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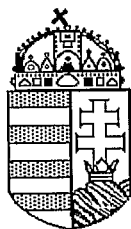Document type: Certified copy of priority document

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MAGYAR KÖZTÁRSASÁG

ELSŐBBSÉGI TANÚSÍTVÁNY

Ügyszám: P0700792

A Magyar Szabadalmi Hivatal tanúsítja, hogy

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Magyarországon

2007. 12. 07. napján   29238/07 iktatószám alatt,

Eljárás amin funkciós foszforsavamidok előállítására és azok alkalmazása epoxi gyantákhoz égésgátlóként és térhálósítóként

című találmányt jelentett be szabadalmazásra.

Az idefűzött másolat a bejelentéssel egyidejűleg benyújtott melléklettel mindenben megegyezik.

Budapest, 2008. év 12. hó 22. napján

A kiadmány hiteléül: Szabó Richárd osztályvezető

The Hungarian Patent Office certifies in this priority certificate that the said applicant(s) filed a patent application at the specified date under the indicated title, application number and registration number. The attached photocopy is a true copy of specification filed with the application.
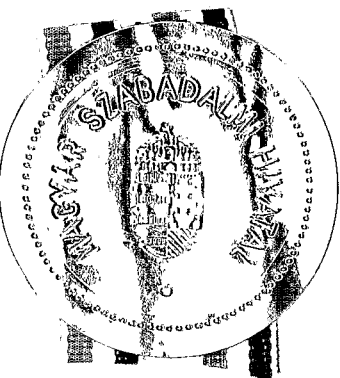
Process for the preparation of amine functional phosphoric amides and their use as flame retardant and curing agent for epoxy resins

Subject of the invention

The present invention relates to a novel improved process for preparing amine functional phosphoric amides, which are useful flame retardants and curing agents especially for epoxy resins. The inventive method offers a simple, cost-effective and environmentally friendly method using inexpensive starting materials.

Background of the invention

Epoxy resins have found use in various industrial applications in the last 50 years since they have been commercially available, due to their excellent characteristics as toughness, chemical, mechanical and electrical resistance, low shrinkage on cure and high adhesion to many substrates. They are widely used for surface coatings, castings, laminates, adhesives, composites, potting and painting materials, especially in application areas where their technical advantages balance their higher costs compared to other thermosetting polymers, e.g. electronic and electrical industry, transportation industry. The main deficiency of epoxy resins is their flammability. In order to meet application requirements their flame retardant properties have to be improved by maintaining other important characteristics as thermal and mechanical properties, and also considering environmental issues as risks for human life and environment, waste treatment and recycling.

The application of halogenated epoxy components as the diglycidyl ether of tetrabromobisphenol A is a highly effective method for the preparation of flame retarded epoxy resin systems, as according to description JP57092017, however the increasing focus on the health and environmental compatibility of flame retardants has resulted in a steady decline in the acceptance of halogen-containing products. Public perception of the environmental impact of combustion of certain halogenated flame retardants during incineration has become an issue in Europe because of the possible production of dibenzodioxins and dibenzofurans.

The sustainable development concept applied to this field implies that fire retardants should involve a low impact on health and environment during the entire life cycle including recycling and disposal. According to the new directives of the European Parliament (Directives on Waste Electrical and Electronic Equipment (WEEE) and on the Restriction of the Hazardous Substances in Electrical and Electronic Equipment (RoHS))

from July 2006 halogenated flame retardants containing polybrominated biphenyls and diphenylethers are banned.

Considering the above mentioned drawbacks substantial amount of research and development has been focused on the replacement of these halogen-containing flame retardants by halogen-free products.

As it is disclosed in the US Patent No. 6,130,282 effective flame retardancy can also be reached by the incorporation of metal hydroxides such as $Mg(OH)_2$ or $Al(OH)_3$. Their effect is based on the endothermic thermal decomposition and the cooling effect of the evolved water. However, for an appropriate flame retardant effect metal hydroxides need to be incorporated in large amounts as high as 30-40 weight%, which increases the viscosity of the epoxy resin and deteriorates the mechanical properties making impossible to use it in many application areas.

As an environmental alternative for the halogen-containing type flame retardants, organophosphorous compounds have been recognized and developed over a number of years and thus have found use as additives in a variety of polymeric materials. Many organophosphorous additives are of low molecular weight and are therefore somewhat volatile, causing their partial loss from the polymer during either high temperature processing by migration to the surface or in the early stages of combustion. Additionally, their transition into the gaseous phase may cause the smoke of the burning material to become loaded with toxic phosphorus-containing compounds. Clearly, there is a need to increase the permanence of the additive within the polymer matrix in order to maximize the fire retardancy and to reduce the evolution of toxic species.
The incorporation of the organophosphorus functionality within the polymeric structure may offer solution to this problem.

The US patent No. 3,981,832 discloses phosphorus-containing flame retardant additives, which are used in a mixture made of ammonium polyphosphate, pentaerythritol and melamine. Nevertheless it also has to be calculated with the disadvantages of solid additives in this case as increase in viscosity due to the large amount of flame retardant additive needed and therefore deterioration of mechanical properties.

The US patent No. 6,486,235 discloses aromatic phosphoric ester derivatives, which are also used for making epoxy resins flame retardant, but these additives also increase the

viscosity and in many cases they weaken the mechanical properties of the epoxy resin as well, moreover the small molecule additives tend to migrate from the polymer matrix.

There are several patents dealing with the application of phosphorus-containing reactive amine type flame retardants (e.g. CN1916049, DE19857697A1), which can be reactively incorporated into the epoxy resin matrix and do not show the above mentioned drawbacks of the additive type flame retardants as increase of the viscosity, migration from the polymer matrix and decrease of the mechanical properties.

However, the known syntheses of the latter phosphorus-containing reactive amine type flame retardants are complicated, multi-step processes applying expensive and/or hazardous halogen-containing phosphorylating agents as starting materials.

Such a process is described in the recent literature [A. Toldy, P. Anna, I. Csontos, A. Szabó and Gy. Marosi; Intrinsically flame retardant epoxy resin – Fire performance and background – Part I, Polymer Degradation and Stability, In Press, Corrected Proof, Available online 15 August 2007, http://dx.doi.org/10.1016/j.polymdegradstab.2007.04.017], where phosphorus containing trifunctional amines are synthesized by the reaction of phosphorus oxychloride and ethanolamine or ethylenediamine. The achieved yield of the reactions is 90 and 80%, respectively, however both syntheses are multistep, complex reactions, with long reaction times and using a halogen-containing, expensive fine chemical as starting material.

Mauerer discussed the synthesis of TAPP [bis(3-aminophenyl)-phenyl phosphate], which was based on a transesterification of triphenyl phosphate with 3-aminophenol. According to the author the reaction yields incomplete replacement of the bound phenol by the 3-aminophenol. Beside the main product TAPP, traces of 3-aminophenyldiphenyl phosphate and oligo-3-aminophenyl phosphates are obtained. This suggests that quantitative replacement of phosphates by amines cannot be awaited. [Polymer Degradation and Stability 88, 1 (2005), pp. 70-73.]

Object of the invention

As it comes from the above, there is continued demand on phosphorus-containing reactive amine type flame retardants or with other words for amine functional phosphoric amides and consequently novel and improved methods for their synthesis is also of great industrial importance. Thus the object of the present invention was to find a simple, short

and inexpensive synthesis for preparing different amine functional phosphoric amides based on orthophosphoric acid or esters thereof.

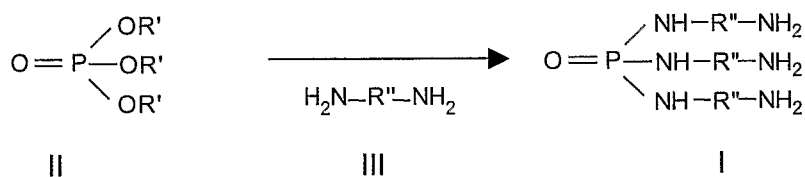## Short description of the invention

We came to the unexpected recognition that by transamidation of various esters of orthophosphoric acid by di- or polyamines useful amine functional phosphoric amides can be synthesized, which can be effectively used in epoxy resins as flame retardants and which neither influence negatively the viscosity of the epoxy resin mixture, nor do they weaken the mechanical properties of the cured resin.

Transamidation reactions are well known in peptide chemistry and generally mean the reaction between an amine and an ester or amide compound resulting in an amide. Nevertheless, there was no indication in the state of art that amine functional phosphoric amides can be prepared by a simple, cost effective reaction starting from orthophosphoric acid and di- or polyamines, the literature [O. Maurer, see above] rather suggested that by such reactions no complete replacement of the phosphate ester groups can be achieved.

The present invention also relates to the use of amine functional phosphoric amides prepared by the inventive process as curing agent and flame retardant in epoxy resins.

Detailed description of the invention

The invention relates to a process for the preparation of amine functional phosphoric amides according to general formula (I) which comprises reacting an orthophosphoric acid ester of general formula (II) with an amine of general formula (III) optionally in the presence of a catalyst

$$
\begin{array}{ccc}
\overset{\displaystyle /OR'}{O=P-OR'} & \xrightarrow{\qquad\qquad} & \overset{\displaystyle /NH-R''-NH_2}{O=P-NH-R''-NH_2} \\
\underset{\displaystyle \backslash OR'}{} & H_2N-R''-NH_2 & \underset{\displaystyle \backslash NH-R''-NH_2}{} \\
\text{II} & \text{III} & \text{I}
\end{array}
$$

wherein

R' is an optionally substituted straight or branched aliphatic group, which can be saturated or unsaturated, or an optionally substituted aromatic group,

R'' is a optionally substituted straight or branched aliphatic group, which can be saturated or unsaturated, or an optionally substituted aromatic group.

In the inventive process a phosphate ester of orthophosphoric acid of general formula (II) is transamidated by various diamine or polyamine compounds of general formula (II).

In the above reaction an alcohol of the general formula R'OH is produced from the starting ester, which can be evaporated from the mixture at the and of the reaction, optionally together with the solvent (if any) or with the remaining unreacted lower boiling point amine component.

Reactants

In the present specification phosphoric acid means orthophosphoric acid (H_3PO_4).

In the general formula (II) R' is an optionally substituted straight or branched C_1-C_{18} alkyl group, a C_3-C_6 cycloalkyl group or C_6-C_8 aryl group, preferably a C_1-C_8 alkyl group. The further preferred groups are the methyl, ethyl, propyl or butyl groups or the phenyl, benzyl, toluyl or xilyl groups.

As phosphate esters of general formula (II) not only symmetrically trisubstituted esters of orthosposphoric acid but mixed esters of thereof can be used as well. However, aliphatic esters such as trimethyl phosphate, triethyl phosphate or phosphate esthers of other alcohols with short carbon chain or their mixture and further aromatic phosphate esters such as triphenyl phosphate and cycloaliphatic phosphate esters can be used advantageously. It is also within the scope of the present invention if a mixture of different phosphate esters is transamidated by the inventive process.

In the context of the present invention aliphatic compounds mean acyclic or cyclic, saturated or unsaturated carbon compounds, excluding aromatic compounds.

The amine of general formula (III) can be generally a di- or a polyamine, wherein R" is an optionally substituted straight or branched aliphatic group, which can be saturated or unsaturated, or an optionally substituted aromatic group.
In a preferred embodiment R" is an optionally substituted straight or branched C_1-C_{18} alkylene group, a C_3-C_6 cycloalkylene group or C_6-C_8 arylene group.
In a further preferred embodiment R" is a C_1-C_8 alkylene group, preferably a C_1-C_6 alkylene group.

In a further preferred embodiment R" is selected from aromatic groups including phenylene, benzylene, tolylene or xilylene group or from aliphatic groups including methylene, ethylene, propylene, butylene or hexamethylene group or from

aminosubsituted groups such as diethylene-amino, triethylene-diamino, dipropylene-amino, pentaethylene-tetraamino group.

The R" and R' groups, such as alkyl, alkylene, aryl, arylene, cycloalkyl, cycloalkylene etc. groups mentioned above are unsubstituted or substituted with preferably one to five substituents independently selected from amino, oxo, halogen, such as F, Cl, Br, I, hydroxy, C_1-C_4 alkyl, trifluoromethyl, trifluoromethoxy, C_1-C_4 alkoxy, alkyl/aryl spiroborane residue, alkyl/aryl silane residue.

As described above, according to the present invention the amines of the general formula (III) have at least two, but optionally more than two primary amino groups in terminal position or as pendent groups in the R" residue, and they can be also positioned in a side chain if R" represents e.g. a branched chain aliphatic group, such as e.g. an alkylene group. Further, both primary diamines and primary polyamines can be in the inventive process.

If the above groups are oxo substituted it means that the have an –O– moiety in the chain, however, the above cited preferred ranges of carbon atom numbers are not effected therewith. For example, an oxo substituted C_2-C_8 alkylene group can be e.g. an alkoxy-alkyl gropup having the same number of carbon atoms.
Alkyl/aryl spiroborane residues and alkyl/aryl silane residues are derived from e.g. R-O-C(CO)$_2$-B-O-R- and R-O-(Si-R$_2$-O)-Si-O-R- groups, respectively.

As amine compounds aliphatic diamines can be advantageously applied, such as ethylenediamine, diethylenetriamine, hexamethylenediamine; polyamines containing one or more cycloaliphatic units as 1,2-diamino cyclohexane, bis(paraaminocyclohexyl)methane; aromatic diamines as meta phenylenediamine, bis (paraaminodipehyl)methane, etc. or their mixture. Liquid amines are preferred because in this case no additional solvent is needed to carry out the reaction, the amine being in excess serves as a solvent per se. Aromatic amines can be also advantageous because the aromatic compounds promote the formation of an intumescent char during burning, which enhances the flame retardant effect in the epoxy resin.

In the above general formulae both R' and R" can be independently the same or different groups. This means that not only symmetrically trisubstituted but also mixed esters of the phosphoric acid can be used. Further, although using a chemically homogenous mixture of di- or polyamines of the general formula (III) could be advantageous for cost or

technical considerations, it is possible to use a mixture of different di- or polyamines, which lead to a non-uniformly substituted product of the general formula (I). In this latter case within one molecule of the end product of the formula (I) the R" groups can be the same or different. Depending on the reaction mixture and the workflow applied, differently N-trisubstrued phosphoric acid amides can be prepared or a mixture of symmetrically N-trisubstituted phosphoric acid amides can be prepared as well. The chemical structure of the end product of the general formula (I) can be controlled by the feed of the components, as e.g. the different amine components can be added sequentially or in a mixture of more than one di- or polyamine.

Catalyst

If the use of a catalyst is desirable to reduce the reaction time, it can be selected from the well known transesterification reactions catalysts. These include from alkali metal alcoholates, preferably from C_1 to C_{18} alkali metal alcoholates, more preferably sodium ethylate; solid acid type catalysts, preferably a clay catalyst, more preferably montmorillonite, hidrotalcite or nanodispersed montmorillonit.

In case of using a solid acid type catalysts, preferably a clay catalyst, such as montmorillonite, hidrotalcite or nanodispersed montmorillonit the catalyst can be left in reaction mixture without any further processing as clay nanoparticles have synergistic flame retardant effect with phosphorus-containing flame retardants. Thereby the use of clay catalysts can be advantageous both for the reaction both for the end product.

Clays (also designated as clay minerals) are generally defined as hydrous aluminium phyllosilicates, which can have variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations. Clays have structures similar to the micas. Clay minerals include the following groups: kaolinite group which includes the minerals kaolinite, dickite, halloysite and nacrite; serpentine group; smectite group which includes pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite and montmorillonite; illite group which includes the clay-micas; chlorite group which includes a wide variety of similar minerals with considerable chemical variation. [Wikipedia, www.wikipedia.org]
According to the invention smectite type clays, preferably montmorillonit or hydrotalcit or nanodispersed froms thereof can be used as a catalyst.

Solvent

The reaction can be carried out in the presence of an appropriate additional solvent, preferably in a non-aqueous apolar solvent, such as toluene, benzene, xylene or hexane or in an aprotic polar solvent, such as acetone, acetonitrile or tetrahydrofurane.

It is also possible to perform the reaction in the absence of an additional solvent, especially if liquid amines of the general formula (III) are used. In case of using liquid amine reagents such as ethylene diamine, no additional solvent is needed (the solvent is the amine component itself) as the excess of the liquid amine not only shifts the equilibrium of the reaction to the formation of amide and alcohol, but also serves as a solvent. The amine has to be added preferably in excess to the desired molar ratio.

In case of amines which are solid at room temperature (RT) working without an additional solvent is still possible, however one has to work at elevated temperatures, above the melting point of the amine with regard to eventual decomposition of the starting materials and the end product, to side reactions and to eventual polymerization or oligomerization of the amine functional phosphoric amide end product. The person skilled in the art is able to determine the reaction conditions applicable for a certain combination of reagents and catalysts.

In case of solid amines non-aqueous apolar solvents as e.g. toluene, benzene, xylene or hexane or aprotic polar solvent such as e.g. acetone, acetonitrile or tetrahydrofurane can be used as solvent, which is removed by vacuum-distillation after the reaction took part.

Alcohols are generally not preferred solvents as they would shifts the equilibrium of the reaction backwards.

Reaction parameters

As said above, if there is no additional solvent applied, the reaction can be carried out at a temperature between the melting point and the boiling point of the amine, which serves as the reaction solvent. However, it is preferable to work at lower temperatures, e.g. between 0°C and 150°C, 0°C and 100°C or more preferably between RT and 100°C.

Consequently, if higher melting amines of the general formula (III) have to be used, the use of an additional solvent makes it possible to reduce the reaction temperature, and work e.g. between 0°C and 150°C, 0°C and 100°C or preferably between RT and 100°C or preferably between RT and the boiling point of the additional solvent under reflux.

After the reaction took part the excess of the amine can be removed by vacuum-destillation together with the formed alcohol. The vacuum used for vacuum-distillation of the excess of amine or the solvent is preferably in the range of 0.1-1 Hgmm or better. Worse vacuum can lead to longer distillation process and polymerization of the end-product.

If the reaction time or temperature exceeds the applicable limit, polymerization of the endproduct can occur.

The epoxy components

As epoxy component the traditional glycidyl ether of bisphenol A or its derivatives can be used. Alkyl di and polyglycidyl ethers, also known as reactive dilutants, as 1,4-butanol glycidyl ether, glycerine triglycidyl ether, pentaerythrite tetraglycidyl ether and others; mono glycidyl ethers as butyl glycidyl ether, phenyl glycidyl ether can be also used as components containing epoxy functionality.
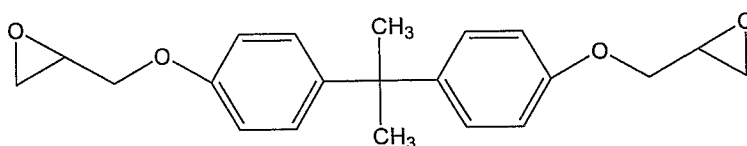
DGEBA (diglycidyl ether of bisphenol A)
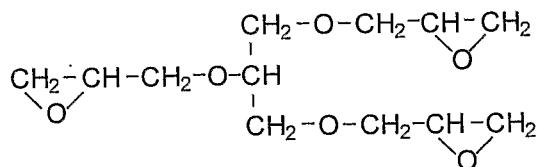
Glycerine triglycidyl ether
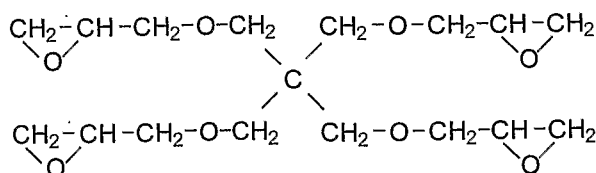
Pentaerythrite tetraglycidyl ether

As traditional additives for epoxy resins the following additives can be considered: fillers, as silica, calcium carbonate, layered and fibrous reinforcing materials, talc, mica,

nanosilicates, hidrotalcite, montmorillonite, sepiolite, glass fibre, natural and synthetic fibres and additives facilitating the application as wetting and antifoaming agents, etc.

The epoxy resin described in this invention can be also used together with traditional flame retardants as metal hydroxides, phosphorus-containing additives as ammonium polyphosphate, non-reactive alkyl and aryl phosphate esthers, halogen-containing additives, etc. according to the needs.

Testing methods

The advantages of the phosphorus-containing amine component described in this invention are the unchanged viscosity during the production, appropriate mechanical strength and component stability of the crosslinked resin, which can be demonstrated applying the following testing methods:

The fire resistance was characterized by limiting oxygen index measurement (LOI, according to ASTMD 2863), UL-94 test (according to ASTM 1356-90 and ANSI//ASTM D-635/77, respectively), Mass Loss Calorimeter (according to ISO 13927, Fire Testing Technology, heat flux of 50 kW/m2), and Glow Wire Flammability Index test (GWFI, PTL DR. GRABENHORST, D-8652 Stadtsteinach, T03.34 type apparatus, according to IEC 60695-2-12).

LOI measurements were done using OXINDEX apparatus built by MÜKI. LOI value represents the minimum concentration of oxygen (expressed as percent by volume) in a mixture of oxygen and nitrogen that will support flaming combustion of a material that is initially at room temperature. A higher value indicates a less flammable material.

UL-94 test determines the material's tendency either to extinguish or to spread the flame once the specimen has been ignited. Specimens are oriented in either a horizontal or vertical position, depending on the specifications of the relevant test method, and are subjected to a defined flame ignition source for a specified period of time. From lowest (least flame retardant) to highest (most flame retardant), the classifications are:

HB: slow burning on a horizontal specimen; burning rate <76 mm/min for thickness <3 mm.

The three vertical ratings, V2, V1 and V0 indicate that the material was tested in a vertical position and self-extinguished within a specified time after the ignition source was removed:

V2: burning stops within 30 seconds on a vertical specimen; drips of flaming particles are allowed.

V1: burning stops within 30 seconds on a vertical specimen; no drips allowed.

V0: burning stops within 10 seconds on a vertical specimen; no drips allowed.

The mass loss calorimeter (MLC) measures mass loss rate, time to ignition and heat release rate during the burning of material or product specimens. At the core of the instrument is a radiant electrical heater in the shape of a truncated cone. This heating element irradiates a flat horizontal sample, 100 mm x 100 mm and up to 50 mm thick, placed beneath it, at a preset heating flux of up to 100 kW/m2 (in our case 50 kW/m2.). The sample is placed on a load cell for continuous monitoring of its mass as it burns. Ignition can be optionally forced by an intermittent spark igniter located above the sample. The glow wire flammability index (GWFI) test is used to simulate the effect of heat as may arise in malfunctioning electrical equipment, such as with overloaded or glowing components. Test results provide a way of comparing the ability of materials to extinguish flames and their ability to not produce particles capable of spreading fire. The glow wire is heated via electrical resistance to a specified elevated temperature. A test specimen is held for 30 seconds against the tip of the glow wire with a force of 1 N. After the glow wire is removed, the time for the flames to extinguish is noted along with details of any burning drops. Cotton is placed beneath the specimen during the test to determine the effects of burning drops. The glow wire flammability index is the highest temperature which satisfies one of the following conditions in three successive tests:

- there is no flame and no glowing (no ignition) or

- burning or glowing time is less than 30 seconds after removal of the glow wire and the cotton does not ignite.

Glow wire temperatures: 550, 600, 650, 700, 750, 800, 850, 900, 960°C

GWFI 650°C: for electronic appliances which cannot be left without attendance during use,

GWFI 750°C: the device can be left without attendance,

GWFI 850°C: even current may flow on the flame retarded part,

GWFI 960°C: can be used in electrical and electronic equipment for unattended use continuously loaded, or equipment to be used near the central supply point of a building; both in parts in contact with, or retaining in position current-carrying parts and in enclosures and covers not retaining current-carrying parts in position. Suitable for all kinds of electronic application.

Rheological characterization of the epoxy resin components was done on TA Instruments AR2000 type rheometer. The measurements were done with flow procedure applying the following parameters: parallel plate geometry, upper plate diameter: 40 mm, lower plate: Peltier plate, gap: 1000 μm, temperature: 25°C; in case of steady state flow step measurements the shear rate ranged from 1-10 1/s in 4 linear steps.

Shore A type hardness was determined according to the standard MSZ 13636-73. The Shore durometer measures the depth of an indentation in the material created by a given

force on a standardized presser foot. The value of the hardness (ranging from 0 to 100, with higher values indicating a harder material) depends on the depth of the indenter's penetration.
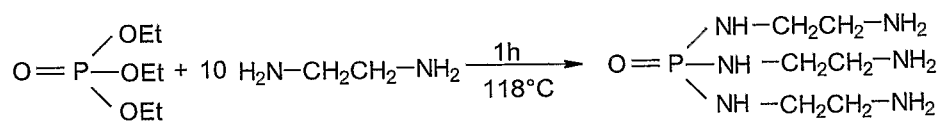
The extraction test was carried out to demonstrate the component stability of the cured epoxy resin. The extraction was done by Soxhlet-extractor using 350 cm3 benzine (boiling point in the region of 80-110°C) as extraction solvent, the turn over ratio of the solvent was 5 and the mass of the cured epoxy resin was 10 g. After extraction the mass loss of the dried sample is characteristic for the component stability of the resin: the smaller the mass loss is, the higher is the component stability.

The following examples are given to further illustrate the present invention, but they are not intended to limit or define the scope of protection, which is specified by the claims and the corresponding parts of the description.

Examples
Examples for the synthesis
Example 1

$$O = P \Big(\begin{array}{c} OEt \\ -OEt \\ OEt \end{array} + 10 \ H_2N-CH_2CH_2-NH_2 \xrightarrow[118°C]{1h} O = P \Big(\begin{array}{c} NH-CH_2CH_2-NH_2 \\ -NH-CH_2CH_2-NH_2 \\ NH-CH_2CH_2-NH_2 \end{array}$$

To 36.7 ml (0.55 mol) of $H_2NCH_2CH_2NH_2$ 9.3 ml (0.055 mol) of $P(O)(OEt)_3$ was added dropwise and the mixture was stirred at the boiling point of $H_2NCH_2CH_2NH_2$, at 118°C for 1 hours. Instead of the necessary 3 equivalents of $H_2NCH_2CH_2NH_2$ 10 equivalents were used in order to shift the equilibrium in the direction of the required trisubstituted product. The excess of $H_2NCH_2CH_2NH_2$ was removed by vacuum distillation to give the liquid, yellowish brown product in 93% yield. The crude mixture was analyzed by ^{31}P NMR chemical shifts, mass spectroscopical data obtained from MS FAB and FTIR spectra.

^{31}P NMR (DMSO) δ: 6.64
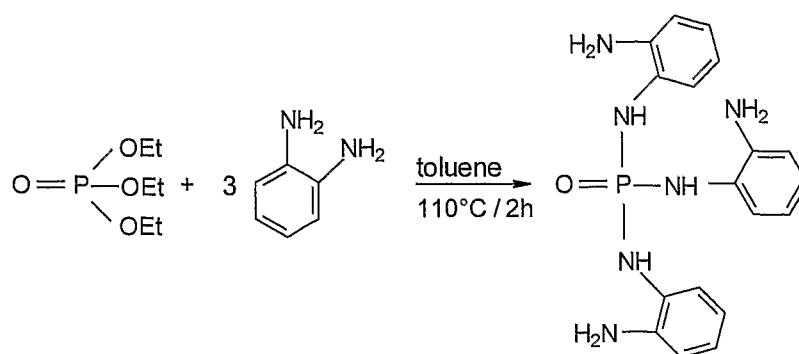
MS, m/z (rel. int.):   225 (M^+, 64)

FTIR (cm-1) 740 (P-N-C), 950 (P-N-C), 1216 (P=O), 3354 (N-H)

Amine number: 500±5 mg KOH/g

Example 2

To the solution of 70 ml toluene and 7.136 g (0.066 mol) of $H_2NC_4H_4NH_2$ 3.72 ml (0.022 mol) of $P(O)(OEt)_3$ was added and the mixture was stirred at the boiling point of toluene, at 110°C for 2 hours. The solvent was removed by vacuum distillation to give the solid, dark violet product in 90% yield. The crude mixture was analyzed by ^{31}P NMR chemical shifts, mass spectroscopical data obtained from MS FAB and FTIR spectra.

^{31}P NMR ($CDCl_3$) δ: -0.85

MS, m/z (rel. int.):   307 (M^+, 6) (disubstituted product)

FTIR (cm^{-1}) 748 (P-N-C), 927 (P-N-C), 1273 (P=O), 3363 (N-H)

Amine number: 307±5 mg KOH/g

Example 3
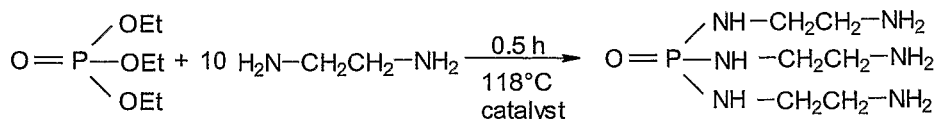
To 36.7 ml (0.55 mol) of $H_2NCH_2CH_2NH_2$ 0.5 g of untreated montmorillonite catalyst (product of Microtec, Eurotrade) was added, then 9.3 ml (0.055 mol) of $P(O)(OEt)_3$ was added dropwise and the mixture was stirred at the boiling point of $H_2NCH_2CH_2NH_2$, at 118°C for 0.5 hour. Instead of the necessary 3 equivalents of $H_2NCH_2CH_2NH_2$ 10 equivalents were used in order to shift the equilibrium in the direction of the required trisubstituted product. The excess of $H_2NCH_2CH_2NH_2$ was removed by vacuum distillation to give the liquid, yellowish brown product in 93% yield. The catalyst was left in the product, as it serves as flame retardant additive as well. The crude mixture was analyzed by ^{31}P NMR chemical shifts, mass spectroscopical data obtained from MS FAB and FTIR spectra.

^{31}P NMR (DMSO) δ: 6.64

MS, m/z (rel. int.):   225 (M^+, 64)

FTIR (cm-1) 740 (P-N-C), 950 (P-N-C), 1216 (P=O), 3354 (N-H)

Amine number: 450±5 mg KOH/g

Examples for the epoxy resin compositions

In Table 1 the compositions of example 4 and 5 serve as comparative examples, while example 6 and 7 make use of the amine functional phosphoric amide flame retardant prepared according to the present invention.

Table 1 Composition (mass%) and properties of epoxy resin samples

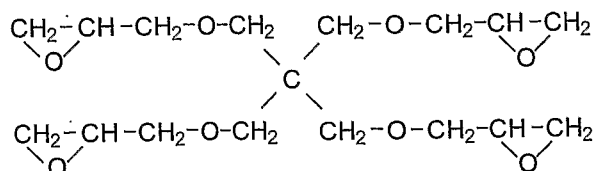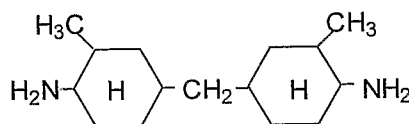| Components	example 4	example 5	example 6	example 7
Eporezit AH-16 epoxy component	74.0	54.5	67.5	63.0
Eporezit T-58 amine type hardener	26.0	19.1	-	-
Triethyl phosphate additive flame retardant	-	26.4	-	-
Hardener according to the invention	-		32.5	-
Hardener according to the invention with Na MMT catalyst	-	-	-	37.0
Properties				
Complex viscosity at 25°C, Pa.s	1.15	0.92	1.15	1.26
LOI, (%)	21	25	39	40
UL-94	HB	V2	V0	V0
Glow wire flammability index (°C)	550	650	960	960
Shore A type hardness	99	55	99	99
Mass loss after extraction (%)	0	15	0	0

Example 4

The first comparative sample consists of AH-16 epoxy component and T-58 curing agent without any flame retardants.

Eporezit AH-16 epoxy resin was applied with Eporezit T-58 curing agent, supplied by P+M Polimer Kémia Kft., Hungary. Their characteristics are summarized in Table 2 and Table 3.

$$CH_2-CH-CH_2-O-CH_2 \quad\quad CH_2-O-CH_2-CH-CH_2$$
$$\underset{O}{\diagdown\diagup} \quad\quad\quad \diagdown\;\diagup \quad\quad\quad \underset{O}{\diagdown\diagup}$$
$$C$$
$$\diagup\;\diagdown$$
$$CH_2-CH-CH_2-O-CH_2 \quad\quad CH_2-O-CH_2-CH-CH_2$$
$$\underset{O}{\diagdown\diagup} \quad\quad\quad\quad\quad\quad\quad \underset{O}{\diagdown\diagup}$$

Eporezit AH-16

$$H_3C \quad\quad\quad\quad\quad CH_3$$
$$H_2N-(\,H\,)-CH_2-(\,H\,)-NH_2$$

Eporezit T-58

Table 2 Characteristics of the applied epoxy resins

Type of epoxy resin	Epoxy equivalent	Viscosity on 25 °C	Density on 25 °C	General description
		(mPa.s)	(g/cm3)	
Eporezit AH-16	160-175	800-1800	1.24	non modified, resin like reactive dilutant

Table 3 Characteristics of the applied curing agent

Type of curing agent	Amine number	Viscosity on 20 °C	Density on 20 °C	General description
		(mPa.s)	(g/cm3)	
Eporezit T-58	460-480	100-200	0.944	curing agent

In case of sample 3 appropriate amounts according to Table 1 of AH-16 epoxy component and T-58 hardener were mixed in a glass beaker by a glass rod for one minute. After homogenization viscosity measurements where done from the mixture and from the rest of it 15 mm x 125 mm x 3mm and 100 mm x100 mm x3mm samples were made for flame

retardancy tests, mechanical characterization and extraction test, which were done after 1 week of curing at room temperature. The properties of the sample are given in Table 1.

Example 5

Example 4 is also a comparative sample consisting of AH-16 epoxy component, T-58 curing agent and an additive flame retardant according to the compositions described in Table 1. The properties of the sample are also given in Table 1.

Example 6

Example 6 made according to this invention serves to demonstrate the advantages of the flame retarded epoxy resin made with amine functional phosphoric amide flame retardant. The phosphoric amine applied in this example was synthesized according to the following method:

To 9.3 ml (0.055 mol) of $P(O)(OEt)_3$ 36.7 ml (0.55 mol) of $H_2N-CH_2CH_2-NH_2$ was added and the mixture was stirred at the boiling point of $H_2N-CH_2CH_2-NH_2$, at 118°C for 3 hours. Instead of the necessary 3 equivalents of $H_2N-CH_2CH_2-NH_2$ 10 equivalents were used in order to shift the equilibrium in the direction of the required trisubstituted product. The excess of $H_2N-CH_2CH_2-NH_2$ was removed by vacuum distillation to give the product in 93% yield. The crude mixture was analyzed by 31P NMR chemical shifts, mass spectroscopical data obtained from MS FAB, Raman and IR spectra. The amine synthesized this way has an amine number of 500±5 mg KOH/g. Amine number of the curing agent was determined by titration according to ASTM D2074-92(1998).

The epoxy resin sample was made from the amine synthesized according to this example, according to the composition listed in Table 1 and method described in case of Example 4. The properties of this sample are summarized in Table 1.

Example 7

Example 7 is also a sample according to the invention, which serves to demonstrate the advantages of the flame retarded epoxy resin made with amine functional phosphoric amides flame retardant. The curing agent used in this sample was synthesized as described in Example 3. The amine number, determined according to the method described in case of Example 6, was 450±5 mg KOH/g.

The epoxy resin sample was made from the amine synthesized according to this example, according to the composition listed in Table 1 and method described in case of Example 4. The properties of this sample are summarized in Table 1.

Summary of the results

The epoxy resins flame retarded this way reach LOI value 40 and V-0 UL-94 rating, 960 °C GWFI value compared to the LOI value of 21, HB UL-94 rating and 550°C GWFI value of the reference epoxy resin. Also the peak of the heat release rate measured by Cone calorimeter is reduced to its 1/10 compared to non flame retarded epoxy resin, furthermore a shift in time can be observed, which reduces the time to escape in case of fire event. According to these outstanding results the epoxy resins flame retarded by these amine functional phosphoric amides are appropriate for all electronic appliances, the GWFI value of 960°C means that they can be used in equipment for unattended use continuously loaded under stringent conditions. Varying the ratio of the not phosphorus-containing curing agent and the phosphorus-containing one every demand for flame retardancy can be fulfilled cost-effectively.

It will be appreciated that the examples are set forth above serve to illustrate the practice of the invention, but various modifications and changes may be made without departing from the spirit and scope of the present invention.

The amine functional phosphoric amide compound acts as flame retardant similarly as the so called intumescent additive systems: during the high temperature ignition phosphorous oxide is formed on the surface of the polymer, which abstracts water from the structure of the epoxy resin and forms a phosphorocarbonaceous layer on the surface blown up by the evolved nitrogen-containing gases from the decomposed amine parts of the matrix. The so formed intumescent layer protects the rest of the resin from the ignition source, hinders the leaving of flammable gases from the incalescent resin and the mixing of these flammable gases with the oxygen of the environment.

The process provided by the present invention makes possible to produce different amine functional phosphoric amides of the general formula (I) for use in epoxy resins. These compounds contain phosphorous and can be used both as crosslinking agent and as reactive flame retardant.

The inventive transamidation synthesis is a cost-effective and environmentally-friendly, simple way to prepare said amine functional phosphoric amides from phosphate esters and di or polyamines. The invention is thus of great advantage to epoxy resin products that should satisfy high standards of security, especially inflammability in e.g. automotive parts and housings.
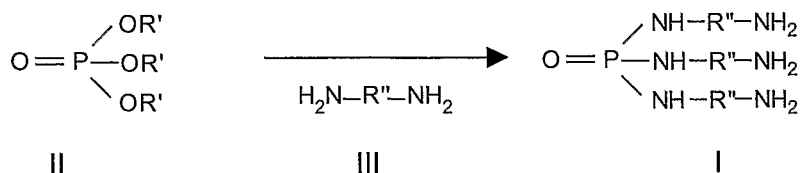
The synthesized amines can substitute the traditional epoxy resin curing agents additionally providing excellent flame retardancy: the epoxy resins flame retarded this way have an LOI value of 39% and V-0 UL-94 rating, 960°C GWFI value and also the peak of the heat release rate measured by Cone calorimeter is reduced to its 1/10 compared to non flame retarded epoxy resin.

Further, they are well-soluble in epoxy components, furthermore they do not increase significantly the viscosity of the polymer matrix, so they do not shorten the pot life of the epoxy resin. The synthesized amines contain 5-15 mass% of phosphorus. The traditional curing agent can be replaced partially or fully by them. In case of full replacement about 25-35 mass% of the phosphorus-containing amine is needed, which means that the epoxy resin composition contains 2.5-4.5% of phosphorus, which provides an excellent flame retardant effect. The mechanical properties of the cured resin are as good as of the original resin.

Claims

1. Process for the preparation of amine functional phosphoric amides according to general formula (I) which comprises reacting an orthophosphoric acid ester of general formula (II) with an amine of general formula (III) optionally in the presence of a catalyst

$$O=P\begin{array}{c}/OR'\\-OR'\\\backslash OR'\end{array} \qquad \xrightarrow{\qquad H_2N-R''-NH_2 \qquad} \qquad O=P\begin{array}{c}/NH-R''-NH_2\\-NH-R''-NH_2\\\backslash NH-R''-NH_2\end{array}$$

$$\text{II} \qquad\qquad\qquad \text{III} \qquad\qquad\qquad \text{I}$$

wherein

R' is an optionally substituted straight or branched aliphatic group, which can be saturated or unsaturated, or an optionally substituted aromatic group,

R" is an optionally substituted straight or branched aliphatic group, which can be saturated or unsaturated, or an optionally substituted aromatic group.

2. Process of claim 1, wherein R' is an optionally substituted straight or branched C_1-C_{18} alkyl group, a C_3-C_6 cycloalkyl group or C_6-C_8 aryl group.

3. Process of claim 1 or 2, wherein R' is a C_1-C_8 alkyl group, preferably methyl, ethyl, propyl or butyl group.

4. Process of any one of the preceding claims, wherein R' is phenyl, benzyl, toluyl or xilyl group.

5. Process of any one of the preceding claims, wherein R' is ethylene group.

6. Process of any one of the preceding claims, wherein R" is an optionally substituted straight or branched C_1-C_{18} alkylene group, a C_3-C_6 cycloalkylene group or C_6-C_8 arylene group.

7. Process of any one of the preceding claims, wherein R" is a C_1-C_8 alkylene group, more preferably methylene, ethylene, propylene, butylenes or hexamethylene group or diethylene-amino, triethylene-diamino, dipropylene-amino, pentaethylene-tetraamino group.

8. Process of any one of the preceding claims, wherein R" is phenylene, benzylene, tolylene or xilylene group.

9. Process of any one of the preceding claims, wherein R" is phenylene or xylilene group.

10. Process of any one of the preceding claims, wherein R' and R" groups, such as the alkyl, alkylene, aryl, arylene, cycloalkyl, cycloalkylene groups are unsubstituted or substituted with preferably one to five substituents independently selected from amino, oxo, halogen, hydroxy, C_1-C_4 alkyl, trifluoromethyl, trifluoromethoxy, C_1-C_4 alkoxy, alkyl/aryl spiroborane residue, alkyl/aryl silane residue.

11. Process of any one of the preceding claims, wherein a catalyst is used which is selected from alkali metal alcoholates, preferably from C_1 to C_{18} alkali metal alcoholates, more preferably sodium ethylate; solid acid type catalysts, preferably a clay catalyst, more preferably montmorillonite, hidrotalcite or nanodispersed montmorillonit.

12. Process of any one of the preceding claims, wherein the reaction is carried out without an additional solvent in the excess of the amine as solvent.

13. Process of any one of the preceding claims, wherein the reaction is carried out in an additional solvent, preferably in a non-aqueous apolar solvent, such as toluene, benzene, xylene or hexane or in an aprotic polar solvent, such as acetone, acetonitrile or tetrahydrofurane.

14. Process of any one of the preceding claims, wherein the reaction is carried out at a temperature ranging from room temperature to the boiling point of the applied solvent.

15. Process of any one of the preceding claims, wherein the reaction is carried at a temperature between 0°C and 150°C, preferably between 0°C and 100°C, more preferably between RT and the boiling point of the additional solvent.

16. The use of amine functional phosphoric amide synthesized according to the method of any of the claims 1 to 11 as curing agent and flame retardant in epoxy resins.