MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS—1963
Conventional Application for a Patent

We, CIBA-GEIGY AG

of Klybeckstrasse 141, 4002 Basle, Switzerland

hereby apply for the grant of a Patent for an invention entitled

"METAL COMPLEXES AND POLYMERS DERIVED THEREFROM"

which is described in the accompanying complete specification.

This application is a Convention Application and is based on the application numbered 4719/75

for a patent or similar protection made in Switzerland

on 14th April, 1975

My address for service is:

Care: SPRUSON & FERGUSON

PATENT ATTORNEYS

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SYDNEY, NEW SOUTH WALES.

AUSTRALIA.

Dated this FIRST day of APRIL 1976

CIBA-GEIGY AG

By: [Signature]

Registered Patent Attorney

To: The Commissioner of Patents
In support of the Convention Application made by CIBA-GEIGY AG for a patent for an invention entitled:

"METAL COMPLEXES AND POLYMERS DERIVED THEREFROM"

We, André Hühn and ) of CIBA-GEIGY AG, Klybeckstrasse 141, Arnold Seiler ) Basle, Switzerland

do solemnly and sincerely declare as follows:

1. We are authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141 on the Act was(we) made in Switzerland on the 14th day of April, 1975

by CIBA-GEIGY AG, Basle, Switzerland

3. Jürgen Habermeier, Alemannenweg 12, 4148 Pfeffingen, Switzerland, and

   Godwin Berner, Reichenbergerstrasse 9, 6149 Fürth/Odenwald, Germany

are the actual inventor(s) of the invention and the which the applicant is entitled to make the application are as follows:

The applicant is the assignee of the said

Jürgen Habermeier and Godwin Berner

4. The basic application(s) referred to in paragraph 2 of this Declaration was(we) the first application(s) made in a Convention country in respect of the invention the subject of the application.

DECLARED at Basle, Switzerland, this 19th day of March, 1976

CIBA-GEIGY AG

To: The Commissioner of Patents
COMPUTER SPECIFICATION
(ORIGINAL)

FOR OFFICE USE:

Application Number: 1296176
Lodged: 13 APR 1976

Complete Specification Lodged: 13 APR 1976
Accepted: LAPPED S.47 D(1)
PUBLISHED: 101/08 10/04

Priority: 14.4.75 CH 4719/75

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Actual Inventors: JÜRGEN HABERMEIER and GODWIN BERNER

Complete Specification for the invention entitled:
"METAL COMPLEXES AND POLYMERS DERIVED THEREFROM"

The following statement is a full description of this invention, including the best method of performing it known to me/us:
The present invention provides metal complexes obtained from N-hydroxyalkylated or aminoalkylated, branched \( \alpha \)-aminocarboxylic acids and divalent metal cations.

Metal complexes are known in the art as dyes and pigments. They have also attained importance in the form of chelate polymers. A prerequisite for the use of metal complexes as intermediates for obtaining polymers or as additives is their resistance to heat under the manufacturing or processing conditions, especially under oxidative influences.

Metal complexes of 2-hydroxyethyl-\( \alpha \)-aminoacetic acid and suitable divalent metal ions of which, for example, iron, copper, nickel and zinc complexes are known, possess two free hydroxyl groups. On account of this diol function these metal complexes are of particular interest for the manufacture of linear and also thermoplastic polyesters.

For example, the polycondensation of nickel-bis-(\( \beta \)-hydroxyethylglycine) with phthalic anhydride in vacuo at 170°C is described in "Gummi, Asbest, Kunststoffe", 1962, page 974. However, in this process only insoluble and infusible oligomers are obtained, and no higher molecular weights are obtained. A further disadvantage is that,
in the anhydride method, the choice of starting products is in general restricted to dicarboxylic acids which are able to form inner anhydrides, since when using mixed anhydrides break-off-reactions can prematurely prevent the chain formation. A stable metal complex with diol functions which is suitable for obtaining polyesters by means of straightforward, economic processes, such as the polycondensation of dicarboxylic acid diesters and diols in the melt and/or solid phase at temperatures of above app. 200°C, or by the acid chloride method, has not been described hitherto.

The present invention has for its object the provision of soluble metal complexes of α-aminocarboxylic acids with diol function or diamine function which have a sufficiently high resistance to heat, especially under oxidative influences, and which are suitable primarily for obtaining chelate polymers by the conventional economic processes and can be used in particular as co-components.

It is a further object of the invention to provide soluble and fusible polymers which can be processed by the customary methods of processing, for example injection moulding or extrusion, to give moulded articles of all kinds.
Accordingly, the invention provides metal complexes of N-hydroxyalkylated or aminoaalkylated, branched \( \alpha \)-aminocarboxylic acids and divalent metal cations, of the formula I

\[
(X-\overset{1}{\text{CH}}-\overset{2}{\text{CH}}-\overset{3}{\text{NH}}-\overset{4}{\text{CR}^3 \text{R}^4 \text{COO}})_2 \text{M} \tag{I}
\]

wherein

- \( X \) represents hydroxyl or aminomethyl,
- \( R^1 \) represents a hydrogen atom, alkyl of 1 to 4 carbon atoms or phenyl,
- \( R^2 \) represents hydrogen, and, except when \( R^1 \) is hydrogen, also represents alkyl of 1 to 4 carbon atoms, or \( R^1 \) and \( R^2 \) together represent tetramethylene,
- \( R^3 \) and \( R^4 \) are the same or different and each independently represents alkyl of 1 to 4 carbon atoms, cycloalkyl, substituted or unsubstituted phenyl or benzyl, or together they represent tetramethylene or pentamethylene, and
- \( M \) represents a divalent copper, zinc, cobalt or, in particular, nickel, cation.

\( R^2 \) is preferably hydrogen and \( R^3 \) and \( R^4 \) are preferably the same.

Each of \( R^1 \) and \( R^2 \) is preferably a hydrogen atom,
alkyl of 1 to 2 carbon atoms, phenyl, and together represent tetramethylene.

\( R^3 \) and \( R^4 \) can have the same meanings as previously given for \( R^1 \) and \( R^2 \) and, in addition, represent cycloalkyl containing preferably 5 or 6 ring members, a substituted or unsubstituted phenyl and benzyl group or represent the pentamethylene radical. Where the phenyl and benzyl groups are substituted, preferred substituents are alkyl radicals of 1 to 6 carbon atoms, for example methyl, ethyl, propyl, isopropyl, butyl, tert. butyl, hexyl.

Suitable values for \( R^1 \) and \( R^2 \) are, for example, hydrogen, methyl, ethyl, propyl, isopropyl, butyl, tert. butyl.

Suitable groups and radicals represented by \( R^3 \) and \( R^4 \) are in addition: phenyl, benzyl, methylphenyl, dimethylphenyl, butylphenyl, methylbutyl, propylphenyl, hexylphenyl, dodecylphenyl, p-methylbenzyl, decylbenzyl, cyclopentyl, cyclohexyl, cycloheptyl, methylcyclohexyl.

If \( X \) is aminomethyl, \( R^1 \) and \( R^2 \) preferably represent a hydrogen atom and \( M \) represents in particular a nickel atom.

\( R^1 \) represents in particular hydrogen, methyl, ethyl, phenyl, or together with \( R^2 \) represents tetra-
methylene, and each of \( R^3 \) and \( R^4 \) represents methyl, ethyl, phenyl, or together they represent pentamethylene.

The compounds of the present invention can be illustrated by the following structural formula

\[
\begin{align*}
\text{OC} & \quad \text{R}^4 \\
\text{O} & \quad \text{NH} - \text{CH} - \text{CH} - X \\
\text{X} & \quad \text{CH} - \text{CH} - \text{HN} \\
\text{R}^1 & \quad \text{R}^2 \\
\text{R}^3 & \quad \text{R}^4
\end{align*}
\]

The compounds of the formula I are obtained by reacting aminocarboxylic acids of the formula II

\[
\begin{align*}
\text{X} & \quad \text{CH} - \text{CH} - \text{NH} - \text{CR}^3 \text{R}^4 - \text{COOH} \\
\text{R}^1 & \quad \text{R}^2
\end{align*}
\]

wherein \( X \) and \( R^1 \) to \( R^4 \) are as defined hereinbefore, with metal salts or metal complexes, in particular those of divalent nickel, zinc, copper or cobalt.

The aminocarboxylic acids of the formula II are to some extent known and to some extent new compounds. N-Hydroxyethyl-\( \alpha \)-aminocyclohexanecarboxylic acid and 1-methyl-1-hydroxyethylaminopropionic acid are described,

A general, new process consists in decomposing aqueous solutions of aminoalkylated or hydroxyalkylated hydantoins of the formula III

\[
\begin{align*}
\text{III} \\
\begin{array}{c}
\text{R}^1 \\
\text{R} \quad \text{R}^2 \\
\text{X-C-H-C-N-C-N-C-H-X}
\end{array}
\end{align*}
\]

wherein \( R^1 \) to \( R^4 \) and \( X \) are as defined in formula I, in the presence of a metal hydroxide, and isolating the aminocarboxylic acid by known methods. The reaction is normally carried out with barium hydroxide at temperatures from 80°C to below the decomposition point of the hydantoins of the formula III and under normal pressure or overpressure. The working up is advantageously effected by neutralising the reaction mixture with carbon dioxide, whereupon the excess barium hydroxide precipitates as carbonate and can be filtered off. Afterwards the desired aminocarboxylic acid can be isolated from the solution by precipitating it with acetone. However, it is also possible to evaporate
the water and ethanolamine which has formed and to purify the residue by recrystallisation. Further details can be inferred from Examples 1 and 2.

Hydroxyalkylated and aminoalkylated hydantoins of the formula III, which are required for the process of this invention, are known compounds which are obtained by reacting epoxides with hydantoins. Examples are described in German Offenlegungsschriften 1'813'003, 1'912'026 and 1'966'743. The manufacture of N-bis-γ-aminopropyl-hydantoins by reacting acrylonitrile with corresponding hydantoins is disclosed in Japanese patent 276'504.

Suitable metal salts of nickel, zinc, copper and cobalt for obtaining the metal complexes of this invention are derived, for example, from the inorganic acids, such as carbonic acid, sulphuric acid, phosphoric acid, phosphorous acid, hydrochloric acid, hydrobromic acid, nitric acid, hydrogen sulphide, and from organic acids, such as monocarboxylic or dicarboxylic acids, for example formic acid, acetic acid, propionic acid, benzoic acid, or from sulphonic acids or phosphonic acids. It is also possible to use metal hydroxides instead of the salts. Among the suitable metal complexes particular mention may be made of the acetylacetonates.
Preferred salts are the carbonates of nickel, zinc, copper and cobalt.

The process for the manufacture of the complexes of this invention is carried out as a rule in two advantageous embodiments, either in solution or in the melt. Suitable solvents are water or polar organic solvents, such as dimethyl formamide, dimethyl sulphoxide or hexamethylphosphoric triamide. The reaction is carried out normally at elevated temperatures of about 50°C-250°C, depending on the nature of the solvent. If water is used as solvent, metal carbonates are preferably used as metal salts. Since the acid corresponding to the metal salt is liberated during the reaction in solution, it is advisable to add an acid acceptor, such as sodium bicarbonate, or to carry out the reaction in a buffered solution. The complexes are isolated as a rule by filtering off the crystalline products. The reaction in the melt is normally carried out when chelating metal complexes, such as acetylacetonates, with the aminocarboxylic acids of this invention. The temperature here can be up to more than 50°C above the melting point of the metal complex.

The compounds of the invention are coloured and crystalline, and they are characterised by a surprisingly
high stability, in particular an excellent resistance to heat under oxydative influences. They are also soluble in many starting components for the polymer manufacture, for example in glycols. They are therefore suitable for the manufacture of chelate polymers with high molecular weights by conventional processes.

Because of their stability, the compounds of the present invention, for example the nickel salts, can also be used as light stability agents in polyolefins, such as polyethylene, polypropylene, polybutylene, or copolymers. Further fields of use are as biocides, for example in antifouling paints, in which case, for example, the diols of the formula I can also be polymerised into the coating.

In addition to their stability, the compounds of the invention have surprisingly good solubility in monomers, for examples diols and diamines which are used for obtaining polymers derived from polyesters, polyamides, polyurethanes or polyureas. They are therefore eminently suitable as comonomers for manufacturing these polymers, which are obtained as polymers containing metal ions in the polymer chain.

The present invention therefore also provides
copolymers which contain metal ions and belong to the group of the linear and crosslinked polyurethanes, the linear polyesters, polyamides, polyureas, polyester amides and polyurethane ureas, and which contain up to 15 molar percent, referred to the polymer, of divalent radicals of at least one metal complex of the formula I.

Preferably the copolymers of the present invention contain up to 10 molar percent, in particular 2.5 to 7.5 molar percent, of radicals of a metal complex of the formula I.

By polyester amides are meant copolymers of dicarboxylic acids, optionally hydroxycarboxylic acids or aminocarboxylic acids as co-component, diols and diamines. By polyurethane ureas are meant copolymers of at least difunctional isocyanates and amines and polyols.

The linear polyesters are based on aliphatic and aromatic dicarboxylic acids, diols, and, optionally, hydroxycarboxylic acids as comonomers. They can in this connection be monopolyesters or copolyesters. It is therefore possible for the polyesters to contain one or more dicarboxylic acids, one or more diols, and, in addition, one or more hydroxycarboxylic acids.

Suitable dicarboxylic acids are linear and
branched, saturated and unsaturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids, cycloaliphatic dicarboxylic acids and dicarboxylic acids which contain amido or imido groups or N-heterocyclic rings.

Examples of possible aliphatic dicarboxylic acids are: malonic acid, dimethyl malonic acid, succinic acid, octadecylsuccinic acid, pimelic acid, adipic acid, trimethyladipic acid, sebacic acid, azelaic acid, maleic acid, fumaric acid, methylmaleic acid, and dimeric acids (dimerisation products of unsaturated aliphatic carboxylic acids, such as oleic acid).

Examples of possible cycloaliphatic dicarboxylic acids are: 1,3-cyclobutanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid, 1,3- and 1,4-cyclohexanedicarboxylic acid, 1,3- and 1,4-dicarboxylmethylcyclohexane, 4,4'-dicyclohexyldicarboxylic acid.

Examples of suitable dicarboxylic acids are: terephthalic acid, isophthalic acid, o-phthalic acid, 1,3-, 1,4-, 2,6- or 2,7-naphthalenedicarboxylic acids, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenylsulphone-dicarboxylic acid, 1,1,3-trimethyl-5-carboxyl-3-(p-carboxylphenyl)-indane, 4,4'-diphenyl ether dicarboxylic acid, bis-p-(carboxyl-
phenyl)-methane.

It is known that dicarboxylic acids which contain amido groups are obtained by reacting diamines or aminocarboxylic acids with dicarboxylic acids or derivatives thereof that form the carboxy amide group. These dicarboxylic acids are described, for example, in German Offenlegungsschrift 2'453'448, 2'150'808 and in US patent 2,925,405.

Dicarboxylic acids which contain imido groups are also known and are described, for example, in German Offenlegungsschrift 2'453'448 and in US patent 3,217,014. N-Carboxyl-methyltrimellitic imide may be cited as an example.

Possible hydroxycarboxylic acids are aliphatic, cycloaliphatic, cycloaliphatic-aliphatic, aromatic and aromatic-aliphatic acids. As examples there may be mentioned: glycollic acid, β-propionic acid, β- or γ-hydroxybutyric acid, p-hydroxy-cyclohexanecarboxylic acid, para-hydroxymethyl-cyclohexanecarboxylic acid, m- or p-hydroxybenzoic acid, p-hydroxyphenylacetic acid.

Suitable diols are the aliphatic glycols, in particular those containing 2 to 10 carbon atoms in the molecule, cycloaliphatic and cycloaliphatic-aliphatic
diols, such as 1,4-dihydroxycyclohexane, 1,4-dihydroxy-
methylcyclohexane, aromatic and aromatic-aliphatic diols, such as hydroquinone, p-xylylene glycol or 2,5-dichloro-
p-xylylene glycol, polyoxyalkylene glycols, such as di-
ethylene glycol, triethylene glycol, polyethylene glycol, bis(p-hydroxyphenyl)methylene, bis(p-hydroxyphenyl)ethyl-
idene or bis(p-hydroxyphenyl)propylidene and bis-(p-hydroxy-
phenyl)sulphone or bis(p-hydroxyphenyl) ether.

Further suitable diols are those that contain
N-heterocyclic rings. These are principally the β-hydroxy-
alkylated hydantoins, alkylene-bishydantoins and benzimid-
azolones, which can be partially or completely halogenated, in particular chlorinated and/or brominated, in the phenyl nucleus. These diols are described, for example, in German Offenlegungsschrift 2'453'448.

Preferably the polyesters contain at least 40 molar percent of terephthalic acid and at least 40 molar percent of aliphatic diols which contain 2 to 10, especially 2 to 4, carbon atoms, or 1,4-dihydroxymethylcyclohexanes, referred to the pure polyester. In particular, the poly-
esters contain only linear aliphatic diols containing 2 to 4 carbon atoms and one diol of the formula I.

The copolyesters of the present invention are
obtained by known methods by polycondensing dicarboxylic acids, or the polyester-forming derivatives thereof, with diols and a metal complex of the formula I.

The known processes for obtaining the polyesters of this invention are, for example, solvent or azeotropic condensation, interface condensation, melt or solid phase condensation, and also combinations of these methods, depending on which polyester-forming derivatives and reaction catalysts are used.

As polyester-forming derivatives of the dicarboxylic acids there are used principally the low molecular di-alkyl esters containing 1 to 4 carbon atoms in the molecule, preferably dimethyl ester or diphenyl ester. The acid di-halides, in particular the acid dichlorides and anhydrides, are also suitable.

The polyesters of the present invention can be obtained by esterifying dicarboxylic acids, or transesterifying low molecular dialkyl esters thereof, at 50° to 250°C, with diols and a metal complex of the formula I, in an inert atmosphere, for example in an atmosphere of nitrogen, in the presence of catalysts and while simultaneously removing the water or alkanol that forms, and subsequently carrying out the polycondensation at temperatures below the de-
composition temperature and under reduced pressure, in the presence of specific catalysts, until the polycondensation products have the desired viscosity.

As esterification catalysts it is possible to use, in known manner, amines, inorganic or organic acids, for example hydrochloric acid or p-toluenesulphonic acid, or also metals or metal compounds which are also suitable as transesterification catalysts.

Since some catalysts tend to promote the transesterification and others the polycondensation, it is advantageous to use a combination of several catalysts. Suitable transesterification catalysts are, for example, the oxides, salts or organic compounds of the metals calcium, magnesium, zinc, cadmium, manganese, titanium and cobalt. The metals themselves can also be used as catalysts. The polycondensation is catalysed, for example, by metals like lead, titanium, germanium, tin and, in particular, antimony or compounds thereof. These catalysts can be added to the reaction mixture together or separately.

These catalysts are used in amounts of approximately 0.001 to 1 percent by weight, referred to the acid component.

In the manufacture of the polyesters of this
invention it is particularly advantageous to use those catalysts which promote both the transesterification and the polycondensation. Such catalysts are primarily mixtures of different metals or metal compounds as well as corresponding metal alloys.

The polycondensation is carried out until the polyesters have attained the desired viscosity. Depending on the nature of the catalyst used and on the size of the batch, the reaction times are from about 30 minutes to several hours. The resultant polyester melt, after it has been removed from the reaction vessel and cooled, is granulated or shredded in the usual way.

Another process for obtaining the polyesters of this invention consists in polycondensing dicarboxylic dihalides, preferably the dichlorides, with the diols in the presence of a basic catalyst in the temperature range from 0° to 100°C, with attendant dehydrohalogenation. Preferably amines or quaternary ammonium salts are used as basic catalysts. The amount of basic catalyst can be from 0.1 to 100 molar percent, referred to the acid halides. This process can be carried out in the presence of a further suitable solvent in which the metal complexes also dissolve.
The polycondensation can also be carried out in such a manner that the starting compounds are initially condensed in the melt to a certain viscosity. Then the precondensate obtained is granulated, for example using an underwater granulator, and the granulate is dried and then subjected to a solid phase condensation in vacuo and at a temperature below the melting point of the granulate. Higher viscosities can thereby be attained.

A particularly advantageous process for obtaining the polyesters of the present invention consists in starting from a polyester, in particular one based on polyalkylene terephthalate, which has a relative viscosity of 1.3 to 4, and fusing and reacting it together with the metal complex until the metal complex is incorporated into the polyester. The viscosity of the polyester falls in the process. However, it can be raised again by subsequently subjecting the resultant granulate to an after-condensation, for example a solid phase condensation.

It is also possible to add the metal complex of the formula I in solution to the polyester, preferably in a diol from which the polyester is synthesised, and afterwards to heat and react it.

The polyamides according to the invention are
obtained in principle by the same or similar processes as the polyesters. To this end the same dicarboxylic acids or polyamide-forming derivatives thereof, such as diesters or dihalides, are polymerised with diamines and diamines of the formula I.

The polyamides are preferably synthesised from terephthalic acid, aliphatic dicarboxylic acids which preferably contain 6 to 12 carbon atoms, alkylenediamines of 2 to 12, in particular 6 to 12, carbon atoms, and cycloaliphatic diamines.

In addition to terephthalic acid, particularly preferred components are adipic acid, hexamethylenediamine, which can also be alkylated, and cyclohexane-bis-methylene as well as 1,12-dodecylenediamine. Polyamides which are based on polyamide 66 are especially preferred.

The diamines of the formula I can also be polymerised into the polyamide by the previously mentioned process by fusing them together with a polyamide.

The polyurethanes of the present invention are obtained by the polyaddition of polyols and diols of the formula I to polyfunctional isocyanates. As a rule, the procedure to be followed is that the reaction is initiated at low temperatures in the region of 50°C and afterwards brought to completion at temperatures up to those below
the decomposition temperature of the resultant polymer.

Both aliphatic and aromatic diisocyanates or triisocyanates are suitable, for example diphenylmethane-4,4'-diisocyanate, hexamethylene diisocyanate, isophoron diisocyanate, 1-methyl-cyclohexyl-2,6-diisocyanate, tolylene-2,4- or -2,6-diisocyanate, naphthalene-1,5-diisocyanate or triphenylmethane-4,4',4''-triisocyanate.

 Preferably aliphatic diols are used besides the diisocyanates for obtaining the linear polyesters, for example alkylenediols of 2 to 12 carbon atoms, in particular butane-1,4-diol, polyethers of these diols, such as bis-ethylene glycol, triethylene glycol, polyethylene oxides, polypropylene oxides, polybutylene oxides, polytetrahydrofuran, polythioethers, for example of monothio-ethylene glycol, polyacetals which are derived from formaldehyde or other aldehydes, and linear polyesters which are obtained from dicarboxylic acids, in particular adipic acid and an excess of diols.

For obtaining branched polyurethanes there are used at least trifunctional polyols, such as glycerol, trimethylolpropane, pentaerythritol, and branched polyesters which are obtained by reacting dicarboxylic acids, for example adipic acid and phthalic acid, with an excess
of diols or triols or tetrols. The molecular weight of the polymeric dihydroxy or polyhydroxy component is in general between about 800 and 3000.

The polyureas of the present invention are obtained by reacting diisocyanates with diamines and di-amines of the formula I in a manner similar to that employed in the manufacture of the polyurethanes. Particularly suitable amines are aliphatic amines and cyclo-aliphatic amines of 2 to 12 carbon atoms and aromatic amines, for example phenylenediamine.

In the working up of the polyester melt, or before the polymerisation reaction or after the completion of the reaction in the melt phase, it is possible to add to the reaction mass inert additives of all kinds, for example reinforcing fillers, in particular 5 to 50 percent by weight of sized glass fibres, inorganic or organic pigments, fluorescent brighteners, matting agents, crystallisation promoters, mould release agents or flame-proofing agents.

If the polymerisation is carried out batchwise, the inert additives can be added during the final condensation steps, for example in the solid phase condensation or also at the conclusion of the melt condensation.
The polymers of the present invention of which the thermoplastic polyamides, polyurethanes, and, in particular, polyesters, are preferred, are partly crystalline to amorphous coloured polymers, depending on which starting components are used and in what ratios they are used. They are preeminently suitable for manufacturing moulded articles of all kinds by the customary moulding processes, such as casting, moulding, laminating, injection moulding, injection blow moulding and extruding. It is also possible to use them for surface coating by the customary methods, for example sintering, electrostatic coating or dipping processes.

The unsaturated polyesters can be further processed with conventional coreactants, such as polystyrene, and with conventional processing assistants to give moulded articles of crosslinked polyesters.

Examples of moulded articles are technical apparatus parts, such as casings or gear wheels, containers, sheets, boards, films, filaments and semi-finished products which can be machined.

The polymers of the present invention have a surprisingly high E-module and stiffness as well as good electrical surface properties.
The following Examples will serve to illustrate the invention. The polyesters are characterised more closely by means of the following characteristic data, which are measured by differential thermoanalysis from a sample which has been tempered for 3 minutes at 30°C above the melting point or softening point and then rapidly chilled. The chilled sample is heated by means of a Perkin-Elmer "DSC-1B" differential scanning calorimeter with a heating speed of 16°C/min. The thermogram of the sample shows the glass transition temperature (T), the crystallisation temperature (T<sub>k</sub>) and the melt temperature (T<sub>s</sub>) and the softening temperature (T<sub>e</sub>). The critical moment in the sudden increase of the specific heat in the thermogram indicates the glass transition temperature, the tip of the exothermic peak indicates the crystallisation temperature and the tip of the endothermic peak indicates the melt temperatures. The relative viscosity of the polycondensates is determined in solutions of 1 g of polyester in 100 ml of a mixture consisting of equal parts of phenol and tetrachloroethane at 30°C.

The molar percentages refer to the polymer.
A) Manufacture of the β-hydroxyethyl-α-amino acids

a) Manufacture of N-β-hydroxyethyl-α-amino-cyclo-
hexanecarboxylic acid

24.3 g of 1,3-dihydroxyethyl-5,5-pentamethylene hydantoin together with 185 g of Ba(OH)$_2$ x $8$ H$_2$O and 300 ml of water are kept for 3 hours at 160°C in a shaking autoclave. Carbon dioxide is passed into the chilled reaction mixture until a pH of 7 is attained, then the precipitated BaCO$_3$ is filtered off with suction and washed repeatedly with water. The filtrate is concentrated to dryness and recrystallised from methanol/water (5:1).

Yield : 15.8 g = 94% of theory (flakes)
Melting point: 282°-285°C (sublimation)
Acid number : calculated 299.5
found 305

The infrared and nuclear magnetic resonance spectra accord with the structure of the above product.

b) Manufacture of N-β-hydroxyethyl-l-methyl-α-
aminopropionic acid

78 g of 1,3-dihydroxyethyl-5,5-dimethyl hydantoin to-
gether with Ba(OH)$_2$ x 8 H$_2$O and 300 ml of water are kept for 3 hours at 160°C in a shaking autoclave. Carbon dioxide is passed into the chilled reaction mixture until a pH of 7 is attained, then the precipitated BaCO$_3$ is filtered off with suction and repeatedly washed with water. The filtrate is concentrated to dryness and recrystallised from ethanol/water (8:1).

Yield : 80.7% of theory (needles)
Melting point: 285°-288°C (sublimation)
Acid number : calculated 380.9
              found 392

The infrared and nuclear magnetic resonance spectra accord with the structure of the above product.

B) Manufacture of the metal complexes

Example 1 Nickel-bis-(N-β-hydroxyethyl-α-aminocyclohexanecarboxylate)

16.71 g of N-hydroxyalkyl-α-amino-cyclohexanecarboxylic acid are dissolved in 200 ml of hot water and 5.89 g of
nickel carbonate are added with stirring. Slight foaming occurs and a turquoise blue precipitate forms. Stirring is continued for 1 hour at 85°C and the precipitate is collected by suction filtration. The substance is washed with cold water and acetone and dried overnight at 130°C.

Yield : 19.2 g = 90.1% of theory
Melting point: > 300°C (decomp.)
Ni. : calculated 13.62%
    found 13.23%

The heat resistance was measured by thermoanalysis (TA - 1, Mettler):

start of the weight increase in air : 250°C
(definition: lowest decrease greater than 1%/min)
temperature of the maximum change in weight in air : 285°C
temperature of maximum change in weight in a nitrogen atmosphere : 300°C
Example 2  Nickel-bis-(N-β-hydroxyethyl-α-methyl-α-aminopropionate

18.8 g of N-hydroxyalkylamino-isobutyric acid are dissolved in water and 7.5 g of nickel carbonate are added. The mixture is heated, with stirring, to app. 85°C, when slight foaming occurs and the solution turns dark blue in colour. The solution is filtered hot and blue crystals fall out of the filtrate on cooling. These crystals are washed with a small amount of cold water and dried. The substance is dried overnight in vacuo at 130°C.

Yield : 16 g = 71% of theory
Melting point: > 300°C (with decomp.)
Ni : calculated 16.74%
     found 16.5%

Example 3  Copper-bis-(N-β-hydroxyethyl-α-amino-cyclohexanecarboxylate)

5.6 g of N-hydroxyethylaminocyclohexanecarboxylic acid are dissolved in 200 ml of hot water and 1.85 g of copper carbonate are added with stirring. Slight foaming thereupon occurs and the solution turns dark blue in colour.
The solution is filtered hot and, on cooling, blue crystals precipitate. These crystals are washed with a small amount of cold water and acetone. The substance is dried overnight at 130°C in vacuo.

Example 4  Zinc-bis-(N-β-hydroxyethyl-α-methyl-α-aminopropionate)

A solution of 1.47 g of 1,3-dihydroxyethyl-5,5-dimethylamino acid and 1.6 g of zinc acetylacetonate in 100 ml of water is heated gradually to 50°C with stirring. After a reaction time of 5 hours the batch is filtered and the filtrate is concentrated almost to dryness. The residue is washed repeatedly with acetone and filtered off with suction.

Yield : 1.6 g = 89.6% of theory
Melting point: 223°-225°C
Zn calculated 18.3%
found 18.2%

Example 5 (comparison example)

The heat resistance of the nickel compound of the invention and of nickel-bis-(N-β-hydroxyethyl-α-aminoacetic acid), identified as I in the Table, is determined in an atmosphere of nitrogen and in air by differential thermo-analysis (DTA) and differential thermogravimetry (DTG). It is evident from the Table that the heat resistance, and especially the resistance to the influence of heat and oxygen, of the compounds of the invention is improved.
<table>
<thead>
<tr>
<th>Determinants</th>
<th>I</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start of the decrease in weight in an N₂ atmosphere</td>
<td>230</td>
<td>256</td>
<td>260</td>
</tr>
<tr>
<td>(6 l/h) - (1%/min) (DTG)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of the maximum change in weight in an N₂ atmosphere</td>
<td>282</td>
<td>300</td>
<td>290</td>
</tr>
<tr>
<td>(6 l/h) - DTG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exothermic procedure in dry air (6 l/h)</td>
<td>185</td>
<td>245</td>
<td>245</td>
</tr>
<tr>
<td>Start of the heat procedure under oxydative influences</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example 6: Nickel-bis-(N-3-aminopropyl-α-aminocyclohexanecarboxylate

10 g (0.1 mole) of N-3-aminopropyl-α-aminocyclohexane-carboxylic acid are dissolved at 80°C in 200 ml of water. On adding 5.9 g (0.05 mole) of nickel carbonate CO₂ evolves and a change in colour to blue occurs. Stirring is continued for half an hour at 80°C and the solution is then concentrated to dryness. The residue is dissolved in 200 ml of absolute methanol and precipitated by adding acetone, to give a light blue compound which is dried in vacuo at 150°C.

Yield: 7.3 g = 32% of theory
Melting point: from 265°C with decomposition
Nickel content (theory): 12.8%
Nickel content (found): 12.4%

Example 7: Polyester based on sebacic acid and ethylene glycol

Ethylene glycol (0.095 mole), sebacic dichloride (0.1 mole) and metalliferous nickel-bis-(N-β-hydroxyethyl-α-methyl-
α-aminopropionate (compound 2) (0.005 mole) are put into a polycondensation apparatus equipped with gas inlet tube, stirrer and distillation head. The temperature is slowly increased with vigorous stirring and while introducing nitrogen. The exothermic condensation reaction starts at app. 30°C and HCl gas evolves. A clear, green solution which slowly solidifies is obtained. While stirring and simultaneously introducing nitrogen the temperature is raised to 160°C, depending on the dicarboxylic chloride, and kept thereat for 2 hours. A vacuum is then slowly applied and after about half an hour nitrogen is blown into the apparatus. A light grey polyester with a relative viscosity of 1.08 is obtained.

Example 8 Polyester based on sebacic acid and ethylene glycol

20.225 g (0.1 mole) of sebacic acid, 0.0975 mole of ethylene glycol and 0.0025 mole of compound 2 are put into a polycondensation apparatus equipped with stirrer and distillation head. The bath temperature is increased to 180°C while stirring and introducing nitrogen and a clear, green
solution is obtained. After a reaction time of 2 hours, about 1.5 ml of water have distilled over. The bath temperature is then raised to 220°C. A vacuum is then slowly applied, in the process of which the batch becomes increasingly viscous. After a reaction time of 2 hours nitrogen is blown into the apparatus. A wax-like, light green polymer, which melts completely clear under the melting point microscope, is obtained with a melting point of 64°C-69°C. The relative viscosity is 1.19.

A wax-like, green polyester with a relative viscosity of 1.43 is obtained by using 0.095 mole of ethylene glycol and 0.05 mole of compound 2 and otherwise carrying out the above procedure.

Example 9 Polyester based on polyethylene terephthalate

Dimethyl terephthalate (0.1 mole), ethylene glycol and the catalyst are put into a polycondensation apparatus equipped with stirrer and distillation head. The apparatus is strongly heated in an oil bath, with stirring, to 200°C, and the methanol which is liberated during the transesterification is distilled off. After about 1 hour the methanol is completely distilled off - the amount of distillate is
read off in a graduated receiving vessel. The mixture is then strongly heated to 240°C and then compound 2 is added. The metal complex dissolves under these conditions within app. 1 hour. Subsequently a vacuum is applied which is gradually increased to $10^{-3}$ Torr. The polycondensation is complete after about 2 hours.

The amount of compound 2 added, the catalyst, and the properties of the polyesters obtained are indicated in Table 1.
<table>
<thead>
<tr>
<th>Compound 2 (molar%)</th>
<th>Catalyst</th>
<th>Relative viscosity</th>
<th>T&lt;sub&gt;G&lt;/sub&gt;</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>MnOAc/Sb₂O₃</td>
<td>1.25</td>
<td>75</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>2.5</td>
<td>ZnOAc/Sb₂O₃</td>
<td>1.35</td>
<td>80</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>2.5</td>
<td>ZnOAc</td>
<td>1.22</td>
<td>75</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>2.5</td>
<td>Ca-glycolate/Sb₂O₃</td>
<td>1.24</td>
<td>74</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>2.5</td>
<td>Ge(OR)₄</td>
<td>1.22</td>
<td>67</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>2.5</td>
<td>Sb₂O₃</td>
<td>1.43</td>
<td>70</td>
<td>green, crystalline</td>
</tr>
<tr>
<td>5</td>
<td>Ca-glycolate/Sb₂O₃</td>
<td>1.20</td>
<td>70</td>
<td>green, crystalline</td>
</tr>
</tbody>
</table>
Example 10  Polyester based on polybutylene terephthalate

29.1 g (0.15 mole) of dimethyl terephthalate, 29.7 g (0.33 mole) of butanediol-1,4- and catalytic amounts of dibutyl tin oxide (DBTO) are put into a polycondensation vessel equipped with stirrer and distillation head. The bath temperature is increased to 200°C while stirring and passing in nitrogen. The apparatus is kept at this temperature for 1 hour and app. 12 ml of methanol are distilled off. The bath temperature is then raised to 240°C and compound 2 is added. The batch is kept for about 1 hour at 240°C with stirring and then a vacuum is applied. The vacuum is increased to $10^{-3}$ Torr and after about 2 hours nitrogen is blown into the apparatus. The amount of compound 2 added, the catalyst, and the properties of the polyester obtained are indicated in Table 2.
### Table 2

<table>
<thead>
<tr>
<th>Compound (molar%)</th>
<th>Catalyst</th>
<th>Properties</th>
<th>appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>ZnOAc/Sb$_2$O$_3$</td>
<td>1.44</td>
<td>TK $^\circ$C</td>
</tr>
<tr>
<td>2.5</td>
<td>Ca-glycolate/Sb$_2$O$_3$</td>
<td>1.69</td>
<td>TK $^\circ$C</td>
</tr>
<tr>
<td>2.5</td>
<td>Ge(OR)$_4$</td>
<td>1.34</td>
<td>TK $^\circ$C</td>
</tr>
<tr>
<td>2.5</td>
<td>DBTO</td>
<td>1.84</td>
<td>TK $^\circ$C</td>
</tr>
<tr>
<td>2.5</td>
<td>DBTO</td>
<td>1.99</td>
<td>TK $^\circ$C</td>
</tr>
</tbody>
</table>
Example 11 Polyester based on polyethylene terephthalate with compound 2 and a further component

The procedure of Example 9 is carried out, but using the additional components listed in Table 3.
<table>
<thead>
<tr>
<th>Co-component (molar%)</th>
<th>Compound 2 (molar%)</th>
<th>Catalyst</th>
<th>Properties</th>
<th>appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>phenylindane-dicarboxylic acid</td>
<td>2.5</td>
<td>DBTO</td>
<td>1.30</td>
</tr>
<tr>
<td>12.5</td>
<td>dimethylisophthalate</td>
<td>2.5</td>
<td>DBTO</td>
<td>1.28</td>
</tr>
<tr>
<td>12.5</td>
<td>dimethylisophthalate</td>
<td>2.5</td>
<td>Ca-glycolate</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td>12.5</td>
<td>bisphenol-A-diglycol-ether</td>
<td>2.5</td>
<td>DBTO</td>
<td>1.38</td>
</tr>
<tr>
<td>7.5</td>
<td>dimethyl sebacate</td>
<td>2.5</td>
<td>DBTO</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Example 12  Polyester based on polybutylene terephthalate

22 g of polybutylene terephthalate (υ_rel = 2.20) and compound 2 are put into a polycondensation apparatus equipped with stirrer and distillation head. The apparatus is strongly heated to 250°C and the reactants are fused while introducing nitrogen. A vacuum is then applied and after a reaction time of about half an hour a completely clear, green melt is obtained. After a further reaction time of 2 hours at 250°C nitrogen is blown into the apparatus. Transparent, green polymers with a setting point of app. 223-226°C are obtained.

The amount of compound 2 added and the properties of the polyesters obtained are indicated in Table 4.
Table 4

<table>
<thead>
<tr>
<th>Compound 2 (% by weight)</th>
<th>Relative viscosity</th>
<th>$T_K$ °C</th>
<th>$T_G$ °C</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.82</td>
<td>39</td>
<td>-</td>
<td>amorphous</td>
</tr>
<tr>
<td>8</td>
<td>1.48</td>
<td>59</td>
<td>40</td>
<td>amorphous</td>
</tr>
<tr>
<td>16</td>
<td>1.42</td>
<td>-</td>
<td>-</td>
<td>amorphous</td>
</tr>
<tr>
<td>20</td>
<td>1.39</td>
<td>-</td>
<td>46</td>
<td>amorphous</td>
</tr>
<tr>
<td>24</td>
<td>1.24</td>
<td>91</td>
<td>50</td>
<td>amorphous</td>
</tr>
</tbody>
</table>
Example 13  Polyurethanes

A mixture of ethylene glycol and compound 2 is put into a reaction vessel equipped with stirrer, drip funnel and cooler. The mixture is heated to 55°C with vigorous stirring. The diisocyanate (0.1 mole) is then slowly added dropwise in the course of about 1 hour and the temperature is raised to 200°C during this time.

Composition and properties of the polyurethanes obtained are indicated in Table 5.
Table 5

<table>
<thead>
<tr>
<th>Compound 2 (molar%)</th>
<th>Properties</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>diisocyanate</td>
<td>T&lt;sub&gt;G&lt;/sub&gt; °C</td>
<td>relative viscosity</td>
</tr>
<tr>
<td>2.5</td>
<td>isophorondi-isocyanate</td>
<td>109</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>isophorondi-isocyanate</td>
<td>113</td>
<td>1.37</td>
</tr>
<tr>
<td>2.5</td>
<td>hexamethylene diisocyanate</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
CLAIMS
CLAMS: The claims defining the invention are as follows:

1. Metal complexes obtained from N-hydroxyalkylated or aminoalkylated, branched \( \alpha \)-aminocarboxylic acids and divalent metal cations, of the formula

\[
\text{(I)}
\]

\[
(X - \text{CH} - \text{CH} - \text{NH} - \text{CH}^\text{3} \text{R}^4 - \text{COO})_2^\text{M}
\]

wherein

- \( X \) represents hydroxyl or aminomethyl,
- \( R^1 \) represents a hydrogen atom, alkyl of 1 to 4 carbon atoms or phenyl,
- \( R^2 \) represents hydrogen, and, except when \( R^1 \) is hydrogen, also represents alkyl of 1 to 4 carbon atoms, or
- \( R^1 \) and \( R^2 \) together represent tetramethylene,
- \( R^3 \) and \( R^4 \) are the same or different and each independently represents alkyl of 1 to 4 carbon atoms, cycloalkyl, substituted or unsubstituted phenyl or benzyl, or together they represent tetramethylene or pentamethylene, and
- \( M \) represents a divalent copper, zinc, cobalt or nickel cation.

2. Metal complexes of the formula I according to claim 1, wherein alkyl contains 1 to 2 carbon atoms, cyclo-
alkyl contains 5 or 6 ring members, and phenyl or benzyl is substituted by 1 to 6 carbon atoms.

3. Metal complexes of the formula I according to claims 1 to 2, wherein $R^2$ is hydrogen.

4. Metal complexes of the formula I according to claims 1 to 3, wherein $R^3$ and $R^4$ are the same.

5. Metal complexes of the formula I according to claims 1 to 4, wherein $R^1$ represents hydrogen, methyl, ethyl or phenyl.

6. Metal complexes of the formula I according to claims 1 to 5, wherein each of $R^3$ and $R^4$ independently represents methyl, ethyl or phenyl or together represent pentamethylene.

7. Metal complexes of the formula I according to claims 1 to 6, wherein M is a nickel cation.
8. Copolymers which contain metal ions selected from the group of the linear and crosslinked polyurethanes, the linear polyesters, polyamides, polyureas, polyester amides and polyurethane ureas, and which contain up to 15 molar percent, referred to the polymer, of divalent radicals of at least one metal complex of the formula I according to claims 1 to 7.

9. Copolymers according to claim 8 which contain up to 10 molar percent, in particular 2.5 to 7.5 molar percent, of radicals of a metal complex of the formula I.

10. Copolymers according to either of claims 8 or 9, wherein the dicarboxylic acid radicals in the polyesters consist of at least 40 molar percent of terephthalic acid radicals.

11. Copolymers according to claims 8 to 10 which contain as remaining diol component an alkylene diol of 2 to 10 carbon atoms, in particular a linear alkylene diol of 2 to 4 carbon atoms.
12. Copolymers according to claims 8 or 9, wherein the polyamide is built up from terephthalic acid or aliphatic dicarboxylic acid radicals of 6 to 12 carbon atoms, and alkylenediamine radicals of 2 to 12, in particular of 6 to 12 carbon atoms, or cycloaliphatic diamine radicals.

13. Copolymers according to claims 8, 9 and 12, wherein the polyamide consists of adipic acid radicals and hexamethylenediamine radicals or of cyclohexane-bis-methylamine radicals or terephthalic acid radicals, and of cyclohexane-bis-methylamine radicals or hexamethylenediamine radicals as well as of diamine radicals of the formula I.

14. Copolymers according to claims 8 or 9 wherein the polyurethanes are synthesised from aliphatic or aromatic diisocyanates or triisocyanates and aliphatic lower or higher molecular weight diols or polyols.

15. Copolymers according to claim 14 which contain as isocyanate: diphenylmethane-4,4'-diisocyanate, hexamethylene diisocyanate, isophoron diisocyanate, 1-methylcyclohexyl-4,6-diisocyanate, toluylene-2,4- or -2,6-di-
isocyanate, naphthalene-1,5-diisocyanate or triphenylmethane-4,4',4''-triisocyanate.

16. Copolymers according to either of claims 14 or 15 which contain as diols or polyols: alkylenediols, polyethers, polyacetals, polythioethers, triols, tetrols or polyesters of dicarboxylic acids with diols and/or triols or tetrols.

17. Use of metal complexes of the formula I according to claims 1 to 7 as co-components for the manufacture of copolymers which contain metal ions selected from the group of the linear or crosslinked polyurethanes, of the linear polyesters, polyamides, polyureas, polyester amides and polyurethane ureas.

DATED this FIRST day of APRIL, 1976

CIBA-GEIGY AG

Patent Attorneys for the Applicant
SPRUSON & FERGUSON