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(71) Demandeur/Applicant: BAYER AKTIENGESELLSCHAFT, DE
(72) Inventeurs/Inventors: HAUSSTATTER, BERND, DE; MAZANEK, JAN, DE; SCHMALSTIEG, LUTZ, DE; GERTZMANN, ROLF, DE
(74) Agent: SWABEY OGILVY RENAULT

(54) Titre/Title: LIANTS D'EMAILS ISOLANTS A STRUCTURE D'UREE ET/OU D'HYDANTOINE
ELECTRICAL INSULATING ENAMEL BINDERS HAVING A UREA AND/OR HYDANTOIN STRUCTURE

(57) Abrégé/Abstract:
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Abstract

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The present invention relates to novel binders for electrical insulating enamels, the resulting enamels being distinguished by high temperature stability and good solderability.

The electrical and electronics industry today requires large amounts of coated wires for the production of motors, transformers, picture tubes and other products. Since the design of modern machines increasingly demands smaller motors, coils, transformers etc., and they work at a higher temperature than their larger equivalent, increased demands are being made of the temperature stability of the wire coatings. In the present application, the temperature stability is defined by the softening temperature of the coating. In many applications, the products are also required to be quickly solderable in order to connect the ends of the coated wires rapidly and simply to other components in an electrically conducting manner.

The electrical insulating enamel coating compositions conventionally used today include conventional coatings having high temperature stability in which polyhydantoins (e.g. FR-A 1 484 694, DE-A 246020), polyimides, polyamide imides (e.g. DE-A 3 544 548, DE-A 3 714 033, DE-A 3 817 614) or polyester amide imides (e.g. US-A 3 652 471, US-A 4 997 891, DE-A 3 249 497) form the main binder component. Wires coated with such products cannot be soldered below a temperature of from 400 to 450°C.

By contrast, electrical insulating enamels based on polyurethane permit rapid solderability at comparatively low temperatures. The binders in the wire enamels used in such cases are based on combinations of polyester polyols and phenol or alkanol-blocked polyisocyanates (DE-A 1 170 096 or DE-A 2 626 175). An improvement in the solderability can be achieved by combining blocked polyisocyanates with hydroxy-functional oligourethanes, e.g., DE-A-1 644 794.
In S. Darling, "International Wire Standards-Progress Towards Harmonization" in Proceedings 19th EEI Conference, Chicago 25th to 28th Sept. 1989, p. 56, polyester imides having a temperature index of 180°C are described as being solderable, but solderability is likewise only present at temperatures above 400°C.

Polyester imides having a high hydroxyl group content, in combination with heat-resistant blocked polyisocyanates, are solderable at 370°C, but they exhibit markedly deteriorating properties in respect of the tan δ break point and the softening temperature as compared with conventional polyester imides. Amide-imide-polyurethane combinations, which are described in EP-A 365 877, also have similar disadvantages. EP-A 752 434 describes raising the softening temperature of solderable wires by introduction of amide/imide-group containing blocked polyisocyanates. Although a marked improvement in solderability is achieved thereby as compared with US-A 4 997 891, the softening temperature is not improved.

From EP-A 231 509 there are known polyisocyanates containing carbodiimide and/or uretonimine groups and their use in wire enamelling. Depending on the reaction partner, such polyisocyanates are suitable for the production of solderable (Example 1 of EP-A 231 509) or, alternatively, heat-resistant enameled wires (Example 3 of EP-A 231 509).

According to the teaching of EP-A 287 947, heat-resistant electrical insulating enamels are obtained using unsaturated carboxylic acids in combination with polyisocyanates containing carbodiimide and/or uretonimine groups. If in the production of the wire enamel having hydantoin structures there is used an isocyanurate-containing compound (EP-A 287 947 Example 3), then there is obtained a wire enamel that is solderable at 420°C and has a softening temperature of 250°C; if the mixture contains no further OH components other than the OH-
containing blocking agents, then non-solderable products having softening temperatures $> 300^\circ \text{C}$ are obtained (EP-A 287 947 Example 2).

The use of $N,N',N''$-tris-(2-hydroxyethyl)-isocyanurate as an additive for polyurethane-based wire enamels also leads to heat-resistant enamelled wires (DE-A 3 133 571).

US-A 5,254,659 describes the production of heat-resistant, solderable wire enamels from polyimides and imide-modified polyurethanes. Owing to the low solids content of the binders and to the solvents, which are unconventional in the wire enamels industry and, moreover, are comparatively expensive, such products are definitely used only in exceptional cases and for the coating of thin wires.

It may be stated in summary that the teaching of the prior-known prior art amounts either to the production of electrical insulating enamels having a high level of heat resistance ($> 270^\circ \text{C}$) that are not solderable or can be soldered only very slowly at $390^\circ \text{C}$, or to the production of electrical insulating enamels that are rapidly solderable at $390^\circ \text{C}$ but have a level of heat resistance of only $\leq 270^\circ \text{C}$.

The object of the invention was, therefore, to provide a coating composition for heat-resistant substrates, especially for the wire-enamelling of wires, that combines both advantages - heat resistance $> 270^\circ \text{C}$ on the one hand and improved solderability at a temperature of $390^\circ \text{C}$ on the other hand.

It has been possible to achieve that object by means of the electrical insulating enamel binders according to the invention that are described in greater detail below. The invention is based on the surprising finding that, by using hydroxy-functional compounds containing particular urea and/or hydantoin groups, it is possible to produce electrical insulating enamels that are solderable at temperatures of $< 400^\circ \text{C}$ in spite of their excellent temperature stability.
Accordingly, the invention provides binders for electrical insulating enamels consisting of:

5   A) at least one hydroxy- and/or amino-functional polyurethane containing urea and/or hydantoin groups,
B) at least one blocked isocyanate component containing ester and/or imide and/or amide and/or urethane groups,
C) organic solvents, and
D) optionally further auxiliary substances and additives,

characterised in that the polyurethane component A) is prepared by reacting

a) from 15 to 40 wt.% of an organic polyisocyanate or of a mixture of organic polyisocyanates with
b) from 5 to 20 wt.% of at least one aspartic acid ester and
c) from 5 to 50 wt.% of a polyhydroxy compound having a molar weight from 62 to 3000 g/mol. in
d) from 25 to 50 wt.% of a solvent or of a solvent mixture.

From EP-A 743 333 there are known hydroxy-functional polyurethane prepolymer having a hydantoin or urea structure, such as are also to be used in principle as component A) in the wire enamel binders according to the invention. According to that teaching, those compounds are distinguished by improved thermal stability and are suitable especially as binders for the coating of sheet steel. US-A 3,549,599 describes the preparation of polyhydantoins from aspartic acid esters, as well as the high temperature stability of the products obtained therewith. Even in conjunction with other publications, the person skilled in the art will find in that teaching no indication as regards either the production of solderable wire enamel binders having
high temperature stability, or the use of those substances in the production of solderable wire enamel binders.

For the preparation of the hydroxy- and/or amino-functional polyurethanes A) to be used according to the invention there are suitable as starting polyisocyanates a) aromatic, aliphatic or cycloaliphatic polyisocyanates, preferably polyisocyanates having a uniform molecular weight or an average molecular weight in the mean of from 140 to 500 with an average NCO functionality in the statistical mean of not more than 2.6.

Such polyisocyanates are, for example, 1,4-phenylene diisocyanate, 2,4- and 2,6-diisocyanatotoluene (TDI) as well as any desired mixtures of those isomers, 4,4', 2,4'- and 2,2'-diisocyanatodiphenylmethane (MDI) or any desired mixtures of those isomers or mixtures of those isomers with their higher homologues, as are obtained in a manner known per se by phosgenation of aniline/formaldehyde condensation products, 1,5-naphthylene diisocyanate, 1,4-butane diisocyanate, 2-methylpentane 1,5-diisocyanate, 1,5-hexane diisocyanate, 1,6-hexane diisocyanate (HDI), 1,3- and 1,4-cyclohexane diisocyanate and any desired mixtures of those isomers, 2,4- and 2,6-diisocyanato-1-methylcyclohexane and any desired mixtures of those isomers, 3,5,5-trimethyl-3-isocyanatomethyl cyclohexaneisocyanate (IPDI), and dicyclohexylmethane 2,4'- and 4,4'-diisocyanate and any desired mixtures of those diisocyanates.

There are preferably used as the starting polyisocyanates a) those having aromatically bonded isocyanate groups having an average NCO functionality in the statistical mean of from 2 to 2.2 and an average molecular weight optionally in the statistical mean of from 174 to 300.

Diisocyanates that are most particularly preferably to be used are 2,4-diisocyanatotoluene and 2,6-diisocyanatotoluene, the technical mixtures consisting of those
isomers, and 4,4'-, 2,4'- and 2,2'-diisocyanatodiphenylmethane or any desired mixtures of those isomers or mixtures of those isomers with their higher homologues, as are obtained in a manner known *per se* by phosgenation of aniline/formaldehyde condensation products, or alternatively any desired mixtures of the aromatic polyisocyanates mentioned here.

For the preparation of the hydroxy- and/or amino-functional polyurethanes A) that are to be used according to the invention there are suitable as component b) aspartic acid esters of the general structural formula (a)

\[
\begin{align*}
X & \quad \text{NH} \quad \text{CH} \quad \text{COOR}^1 \\
& \quad \text{CH}_2 \quad \text{COOR}^2 \\
& \quad \text{m}
\end{align*}
\]

(a),

which are obtained according to the teaching of EP-A 403 921, DE-A 1 670 812 and DE-A 2 158 945 in a known manner by reacting a component of formula (i) containing primary amine groups

\[
X \quad [\text{NH}_2]_m
\]

(i)

with fumaric acid esters and/or maleic acid esters of formula (ii)

\[
\begin{align*}
\text{R}^1 & \quad \text{O} \quad \text{C} = \text{O} \\
& \quad \text{O} \quad \text{C} = \text{O} \\
& \quad \text{R}^2
\end{align*}
\]

(ii)

wherein
X represents an m-valent organic radical optionally containing one or more hetero atoms, as can be obtained by removing the primary amino group or groups from a corresponding mono- or poly-amine containing (cyclo-)aliphatically or araliphatically bonded primary amino groups and having a molecular weight in the range from 60 to 6000, which radical may contain further functional groups that are reactive towards isocyanate groups and/or inert at temperatures up to 100°C.

Suitable fumaric or maleic acid diesters of formula (ii) are compounds in which $R^1$ and $R^2$ represent organic radicals having from 1 to 9 carbon atoms. Preference is given to radicals $R^1$ and $R^2$ having from 1 to 4 carbon atoms, it also being possible for $R^1$ and $R^2$ to represent identical radicals.

As amines (i) there are used difunctional amines ($m = 2$) or mixtures of difunctional amines and amines having a higher functionality ($m = 2$ and $m > 2$), so that the mean functionality of the aspartic acid esters is $\geq 2$. There are suitable preferably mixtures of difunctional ($m = 2$) and trifunctional ($m = 3$) amines, the equivalence ratio of difunctional amines to trifunctional amines being from 1:2 to 5:1. There are particularly preferably suitable mixtures in which the equivalence ratio of difunctional amines to trifunctional amines is from 1:1.5 to 3:1.

Examples of suitable difunctional amines (i) are ethylenediamine, 1,2-diaminopropane, 1,4-diaminobutane, 2,5-diamino-2,5-dimethylhexane, 1,5-diamino-2-methylpentane (Dytek® A from DuPont), 1,6-diaminohexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, 1,12-diaminododecane, 1-amino-3,3,5-trimethyl-5-aminomethylene cyclohexane (IPDA), 2,4- and/or 2,6-hexahydrotoluenediamine (H₆TDA), isopropyl-2,4- and/or -2,6-diaminocyclohexane, 1,3-bis-(aminomethyl)-cyclohexane, 2,4'- and/or 4,4'-diamino-dicyclohexylmethane, 3,3'-dimethyl-4,4'-diamino-dicyclohexylmethane (Laromin® C 260 from BASF), the isomeric diaminodicyclohexylmethanes having a methyl group as substituent at the
nucleus (= C-monomethyl-diaminodicyclohexylmethanes), 3(4)-aminomethyl-1-methylcyclohexylamine (AMCA) and 1,3-bis-(aminomethyl)-benzene.

Examples of amines having a functionality of three or more are 4-aminomethyl-1,8-octanediamine; 2,2',2"-triaminotriethylamine, 1,3,5-tris-(aminomethyl)-2,4,6-triethylbenzene, tris-1,1,1-aminooethylethane, 1,2,3-triaminopropane, tris-(3-amino-propyl)-amine and N,N,N',N'-tetrakis-(2-aminoethyl)-ethylenediamine.

In principle, there are suitable as amines (i) also mixtures of monoamines (m = 1) or diamines (m = 2) containing further groups that are reactive towards isocyanates at from 20 to 200°C, with amines having a higher functionality (m > 2), so that the mean functionality of the aspartic acid esters, taking into account all groups that are reactive towards isocyanates in the temperature range from 20 to 200°C, is ≥ 2 and < 3.5.

Examples of suitable hydroxy-functional amines (i) are 2-amino-ethanol, aminopropanols, 3-amino-1,2-propanediol, aminobutanol and 1,3-diamino-2-propanol.

In principle, it is also possible to use low molecular weight polyether polyamines having aliphatically bonded primary amino groups, as are marketed, for example, by Huntsman under the name Jeffamin®.

The preparation of the aspartic acid esters b) may be effected either in solution or without a solvent. In both cases, an equimolar reaction of the amine with the fumaric or maleic acid diester is preferably carried out. In order to vary application-related properties of the wire coatings in a targeted manner, the equivalence ratio of maleic or fumaric acid ester to amine i) may be varied from 1.2:1 to 1:2. In the case where mixtures of aspartic acid esters are used, the aspartic acid esters may be prepared separately or in one reaction vessel.
Suitable polyhydroxy compounds c) for the preparation of the hydroxy- and/or amino-functional polyurethanes A) to be used according to the invention are any desired araliphatic, aliphatic or cycloaliphatic polyhydroxy compounds, preferably polyhydroxy compounds having a uniform molecular weight or an average molecular weight in the mean of from 62 to 3000 with an average OH functionality in the statistical mean of not more than 3. There come into consideration as low molecular weight polyhydroxy compounds c) preferably diols and/or triols having a molecular weight in the range from 62 to 350 and, less preferably, also polyhydroxy compounds having molecular weights from 350 to 3000. Suitable polyhydroxy compounds c) having a molecular weight in the range from 62 to 350 are, for example, ethylene glycol, propanediols, butanediols, hexanediols, di-, tri- or tetra-ethylene glycol, di-, tri- or tetra-propylene glycol, neopentyl glycol, 2-ethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-bis(hydroxymethyl)-cyclohexane, 2,2-bis(4-hydroxycyclohexyl)-propane, glycerol, hexanetriol and N,N',N''-tris-(2-hydroxyethyl)-isocyanurate (THEIC). Higher molecular weight polyhydroxy compounds c) are, for example, the known polyhydroxy polyesters, as are obtained from dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid or adipic acid with excess polyols of the above-mentioned type. It is also possible to use as higher molecular weight polyols c) polyhydroxy polyethers known per se, as are obtainable by alkoxylation of low molecular weight starter molecules.

Mixtures of the above-mentioned hydroxy-functional compounds may also be used as the polyhydroxy compound c).

There are used as solvents d) the solvents conventionally employed in wire enamelling, in order to adjust the viscosity of the products to a level necessary for processing. Particularly suitable as solvents are phenols, cresols, xylenols and their technical isomeric mixtures, benzyl alcohol, 2-methoxypropyl acetate, butyl acetate, N-methylpyrrolidone, hydrocarbons or hydrocarbon mixtures that are liquid at room
temperature, as well as mixtures of the mentioned solvents. Solvent mixtures of the mentioned solvents are preferred.

According to a preferred embodiment for the preparation of the hydroxy- and/or amino-functional polyurethanes A), the polyisocyanate a) is diluted with the solvent or the solvent mixture d) in a weight ratio of from 3:1 to 1:3, preferably from 1.5:1 to 1:1.5. The isocyanate-reactive components b) and c) are mixed together in a weight ratio of from 1:10 to 4:1, preferably from 1:2 to 2:1, and diluted with the solvent or solvent mixture d) in a weight ratio of from 1:10 to 2:1, preferably from 1:1.5 to 1.5:1. The mixture containing the isocyanate-reactive components b) and c) is adjusted to a temperature of from 10 to 150°C, preferably from 20 to 80°C. The solution containing component a) is added to that mixture. The reaction mixture is stirred at a temperature of from 10 to 150°C, preferably from 20 to 80°C, until no further free isocyanate groups can be detected.

The reaction mixture is then preferably stirred at from 80 to 120°C in order to induce or complete hydantoin formation and remove by distillation, optionally under reduced pressure, the alcohol separated during the reaction, or leave it in the reaction mixture.

In a further embodiment for the preparation of the hydroxy- and/or amino-functional polyurethanes A), the polyisocyanate a) is diluted with the solvent or the solvent mixture d) in a weight ratio of from 3:1 to 1:3, preferably from 1.5:1 to 1:1.5. The isocyanate-reactive components b) and c) are mixed together in a weight ratio of from 1:10 to 4:1, preferably from 1:2 to 2:1, and diluted with the solvent or solvent mixture d) in a weight ratio of from 1:10 to 2:1, preferably from 1:1.5 to 1.5:1. The mixture containing isocyanate-reactive components b) and c) is adjusted to a temperature of from 10 to 150°C, preferably from 20 to 100°C. That mixture is added to the solution containing component a). The reaction mixture is stirred at a
temperature of from 10 to 150°C, preferably from 20 to 100°C, until no further free isocyanate groups can be detected.

In further embodiments, it is also possible to use the whole of the solvent for diluting only individual components. A further embodiment for the preparation of the hydroxy- and/or amino-functional polyurethanes A) may consist, for example, in a two-stage reaction procedure, in which the polyisocyanate a) is first reacted with the aspartic acid ester or aspartic acid ester mixture b) before the polyhydroxy compounds c) are reacted with the remaining polyisocyanate a). A further embodiment may consist in first adding only the polyhydroxy-functional compounds c) to the polyisocyanate a) and adding the aspartic acid ester or the aspartic acid ester mixture b) to the isocyanate only once the first reaction is complete.

In order to accelerate the reaction of the NCO groups with compounds that are reactive towards NCO groups it is possible to use the catalysts known in polyurethane chemistry and described by way of example in Kunststoffhandbuch (eds. Becker/Braun), Vol. 7, Polyurethane, p. 92 ff, Carl Hanser Verlag, Munich Vienna 1983. The catalysts are optionally used in an amount of from 0.01 to 5.0 %, based on the polyisocyanates a).

The binders according to the invention for wire enamels are produced by mixing the hydroxy- and/or amino-functional polyurethanes A) at room temperature with blocked enamel polyisocyanates B), organic solvents C) and, optionally, auxiliary substances and additives D) known per se in the technology of wire enamel coating, the isocyanate-reactive component A) being used in such amounts that an equivalent ratio of hydroxy- and/or amino-functional groups of component A) to blocked isocyanate groups of component B) of from 1:2 to 1.5:1, preferably from 1:1.5 to 1.3:1, is maintained.
There may be used as the blocked enamel polyisocyanates B) the resins, known *per se* from the technology of wire enamelling, that have ester and/or amide and/or imide and/or urethane structures and contain blocked isocyanate terminal groups. There may preferably be used as component B) polyamide imides and/or polyimides having an amide and/or imide structure content of from 0.5 to 10 wt.% (calculated as -CO-N<, mol. wt. = 42). There may particularly preferably be used as component B) polyurethanes that have a urethane group content of from 2 to 20 wt.%, especially that have a urethane group content of from 4 to 15 wt.%, and that are terminated by blocked NCO groups.

There come into consideration as the solvent component C) all organic solvents, conventionally employed in the technology of enamels, that are inert towards isocyanate groups, such as, for example, ethyl acetate, butyl acetate, ethylene glycol monomethyl or monoethyl acetate, 1-methoxypropyl-2-acetate, 2-butanone, 4-methyl-2-pentanone, cyclohexanone, toluene, xylene, solvent naphtha or mixtures thereof. Also usable, but less preferred, are plasticisers such as, for example, those based on phosphoric acid, sulfonic acid or phthalic acid esters. In addition to the enamel solvents that are inert towards NCO groups, it is also possible, however, to use a proportion of solvents that are reactive towards NCO groups. There are suitable preferably monofunctional, aliphatic, cycloaliphatic, araliphatic alcohols or, alternatively, phenols such as, for example, isopropanol, n-butanol, n-octanol, 2-methoxyethanol, 2-ethoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, 1-methoxy-2-propanol, cycloalkonols such as benzyl alcohol, or phenols such as cresol, xylenol as well as their technical isomeric mixtures.

It is possible to use according to the invention as auxiliary substances and additives D) the catalysts, pigments and/or flow agents known *per se* from the technology of electrical insulating enamels.
The electrical insulating enamel binders according to the invention are stable to storage at room temperature or moderately elevated temperature (up to about 50°C) and, on heating to temperatures above 60°C, preferably from 100 to 500°C and especially from 180 to 400°C, react completely to form crosslinked plastics with simultaneous evaporation of any volatile constituents that may be present. The enamels are applied by the immersion, roller application, nozzle or suction felt processes known per se, application being followed by drying, that is to say hardening, of the enamel layers in conventional drying ovens in a temperature range from 100 to 500°C and especially from 180 to 400°C.

Of the properties of the electrical insulating enamel binders according to the invention, special mention is to be made of the good solderability and the high softening temperature and high heat-shock temperature of the resulting products as compared with conventional known products of the prior art. Because of the excellent electrical and mechanical properties of the binders according to the invention, the products are suitable also for the production of insulating fabrics or for the impregnation of electric motors.
Examples

Example 1
Preparation of an aspartic acid ester

53.6 g of 4-aminomethyl-1,8-octanediamine and 109.3 g of 2-methyl-1,5-pentanediamine are placed in a vessel, and 406.2 g of maleic acid dimethyl ester are added thereto, with stirring, so that a temperature of 50°C is not exceeded in the reaction mixture. Stirring is then continued for 20 hours at 60°C.

Example 2
Preparation of an enamel polyisocyanate A)

15 68.3 g of the aspartic acid ester of Example 1 are homogenised with 75.7 g of trimethylolpropane, 31.3 g of 1,3-butanediol, 36.9 g of diethylene glycol and 227.1 g of cresol and added dropwise to a mixture, heated to 80°C, of 242.0 g of 4,4′-MDI (Desmodur 44 M® from Bayer AG) dissolved in 227.1 g of MPA. The reaction temperature is maintained at a maximum of 120°C, taking into account the exothermicity, until the free NCO content is less than 0.5%. The calculated OH content is 2.9 %.

Example 3
Preparation of an enamel polyisocyanate A)

25 63.8 g of the aspartic acid ester of Example 1 is homogenised with 54.9 g of trimethylolpropane, 25.3 g of 1,3-butanediol, 29.8 g of diethylene glycol and 200.0 g of cresol and added dropwise to a mixture, heated to 80°C, of 226.1 g of 4,4′-MDI (Desmodur 44 M® from Bayer AG) dissolved in 200.0 g of MPA. The reaction
temperature is maintained at a maximum of 120°C, taking into account the exothermicity, until the free NCO content is less than 0.5 %. The calculated OH content is 2.9 %.

In the following Examples relating to the coating of copper wires, a horizontal wire enamelling installation from Aumann, Espelkamp, FRG, type FLK 240 having an oven length of 2.4 m (modified slightly for medium-diameter wires) was used. Copper wire having a diameter of 0.5 mm was enamelled by means of nozzle application in 7 passages at an oven temperature of 450°C/500°C at a rate of 12-18 m/min.

The reaction components used for the compounds (A) according to the invention containing Zerewitinoff atoms were cresol-blocked polyisocyanates (B 1 or B 2).

Component B 1 was obtained by the dropwise addition of a mixture of 375.2 g of trimethylolpropane, 1026.0 g of cresol, 155.4 g of n-butanol, 0.4 g of diazabicyclooctane and 8.1 g of dibutyltin dilaurate to 2500 g of 4,4'-MDI (Desmodur® 44 M from Bayer AG) at 80°C (blocked NCO content is 9.8 %).

There was used as component B 2 a commercially available blocked polyisocyanate (Desmodur® VP LS 2018) from Bayer (blocked NCO content is 9.5 %).

Example 4

Production of an electrical insulating enamel according to the invention

94.2 g of polyisocyanate C, which had been dissolved in 87.2 g of cresol and 87.1 g of xylene, were added to 131.5 g of the OH-functional enamel resin prepared according to Example 1.
A wire coated with that enamel is solderable at 390°C within 5 seconds, the tan δ break point is 180°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 280°C. The enamel film exhibits a high degree of flexibility: after 15% pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5% pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 5

Production of an electrical insulating enamel according to the invention

78.1 g of polyisocyanate B 2, which has been dissolved in 79.1 g of cresol and 79.0 g of xylene, are added to 163.8 g of the OH-functional enamel resin prepared according to Example 2.

A wire coated with that enamel is solderable at 390°C within 5 seconds, the tan δ break point is 173°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 280°C. The enamel film exhibits a high degree of flexibility: after 15% pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable without pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 6

Production of an electrical insulating enamel according to the invention

82.3 g of polyisocyanate B 1, which has been dissolved in 81.2 g of cresol and 81.1 g of xylene, are added to 155.4 g of the OH-functional enamel resin prepared according to Example 2.
A wire coated with that enamel is solderable at 390°C within 8 seconds, the tan δ break point is 179°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 290°C. The enamel film exhibits a high degree of flexibility: after 15 % pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5 % pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 7

Production of an electrical insulating enamel according to the invention

91.2 g of polyisocyanate B 1, which has been dissolved in 85.6 g of cresol and 85.6 g of xylene, are added to 137.7 g of the OH-functional enamel resin prepared according to Example 2.

A wire coated with that enamel is solderable at 390°C within 6 seconds, the tan δ break point is 179°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 290°C. The enamel film exhibits a high degree of flexibility: after 10 % pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5 % pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 8

Production of an electrical insulating enamel according to the invention

98.3 g of polyisocyanate B 1, which has been dissolved in 89.2 g of cresol and 89.1 g of xylene, are added to 123.4 g of the OH-functional enamel resin prepared according to Example 1.
A wire coated with that enamel is solderable at 390°C within 9 seconds, the tan δ break point is 184°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 290°C. The enamel film exhibits a high degree of flexibility: after 5 % pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5 % pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 9

Production of an electrical insulating enamel according to the invention

106.5 g of polyisocyanate B 1, which has been dissolved in 93.3 g of cresol and 93.1 g of xylene, are added to 107 g of the OH-functional enamel resin prepared according to Example 1.

A wire coated with that enamel is solderable at 390°C within 6 seconds, the tan δ break point is 191°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 300°C. The enamel film exhibits a high degree of flexibility: after 5 % pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5 % pre-extension on a 0.5 mm pin after 30 minutes at 200°C.

Example 10

Production of an electrical insulating enamel according to the invention

112.8 g of polyisocyanate B 1, which has been dissolved in 96.2 g of cresol and 96.2 g of xylene, are added to 94.4 g of the OH-functional enamel resin prepared according to Example 1.
A wire coated with that enamel is solderable at 390°C within 9 seconds, the tan δ break point is 190°C, the softening temperature according to IEC 851, Part 6, 4.1.2, is 290°C. The enamel film exhibits a high degree of flexibility: after 5 % pre-extension, the wire can be wound round a 0.5 mm cylindrical pin without the enamel film exhibiting cracks. The heat shock is acceptable with 5 % pre-extension on a 0.5 mm pin after 30 minutes at 200°C.
Patent claims

1. Binder for electrical insulating enamels, consisting essentially of

   A) at least one hydroxy- and/or amino-functional polyurethane containing urea and/or hydantoin groups,
   B) at least one blocked isocyanate component containing ester and/or imide and/or amide and/or urethane groups,
   C) organic solvents, and
   D) optionally further auxiliary substances and additives,

   characterised in that the polyurethane component A) is prepared by reacting

   a) from 15 to 40 wt.% of an organic polyisocyanate or of a mixture of organic polyisocyanates with
   b) from 5 to 20 wt.% of at least one aspartic acid ester and
   c) from 5 to 50 wt.% of a polyhydroxy compound having a molar weight from 62 to 3000 g/mol. in
   d) from 25 to 50 wt.% of a solvent or of a solvent mixture.

2. Binder for electrical insulating enamels according to claim 1, characterised in that the polyisocyanate/polyisocyanate mixture a) used for preparing the hydroxy- and/or amino-functional polyurethane component A) containing urea and/or hydantoin groups contains aromatically bonded isocyanate groups having an average NCO functionality in the statistical mean of from 2 to 2.2 and an average molecular weight optionally in the statistical mean of from 174 to 300.

3. Binder for electrical insulating enamels according to claims 1 and 2, characterised in that the aspartic acid ester b) used for preparing the hydroxy-
and/or amino-functional polyurethane component A) contains difunctional amines and amines having a higher functionality in a ratio of from 1:2 to 5:1.

4. Binder for electrical insulating enamels according to claims 1 to 3, characterised in that the aspartic acid ester b) that is used contains difunctional amines and trifunctional amines in a ratio of from 1:1.5 to 3:1.

5. Binder for electrical insulating enamels according to claims 1 to 4, characterised in that the aspartic acid ester b) used for preparing the hydroxy-and/or amino-functional polyurethane component A) contains, other than the secondary amine groups, no further groups that are reactive towards isocyanates in the range from 10 to 150°C.

6. Binder for electrical insulating enamels according to claims 1 to 5, characterised in that the isocyanate-reactive aspartic acid esters b) and polyhydroxy compounds c) used for preparing the hydroxy- and/or amino-functional polyurethane component A) are used in a weight ratio of from 1:10 to 4:1.

7. Binder for electrical insulating enamels according to claims 1 to 6, characterised in that the isocyanate-reactive aspartic acid esters b) and polyhydroxy compounds c) used for preparing the hydroxy- and/or amino-functional polyurethane component A) are used in a weight ratio of from 1:2 to 2:1.

8. Binder for electrical insulating enamels according to claims 1 to 7, characterised in that the polyhydroxy compounds c) used for preparing the hydroxy- and/or amino-functional polyurethane component A) have molar weights of from 62 to 350.
9. Binder for electrical insulating enamels according to claims 1 to 8, characterised in that blocked isocyanates containing urethane groups are used as component B).

10. Use of hydroxy- and/or amino-functional polyurethanes containing urea and/or hydantoin groups according to claim 1 in the production of electrical insulating enamels.

11. Use of hydroxy- and/or amino-functional polyurethanes containing urea and/or hydantoin groups according to claim 10 in combination with polyurethanes containing blocked isocyanate groups in the production of electrical insulating enamels.

12. Enamels produced from binder mixtures according to claims 1 to 9.