Low–solvent or solvent–free printing–ink or coatings binders comprise (a): from 30 to 98 % by weight of polyesters, as component A, obtainable by reacting (a1) hydroxyl– and/or amino–terminated oligomers, as component A1, (a2) at least one polyanhydride compound having at least two carboxylic anhydride groups, as component A2, with or without (a3) at least one monoanhydride of a polycarboxylic acid, as component A3, (b) from 70 to 2 % by weight of cross–linker for cross–linking the polyesters of component A, as component B, and (c) from 0 to 30 % by weight, based on the sum of the amounts of components A and B, of at least one solvent.
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Low-emission curable printing-ink or coatings binders

The invention relates to low-emission, curable binders for coatings or printing inks, to processes for their preparation, to coating materials and printing inks comprising them, to polyesters used for their preparation, and to the use thereof for coating, printing and/or impregnating substrates or shaped articles, especially metallic vessels, packaging or parts thereof.

The coating or coloring of different shaped articles and packaging, for example metallic packaging for foodstuffs, such as cans, is carried out using low-solvent or solvent-free coatings binders based on oligomeric polyesters.

US 4,256,622 describes curable hydroxy resin compositions which consist of hydroxyl-containing polyesters, polyglycol monoethers, amino resins and catalysts. Customary commercial polyesters are employed. As the polyglycol monoether use is made, for example, of propylene glycol monomethyl ether.

DE-A-27 21 989 describes liquid coating compositions with a low-solvent or solvent-free base. They comprise amino resins and at least bifunctional polyesters which are built up from polyols and dicarboxylic acids.

For the protective and decorative coating of packaging containers made from metal, for example cans and buckets for foodstuffs and nonfoods, deep-drawn cans, especially beverage cans, and also jar closures, crown corks and other lids, use is made almost exclusively of coating materials and printing inks which are solutions in organic solvents.

EP-B-0 002 718 describes the use of a coating material based on epoxy resin and on a trimellitic anhydride ester mixture for the interior coating of metal containers for foodstuffs or beverages. For this purpose,
a diester is prepared from trimellitic anhydride and ethylene glycol and is dissolved, together with an epoxy resin, in an organic solvent.

Low-solvent or solvent-free coating materials and printing inks have not met the technical requirements placed on them. When used in conjunction with metal packaging, especially for foodstuffs, they are required to exhibit high levels of adhesion, abrasion resistance, deformability and sterilizability, since beverage cans, for example, after coating or printing are filled, shaped and sterilized under hot conditions. In the course of coating or printing the articles, the solvent employed in the coating materials and printing inks used to date escapes and can in general not be recovered. However, for reasons of environment and economics there is a need for low-solvent or solvent-free coating materials and printing inks.

It is an object of the present invention, therefore, to provide low-solvent or solvent-free printing-ink or coatings binders, and also coating materials and printing inks, which meet the above requirements.

We have found that this object is achieved by providing low-solvent or solvent-free printing-ink or coatings binders comprising

a: from 30 to 98% by weight of polyesters, as component A, which can be prepared by reacting

a1: hydroxyl- and/or amino-terminated oligomers, as component A1, which are built up from

all: at least one polyfunctional carboxylic acid as component A11.
a12: at least one polyfunctional hydroxy compound and/or amino compound as component A12.

and optionally

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a13: at least one monofunctional hydroxy compound and/or amino compound and/or monocarboxylic acid as component A13.

component A12 being employed in an excess of equivalents relative to A11, so that hydroxyl- and/or amino-terminated oligomers are formed even in the case of complete condensation.

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a2: at least one polyanhydride compound having at least two carboxylic anhydride groups, as component A2.

and optionally

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a3: at least one monoanhydride of a polycarboxylic acid, as component A3.

b: from 70 to 2% by weight of crosslinker for crosslinking the polyesters of component A, as component B.

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it being possible for free carboxyl groups present in component A and possibly B to be at least partially neutralized with bases, and

c: from 0 to 30% by weight, based on the sum of the amounts of components A and B, of at least one solvent, as component C.
Externally crosslinked polyesters, especially those crosslinked by means of amino resin, require a relatively high molecular weight, i.e. a high degree of polycondensation, in order to satisfy the above technical requirements of the finished coating. Because of this high molecular weight, the polyesters used to date are generally solid or of very high viscosity and have to be dissolved in organic solvents. The known crosslinkable polyesters which are liquid at room temperature have a limited degree of condensation. They are linear or branched and carry terminal functional groups. They are crosslinked by way of these terminal functionalities. Attempts to employ such known polyesters for metal packaging, especially cans, showed that it was not possible to achieve the high requirements, especially in respect of deformability and sterilizability, using these polyesters. The printing-ink or coatings binders provided in accordance with the invention include, as component A, polyesters which are functionalized in the molecule chain and not just terminally. By using these polyesters of the invention, which are described in more detail below, it is possible to provide low-solvent or solvent-free printing-ink or coatings binders, and, respectively, coating materials or printing inks, which meet the requirements after crosslinking or curing.

Component A

Component A is present in the novel low-solvent or solvent-free printing-ink or coatings binders in an amount of from 30 to 98, preferably from 40 to 90 and, in particular, from 60 to 90% by weight.

The polyesters of component A can be prepared by reacting a mixture of the following components A1, A2 and, if desired, A3.
Component A1

Components A1 are hydroxyl- and/or amino-terminated oligomers which are built up from the following components A11, A12 and, if desired, A13.

Components A11 are at least one polyfunctional carboxylic acid. Suitable polyfunctional carboxylic acids are di-, tri- and higher polybasic carboxylic acids, preferably dicarboxylic acids. Depending on the desired properties the polyfunctional carboxylic acid can be aliphatic, aromatic or mixed aliphatic/aromatic. Examples of suitable polyfunctional carboxylic acids are phthalic acid in its isomeric forms and linear terminal C3·12-, preferably C4·10-alkylenedicarboxylic acids, especially adipic acid. Examples of other suitable acids are suberic acid, tetrahydrophthalic acid, endomethylenetetrahydrophthalic acid, hexahydrophthalic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid, trimellitic acid and pyromellitic acid.

Components A12 are at least one polyfunctional hydroxy compound and/or amino compound. The polyfunctional hydroxy compound and/or amino compound in this case has 2 or more, preferably 2 to 4, hydroxyl and/or amino groups. Examples of compounds suitable as component A12 are linear aliphatic terminal diols, such as C2·12-, preferably C2·6-diols, especially ethylene glycol and 1,6-hexanediol. It is also possible to employ aromatic or mixed aromatic/aliphatic hydroxy and/or amino compounds. Examples, in addition to ethylene glycol and hexanediol, are 2-methylpropanediol, polyethylene glycols, propylene glycols, polypropylene glycols, butanediol isomers, neopentyl glycol, trimethylolpropane, glycerol, pentaerythritol, bisphenol A, and hydrogenated bisphenol A. It is also possible to employ OH-polyfunctional polymers, such as hydroxyl-modified polybutadienes or hydroxyl-carrying polyurethane prepolymer and epoxy resins. Also of importance are alkoxylated OH-functional substances, such as the ethoxylate and propoxylate products of the above-described polyols.
and also polyalkylene oxide polyols, polytetrahydrofurandiols and polycaprolactonediols.

In addition there may be present as component A13, if desired, at least one monofunctional hydroxy compound and/or amino compound and/or monocarboxylic acid.

By using the monofunctional compounds it is possible to control the molecular weight of the oligomers of component A1. The introduction of amide and imide structures is also possible. This is described, for example, in DE-A-15 70 273 and DE-A-17 20 323. By selecting suitable starting materials it is possible to alter the properties of the hydroxyl- and/or amino-terminated oligomers. By using longer-chain, unbranched compounds, such as hexanediol or adipic acid, it is possible to improve the elasticity of the end products. The use of branched compounds, such as neopentyl glycol, leads to compounds which are more resistant to hydrolysis. The use of aromatic compounds, such as isomers of phthalic acid, or hydrogenated bisphenol A, leads to end products which are more scratch-resistant and temperature-stable. The starting materials can be selected in accordance with these generally known aims and/or properties.

It is advantageous in many cases to start from the esters of the carboxylic acids and to prepare the polyesters by transesterification at elevated temperatures, since these transesterifications proceed in some cases more readily and more rapidly than direct esterification. In addition, by using polyfunctional amines it is also possible to obtain polyesters having amide structures. The amounts of components A11, A12 and A13 are chosen so that the resulting oligomers are hydroxyl- and/or amino-terminated. The molar fraction of the hydroxy or amino compounds is therefore higher than that of the acid compounds. The excess of equivalents of hydroxyl and/or amino components relative to carboxyl components is from 5 to 200, preferably from 5 to 100 and, with particular
preference, from 20 to 50%. In this case, hydroxy compounds and amine compounds are calculated together. By means of this excess the products obtained, even in the case of complete polycondensation, are only of relatively low molecular mass, i.e. are oligomers, which are hydroxyl-terminated or, if amine compounds are used as well, are both hydroxyl- and amino-terminated. The additional use of monofunctional carboxylic or hydroxy compounds allows further regulation of the degree of condensation and control of the functionalization of the oligomers. To prepare component A1 it is also possible to employ polyfunctional natural substances or derivatives thereof, such as linseed oil fatty acid, coconut fatty acid, castor oil, castor oil fatty acid and dimeric and polymeric fatty acids. In general these oligomeric polyesters are functionalized only at the ends. By means of polyfunctional starting materials, such as triols, branches are in fact introduced into the polymer backbone and may, in turn, be functionally terminated. Direct functionalization of a polymer main chain, however, is not achieved by this means. The average molecular weight of the oligomers is from 200 to 5000, preferably from 300 to 1000.

The novel polyesters attain their valuable properties by functionalization in the polymer main chain. For this purpose the hydroxyl- and/or amino-terminated oligomers of component A1 are reacted with polyanhydride compounds of component A2.

Component A2

As component A2 use is made of at least one polyanhydride compound having at least two carboxylic anhydride groups. The polyanhydride compound has at least four carboxyl groups, forming two carboxylic anhydride groups. In addition, the compound may have further carboxyl groups, present as such or in the form of anhydride groups. It is preferred to employ the anhydrides of aromatic or partly aromatic tetracarboxylic acids. For example, compounds of the formula (I)
are employed where

A is a C\textsubscript{2-20} radical which can contain aromatic, aliphatic and/or
cycloaliphatic radicals, O, NR\textsuperscript{1}, S and/or SO\textsubscript{2} in the chain or
can be substituted by one or more of the organic radicals or
halogen atoms.

X is O, NR\textsuperscript{2} or S, and

R\textsuperscript{1} and R\textsuperscript{2} independently are H, C\textsubscript{1-5}-alkyl, C\textsubscript{6-12}-aryl, C\textsubscript{7-13}-aralkyl or C\textsubscript{7-13}-
alkaryl.

The compounds of the formula (I) have units which are derived from
trimellitic acid. These units can be linked by way of ester, thioester or
amide bonds to the radical A to form a molecule. The radical A is an
organic C\textsubscript{2-20} radical. It is composed of aromatic, aliphatic and/or
cycloaliphatic radicals which can contain O, NR\textsuperscript{1}, S and/or SO\textsubscript{2} as
heteroatoms in the chain. They may be substituted, moreover, by one or
aromatic, aliphatic and/or cycloaliphatic radicals, and by halogen atoms.

For example, A can be a linear unbranched alkyl radical which is attached
by way of the terminal carbon atoms to the radicals X. Such a radical
preferably has 1 to 12, particularly preferably 1 to 6 carbon atoms. The
simplest example of an aromatic radical is a phenylene radical. Examples
of combined aliphatic and aromatic radicals are radicals derived from bisphenol A. Preferred radicals are alkyl radicals from \( \text{C}_2 \) to \( \text{C}_6 \).

Compounds of the formula (I) can be obtained by reacting trimellitic anhydride with diols, dithiols or diamines. Examples of anhydrides of this kind which can be employed in accordance with the invention are described in EP-A-0 002 718, US 3,435,002 and US 3,749,722.

As component A2 it is also possible to employ compounds of the formula (II)

\[
\begin{align*}
\text{O} & \quad \text{B} & \quad \text{O} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} & \quad \text{O} \\
\end{align*}
\]

where

\( B \) is -\text{CO}-, a single bond, -\text{O}-, -\text{S}-, \text{SO}_2-., -\text{O-Phe-O-}, -\text{C(CH}_3)_2-., -\text{CH}_2- \) or -\text{CO-NH-}.

\( \text{Ph} \) here is phenylene.

Examples of suitable compounds are benzophenetetracarboxylic dianhydride, pyromellitic dianhydride, oxydiphthalic dianhydride, diphenyl sulfone tetracarboxylic dianhydride, biphenyltetra carboxylic dianhydride, methylbiscyclohexanetetracarboxylic dianhydride and diphenyl methanetetracarboxylic dianhydride.

Examples of preferably used tetracarboxylic dianhydrides are pyromellitic dianhydride, benzophenetetracarboxylic dianhydride, biphenyltetra carboxylic dianhydride and oxydiphthalic dianhydride, and also partial
esters and/or partial amides of polycarboxylic acids which also contain at least two anhydride functions in the molecule. Such partial esters or partial amides can be obtained, for example, by reacting tetracarboxylic dianhydrides with a stoichiometric deficit, based on the anhydride groups, of poly-hydroxyl- or -amino-functional substances. Since the reactivity of the anhydride groups is changed by these reactions, addition takes place preferably only onto one anhydride group of the tetracarboxylic dianhydrides. In the majority of cases a stochastic mixture of the possible reaction products is obtained, with a predominant proportion of substances having at least two anhydride functions in a molecule, which are derived from two tetracarboxylic dianhydride molecules linked by way of the poly-hydroxyl- or -amino-functional substance. Corresponding mixtures can readily be employed for reaction with the oligomers of components A1, no disruption being caused by the byproduct fractions.

Component A3

As component A3 it is possible, if desired, to employ at least one monoanhydride of a polycarboxylic acid. This monoanhydride can be derived from a polycarboxylic acid having more than 2 carboxyl groups. The polycarboxylic acid can be aliphatic, aromatic or mixed aliphatic/ aromatic. Examples of suitable monoanhydrides are phthalic anhydride, maleic anhydride, malonic anhydride and, preferably, trimellitic anhydride. Further suitable monoanhydrides are the anhydrides of partial esters of tetracarboxylic acids. Further influence over the end properties of the coatings can be exerted by way of the ester radical of these compounds.

As component A3 it is preferred to employ phthalic anhydride, maleic anhydride, malonic anhydride or trimellitic anhydride, preferably trimellitic anhydride.
Reaction of the polyanhydride compound of component A2 with the oligomer of component A1 opens the anhydride groups, and bonding to the oligomers of component A1 takes place by way of in each case one of the carboxyl groups of each anhydride function. In this way there are carboxyl groups within the chain of the polyesters. It is therefore possible to obtain polyesters whose chain contains free carboxyl groups which are capable of reaction. By using monoanhydrides of component A3 in the condensation of components A1, A2 and A3 it is possible to adjust the molecular weight, and thus the softening point and viscosity, of the resulting polyesters.

Preferably, the polyesters of component A have a degree of condensation such that they are in liquid form at room temperature (25°C). At 25°C they preferably have a viscosity of not more than 100,000 mPas, preferably not more than 20,000 mPas and, with particular preference, 5000 mPas.

In order to ensure that the chain extension does not excessively increase the molecular weight and thus the viscosity of the polyesters, it is preferred to react only some of the hydroxyl and/or amino groups that are present in component A1 with dianhydrides. If a greater increase in the number of carboxyl groups in the molecule is required, it is possible in accordance with the invention to obtain carboxyl groups on the remaining terminal hydroxyl groups by reactions with monoanhydrides of polycarboxylic acids as component A3.

By selecting appropriate proportions of the components A2 and A3 to A1 it is possible, in addition, to determine whether terminal carboxyl groups or hydroxyl groups and/or amino groups are present. The molar ratio of the functional groups in A2 and A3 to functional groups in A1 is preferably set such that it is predominantly or exclusively terminal carboxyl groups and/or anhydride groups which are present. The carboxyl groups in the polymer main chain, and possibly present as end groups, are highly suitable functional groups for crosslinking with the crosslinkers of component B that are employed in accordance with the invention. In this
case the free carboxyl groups present may be partially or completely neutralized with bases. Neutralization increases the water-solubility of the compounds employed. Hence it is also possible, if desired, to prepare aqueous binder formulations.

In order to prepare component A, components A1, A2 and, if present, A3 are reacted preferably under conditions in which acid anhydride groups present, but essentially no free carboxyl groups, are reacted. For this purpose, the appropriate components are heated together, for example, at from 60 to 140°C, preferably from 60 to 100°C and, in particular, from 60 to 80°C. The reactions in this case can also be accelerated by means of known esterification catalysts, such as tertiary amines or tin compounds. Such catalysts are often used for oligoester and polyester condensation as well and are therefore present in any case in the reaction mixtures. The amount of component A2 co-reacted determines the number of chain linkages and thus the ultimate molecular weight of the polyesters A. Through the selection of the co-reacted component A2 it is possible to determine the arrangement of the carboxyl groups in the chain.

The invention also relates to these polyesters of component A, to the process described for their preparation and their use in the printing-ink or coatings binders, as to coating materials and printing inks as described herein.

Component B

All compounds suitable for crosslinking with component A can be employed as component B. These are preferably amino resins, highly methylolated and highly etherified melamines, benzoguanamines, polyfunctional epoxides, polyfunctional blocked or nonblocked isocyanates, or mixtures thereof.
The nature of the crosslinker of component B may depend on the nature of the functional groups which are still present in the polyester of component A. This may also influence the properties of the novel low-solvent or solvent-free printing-ink or coatings binders. For polyesters of component A having free hydroxyl groups, polyisocyanates for two-component applications which cure even at room temperature are suitable. For single-component coating materials which are stable on storage and can be crosslinked by heating, blocked isocyanates are particularly suitable.

For predominantly carboxyl-functional polyesters of component A, polyfunctional epoxy resins are suitable crosslinkers for formulating coating materials of limited storage life. For the preferred utility in stoving enamels, for example for packaging made from metallic materials, the preferred crosslinkers of component B are highly methylolated and highly etherified ureas, melamines and benzoguanamines. Examples of appropriate commercial products are those from the product lines Cymel® from American Cyanamid, Luwipal® and Plastopal® from BASF AG, or hexamethylolmelamine hexamethyl ether (HMM), which is marketed by various manufacturers.

Crosslinkers of component B, such as epoxy resins or isocyanates, which enter into a defined chemical reaction are judiciously employed in chemically equivalent proportions to the functional groups of components A. Crosslinkers with a less specific action, such as HMM, are employed in proportions which should be determined empirically relative to the polyester of component A that is to be crosslinked. In general, these proportions are from 2 to 60% by weight of component B based on component A. It is also technically logical to employ mixtures of the abovementioned crosslinkers of component B in order to direct particular properties of the coatings.
It is also possible in accordance with the invention to use mixtures of polyesters of component A having different functionality with mixtures of the abovementioned crosslinkers of component B, in which case the different functionalities respond separately. This produces interpenetrating networks which may lead to coatings having very good properties. Examples of such mixed printing-ink or coatings binders are mixtures of oligomeric precursors of the polyesters A, which have undergone little or no reaction with anhydrides and therefore still have a high proportion of hydroxyl groups, with compounds of a kind in which the hydroxyl groups have very largely been converted to carboxyl groups using the abovementioned anhydrides. Crosslinkers for these mixtures are then, for example, blocked polyisocyanates in a mixture with crosslinkers of the HMM type. Owing to the differences in reactivity, stoving forms interpenetrating networks of predominantly urethane-crosslinked hydroxy polyesters and of predominantly HMM-crosslinked carboxy polyesters.

Component C

Suitable solvents as component C are all solvents which do not interact with but are capable of dissolving components A and B. Furthermore, the carboxyl-modified components A, after (partial) neutralization, are highly compatible with water, so that water is a suitable solvent as well.

Preparing the printing-ink or coatings binders

The printing-ink or coatings binders described above are prepared by reacting components A1, A12 and, if present, A13 to give component A1 and then reacting A1, A2 and, if present, A3 to give component A, followed by mixing component A and B, followed if appropriate by at least partial neutralization of free carboxyl groups with bases. components A11, A12, A13, A1, A2, A3, A and B being as defined above and the reaction of A1, A2 and, if present, A3 being conducted preferably under conditions in which
acid anhydride groups present, but essentially no free carboxyl groups, are reacted. Appropriate reaction conditions have been given above. The starting materials for the reaction can be processed without solvent or in a solvent. In each reaction step it is possible for all the starting materials to be introduced together as a mixture and then reacted. Alternatively, they can be metered individually into a reaction mixture. Appropriate methods are known to the skilled worker.

The carboxyl groups present can be neutralized preferably with amines. By neutralization it is possible to increase the solubility or dispersibility of the printing-ink or coatings binders in water.

The above-described printing-ink or coatings binders can be employed without solvent or in low-solvent mixtures. Low-solvent mixtures are those having a solvent content of from 1 to 40%, preferably from 5 to 10%, by weight, based on the overall printing-ink or coatings binder. The solvent content is preferably very low; in particular, no solvent is used. By this means it is possible very greatly to reduce, or, respectively, to avoid, emissions in the course of processing and curing the printing-ink or coatings binders without impairing the processing properties and the characteristics of the resulting coatings or prints. The coating compositions obtained in accordance with the invention are, consequently, low in or free from solvent, produce an extremely low level of emissions, and can be cured, for example, by stoving or designed so as to be self-curing at room temperature.

The novel printing-ink or coatings binders described above can be incorporated into coating materials or printing inks. Novel coating materials or printing inks comprise, as binder, mixtures of

a: component A as described above and
b: component B as described above
and optionally

c: component C as described above, and also

d: customary additives as component D, and

e: from 0 to 70% by weight of water as component E, based on the sum of components A, B, D and, if used, C.

Component D

Examples of customary additives as component D are dyes, fillers and/or color pigments, and also fibrous, matting or gloss-enhancing additives. Further additives are auxiliaries, such as catalysts for crosslinking, surfactants, flow promoters, viscosity regulators, silicone additives, additives for improving the lubricity (mobility) and abrasion, synthetic and natural waxes, and other auxiliaries.

Component E

Water as the diluent of component E serves to disperse the other components, and these aqueous dispersions can be used as coating compositions. In order to obtain aqueous dispersions the novel printing-ink and coatings binders are preferably neutralized, at least partially, and are employed alone or in conjunction with a solvent.

The invention also relates to the use of the above-described printing-ink or coatings binders, or coating materials and printing inks, for coating, printing and/or impregnating substrates or shaped articles, especially metallic vessels, packaging or parts thereof.
The coatings obtained from the novel printing-ink or coatings binders and, respectively, from the novel printing inks or coating materials are pasteurizable and sterilizable. They can also be overprinted or overcoated with excellent intercoat adhesion. In addition, they adhere so firmly that the substrates can be deformed without the coating becoming detached. They are used in particular for coating and/or impregnating two-dimensional or multidimensional, compact, porous, fibrous or particulate substrates, especially of wood, wood materials, metals, glass, including glass fibers, or mineral fibers.

A preferred use is in the coating and/or printing of metal packaging, especially of 2-, 3- or multi-part cans for foodstuffs and nonfoods, beverage cans, jar closures, other lids and crown corks made from metallic materials, such as aluminum or tin-plated, zinc-plated or otherwise coated iron or steel.

Known application techniques in this context are wet offset, dry offset, roller application, application with gravure cylinders, rubber rolls or rubber blankets, sponge printing, pad printing, knife coating, dipping, curtain coating and spraying directly onto the substrate or onto precoated substrates. In the case of printing inks overcoating with clear varnish is also possible.

Thermal curing can be carried out with infrared radiation, in stoving ovens or in hot-air tunnels.

The invention is illustrated in more detail below by means of examples.

**Example 1**

Oligoester with terminal hydroxyl groups
730.8 g of adipic acid (5 mol), 416.7 g of neopentyl glycol (4 mol) and 472.8 g of hexanediol (4 mol) were heated to 200°C in 7 hours under a gentle stream of nitrogen in a stirred flask with distillation device. Cooling gave a liquid, slightly yellowish resin having an acid number of 25 mg of KOH/g and an OH number of 197.3 mg of KOH/g. The resin had a viscosity of 910 mPas at 25°C and virtually Newtonian flow behavior.

Example 2

Carboxyl-containing binder

500 g of the oligoester from Example 1 were mixed at room temperature with 80 g of benzophenonetetracarboxylic dianhydride in a stirred flask and the mixture was then heated at 130°C for 2 hours. The mixture was subsequently cooled to 60°C. 96 g of trimellitic anhydride were added, and heating was continued at 130°C for 2 hours. This gave a yellowish, liquid resin having an acid number of 94 mg of KOH/g. The resin had a viscosity of 9779 mPas at 25°C. Then 80 g of melamine-formaldehyde resin etherified with butanol and/or methanol (for example Luwipal® 044 from BASF AG) were stirred in; the mixture had a viscosity of 7420 mPas at 26°C.

Example 3

Trimellitic ester dianhydride/anhydride mixture

In a stirred flask, 384.0 g of trimellitic anhydride (2 mol) were melted at about 170°C. After heating to 180°C, a mixture of 35.6 g of 1,6-hexanediol (0.30 mol) and 55.8 g of ethylene glycol (0.90 mol) was added dropwise over the course of 20 minutes. The mixture was then held for 2 hours at 190°C and then distilled at a pressure of about 15 mbar until, after about 1 hour, no more condensate was obtained. The residue was then cooled to 150°C, and 168.2 g of methylhexahydronaphthalic anhydride (1 mol)
were stirred in. The resulting mass was cast as a melt and cooled to form a solid, resinous mass.

Example 4

Carboxyl-containing binder

In a stirred flask, 500 g of oligoester from Example 1 were mixed at room temperature with 95 g of anhydride mixture from Example 3 and then this mixture was heated at 130°C for 2 hours. It was then cooled to 60°C, and 96 g of trimellitic anhydride were introduced. The mixture was then heated at 130°C for 2 hours. This gave a yellowish, liquid resin having an acid number of 82 mg of KOH/g. The resin had a viscosity of 74 mPas at 25°C. Then 80 g of Luwipal® 044 from BASF AG were stirred in, after which the mixture had a viscosity of 5326 mPas at 26°C.

Crosslinkability

The binders from Examples 2 and 4 were applied with a doctor blade having a gap height of 25 μm onto bright aluminum panels and the coated panels were stoved at 160°C for 45 minutes in a convection oven. Cooling gave smooth, glossy films which could be rubbed 50 times with an acetone-soaked cotton pad without showing any traces of attack.
20

Claims:

1. A low-solvent or solvent-free printing-ink or coatings binder comprising

   a: from 30 to 98% by weight of polyesters, as component A, obtainable by reacting

   a1: hydroxyl- and/or amino-terminated oligomers, as component A1, which are built up from

   a11: at least one polyfunctional carboxylic acid as component A11,
   a12: at least one polyfunctional hydroxy compound and/or amino compound as component A12.

   and optionally
   a13: at least one monofunctional hydroxy compound and/or amino compound and/or monocarboxylic acid as component A13.

   component A12 being employed in an excess of equivalents relative to A11, so that hydroxyl- and/or amino-terminated oligomers are formed even in the case of complete condensation,

   a2: at least one polyanhydride compound having at least two carboxylic anhydride groups, as component A2.

   and optionally

   a3: at least one monoanhydride of a polycarboxylic acid, as component A3,
b: from 70 to 2% by weight of crosslinker for crosslinking the polyesters of component A, as component B.

it being possible for free carboxyl groups present in component A and possibly B to be at least partially neutralized with bases, and

c: from 0 to 30% by weight, based on the sum of the amounts of components A and B, of at least one solvent, as component C.

2. A binder as claimed in claim 1, wherein dianhydrides of aromatic or partial aromatic tetracarboxylic acids are employed as component A.

3. A binder as claimed in claim 2, wherein compounds of the formula (I)

\[
\begin{align*}
\text{C} & \xrightarrow{X} \text{A} & \xrightarrow{X} \text{C} \\
\text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O}
\end{align*}
\]

where

A is a C_{2-20} radical which can contain aromatic, aliphatic and/or cycloaliphatic radicals, O, NR^1, S and/or SO_{2} in the chain or can be substituted by one or more of the organic radicals or halogen atoms,

X is O, NR^2 or S, and

R^1 and R^2 independently are H, C_{1-5}-alkyl, C_{6-12}-aryl, C_{7-13}-aralkyl or C_{7-13}-alkaryl
are employed as component A2.

4. A binder as claimed in claim 2, wherein compounds of the formula

(II)

where

\[ B = \cdot \text{CO} - , \text{a single bond, } \cdot \text{O} - , \cdot \text{S} - , \cdot \text{SO}_2 - , \cdot \text{O-Ph-O} - , \cdot \text{C(CH}_2)_2 - , \cdot \text{CH}_2 - \]

or \[ \cdot \text{CO-NH} - \]

are employed as component A2.

5. A binder as claimed in any of claims 1 to 4, wherein trimellitic anhydride is employed as component A3.

6. A binder as claimed in any of claims 1 to 5, wherein the components A1, A2 and, if used, A3 are reacted under conditions in which acid anhydride groups present, but essentially no free carboxyl groups, are reacted.

7. A binder as claimed in any of claims 1 to 6, wherein amino resins, highly methylolated and highly etherified melamines and/or benzoguanamines, polyfunctional epoxides, polyfunctional blocked or nonblocked isocyanates, or mixtures thereof, alone or together with other crosslinkers, are employed as component B.
8. A process for preparing a printing-ink or coatings binder as claimed in any of claims 1 to 7 by reacting components A11, A12 and, if used, A13 to give component A1 and then reacting components A1, A2 and, if used, A3 to give component A, followed by mixing components A, B and, if used, C, followed if desired by at least partial neutralization of free carboxyl groups with bases, the reaction of A1, A2 and, if used, A3 preferably taking place under conditions in which acid anhydride groups present, but essentially no free carboxyl groups, are reacted.

9. A coating material or printing ink comprising as binder, mixtures of
   a: component A as defined in any of claims 1 to 6,
   b: component B as defined in claim 1 or 7
   and optionally
   c: component C as defined in claim 1, and also
   d: customary additives as component D, and
   e: from 0 to 70% by weight of water as component E, based on the
   sum of the amounts of components A, B, D and, if used, C.

10. The use of a printing-ink or coatings binder as claimed in any of claims 1 to 7 or of a coating material or printing ink as claimed in claim 9 for coating, printing and/or impregnating substrates or shaped articles, especially metallic vessels, packaging or parts thereof.

11. A polyester as defined as component A in any of claims 1 to 6.

12. A process for preparing a polyester as claimed in claim 11 by reacting components A11, A12 and, if used, A13 to give component A1 and then reacting components A1, A2 and, if used, A3 to give component
A, the reaction of A1, A2 and, if used, A3 preferably taking place under conditions in which acid anhydride groups present, but essentially no free carboxyl groups, are reacted.

13. The use of a polyester as claimed in claim 11 for preparing low-solvent or solvent-free printing-ink or coatings binders, coating materials or printing inks.
**INTERNATIONAL SEARCH REPORT**

A. CLASSIFICATION OF SUBJECT MATTER

| IPC  | C09D167/00 | C09D11/10 | C09D177/12 |

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

| IPC  | C09D | C08G |

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

Electronic data base consulted during the international search (name of data base and, where practical, search terms used):

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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Further documents are listed in the continuation of box C.

| X        | Patent family members are listed in annex. |

* Special categories of cited documents:

*A* document defining the general state of the art which is not considered to be of particular relevance

*E* earlier document but published on or after the international filing date

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*Z* document member of the same patent family

Date of the actual completion of the international search: 16 July 1998

Date of mailing of the international search report: 27/07/1998

Name and mailing address of the ISA

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Authorized officer

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