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(54) Titre : COMBINAISONS DE STABILISANTS POUR DES SYSTEMES POLYMERES
(54) Title: STABILISER COMBINATIONS FOR POLYMER SYSTEMS

(57) Abrégé/Abstract:
The invention relates to stabilising combinations of antioxidants comprising sterically hindered phenol groups and special water-soluble, inorganic phosphorous compounds. The invention also relates to a method for producing graft rubber polymers, obtained by emulsion polymerisation, with improved thermal stability during the drying process, in addition to an improved characteristic profile and to graft rubber polymers obtained by said method. The invention further relates to thermoplastic moulding materials with a modified impact-resistance, in particular ABS moulding materials, which contain said graft rubber polymers as impact-resistance modifiers. The moulding materials are characterised by an improved odour after thermoplastic processing.

ABSTRACT

The invention relates to stabilising combinations of antioxidants comprising sterically hindered phenol groups and special water-soluble, inorganic phosphorous compounds. The invention also relates to a method for producing graft rubber polymers, obtained by emulsion polymerisation, with improved thermal stability during the drying process, in addition to an improved characteristic profile and to graft rubber polymers obtained by said method. The invention further relates to thermoplastic moulding materials with a modified impact-resistance, in particular ABS moulding materials, which contain said graft rubber polymers as impact-resistance modifiers. The moulding materials are characterised by an improved odour after thermoplastic processing.

Stabiliser Combinations for Polymer Systems

The present invention relates to stabilising combinations of antioxidants with sterically hindered phenol groups and special water-soluble inorganic phosphorus compounds, a process for the production of graft rubber polymers obtained by emulsion polymerisation having improved thermal stability during drying as well as an improved property profile, and the graft rubber polymers obtainable by this process. The invention also relates to impact modified thermoplastic moulding compositions, in particular ABS moulding compositions, that contain these graft rubber polymers as impact modifiers. The moulding compositions are characterised by an improved odoriferous behaviour after processing.

Synthetic polymers, in particular those with unsaturated bonds in the molecule chain, are decomposed by the action of oxidising agents (e.g. oxygen, ozone), heat or light, as a result of which the properties are impaired and problems arise in the practical use of the moulded articles produced from the polymers.

In order to prevent such a decomposition, numerous stabilisers for polymers have already been described (see for example EP-A 669 367 and the literature cited therein).

A particular problem and the first object of the present invention is the effective stabilisation in an early stage of polymers produced in aqueous dispersion, aqueous emulsion or aqueous suspension.

It has now surprisingly been found that combinations of antioxidants with sterically hindered phenol groups and special water-soluble inorganic phosphorus compounds are particularly effective in stabilising polymers produced in aqueous dispersion.

Graft rubber polymers, in particular graft rubbers for application areas such as for example impact modifiers for polymer systems, are often produced by the process of

aqueous emulsion polymerisation, in which as a rule a drying process is necessary as the last working-up step.

In particular the rubber fraction contained in the graft rubber polymers exhibits a sensitivity to agents having an oxidising effect (e.g. peroxides, oxygen, ozone), which normally manifests itself in a negative way in the working-up and drying process. This sensitivity is particularly pronounced in rubbers with unsaturated portions in the molecule chain, such as for example polybutadiene.

A particular problem in the working-up of graft rubber polymers produced by polymerisation in aqueous emulsion is accordingly to protect the rubber as soon as possible against oxidative decomposition or other oxidative damage.

Although numerous methods for stabilising graft rubber polymers are described in the literature (see for example Gächter/Müller: Kunstoff-Additive, Carl Hanser Verlag, Munich, Vienna 1979), the disadvantages of these methods however are an insufficient protection of the polymer against oxidative reagents in the aqueous phase as well as the large addition of primary and secondary antioxidants that is accordingly necessary (as a rule sterically hindered phenols and esters of thiodipropionic acid and/or other sulfur-containing compounds), which can involve high expenditure and lead to other problems such as too high a proportion of volatile substances (emission problems) or undesirable changes in properties (e.g. lowering of the modulus of elasticity).

Accordingly, the object of the invention was furthermore to provide emulsion graft rubbers already highly stabilised in an earlier stage, using as small amounts as possible of primary antioxidants present in the form of organic compounds, and/or optionally also as small amounts as possible of correspondingly secondary antioxidants.

It has now been found that graft rubber polymers produced by emulsion polymerisation and having improved stability in the working-up and drying process are obtained by adding specific combinations of compounds with sterically hindered phenolic groups and

special water-soluble inorganic phosphorus compounds in the form of aqueous preparations before the working-up stage.

ABS moulding compositions are two-phase plastics consisting of a thermoplastic copolymer of resin-forming monomers, e.g. styrene and acrylonitrile, in which the styrene may be wholly or partially replaced by α-methylstyrene or methyl methacrylate, this copolymer, also termed SAN resin or matrix resin, forming the outer phase, as well as at least one graft polymer that can be obtained by polymerisation of one or more resin-forming monomers, e.g. the monomers mentioned above, in the presence of a rubber, e.g. butadiene homopolymer or copolymer ("graft base"). This graft polymer ("elastomer phase" or "graft rubber") forms the dispersed phase in the matrix resin.

The aforementioned polymers may in principle be produced by known methods such as emulsion, solution, bulk, suspension or precipitation polymerisation, or by combinations of such processes.

In the processing of such ABS polymers undesirable odours are often produced, especially at high processing temperatures. These intrinsic odours may lead to problems in special applications of the moulded parts (for example in automobile interiors).

In order to solve these problems it has been proposed *inter alia* to add special combinations of zinc oxide and/or magnesium oxide and epoxide group-containing compounds in the compounding stage (see EP-B 849 317).

The modulus of elasticity behaviour and the emission behaviour of the moulding compositions may however be adversely affected by adding epoxide group-containing compounds. Zinc oxide and magnesium oxide may in addition have a negative effect on the gloss behaviour.

A further object of the present invention is accordingly to produce impact modified thermoplastic moulding compositions, in particular ABS polymer moulding compositions, that do not exhibit any undesirable odours after they have been processed

into moulded parts. At the same time the other properties should not be negatively influenced.

It has now been found that this object can be achieved by thermoplastic moulding compositions containing special graft rubbers as impact modifiers.

The present invention provides on the one hand combinations containing

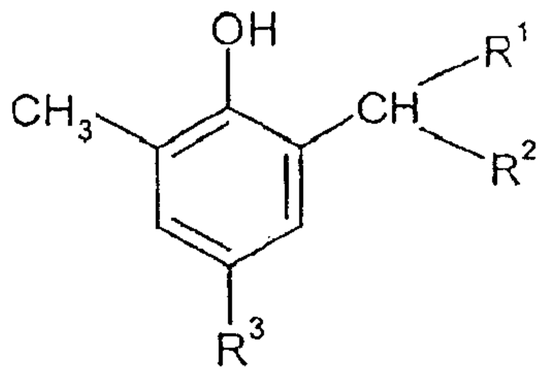
a) 1 to 99 parts by weight, preferably 10 to 90 parts by weight and particularly preferably 20 to 80 parts by weight of at least one antioxidant having at least one sterically hindered phenol group, and

b) 99 to 1 part by weight, preferably 90 to 10 parts by weight and particularly preferably 80 to 20 parts by weight of at least one water-soluble inorganic phosphorus compound selected from the group containing the salts of hypophosporous acid (H_3PO_2) and phosphorous acid (H_3PO_3 and HPO_2).

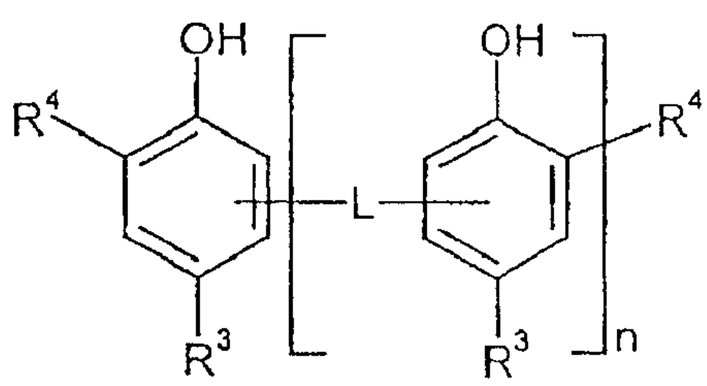
Suitable antioxidants according to component a) are compounds that contain at least one sterically hindered phenol group.

Examples of such compounds are 2,6-di-tert.-butyl-4-methylphenol, 2-tert.-butyl-4,6-dimethylphenol, 2,6-di-tert.-butyl-4-ethylphenol, 2,6-di-tert.-butyl-4-n-butylphenol, 2,6-di-tert.-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert.-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1′-methylundec-1′-yl)-phenol, 2,4-dimethyl-6-(1′-methylheptadec-1′-yl)-phenol, 2,4-dimethyl-6-(1′-methyltridec-1′-yl)-phenol, 2,2′-methylene-bis-(6-tert.-butyl-4-methylphenol), 2,2′-methylene-bis-(6-tert.-butyl-4-ethylphenol), 2,2′-methylene-bis-[4-methyl-6-(α-methylcyclohexyl)-phenol], 2,2′-methylene-bis-(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis-(6-nonyl-4-methylphenol), 2,2′-methylene-bis-(4,6-di-tert.-butylphenol), 2,2′-ethylidene-bis-(4,6-di-tert.-butylphenol), 2,2′-ethylidene-bis-(6-tert.-butyl-4-isobutylphenol), 2,2′-methylene-

bis-[6-(α-methylbenzyl)-4-nonylphenol, 2,2′-methylene-bis-[6-(α,α-dimethylbenzyl)-4-nonylphenol], 4,4′-methylene-bis-(2,6-di-tert.-butylphenol), 4,4′-methylene-bis-(6-tert.-butyl-2-methylphenol), 1,1-bis-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-butane, 2,6-bis-(3-tert.-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol-bis-[3,3-bis-(3′-tert.-butyl-4′-hydroxyphenyl)-butyrane], bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl)-dicylcopentadiene, bis-[2-(3′-tert.-butyl-2′-hydroxy-5′-methylbenzyl)-6-tert.-butyl-4-methylphenyl]-terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)-butane, 2,2-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propane, 4,4′-butylidene-bis-(2-tert.-butyl-5-methylphenol), 2,2′-isobutylidene-bis-(4,6-dimethylphenol), 2,2-bis-(5-tert.-butyl-4-hydroxy-2-methylphenyl~)-4-n-dodecylmercaptobutane, 1,1,5,5,-tetra-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-pentane, triethylene glycol-bis-3-(3-tert.-butyl-4-hydroxy-5-methylphenyl)-propionate, esters of 3,5-di-tert.-butyl-4-hydroxyphenylacetic acid with monohydric or polyhydric alcohols, such as for example with methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxy)-ethyl isocyanurate, N,N′-bis-(hydroxyethyl)-oxalic acid diamide, 3-thiaundecanol, 3-thiopentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane, for example octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate, 1,6-hexanediol-bis-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate or tetrakis[methylene-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate]-methane, mixed C_{13-15}-alkyl esters of 3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzenepropionic acid, 2,2-thio-bis-(6-tert.-butyl-4-methylphenol), 2,2′-thio-bis-(4-octylphenol), 4,4′-thio-bis-(6-tert.-butyl-3-methylphenol), 4,4′-thio-bis-(6-tert.-butyl-2-methylphenol), 4,4′-thio-bis-(3,6-di-sec.-amylphenol), 4,4′-bis-(2,6-dimethyl-4-hydroxyphenyl)-disulfide, as well as compounds of the general formula (I) or compounds of the general formula (II)



(I)



(II)

wherein $R^1 = C_1$-C_2-alkyl

$R^1 = C_2$-C_{30}-alkyl

$R^3 = C_1$-C_4-alkyl

R^4 = tert.-butyl, cyclohexyl

L = $-CH_2-$, tricyclo[5,2,1,$0^{2,6}$]decan-3,8-ylene and

$n \geq 1$,

as well as arbitrary mixtures of the aforementioned phenols.

Preferred phenols a) are 2,2′-methylene-bis-(6-tert.-butyl-4-methylphenol), 2,2′-methylene-bis-(6-tert.-butyl-4-ethylphenol), triethylene glycol bis-3-(3-tert.-butyl-4-hydroxy-5-methylphenyl)-propionate, octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate, compound (I) where $R^1 = CH_3$, $R^2 = n\text{-}C_{14}H_{29}$ and $R^3 = CH_3$, compound (II) where $R^3 = CH_3$, $R^4 = t\text{-}C_4H_9$, L = tricyclo[5,2,1,$0^{2,6}$]decan-3,8-ylene and $n \leq 1$.

Suitable water-soluble inorganic phosphorus compounds according to component b) are salts of hypophosphorous acid (H_3PO_2) or of phosphorous acid (H_3PO_3 and HPO_2).

In this connection "water-soluble" denotes within the context of the invention a solubility of at least 1 g of salt in 100 g of water. Suitable water-soluble inorganic phosphorus compounds according to b) have a water solubility of preferably at least 2 g of salt in 100 g of water and particularly preferably at least 5 g of salt in 100 g of water (in each case at 50°C).

Examples of such compounds include sodium hypophosphite, potassium hypophosphite, magnesium hypophosphite, calcium hypophosphite, sodium phosphite, potassium phosphite, calcium phosphite as well as mixtures thereof.

Preferred compounds b) are sodium hypophosphite and sodium phosphite.

The combinations according to the invention may additionally contain as component c), organic, non-water-soluble phosphorus-containing stabilisers such as for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris-(nonylphenyl)-phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol phosphite, tris-(2,4-di-tert.-butylphenyl)-phosphite, diisodecylpenta-erythritol diphosphite, bis-(2,4-di-tert.-butylphenyl)-pentaerythritol diphosphite, bis-(2,6-di-tert.-butyl-4-methylphenyl)-pentaerythritol diphosphite, bis-isodecyloxypenta-erythritol diphosphite, bis-(2,4-di-tert.-butyl-6-methylphenyl)-pentaerythritol diphosphite, bis-(2,4,6-tri-tert.-butylphenyl)-pentaerythritol diphosphite, tristearyl-sorbitol triphosphite, tetrakis-(2,4-di-tert.-butylphenyl)-4,4′-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert.-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert.-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocine, bis-(2,4-di-tert.-butyl-6-methylphenyl)-methyl phosphite, bis-(2,4-di-tert.-butyl-6-methylphenyl)-ethyl phosphite as well as mixtures thereof in an amount of up to 50 parts by weight referred to 100 parts by weight of a) + b).

Preferred compounds c) are tris-(2,4-di-tert.-butylphenyl)-phosphite, bis-(2,4-di-tert.-butylphenyl)-pentaerythritol diphosphite and tris-(nonylphenyl)-phosphite.

Furthermore the combinations according to the invention may contain as sulfur-containing component d), sulfur-containing stabilisers such as for example esters of β-thiodipropionic acid (e.g. dilauryl thiodipropionate, distearyl thiodipropionate, dimyristyl thiodipropionate, tridecyl thiodipropionate), mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, dioctadecyl disulfide, pentaerythritol tetrakis-(β-dodecylmercapto)-propionate, compounds obtained by polymerisation of vinyl

monomers such as for example styrene, acrylonitrile, methyl methacrylate in the presence of mercaptans (see for example EP-PS 195 918), as well as mixtures thereof in an amount of up to 50 parts by weight referred to 100 parts by weight of a) + b). Preferred compounds d) are dilauryl thiodipropionate, distearyl thiodipropionate and compounds obtained by polymerisation of vinyl monomers such as for example styrene, acrylonitrile, methyl methacrylate in the presence of mercaptans.

The combinations according to the invention are suitable as agents for stabilising polymers, in particular polymers produced in aqueous dispersion such as for example aqueous emulsion (emulsion polymerisation) or aqueous suspension (suspension polymerisation), against oxidative decomposition or other changes brought about by the action of oxygen.

The present invention accordingly also provides for the use of the combinations according to the invention for stabilising polymers.

Polymers that may be stabilised by the addition of the mixtures according to the invention are for example acrylonitrile-butadiene-styrene terpolymers (ABS), methyl methacrylate-butadiene-styrene terpolymers (MBS), styrene-acrylonitrile copolymers (SAN), α-methylstyrene-acrylonitrile copolymers, polystyrene, impact resistant polystyrene (HIPS), polymethyl methacrylate, polybutadiene, styrene-butadiene rubbers, acrylonitrile-butadiene rubbers, polychloroprene, polyisoprene, acrylate rubbers, ethylene-vinyl acetate rubbers, vinylpyridine-butadiene rubbers, vinylpyridine-styrene-butadiene rubbers, vinylpyridine-acrylonitrile-butadiene rubbers as well as carboxylated rubbers.

The mixtures according to the invention are particularly effective in stabilising ABS polymers, MBS polymers and rubber polymers.

The present invention also provides a process for stabilising polymers, characterised in that a combination containing

a) 1 to 99 parts by weight, preferably 10 to 90 parts by weight and particularly preferably 20 to 80 parts by weight of at least one antioxidant having at least one sterically hindered phenol group, and

b) 99 to 1 part by weight, preferably 90 to 10 parts by weight and particularly preferably 80 to 20 parts by weight of at least one water-soluble inorganic phosphorus compound selected from the group containing the salts of hypophosporous acid (H_3PO_2) and phosphorous acid (H_3PO_3 and HPO_2)

or the individual components of this combination together or individually in the form of an aqueous solution or an aqueous dispersion or an aqueous emulsion or a combination selected from these aqueous forms, is added to the polymer material present in aqueous emulsion or aqueous suspension, followed by working-up according to conventional methods.

Conventional working-up methods include for example precipitation of the emulsion polymers by adding electrolytes such as for example salts or acids, or by vigorous cooling, spray drying of the emulsion, or separation of the polymer by filtration or centrifugation in the case of suspension polymers.

The amounts of the combinations according to the invention used for the stabilisation are 0.1 to 10 parts by weight, preferably 0.2 to 8 parts by weight and particularly preferably 0.5 to 5 parts by weight referred to 100 parts by weight of polymer to be stabilised.

The present invention furthermore provides stabilised polymer materials that can be obtained by a process that involves adding, before the working-up, 0.1 to 10 parts by weight, preferably 0.2 to 8 parts by weight and particularly preferably 0.5 to 5 parts by weight (in each case referred to 100 parts by weight of polymer) of a combination containing

a) 1 to 99 parts by weight, preferably 10 to 90 parts by weight and particularly preferably 20 to 80 parts by weight of at least one antioxidant having at least one sterically hindered phenol group, and

b) 99 to 1 part by weight, preferably 90 to 10 parts by weight and particularly preferably 80 to 20 parts by weight of at least one water-soluble inorganic phosphorus compound selected from the group containing the salts of hypophosporous acid (H_3PO_2) and phosphorous acid (H_3PO_3 and HPO_2).

In this connection the stabiliser mixture is added in the form of an aqueous solution or an aqueous dispersion or an aqueous emulsion or a combination of these aqueous forms to the polymer material to be stabilised that is present in the aqueous emulsion or aqueous suspension. It is also possible to add the individual constituents of the stabiliser mixture in different aqueous forms to the polymer.

Preferably the stabilised polymer materials obtainable by the process according to the invention are graft rubber polymers produced by emulsion polymerisation and containing

I) at least one rubber having a glass transition temperature ≤ 10°C as graft base, and

II) at least one graft shell built up by polymerisation of at least one vinyl monomer in the presence of the rubber.

Suitable rubbers I) are rubbers present in emulsion form having glass transition temperatures ≤ 10°C. Examples of such rubbers include polymers of butadiene, for example polybutadiene, butadiene-styrene copolymers, preferably with styrene contents of 3 to 40 wt.%, butadiene-acrylonitrile copolymers, preferably with acrylonitrile contents of 3 to 20 wt.%, terpolymers of butadiene, styrene and acrylonitrile, copolymers and terpolymers of butadiene with other vinyl monomers such as for example acrylic acid, methacrylic acid, vinylpyridine, C_{1-8}-acrylic acid esters such as for example n-butyl acrylate or 2-ethylhexyl acrylate, C_{1-8}-methacrylic acid esters such as for example methyl

methacrylate, as well as homopolymers and copolymers of C_{1-8}-alkyl acrylates such as for example poly-n-butyl acrylate.

Preferred rubbers I) are polybutadiene, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers.

Particularly preferred are polybutadiene and butadiene-styrene copolymers.

For the production of the graft rubber polymers according to the invention, the rubber is conveniently present in emulsion form. The rubber latices used for the production of the graft rubber polymers have as a rule mean particle diameters of 50 to 1000 nm, preferably 80 to 800 nm and particularly preferably 100 to 600 nm. In this connection monomodal, bimodal, trimodal and multimodal rubber latices may be used.

Suitable vinyl monomers for the construction of the graft shell II) are monomers that can be polymerised in aqueous emulsion in the presence of a rubber latex. Examples of such monomers are vinyl aromatic compounds such as for example styrene or α-methylstyrene, unsaturated nitriles such as for example acrylonitrile or methacrylonitrile, C_{1-8}-acrylic acid esters and C_{1-8}-methacrylic acid esters such as for example n-butyl acrylate, tert.-butyl acrylate or methyl methacrylate, as well as N-substituted maleimides such as for example N-phenylmaleimide.

Particularly suitable are monomer mixtures such as for example styrene/acrylonitrile mixtures, styrene/methyl methacrylate mixtures, styrene/acrylonitrile/methyl methacrylate mixtures, styrene/acrylonitrile/N-phenylmaleimide mixtures. Particularly preferred vinyl monomers are styrene, acrylonitrile as well as mixtures thereof.

The graft rubber polymers according to the invention have a rubber content of 10 to 90 wt.%, preferably 30 to 80 wt.% and particularly preferably 40 to 75 wt.% referred to I) and II).

The graft rubber polymers according to the invention are characterised by an improved stability in the working-up and drying process. Even minor total amounts of organic stabilisers are sufficient to achieve the improved thermal stabilities in the product.

The graft rubber polymers according to the invention are suitable for example as impact modifiers for thermoplastic resins. Examples of such thermoplastic resins include polyvinyl chloride, polymethyl methacrylate, styrene/acrylonitrile copolymers, α-methylstyrene/acrylonitrile copolymers, polyamides, polyethylene terephthalates, polybutylene terephthalates, aromatic polycarbonates, aromatic polyester carbonates as well as combinations selected from these thermoplastic resins.

The present invention accordingly also provides thermoplastic moulding compositions containing

A) at least one graft rubber produced by free-radical emulsion polymerisation of at least one vinyl monomer, preferably styrene and acrylonitrile, in a weight ratio of 90:10 to 50:50, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide, particularly preferably the polymerisation of styrene and acrylonitrile in the presence of at least one rubber present in latex form with a glass transition temperature below 0°C, preferably a butadiene rubber present in latex form, particularly preferably polybutadiene, to which was added, before the working-up, a combination of

a) at least one antioxidant with at least one sterically hindered phenol group, and

b) at least one water-soluble inorganic phosphorus compound selected from salts of hypophosphorous acid (H_3PO_2) or phosphorous acid (H_3PO_3 or HPO_2) in the form of an aqueous solution or dispersion, and

B) at least one thermoplastic rubber-free polymer obtained by polymerisation of at least one resin-forming vinyl monomer, preferably styrene and acrylonitrile, in a weight ratio of 90:10 to 50:50, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide.

In general the moulding compositions according to the invention may contain the graft rubber A) and the thermoplastic rubber-free vinyl polymer B) in arbitrary amounts, normally in the range 5 to 95 parts by weight of A) and 95 to 5 parts by weight of B), preferably 10 to 60 parts by weight of A) and 90 to 40 parts by weight of B), and particularly preferably 15 to 50 parts by weight of A) and 85 to 50 parts by weight of B).

Furthermore the moulding compositions according to the invention may contain further rubber-free thermoplastic resins not built up from vinyl monomers, wherein these thermoplastic resins are used in amounts of up to 1000 parts by weight, preferably up to 700 parts by weight and particularly preferably up to 500 parts by weight (in each case referred to 100 parts by weight of A+B).

For the production of the graft rubber A), 20 to 70 parts by weight, particularly preferably 25 to 60 parts by weight, of at least one vinyl monomer, preferably a mixture of styrene and acrylonitrile, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide, are polymerised in the presence of preferably 30 to 80 parts by weight, particularly preferably 40 to 75 parts by weight (in each case referred to solids) of a rubber latex.

The monomers used in these graft polymers are preferably mixtures of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, particularly preferably in a weight ratio of 80:20 to 65:35.

Suitable rubber present in latex form for the production of the graft rubbers A) are in principle all rubber polymers with a glass transition temperature below 0°C.

Examples of such rubber polymers are polydienes such as for example polybutadiene and polyisoprene, alkyl acrylate rubbers based on C_{1-8}-alkyl acrylates such as for example poly-n-butyl acrylate, polysiloxane rubbers such as for example products based on polydimethylsiloxane.

Preferred rubbers for the production of the graft rubbers A) are butadiene polymer latices, which can be produced by emulsion polymerisation of butadiene and optionally comonomers. This polymerisation process is known and is described for example in Houben-Weyl, Methoden der Organischen Chemie, Makromolekulare Stoffe, Part 1, p. 674 (1961), Thieme Verlag Stuttgart.

As comonomers there may be used up to 50 wt.% (referred to the total amount of monomer used for the butadiene polymer production) of one or more monomers copolymerisable with butadiene. Preferred examples of such monomers are isoprene, chloroprene, acrylonitrile, styrene, α-methylstyrene, C_1-C_4-alkylstyrenes, C_1-C_8-alkyl acrylates, C_1-C_8-alkyl methacrylates, alkylene glycol diacrylates, alkylene glycol dimethacrylates and divinylbenzene. Butadiene alone is preferably used.

The rubber used for the production of the graft rubber A) may be present in the form of a latex with a monomodal, bimodal, trimodal or multimodal particle size distribution. Preferred are rubber latices that have a monomodal, bimodal or trimodal particle size distribution.

The mean particle diameters (d_{50} value) of the monomodal, bimodal, trimodal or multimodal rubber latices used for the production of the graft rubbers A) may vary within wide ranges. Suitable particle diameters are for example between 50 and 600 nm, preferably between 80 and 550 nm and particularly preferably between 100 and 500 nm.

For the production of rubber latices with bimodal, trimodal or multimodal particle size distributions, preferably monomodal rubber latices of different mean particle size and narrow particle size distribution are mixed with one another.

Monomodal rubber latices with a narrow particle size distribution are understood within the context of the invention to mean those latices that have a particle size distribution width (measured as d_{90}-d_{10} from the integral particle size distribution) of 30 to 150 nm, preferably 35 to 100 nm and particularly preferably 40 to 80 nm.

Monomodal rubber latices with a narrow particle size distribution are preferably produced by emulsion polymerisation of suitable monomers, preferably monomer mixtures containing butadiene, particularly preferably butadiene *per se*, according to the so-called seed polymerisation technique, in which first of all a finely particulate polymer, preferably a rubber polymer, particularly preferably a butadiene polymer, is produced as seed latex and is then polymerised further by further conversion with rubber-forming monomers, preferably with monomers containing butadiene, to form larger particles (see for example Houben-Weyl, Methoden der Organischen Chemie, Makromolekulare Stoffe Part 1, p. 339 (1961), Thieme Verlag Stuttgart).

In this connection the seed batch process or the seed feed process is preferably used.

It is also possible in the production of the rubber latices to produce first of all a finely particulate butadiene polymer by known methods and then agglomerate the latter in a known manner in order to adjust the necessary particle size. Relevant techniques are described for example in EP-A 0 029 613; EP-A 0 007 810; DD-A 144 415; DE-A 1 233 131; DE-A 1 258 076; DE-A 2 101 650; GB-A 1 379 391.

In principle the rubber latices may also be produced by emulsifying finely particulate rubber polymers in aqueous media (see for example JP-A 55-125 102).

The differences in the mean particle diameters (d_{50} value from the integral particle size distribution) of the rubber latices used for the mixture in the preferred production of bimodal, trimodal or multimodal particle size distributions are at least 30 nm, preferably at least 60 nm and particularly preferably at least 80 nm.

The gel contents of the rubber latices used for the production of the graft rubbers A) are as a rule not important and may vary within wide ranges. Normally the values are between ca. 30% and 98%, preferably between 40% and 95%.

The gel contents of the rubber latices may in principle be adjusted in a known manner by using suitable reaction conditions (e.g. high reaction temperature and/or polymerisation up to a high conversion, as well as optionally addition of crosslinking substances in order to achieve a high gel content, or for example low reaction temperature and/or termination of the polymerisation reaction before crosslinking has proceeded too far, as well as optionally the addition of molecular weight regulators such as for example n-dodecylmercaptan or t-dodecylmercaptan in order to achieve a low gel content).

As emulsifiers there may be used conventional anionic emulsifiers such as alkyl sulfates, alkyl sulfonates, aralkyl sulfonates, soaps of saturated or unsaturated fatty acids, as well as alkaline disproportionated or hydrogenated abietic acid or tall oil acid; emulsifiers with carboxyl groups are preferably used (e.g. salts of C_{10}-C_{18}-fatty acids, disproportionated abietic acid, hydrogenated abietic acid, emulsifiers according to DE-A 3 639 904 and DE-A 3 913 509).

The determination of the mean particle diameter d_{50} as well as the d_{10} and d_{90} values may be carried out by ultracentrifuge measurements (see W. Scholtan, H. Lange: Kolloid Z. u. Z. Polymere 250, pp. 782 to 796 (1972)).

The specified values for the gel content refer to the determination according to the wire cage method in toluene (see Houben-Weyl, Methoden der Organischen Chemie, Makromolekulare Stoffe, Part 1, p. 307 (1961), Thieme Verlag Stuttgart).

The graft polymerisation in the production of the graft rubbers A) may be carried out so that the monomer mixture is added in portions or continuously to the rubber latex and then polymerised. In this connection special monomer-rubber ratios are preferably maintained.

The graft polymerisation to produce the graft rubber A) may for example be carried out by adding the monomer in such a way that within the first half of the overall monomer addition time 55 to 90 wt.%, preferably 60 to 80 wt.% and particularly preferably 65 to 75 wt.% of the total monomers to be used in the graft polymerisation are metered in, the remaining portion of the monomers being metered in within the second half of the overall monomer addition time. A uniform continuous metering in of the monomers to the rubber latex is preferred.

Molecular weight regulators may in addition be used in the graft polymerisation, preferably in amounts of 0.05 to 2 wt.%, particularly preferably in amounts of 0.1 to 1 wt.% (in each case referred to the total amount of monomers in the graft polymerisation stage). Suitable molecular weight regulators are for example alkylmercaptans such as n-dodecylmercaptan, t-dodecylmercaptan, as well as dimeric α-methylstyrene or terpinolene.

Suitable initiators for the production of the graft rubber A) according to the invention include inorganic and organic peroxides, for example H_2O_2, di-tert.-butyl peroxide, cumene hydroperoxide, dicyclohexyl percarbonate, tert.-butyl hydroperoxide, p-menthane hydroperoxide, azo initiators such as azobisisobutyronitrile, inorganic per salts such as ammonium, sodium or potassium persulfate, potassium perphosphate, sodium perborate as well as redox systems. Redox systems consist as a rule of an organic oxidising agent and a reducing agent, in which connection heavy metal ions may additionally be present in the reaction medium (see Houben-Weyl, Methoden der Organischen Chemie, Vol. 14/1, pp. 263 to 297).

The polymerisation temperature is generally 25°C to 160°C, preferably 40°C to 90°C. The graft polymerisation may be carried out under normal temperature conditions, for example isothermally; however the graft polymerisation is preferably carried out so that the temperature difference between the start and end of the reaction is at least 10°C, preferably at least 15°C and particularly preferably 20°C.

Suitable emulsifiers are for example conventional anionic emulsifiers such as alkyl sulfates, alkyl sulfonates, aralkyl sulfonates, soaps of saturated or unsaturated fatty acids, as well as alkaline disproportionated or hydrogenated abietic or tall oil acids. Emulsifiers with carboxyl groups are preferably employed (for example salts of C_{10-18}-fatty acids, disproportionated abietic acid, hydrogenated abietic acid, emulsifiers according to DE-A 3 639 904 and DE-A 3 913 509).

In the production of the graft rubbers A), there is preferably added to the graft rubber emulsion before the working-up, a combination containing

a) at least one antioxidant containing at least one sterically hindered phenol group,

and

b) at least one water-soluble inorganic phosphorus compound selected from salts of hypophosphorous acid (H_3PO_2) or phosphorous acid (H_3PO_3 and HPO_2)

as described above, in the form of an aqueous solution or dispersion.

The amount of the combination of a) and b) is usually 0.1 to 10 parts by weight, preferably 0.2 to 8 parts by weight and particularly preferably 0.5 to 5 parts by weight (in each case referred to 100 parts by weight of graft rubber to be stabilised).

The amounts of the compounds c) that are optionally additionally used are normally 0.1 to 5 parts by weight, preferably 0.2 to 3 parts by weight and particularly preferably 0.4 to 2 parts by weight (in each case referred to 100 parts by weight of graft rubber to be stabilised).

The amounts of the compounds d) that are optionally additionally used are normally 0.2 to 7 parts by weight, preferably 0.3 to 6 parts by weight and particularly preferably 0.4 to 5 parts by weight (in each case referred to 100 parts by weight of graft rubber to be stabilised).

The addition of the components a) and b) and optionally in addition c) and/or d) added before the working-up takes place in the form of aqueous preparations, in which connection aqueous solutions, aqueous dispersions, aqueous emulsions, aqueous suspensions or combinations of the aforementioned aqueous systems may be used. The addition of the compounds may take place jointly or individually in the form of the aforementioned aqueous systems.

Preferably no sulfur-containing compound is added to the graft rubber emulsion before the working-up.

As rubber-free copolymers B) there are preferably used copolymers of styrene and acrylonitrile in a weight ratio of 95:5 to 50:50, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide.

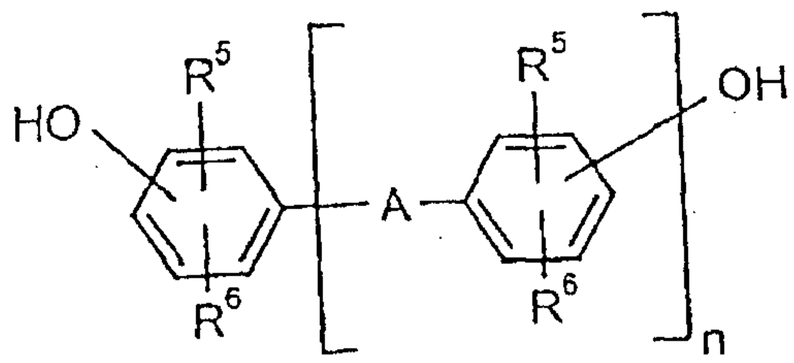
Particularly preferred are those copolymers B) whose acrylonitrile proportion is less than 30 wt.%.

The copolymers preferably have mean molecular weights $\overline{M}_w$ of 20,000 to 200,000 and intrinsic viscosities [η] of 20 to 110 ml/g (measured in dimethylformamide at 25°C).

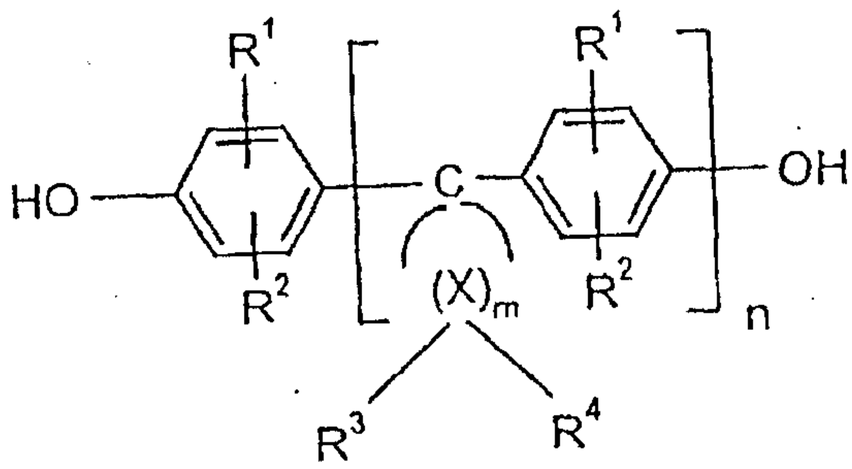
Details of the production of these resins are described for example in DE-A 24 20 358 and DE-A 27 24 360. Vinyl resins produced by bulk polymerisation or solution polymerisation have proved particularly suitable. The copolymers may be added alone or in an arbitrary mixture.

In addition to the thermoplastic resins built up from vinyl monomers, it is also possible to use polycondensates, for example aromatic polycarbonates, aromatic polyester carbonates, polyesters, polyamides as rubber-free copolymer in the moulding compositions according to the invention.

Suitable thermoplastic polycarbonates and polyester carbonates are known (see for example DE-A 14 95 626, DE-A 22 32 877, DE-A 27 03 376, DE-A 27 14 544, DE-A 30 00 610, DE-A 38 32 396, DE-A 30 77 934), which can be produced for example by reacting diphenols of the formulae (III) and (IV)



(III)



(IV)

wherein

A denotes a single bond, C_1-C_5-alkylene, C_2-C_5-alkylidene, C_5-C_6-cycloalkylidene, -O-, -S-, -SO-, -SO_2- or -CO-,

R^5 and R^6 independently of one another denote hydrogen, methyl or halogen, in particular hydrogen, methyl, chlorine or bromine,

R^1 and R^2 independently of one another denote hydrogen, halogen, preferably chlorine or bromine, C_1-C_8-alkyl , preferably methyl, ethyl, C_5-C_6-cycloalkyl, preferably cyclohexyl, C_6-C_{10}-aryl, preferably phenyl, or C_7-C_{12}-aralkyl, preferably phenyl-C_1-C_4-alkyl, in particular benzyl,

m is an integer from 4 to 7, and is preferably 4 or 5,

n is 0 or 1,

R^3 and R^4 may be chosen individually for each X and independently of one another denote hydrogen or C_1-C_6-alkyl, and

X denotes carbon,

with carbonic acid halides, preferably phosgene, and/or with aromatic dicarboxylic acid dihalides, preferably benzenedicarboxylic acid dihalides, by phase interface polycondensation or with phosgene by polycondensation in homogeneous phase (the so-called pyridine process), wherein the molecular weight may be adjusted in a known manner by an appropriate amount of known chain terminators.

Suitable diphenols of the formulae (III) and (IV) include for example hydroquinone, resorcinol, 4,4′-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 2,2-bis-(4-hydroxy-3,5-dimethylphenyl)-propane, 2,2-bis-(4-hydroxy-3,5-dichlorophenyl)-propane, 2,2-bis-(4-hydroxy-3,5-dibromophenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3-dimethylcyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5,5-tetramethylcyclohexane or 1,1-bis-(4-hydroxyphenyl)-2,4,4-trimethylcyclopentane.

Preferred diphenols of the formula (III) are 2,2-bis-(4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane; the preferred phenol of the formula (IV) is 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Mixtures of diphenols may also be used.

Suitable chain terminators include for example phenol, p-tert.-butylphenol, long-chain alkylphenols such as 4-(1,3-tetramethylbutyl)-phenol according to DE-A 2 842 005, monoalkylphenols, dialkylphenols with a total of 8 to 20 C atoms in the alkyl substituents according to DE-A 3 506 472, such as p-nonylphenol, 2,5-di-tert.-

butylphenol, p-tert.-octylphenol, p-dodecylphenol, 2-(3,5-dimethylheptyl)-phenol and 4-(3,5-dimethylheptyl)-phenol. The necessary amount of chain terminators is in general 0.5 to 10 mole %, referred to the sum of the diphenols (III) and (IV).

The suitable polycarbonates and/or polyester carbonates may be linear or branched; branched products are preferably obtained by incorporating 0.05 to 2.0 mole %, referred to the sum total of diphenols employed, of trifunctional or higher functional compounds, for example those with three or more than three phenolic OH groups.

The suitable polycarbonates and/or polyester carbonates may contain aromatically bound halogen, preferably bromine and/or chlorine; however, they are preferably halogen-free.

The polycarbonates/polyester carbonates have mean molecular weights ($\overline{M}_w$, weight average) determined for example by ultracentrifugation or light scattering measurements, of 10,000 to 200,000, preferably 20,000 to 80,000.

Suitable thermoplastic polyesters are preferably polyalkylene terephthalates, i.e. reaction products of aromatic dicarboxylic acids or their reactive derivatives (for example dimethyl esters or anhydrides) and aliphatic, cycloaliphatic or arylaliphatic diols and mixtures of such reaction products.

Preferred polyalkylene terephthalates can be produced from terephthalic acids (or their reactive derivatives) and aliphatic or cycloaliphatic diols containing 2 to 10 C atoms according to known methods (Kunstoff-Handbuch, Vol. VIII, p. 695 ff, Carl Hanser Verlag, Munich 1973).

In preferred polyalkylene terephthalates 80 to 100 mole %, preferably 90 to 100 mole % of the dicarboxylic acid radicals are terephthalic acid radicals, and 80 to 100 mole %, preferably 90 to 100 mole % of the diol radicals are ethylene glycol and/or butanediol-1,4 radicals.

The preferred polyalkylene terephthalates may in addition to ethylene glycol radicals and/or butanediol-1,4 radicals also contain 0 to 20 mole % of radicals of other aliphatic diols with 3 to 12 C atoms or cycloaliphatic diols with 6 to 12 C atoms, for example radicals of propanediol-1,3, 2-ethylpropanediol-1,3, neopentyl glycol, pentanediol-1,5, hexanediol-1,6, cyclohexanedimethanol-1,4, 3-methylpentanediol-1,3 and -1,6, 2-ethylhexanediol-1,3, 2,2-diethylpropanediol-1,3, hexanediol-2,5, 1,4-di(β-hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-β-hydroxyethoxyphenyl)-propane and 2,2-bis-(4-hydroxypropoxyphenyl)-propane (DE-A 24 07 647, 24 07 776, 27 15 932).

The polyalkylene terephthalates may be branched by the incorporation of relatively small amounts of trihydric or tetrahydric alcohols or tribasic or tetrabasic carboxylic acids, such as are described in DE-A 1 900 270 and US-A 3,692,744. Examples of preferred branching agents include trimesic acid, trimellitic acid, trimethylolethane and trimethylolpropane, and pentaerythritol. It is advisable to use not more than 1 mole % of the branching agent referred to the acid component.

Particularly preferred are polyalkylene terephthalates that have been produced solely from terephthalic acid and its reactive derivatives (e.g. the dialkyl esters) and ethylene glycol and/or butanediol-1,4, and mixtures of these polyalkylene terephthalates.

Preferred polyalkylene terephthalates are also copolyesters that are produced from at least two of the alcohol components mentioned above; particularly preferred copolyesters are poly-(ethylene glycol butanediol-1,4)-terephthalates.

The preferably suitable polyalkylene terephthalates generally have an intrinsic viscosity of 0.4 to 1.5 dl/g, preferably 0.5 to 1.3 dl/g, in particular 0.6 to 1.2 dl/g, in each case measured in phenol/o-dichlorobenzene (1:1 parts by weight) at 25°C.

Suitable polyamides are known homopolyamides, copolyamides and mixtures of these polyamides. These may be partially crystalline and/or amorphous polyamides.

Suitable as partially crystalline polyamides are polyamide-6, polyamide-6,6, mixtures and corresponding copolymers of these components. Also suitable are partially crystalline polyamides whose acidic component consists wholly or partially of terephthalic acid and/or isophthalic acid and/or suberic acid and/or sebacic acid and/or azelaic acid and/or adipic acid and/or cyclohexanedicarboxylic acid, whose diamine component consists wholly or partially of m- and/or p-xylylenediamine and/or hexamethylenediamine and/or 2,2,4-trimethylhexamethylenediamine and/or 2,2,4-trimethylhexamethylenediamine and/or isophorone diamine, and whose composition is in principle known.

There should also be mentioned polyamides that are produced wholly or in part from lactams containing 7 to 12 C atoms in the ring, optionally with the co-use of one or more of the starting components mentioned above.

Particularly preferred partially crystalline polyamides are polyamide-6 and polyamide-6,6 and their mixtures. Known products may be used as amorphous polyamides. These are obtained by polycondensation of diamines such as ethylenediamine, hexamethylenediamine, decamethylenediamine, 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine, m- and/or p-xylylenediamine, bis-(4-aminocyclohexyl)-methane, bis-(4-aminocyclohexyl)-propane, 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 2,5- and/or 2,6-bis-(aminomethyl)-norbornane and/or 1,4-diaminomethylcyclohexane with dicarboxylic acids such as oxalic acid, adipic acid, azelaic acid, decanedicarboxylic acid, heptadecanedicarboxylic acid, 2,2,4- and/or 2,4,4-trimethyladipic acid, isophthalic acid and terephthalic acid.

Also suitable are copolymers that are obtained by polycondensation of several monomers, as well as copolymers that are produced by the addition of aminocarboxylic acids such as ε-aminocaproic acid, ω-undecanoic acid or ω-aminolauric acid or their lactams.

Particularly suitable amorphous polyamides are the polyamides produced from isophthalic acid, hexamethylenediamine and further diamines such as 4,4′-diaminodicyclohexylmethane, isophorone diamine, 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine, 2,5- and/or 2,6-bis-(aminomethyl)-norbornene; or from isophthalic acid, 4,4′-diaminodicyclohexylmethane and ε-caprolactam; or from isophthalic acid, 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane and laurinlactam; or from terephthalic acid and the isomeric mixture of 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine.

Instead of pure 4,4′-diaminodicyclohexylmethane there may also be used mixtures of the position isomeric diaminodicyclohexylmethanes that are composed of

70 to 99 mole % of the 4,4′-diamino isomer
10 to 30 mole % of the 2,4′-diamino isomer
0 to 2 mole % of the 2,2′-diamino isomer, and

optionally suitably higher condensed diamines that are obtained by hydrogenation of industrial quality diaminodiphenylmethane. Up to 30% of the isophthalic acid may be replaced by terephthalic acid.

The polyamides preferably have a relative viscosity (measured in a 1 wt.% solution in m-cresol at 25°C) of 2.0 to 5.0, particularly preferably of 2.5 to 4.0.

The production of the moulding compositions according to the invention is carried out by mixing the components A) and B) as well as optionally further constituents in conventional mixing units (preferably on multiroll stands or in mixer-extruders or internal kneaders).

The present invention accordingly also provides a process for the production of the moulding compositions according to the invention, in which the components A) and B) and optionally further constituents are mixed, compounded at elevated temperature, in general at temperatures from 150° to 300°C, and extruded.

The necessary or expedient additional additives, e.g. UV stabilisers, antistatics, lubricants, mould release agents, flameproofing agents, fillers or reinforcing agents (glass fibres, carbon fibres, etc.) and colourants may be added to the moulding compositions according to the invention during production, working-up, further processing and final processing.

The final processing may be undertaken in conmmercially available processing units and includes for example injection moulding processing, panel extrusion optionally followed by heat forming, cold forming, extrusion of pipes and profiled sections, or calender processing.

The present invention furthermore provides for the use of the moulding compositions according to the invention for the production of moulded parts as well as the moulded parts *per se*.

Examples

The invention is described in more detail in the following examples. The specified parts are always parts by weight and refer in each case to solid constituents and/or polymerisable constituents.

Examples relating to the thermal stability of stabilised polymers

The stability was determined by measuring the temperature (T_m) at which the exothermic reaction exhibits a maximum, by means of differential scanning calorimetry (DSC).

All DSC measurements were carried out using a DSC-2 calorimeter from Perkin-Elmer (oxygen as rinsing gas, oxygen flow rate of 60 ml/min). The heating rate in the dynamic measurement was constant at 20 K/min.

The following were used as polymers:

Polymer I (graft rubber obtained by polymerisation of 41 parts by weight of a styrene/acrylonitrile = 73:27 mixture in the presence of 59 parts by weight of a polybutadiene latex),

Polymer II (polybutadiene produced by emulsion polymerisation) and

Polymer III (butadiene/acrylonitrile = 64:36 polymer produced by emulsion polymerisation of a corresponding butadiene/acrylonitrile mixture.

The following substances were used in carrying out the tests described hereinafter:

A) octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076 from Ciba, Basel, Switzerland)

B-1) sodium hypophosphite

B-2) sodium phosphite

The incorporation of the stabilisers or stabiliser combinations specified in Table 1 was performed by adding the stabiliser components present in aqueous solution or aqueous dispersion (Irganox® 1076 as 25% aqueous dispersion obtained by dispersing the sodium salt of disproportionated abietic acid, sodium hypophosphite and sodium phosphite as 10% aqueous solution) to the polymers present in emulsion form.

The working-up was performed by coagulation with a magnesium sulfate/acetic acid = 1:1 mixture in the form of a 1% aqueous solution, washing with water and drying at 40°C *in vacuo*.

Table 1

Example	Polymer	Stabiliser (parts by weight per 100 parts by weight of polymer)	Thermal Stability in DSC Measurement T_m (min)
1	I	1 A + 1 B-1	229
2	I	1 A + 1 B-2	231
3 (Comparison)	I	1 A	226
4 (Comparison)	I	1 B-1	204
5 (Comparison)	I	--	204
6	II	1 A + 1 B-1	215
7 (Comparison)	II	1 A	201
8 (Comparison)	II	1 B-1	190
9 (Comparison)	II	--	195
10	III	1 A + 1 B-1	268
11 (Comparison)	III	1 A	260
12 (Comparison)	III	1 B-1	214
13 (Comparison)	III	--	212

From the results shown in Table 1 it is evident that the stabiliser combinations according to the invention lead to a significantly improved oxidation stability of the polymers

treated therewith. This is particularly surprising since the sole use of the components B-1 or B-2 did not exhibit any stabilising effect.

Examples relating to the thermal stability of stabilised graft rubbers

The following substances were used in carrying out the tests described hereinbelow:

As graft rubber there was used a mixture consisting of a first graft rubber latex I (obtained by polymerisation of 50 parts by weight of a styrene/acrylonitrile mixture (73:27) in the presence of 50 parts by weight of a polybutadiene latex with a mean particle size d_{50} of 125 nm) and a second graft rubber latex II (obtained by polymerisation of 41 parts by weight of a styrene/acrylonitrile mixture (73:27) in the presence of 59 parts by weight of a polybutadiene latex with a mean particle size d_{50} of 345 nm), the weight ratio of graft rubber I to graft rubber II being 1:1.

The following stabilisers were added to the graft rubber in the amounts given in Table 2:

A) octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076 from Ciba, Basel, Switzerland)

B) sodium hypophosphite

C) tris-(2,4-di-tert.-butylphenyl)-phosphite (Irgafos® 168 from Ciba, Basel, Switzerland)

D-1) dilauryl thiodipropionate (Irganox® PS 800 from Ciba, Basel, Switzerland)

D-2) sulfur-containing polymer of styrene, acrylonitrile and tert.-dodecylmercaptan, present in latex form and produced according to EP-B 195 918, Example 1.

The incorporation of the stabilisers was achieved by adding the substances present in the form of aqueous solutions or aqueous dispersions to the graft rubber latices.

Working-up was carried out in each case by precipitation with a 1:1 mixture of magnesium sulfate and acetic acid in the form of a 1% aqueous solution, washing with water, and drying at 40°C *in vacuo*.

The thermal stability of the graft rubbers was measured by determining the oxidative discolouration using a Metrastat PSD 260 test system (manufacturer: PSD-Prüfgeräte-Systeme Dr. Stapfer GmbH, Düsseldorf). The graft rubber powder is stored under air at a specified temperature and the time for discolouration to occur is measured. This simulates the thermal stress exerted during drying.

The stability of the variously stabilised graft rubbers was determined by measuring the time after which a brown discolouration was formed at 180°C.

It is clear from the results given in Table 2 that the graft rubbers according to the invention exhibit very good thermal stabilities, in which even very minor overall amounts of organic stabilisers in the product result in improved or comparable thermal stabilities.

Table 2

Example	Stabiliser (parts by weight per 100 parts by weight of graft rubber)					Overall Amount of Organic Stabiliser (parts by weight per 100 parts by weight of graft rubber)	Metrastat Test (time up to the start of discolouration, in min)
	A	B	C	D-1	D-2		
14	0.75	0.5			1.75	2.50	220
15 (Comparison)	0.75				2.65	3.40	100
16	0.75	0.5		0.6		1.35	210
17 (Comparison)	0.75			0.9		1.65	205
18	0.75	0.5	0.8			1.55	140
19	1.0	0.5	0.8			1.80	150
20 (Comparison)	1.0		0.8			1.80	135

Examples relating to the odoriferous behaviour of stabilised moulding compositions

Components employed:

Graft rubber A1:

Mixture of a first graft rubber latex I (obtained by polymerisation of 50 parts by weight of a styrene/acrylonitrile = 73:27 mixture in the presence of 50 parts by weight of a polybutadiene latex with a mean particle size d_{50} of 125 nm) and a second graft rubber latex II (obtained by polymerisation of 41 parts by weight of a styrene/acrylonitrile = 73:27 mixture in the presence of 59 parts by weight of a polybutadiene latex with a mean particle size d_{50} of 345 nm) in a weight ratio of graft rubber I to graft rubber II of 1:1, a stabiliser combination K1 in the form of an aqueous dispersion being added to the graft rubber before the working-up.

Graft rubber A2:

Graft rubber similar to A1, in which a stabiliser combination K2 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Graft rubber A3:

Graft rubber similar to A1, in which a stabiliser combination K3 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Graft rubber A4:

Graft rubber similar to A1, in which a stabiliser combination K4 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Graft rubber A5:

Graft rubber similar to A1, in which a stabiliser combination K5 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Graft rubber A6:

Graft rubber similar to A1, in which a stabiliser combination K6 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Graft rubber A7:

Graft rubber similar to A1, in which a stabiliser combination K7 in the form of an aqueous dispersion was added to the graft rubber before the working-up.

Stabiliser combinations employed (in each case referred to 100 parts by weight of graft rubber):

K1: 0.75 part of octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076 from Ciba, Basel, Switzerland), 0.8 part of tris-(2,4-di-tert.-butylphenol)-phosphite (Irgaphos® 168, Ciba, Basel, Switzerland), 0.5 part of sodium hypophosphite

K2: 1.0 part of Irganox® 1076, 0.8 part of Irgaphos® 168, 0.5 part of sodium hypophosphite

K3: 1.0 part of Irganox® 1076, 0.8 part of Irgaphos® 168

K4: 0.75 part of Irganox® 1076, 1.75 parts of a polymer of styrene, acrylonitrile and t-dodecylmercaptan, produced according to EP-B 195 918, Example 1, 0.5 part of sodium hypophosphite

K5: 0.75 part of Irganox® 1076, 2.65 parts of a polymer of styrene, acrylonitrile and t-dodecylmercaptan, produced according to EP-B 195 918, Example 1

K6: 0.75 part of Irganox® 1076, 0.6 part of Irganox® PS 800 (Ciba, Basel, Switzerland), 0.5 part of sodium hypophosphite

K7: 0.75 part of Irganox® 1076, 0.9 part of Irganox® PS 800

Resin component B:

Random styrene/acrylonitrile copolymer (styrene/acrylonitrile weight ratio 72:28) with a $\overline{M}_w$ of ca. 85,000 and $\overline{M}_w / \overline{M}_n - 1 \leq 2$ obtained by free-radical solution polymerisation.

Moulding compositions

The polymer components described above are mixed in the proportions given in Table 3 with 2 parts by weight of ethylenediamine bisstearylamide and 0.1 part by weight of a silicone oil in an internal kneader and after granulation are processed at a processing temperature of 240°C into moulded articles by injection moulding.

The odoriferous behaviour was evaluated according to the recommendations of the Verband der Automobilindustrie e.V. (VDA) for determining the odoriferous behaviour of materials used in vehicle interiors, dated October 1992 (VDA 270 C3 smell test, see Kraftfahrwesen e.V. (DKF) documentation, Ulrichstraße 14, Bietigheim-Bissingen).

Evaluation scale for evaluating the smell according to VDA 270

Score 1: not detectable

Score 2: detectable, not unpleasant

Score 3: clearly detectable but still not unpleasant

Score 4: unpleasant

Score 5: extremely unpleasant

Score 6: intolerable

The yellowness index (YI) was determined according to ASTM Norm 1925 (type of light: C, observer: 2°, measurement opening: large area value) according to the equation YI = (128 X-106 Z)/Y, where X,Y,Z = colour co-ordinates according to DIN 5033. The results are also shown in Table 3.

From Table 3 it is clear that the moulding compositions according to the invention have improved yellowness values and in particular exhibit an improved odoriferous behaviour to such an extent that the smell is no longer regarded as unpleasant.

Table 3: Composition and test values of the moulding compositions

Example	A1 parts by wt.	A2 parts by wt.	A3 parts by wt.	A4 parts by wt.	A5 parts by wt.	A6 parts by wt.	A7 parts by wt.	B parts by wt.	YI	Smell eval. (acc. to VDA 270 C3)
21	30	--	--	--	--	--	--	70	30	2.5
22	--	30	--	--	--	--	--	70	31	2.5
23 (Comp.)	--	--	30	--	--	--	--	70	34	3.5
24	--	--	--	30	--	--	--	70	34	3
25 (Comp.)	--	--	--	--	30	--	--	70	36	4.5
26	--	--	--	--	--	30	--	70	33	3
27 (Comp.)	--	--	--	--	--	--	30	70	35	4.5

Patent Claims

1. Combinations containing

a) 1 to 99 parts by weight of at least one antioxidant having at least one sterically hindered phenol group, and

b) 99 to 1 part by weight of at least one water-soluble inorganic phosphorus compound selected from the group containing the salts of hypophosphorous acid (H_3PO_2) and phosphorous acid (H_3PO_3 and HPO_2).

2. Combinations according to claim 1 containing in addition as component c) up to 50 parts by weight of at least one organic phosphorus-containing stabilising compound not soluble in water.

3. Combinations according to claim 1 or 2, containing in addition as component d) up to 50 parts by weight of at least one sulfur-containing stabilising compound.

4. Use of combinations according to claims 1 to 3 for stabilising polymers.

5. Process for stabilising polymers, characterised in that a combination containing

a) 1 to 99 parts by weight of at least one antioxidant having at least one sterically hindered phenol group, and

b) 99 to 1 part by weight of at least one water-soluble inorganic phosphorus compound selected from the group containing the salts of hypophosphorous acid (H_3PO_2) and phosphorous acid (H_3PO_3 and HPO_2)

and/or the individual components of this combination are added together or individually in the form of an aqueous solution or an aqueous dispersion or an

aqueous emulsion or a combination of these aqueous forms, to the polymer material present in aqueous emulsion or aqueous suspension.

6. Process according to claim 5, characterised in that 0.1 to 10 parts by weight of the combination containing a) and b) is/are added per 100 parts by weight of polymer.

7. Process according to claim 5, characterised in that 1 to 99 parts by weight of a) and 99 to 1 part by weight of b), the amounts of a) and b) totalling 100 parts by weight, are added.

8. Process according to claim 5, characterised in that octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate is added as component a) and sodium hypophosphite is added as component b).

9. Process according to claim 5, characterised in that in addition at least one organic phosphorus-containing stabiliser is added as component c).

10. Process according to claim 5, characterised in that in addition at least one sulfur-containing stabiliser is added as component d).

11. Stabilised graft rubber materials obtainable by the process according to claim 5.

12. Stabilised polymer materials according to claim 11, containing as polymer at least one polymer selected from the group containing ABS polymers, MBS polymers and rubber polymers.

13. Stabilised graft rubber materials according to claim 11, containing

I) at least one rubber having a glass transition temperature $\leq 10°C$ as graft base, and

II) at least one graft shell built up by polymerisation of at least one vinyl monomer in the presence of the rubber.

14. Stabilised graft rubber materials according to claim 11, wherein the rubber content is from 10 to 90 wt.% referred to I) and II).

15. Thermoplastic moulding compositions containing

A) at least one graft rubber produced by free-radical emulsion polymerisation of at least one vinyl monomer in the presence of at least one rubber present in latex form and with a glass transition temperature below 0°C, to which was added, before the working-up, a combination of

a) at least one antioxidant with at least one sterically hindered phenol group, and

b) at least one water-soluble phosphorus compound selected from salts of hypophosphorous acid (H_3PO_2) or phosphorous acid (H_3PO_3 or HPO_2) in the form of an aqueous solution or dispersion, and

B) at least one thermoplastic rubber-free polymer obtained by polymerisation of at least one resin-forming vinyl monomer.

16. Compositions according to claim 15, containing

A) at least one graft rubber produced by free-radical emulsion polymerisation of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide, in the presence of at least one butadiene rubber present in latex form, to which has been added, before the working-up, a combination

of

a) at least one antioxidant with at least one sterically hindered phenol group, and

b) at least one water-soluble phosphorus compound selected from salts of hypophosphorous acid (H_3PO_2) or phosphorous acid (H_3PO_3 or HPO_2) in the form of an aqueous solution or dispersion, and

B) at least one thermoplastic rubber-free polymer obtained by polymerisation of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, in which styrene and/or acrylonitrile may be wholly or partially replaced by α-methylstyrene, methyl methacrylate or N-phenylmaleimide.

17. Moulding composition according to claim 15, characterised in that for the production of the component A) styrene and acrylonitrile are added as monomers in a weight ratio of 90:10 to 50:50.

18. Moulding composition according to claim 15, characterised in that the proportion of the component A) is 5 to 95 parts by weight and the proportion of the component B) is 95 to 5 parts by weight.

19. Moulding composition according to claim 15, characterised in that the rubber base of the component A) is a polybutadiene.

20. Moulding composition according to claim 15, characterised in that the antioxidant A) is octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate.

21. Moulding composition according to claim 15, characterised in that the water-soluble phosphorus compound b) is sodium hypophosphite or sodium phosphite.

22. Moulding composition according to claim 15, characterised in that in addition at least one further polymer is present selected from the group containing aromatic polycarbonates, aromatic polyester carbonates, polyesters and polyamides.

23. Process for the production of moulded articles according to claim 15, characterised in that the components A) and B) and optionally further constituents are mixed and are compounded and extruded at elevated temperatures.

24. Use of moulding compositions according to claim 15 for the production of moulded parts.

25. Moulded parts obtainable from moulding compositions according to claim 15.

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