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(54) **STABILISIERTE
ACRYLNITRIL/STYROL/BUTADIEN
FORMMASSEN**

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(57) **ABSTRACT**

The invention relates to a thermoplastic molding composition containing:

from 3 to 94.6% by weight of one or more styrene copolymers as component A

from 5 to 95.2% by weight of one or more impact-modifying graft rubbers having an olefinic double bond in the rubber phase as component B

from 0.2 to 0.9% by weight of a compound of the formula (I) as component C:

from 0 to 0.9% by weight of a mixture of the formula (II) as component D:

from 0 to 0.5% by weight of a compound of the formula (III) as component E:

or from 0 to 0.5% by weight of a compound of the formula (IV):

or from 0 to 0.5% by weight of a compound of the formula (V):

or from 0 to 0.5% by weight of a compound of the formula (VI):

from 0 to 10% by weight of one or more additives, where these differ from components C, D, and E, as component F, and from 0 to 40% by weight of fibrous or particulate fillers as component G, with the proviso that if the amount of component D is 0% by weight the amount of component E is from 0.01 to 0.5% by weight of one or more of the compounds III, IV, V, or VI, where each of the % by weight values is based on the sum weight of components A to G, and the sum of these values does not exceed 100% by weight. The invention also relates to a process to make the thermoplastic composition and the use of the thermoplastic composition.

**STABILISIERTE
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FORMMASSEN**

[0001] The present invention relates to thermoplastic molding compositions comprising styrene copolymers and comprising impact-modifying graft rubbers having an olefinic double bond in the rubber phase.

[0002] There is a very wide variety of known stabilized thermoplastic molding compositions, and these have a wide range of possible uses because their property profile, in particular their good impact resistance, is advantageous for many applications.

[0003] U.S. Pat. No. 4,692,486 discloses stabilizer mixtures comprising compounds of the formulae (I) and (III) of the present application for polypropylene, polyurethane, and polystyrene, where the amounts used of the individual stabilizer components are smaller than or equal to 0.1% by weight.

[0004] DE-A-103 16 198 discloses stabilizer mixtures for a very wide variety of thermoplastic polymers, an example highlighted being polypropylene. The stabilizer mixtures are three-substance mixtures. For each of the three components of said stabilizer mixture, a large number of possible generic and specific compounds are described. Just one of many possibilities described includes stabilizer mixtures which also comprise compounds of the formulae (VI), (VII), and (VIII) of the present application. The amount of each of the three stabilizer components that can be present here is preferably from 0.05 to 1% by weight, based on the organic material. A disadvantage of this embodiment is the marked decrease in multiaxial toughness during weathering.

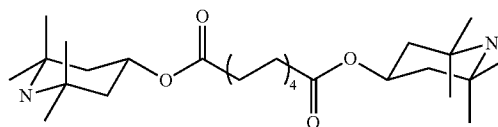
[0005] It was therefore an object of the present invention to provide improved molding compositions based on acrylonitrile/butadiene/styrene molding compositions.

[0006] Novel and improved thermoplastic molding compositions have accordingly been discovered, comprising:

[0007] from 3 to 94.6% by weight of one or more styrene copolymers as component A

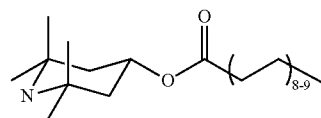
[0008] b) from 5 to 95.2% by weight of one or more impact-modifying graft rubbers having an olefinic double bond in the rubber phase as component B

[0009] c) from 0.2 to 0.9% by weight of a compound of the formula (I) as component C:



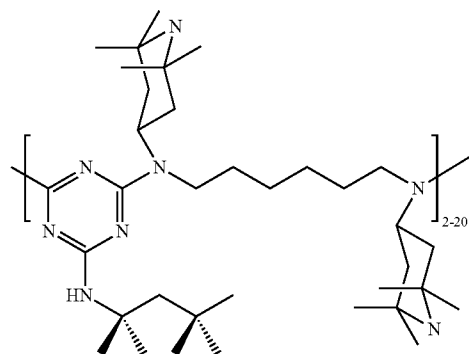
(I)

[0010] d) from 0 to 0.9% by weight of a mixture of the formula (II) as component D:



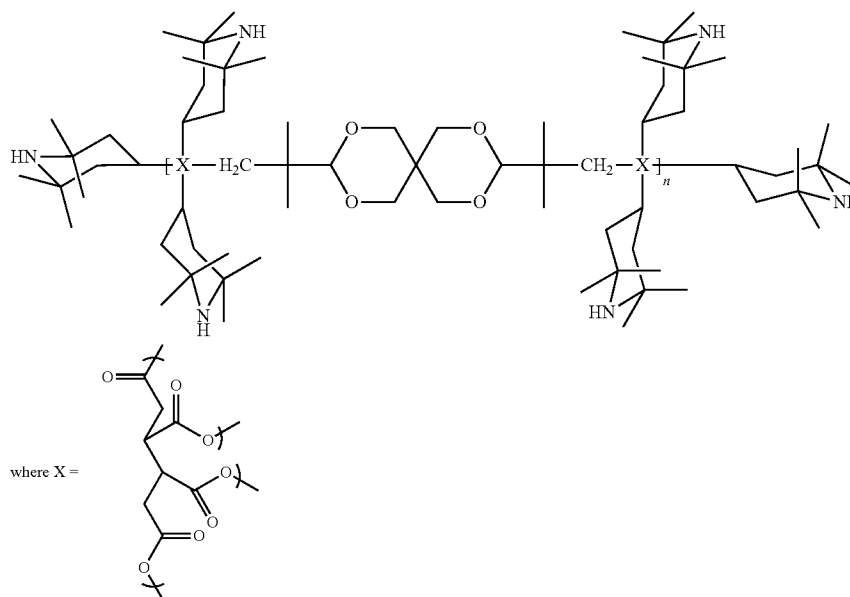
(II)

[0011] e) from 0 to 0.5% by weight of a compound of the formula (III) as component E:



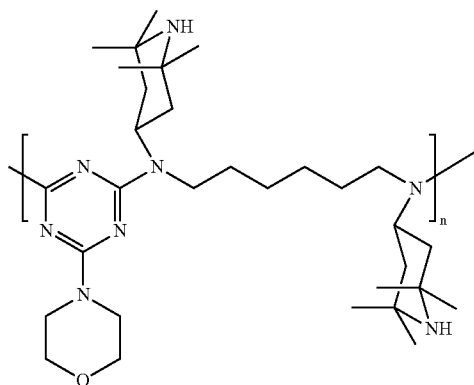
(III)

[0012] or from 0 to 0.5% by weight of a compound of the formula (IV):

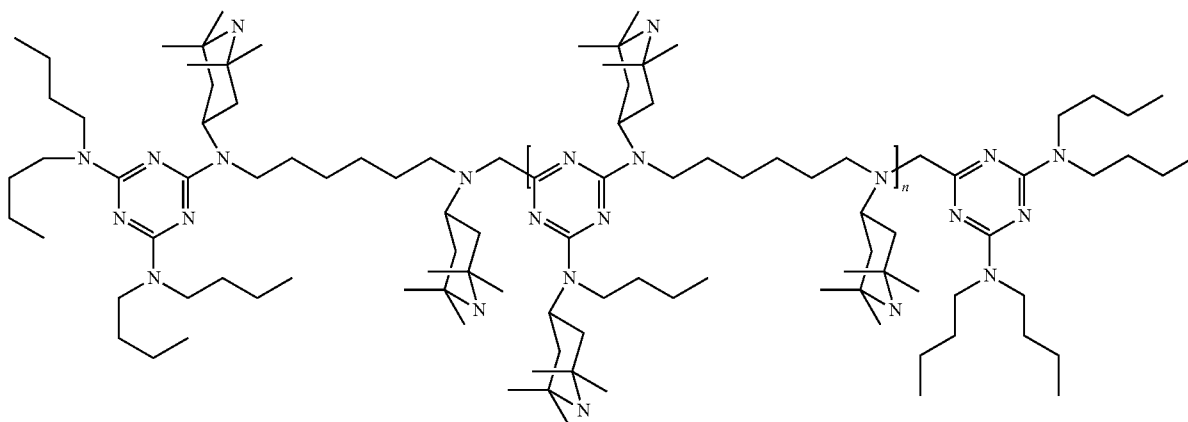


(IV)

[0013] or from 0 to 0.5% by weight of a compound of the formula (V):



[0014] or from 0 to 0.5% by weight of a compound of the formula (VI):



[0015] f) from 0 to 10% by weight of one or more additives, where these differ from components C, D, and E, as component F, and

[0016] g) from 0 to 40% by weight of fibrous or particulate fillers as component G,

with the proviso that if the amount of component D is 0% by weight (i.e. no component D is present), the amount of component E is from 0.01 to 0.5% by weight, preferably from 0.1 to 0.5% by weight, particularly preferably from 0.2 to 0.5% by weight, of one of the compounds III, IV, V, or VI, where each of the % by weight values is based on the sum weight of components A to G, and the sum of these values is 100% by weight.

[0017] Processes for producing said molding compositions have moreover been invented, as also have the use thereof for producing foils, moldings, or fibers, and said foils, moldings, or fibers.

[0018] By virtue of the specific selection, essential to the invention, of each individual component, and specific quantitative proportions thereof, when the molding compositions of the invention are compared with the known stabilized molding compositions they exhibit a further improvement in weathering resistance, i.e. a further improvement in resistance to heat, to light, and/or to oxygen.

[0019] A description follows of the articles, processes, and uses of the invention.

[0020] The molding compositions of the invention comprise, based on the total weight of components A, B, C, D, E, F, and G, which is 100% by weight

[0021] a) from 3 to 94.6% by weight, preferably from 10 to 75% by weight, particularly preferably from 20 to 70% by weight of component A,

[0022] b) from 5 to 95.2% by weight, preferably from 10 to 50% by weight, particularly preferably from 15 to 40% by weight of component B,

[0023] c) from 0.2 to 0.9% by weight, preferably from 0.2 to 0.7% by weight, particularly preferably from 0.3 to 0.6% by weight of component C,

[0024] d) from 0 to 0.9% by weight, preferably from 0.2 to 0.7% by weight, particularly preferably from 0.2 to 0.4% by weight of component D, with the proviso that if the amount of component D is 0% by weight (i.e. no component D is present), the amount of component E is from 0.01 to 0.5% by weight, preferably from 0.1 to 0.5% by weight,

(VI)

particularly preferably from 0.2 to 0.5% by weight, of one of the compounds III, IV, V, or VI,

[0025] e) from 0 to 0.5% by weight, preferably from 0.1 to 0.5% by weight, particularly preferably from 0.2 to 0.4% by weight of component E

[0026] f) from 0 to 10% by weight, preferably from 0 to 8% by weight, particularly preferably from 0 to 5% by weight of component F, and

[0027] g) from 0 to 40% by weight, preferably from 0 to 25% by weight, particularly preferably from 0 to 15% by weight of component G.

[0028] The ratio by weight of component C to component D is generally in the range from 4:1 to 0.25:1, preferably from 4:1 to 1:1, particularly preferably from 3:1 to 1:1.

[0029] The ratio by weight of component D to E is generally in the range from 2:1 to 0.5:1.

Component A:

[0030] The thermoplastic molding compositions of the invention comprise one or more styrene copolymers as component A. Any desired suitable comonomers can be present alongside styrene here in the copolymers. Preference is given to a styrene-acrylonitrile copolymer, alpha-methylstyrene-acrylonitrile copolymer, or N-phenylmaleimide-acrylonitrile copolymer.

[0031] A suitable component A is in principle any of the following that are known to the person skilled in the art and described in the literature: styrene-acrylonitrile copolymers, α -methylstyrene-acrylonitrile copolymers, N-phenylmaleimide-acrylonitrile copolymer, or a mixture of these, as long as the intrinsic viscosity IV of a mixture of these is less than or equal to 85 ml/g (measured to DIN 53727 at 25° C. on a 0.5% strength by weight solution in dimethylformamide; this measurement method also applies to all of the intrinsic viscosities IV mentioned hereinafter).

[0032] Preferred components A are composed of from 50 to 90% by weight, preferably from 60 to 80% by weight, in particular from 65 to 78% by weight, of styrene, and from 10 to 50% by weight, preferably from 20 to 40% by weight, in particular from 22 to 35% by weight, of acrylonitrile, and also from 0 to 5% by weight, preferably from 0 to 4% by weight, in particular from 0 to 3% by weight, of further monomers, where each of the % by weight values is based on the weight of component A, and the sum of these is 100% by weight.

[0033] Further preferred components A are composed of from 50 to 90% by weight, preferably from 60 to 80% by weight, in particular from 65 to 78% by weight, of α -methylstyrene, and from 10 to 50% by weight, preferably from 20 to 40% by weight, in particular from 22 to 35% by weight, of acrylonitrile, and also from 0 to 5% by weight, preferably from 0 to 4% by weight, in particular from 0 to 3% by weight, of further monomers, where each of the % by weight values is based on the weight of component A, and the sum of these is 100% by weight.

[0034] Components A to which preference is likewise given are composed of 50 to 90% by weight, preferably from 60 to 80% by weight, in particular from 65 to 78% by weight, of N-phenylmaleimide, and from 10 to 50% by weight, preferably from 20 to 40% by weight, in particular from 22 to 35% by weight, of acrylonitrile, and also from 0 to 5% by weight, preferably from 0 to 4% by weight, in particular from 0 to 3% by weight, of further monomers, where each of the % by weight values is based on the weight of component A, and the sum of these is 100% by weight.

[0035] Components A to which preference is likewise given are mixtures of said styrene-acrylonitrile copolymers, α -methylstyrene-acrylonitrile copolymers, and N-phenylmaleimide-acrylonitrile copolymers.

[0036] The abovementioned further monomers that can be used are any of the copolymerizable monomers, examples being p-methylstyrene, tert-butylstyrene, vinylnaphthalene, alkyl acrylates, and/or alkyl methacrylates, for example those having C₁-C₈-alkyl radicals, N-phenylmaleimide, or a mixture of these.

[0037] The copolymers of component A can be produced by known methods. By way of example, they can be produced via free-radical polymerization, in particular via emulsion, suspension, solution, or bulk polymerization.

Component B:

[0038] Component B is preferably composed of one or more impact-modifying graft rubbers having an olefinic double bond in the rubber phase. Component B is a graft copolymer with bimodal particle size distribution, and the proportion thereof in the molding compositions of the invention is from 5 to 80% by weight, preferably from 10 to 70% by weight, and particularly preferably from 15 to 60% by weight, based on the entirety of components A, B, C, D, and/or E, and also, if present, F and G. The graft polymer B is composed of a "soft" elastomeric, particulate graft base b1, and of a "hard" graft b2. The swelling index of component B

is generally from 5 to 20, preferably from 6 to 15, and particularly preferably from 7 to 13.

[0039] The proportion of the graft base b1 comprised is from 40 to 90% by weight, preferably from 45 to 85% by weight, and particularly preferably from 50 to 80% by weight, based on component B. The graft base b1 is obtained via polymerization of, based on b1, from 70 to 100% by weight, preferably from 75 to 100% by weight, and particularly preferably from 80 to 100% by weight, of at least one conjugated diene b11, and from 0 to 30% by weight, preferably from 0 to 25% by weight, and particularly preferably from 0 to 10% by weight, of at least one further monoethylenically unsaturated monomer. Conjugated dienes b11 that can be used are butadiene, isoprene, chloroprene, and mixtures thereof. It is preferable to use butadiene or isoprene or a mixture thereof, and butadiene is very particularly preferably used.

[0040] Constituent b1 of the molding compositions can moreover comprise, with concomitant reduction in the amount of the monomers b11, further monomers b12 which vary the mechanical and thermal properties of the core within a certain range. Examples that may be mentioned of these monoethylenically unsaturated comonomers are: styrene, α -methylstyrene, acrylonitrile, maleic anhydride, acrylic acid, methacrylic acid, maleic acid, and fumaric acid.

[0041] It is preferable to use styrene, α -methylstyrene, n-butyl acrylate, or a mixture of these as monomers b12, and it is particularly preferable to use styrene and n-butyl acrylate or a mixture of these, and it is very particularly preferable to use styrene. The amounts used of styrene or n-butyl acrylate, or a mixture of these, are in particular up to 20% by weight in total, based on b1.

[0042] One particular embodiment uses a graft base made of, based on b1:

b11 from 70 to 99.9% by weight, preferably from 90 to 99% by weight, of butadiene, and

b12 from 0.1 to 30% by weight, preferably from 1 to 10% by weight, of styrene.

[0043] The proportion comprised of the graft b2 is from 10 to 60% by weight, preferably from 15 to 55% by weight, and particularly preferably from 20 to 50% by weight, based on component B.

[0044] The graft b2 is obtained via polymerization of, based on b2:

b21 from 65 to 95% by weight, preferably from 70 to 90% by weight, and particularly preferably from 72 to 85% by weight, of at least one vinylaromatic monomer,

b22 from 5 to 35% by weight, preferably from 10 to 30% by weight, and particularly preferably from 15 to 28% by weight, of acrylonitrile, and

b23 from 0 to 30% by weight, preferably from 0 to 20% by weight, and particularly preferably from 0 to 15% by weight, of at least one other monoethylenically unsaturated monomer.

[0045] Styrene and/or α -methylstyrene can be used as vinylaromatic monomers. The monomers mentioned at an earlier stage above for component b12 can be used as other monomers b23. Methyl methacrylate and acrylates, such as n-butyl acrylate, are particularly suitable. Methyl methacrylate MMA is very particularly suitable as monomer b23, and preference is given here to an amount of up to 20% by weight of MMA, based on b2.

[0046] The graft polymers are produced by the emulsion polymerization process. It is usual to polymerize at from 20 to 100° C., but preferably from 30 to 90° C. Conventional emulsifiers are usually used concomitantly, examples being the alkali metal salts of alkylsulfonic acids or of alkylarylsulfonic

acids, other examples being alkyl sulfates, fatty alcohol sulfonates, and salts of higher fatty acids having from 10 to 30 carbon atoms, and other examples are sulfosuccinates, ether sulfonates, and resin soaps. Preference is given to use of the alkali metal salts, in particular the Na salts and K salts, of alkylsulfonates or fatty acids having from 10 to 18 carbon atoms.

[0047] The amounts generally used of the emulsifiers are from 0.5 to 5% by weight, in particular from 0.5 to 3% by weight, based on the monomers used in producing the graft base b1.

[0048] In producing the dispersion it is preferable to use an amount of water such that the solids content of the finished dispersion is from 20 to 50% by weight. Operations are usually carried out with a water/monomer ratio of from 2:1 to 0.7:1.

[0049] Suitable free-radical generators for initiating the polymerization reaction are any of those which decompose at the selected reaction temperature, i.e. either those which decompose solely thermally or those which decompose in the presence of a redox system. Preferred polymerization initiators that can be used are free-radical generators such as peroxides, a preferred example being peroxosulfates (e.g. sodium persulfate or potassium persulfate), and azo compounds, such as azodiisobutyronitrile. However, it is also possible to use redox systems, in particular those based on hydroperoxides, such as cumene hydroperoxide.

[0050] The amount generally used of the polymerization initiators is from 0.1 to 1% by weight, based on the graft base monomers b11 and b12.

[0051] The free-radical generators, and also the emulsifiers, are added to the reaction mixture by way of example batchwise, by adding the total amount at the start of the reaction, or are added batchwise after division into a plurality of portions, at the start and at one or more subsequent junctures, or are added continuously during a certain time interval. The continuous addition process can also follow a gradient, which can by way of example be upward- or downward-inclined, linear, or exponential, or else can be a staged gradient (step function).

[0052] Molecular-weight regulators can moreover be used concomitantly, examples being ethylhexyl thioglycolate, n- or tert-dodecyl mercaptan, and other mercaptans, terpinols, and dimeric α -methylstyrene, or other compounds suitable as molecular-weight regulators. The molecular-weight regulators are added to the reaction mixture batchwise or continuously, as has been described above for the free-radical generators and emulsifiers.

[0053] In order to maintain constant pH, which is preferably from 6 to 9, buffer substances can be used concomitantly, an example being $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$, sodium hydrogen carbonate, or buffers based on citric acid/citrate. The amounts used of regulators and buffer substances are conventional, and there is therefore no need for further information in this respect.

[0054] In one particular preferred embodiment, a reducing agent is added during the grafting of the graft base b1 with the monomers b21 to b23.

[0055] In one particular embodiment, the graft base can also be produced via polymerization of the monomers b1 in the presence of a fine-particle latex, this being known as the seed latex polymerization procedure. This latex is used as initial charge and can be composed of monomers that form elastomeric polymers, or else of the other monomers mentioned above. Suitable seed latices are composed by way of example of polybutadiene or polystyrene.

[0056] In another preferred embodiment, the graft base IA can be produced by what is known as the feed process. In this process, a certain proportion of the monomers b1 is used as initial charge, and the polymerization reaction is initiated, and then the remainder of the monomers ("feed") a1) is added as feed during the polymerization reaction. The parameters for the feed (shape of gradient, amount, duration, etc.) depend on the other polymerization conditions. The principles of the statements made in relation to the mode of addition of the free-radical initiator or of the emulsifier are again applicable here. The proportion of the monomers b1 preferably used as initial charge in the feed process is from 5 to 50% by weight, particularly preferably from 8 to 40% by weight, based on loll. It is preferable that the feed of a1) is added within a period of from 1 to 18 hours, in particular from 2 to 16 hours, very particularly from 4 to 12 hours.

[0057] Graft polymers having a plurality of "soft" and "hard" shells are moreover also suitable, for example those having the structure b1-b2-b1-b2, or b2-b1-b2, especially in the case of relatively large particles.

[0058] The precise polymerization conditions, in particular the nature of and amount of, and the metering procedure for, the emulsifier, and the other polymerization auxiliaries, are preferably selected in such a way that the average particle size of the resultant latex of the graft polymer B, defined via the d50 value of the particle size distribution, is from 80 to 800, preferably from 80 to 600, and particularly preferably from 85 to 400, measured with the aid of HDC (W. Wohlleben and H. Schuch in Measurement of Particle Size Distribution of Polymer Latexes, 2010, Editors: Luis M. Gugliotta and Jorge R. Vega, p. 130-153).

[0059] The reaction conditions are balanced in such a way that the polymer particles of B have bimodal particle size distribution, i.e. a size distribution with two relatively pronounced maxima. The first maximum is more pronounced (comparatively narrow peak) than the second, and is generally at from 25 to 200 nm, preferably from 60 to 170 nm, particularly preferably from 70 to 150 nm. The second maximum is generally at from 150 to 800 nm, preferably from 180 to 700 nm, particularly preferably from 200 to 600 nm. The second maximum here (from 150 to 800 nm) is at particle sizes larger than those of the first maximum (from 25 to 200 nm).

[0060] The bimodal particle size distribution is preferably achieved via (partial) agglomeration of the polymer particles. An example of a procedure for achieving this is as follows: the monomers b1 which form the core are polymerized to a conversion which is usually at least 90%, preferably greater than 95%, based on the monomers used. This conversion has generally been achieved after from 4 to 20 hours. The average particle size d50 of the resultant rubber latex is at most 200 nm and it has a narrow particle size distribution (almost monodisperse system).

[0061] In the second stage, the rubber latex is agglomerated. This is generally achieved via addition of a dispersion of an acrylate polymer. It is preferable to use dispersions of copolymers of (C1-C4-alkyl)acrylates, preferably of ethyl acrylate, with from 0.1 to 10% by weight of monomers forming polar polymers, e.g. acrylic acid, methacrylic acid, acrylamide, or methacrylamide, N-methylolmethacrylamide or N-vinylpyrrolidone. Preference is given to a composition made of from 80 to 98% of ethyl acrylate and from 2 to 20% of methacrylamide, and particular preference is given to a composition made of from 90 to 98% of ethyl acrylate and from 2 to 10% of methacrylamide. The agglomeration dispersion can also optionally comprise a plurality of the acrylate polymers mentioned.

[0062] The concentration of the acrylate polymers in the dispersion used for agglomeration is in general to be from 3 to 40% by weight. The agglomeration process uses from 0.2 to 20 parts by weight, preferably from 1 to 5 parts by weight, of the agglomeration dispersion for every 100 parts of the rubber latex, the calculation in each case being based on solids. The agglomeration process is carried out via addition of the agglomeration dispersion to the rubber. The rate of addition is normally not critical, and the addition generally takes from about 1 to 30 minutes at a temperature of from 20 to 90° C., preferably from 30 to 75° C.

[0063] The rubber latex can also be agglomerated via other agglomeration agents, e.g. acetic anhydride, as well as by means of an acrylate polymer dispersion. Agglomeration via pressure or freezing is also possible (pressure agglomeration or freeze agglomeration). The methods mentioned are known to the person skilled in the art.

[0064] Under the conditions mentioned, only a portion of the rubber particles is agglomerated, and the distribution produced is therefore bimodal. After the agglomeration process here, the proportion of the particles present in the non-agglomerated state (numeric distribution) is generally more than 50%, preferably from 75 to 95%. The resultant partially agglomerated rubber latex is relatively stable, and can therefore be readily stored and transported without coagulation.

[0065] In order to achieve bimodal particle size distribution in the graft polymer B, it is also possible to produce, separately from one another and in a usual manner, two different graft polymers B' and B'' which differ in their average particle size, and to combine the graft polymers B' and B'' in the desired quantitative proportion.

[0066] The polymerization of the graft base b1 is usually conducted in such a way, via selection of the reaction conditions, as to give a graft base with a particular condition of crosslinking. Examples that may be mentioned of parameters essential for this purpose are the reaction temperature and reaction time, the ratio of monomers, regulator, free-radical initiator and, for example in the case of the feed process, the feed rate and the amount, and the juncture of addition, of regulator and initiator.

[0067] A method for characterizing the condition of crosslinking of crosslinked polymer particles is measurement of the swelling index SI, which is a measure of the solvent-swellability of a polymer having some degree of crosslinking. An example of conventional swelling agents is methyl ethyl ketone or toluene. The SI of the ungrafted molding compositions b1 of the invention is usually in the range SI=from 10 to 60, preferably from 15 to 55, and particularly preferably from 20 to 50, in toluene.

[0068] Another method of characterizing the condition of crosslinking is measurement of NMR relaxation times for the labile protons, these being known as T2 times. As the degree of crosslinking of a particular network increases, its T2 times decrease. Usual T2 times for the graft bases b1 of the invention are average T2 times in the range from 2.0 to 4.5 ms, preferably from 2.5 to 4.0 ms, and particularly preferably from 2.5 to 3.8 ms, measured on filmed specimens at 80° C.

[0069] Another measure for characterizing the graft base and its condition of crosslinking is gel content, i.e. the proportion of the product which has been crosslinked and is therefore insoluble in a particular solvent. The solvent used for determination of gel content is usefully the same as that used for determination of the swelling index. Usual gel contents of the graft bases b1 of the invention are in the range from 50 to 90%, preferably from 55 to 85%, and particularly preferably from 60 to 80%.

[0070] The swelling index is determined by way of example by the following method: about 0.2 g of the solid of a graft base dispersion filmed via evaporation of the water is swollen in a sufficient amount (e.g. 50 g) of toluene. After, for example, 24 h the toluene is removed under suction and the specimen is weighed. The specimen is dried in vacuo and again weighed. The swelling index is the ratio of the outgoing weight after the swelling procedure to the outgoing dry weight after the further drying process. The gel content is calculated correspondingly from the ratio of dry outgoing weight after the swelling step to the ingoing weight prior to the swelling step ($\times 100\%$).

[0071] The T2 time is determined via measurement of NMR relaxation of a specimen of the graft base dispersion which has been filmed after removal of water. For this, by way of example, the specimen is dried in air overnight and at, for example, 60° C. dried in vacuo for 3 h and then subjected to measurement using suitable measuring equipment, e.g. minispec equipment from Bruker, at 80° C. The relaxation process is markedly temperature-dependent, and comparison can therefore be made only between specimens subjected to measurement by the same method.

[0072] The conditions used to produce the graft b2 can be the same as those used to produce the graft base b1, and the graft b2 can be produced here in one or more steps of a process. By way of example, for two-stage grafting, styrene and, respectively, α -methylstyrene can first be polymerized alone, and then styrene and acrylonitrile can be polymerized, in two successive steps. This two-stage grafting process (first styrene, then styrene/acrylonitrile) is a preferred embodiment. Further details concerning production of the graft polymers B are described in DE-OS 12 60 135 and 31 49 358.

[0073] It is advantageous in turn to carry out the graft polymerization onto the graft base b1 in aqueous emulsion. The system used for this process can be the same as that used for the polymerization of the graft base, and further emulsifier and initiator can be added here. These do not have to be identical with the emulsifiers and initiators used for producing the graft base a1). By way of example, therefore, it can be advantageous to use a persulfate as initiator for producing the graft base b1 but to use a redox initiator system for polymerizing the graft shell b2. In other respects, the statements made in relation to the production of the graft base b1 apply to the selection of emulsifier, initiator, and polymerization auxiliaries. The monomer mixture to be grafted onto the material can be added to the reaction mixture all at once, batchwise in a plurality of stages, or preferably continuously during the polymerization reaction.

[0074] To the extent that ungrafted polymers are produced from the monomers b2 during the grafting of the graft base b1, the amounts are counted with the mass of component B, and are generally less than 10% by weight of b2.

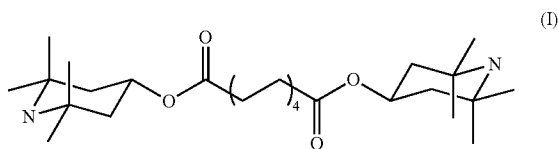
[0075] The graft copolymers B of the invention can be used as they stand, as they are produced in the reaction mixture, for example in the form of latex emulsion or of latex dispersion. However, as an alternative, which is preferable for most applications, they can also be worked up in a further step. Methods of work-up are known to the person skilled in the art. One example of these is isolation of the graft copolymers B from the reaction mixture, e.g. via spray drying or shear, or via precipitation using strong acids, or by means of nucleating agents, such as inorganic compounds, e.g. magnesium sulfate. The graft copolymers B present in the reaction mixture can also be worked up by dewatering them completely or partially. Another possibility is to undertake the work-up by means of a combination of the methods mentioned.

[0076] The SI of the graft polymers is usually in the range SI—from 5 to 20, preferably from 6 to 15, and particularly preferably from 7 to 13.

[0077] Components A and B can be mixed in any desired manner by any of the known methods to produce the molding composition. If, by way of example, these components have been produced via emulsion polymerization, the resultant polymer dispersions can be mixed with one another, and then the polymers can be precipitated together, and the polymer mixture can be worked up. However, the blending of these components preferably takes place via extrusion, kneading, or rolling of the components together, where the components have been previously isolated, if necessary, from the aqueous dispersion or solution obtained during the polymerization reaction. The graft-copolymerization products B obtained in aqueous dispersion can also be dewatered only partially and mixed in the form of moist crumb with the hard matrix A, whereupon full drying of the graft copolymers B then takes place during the mixing process.

Component C:

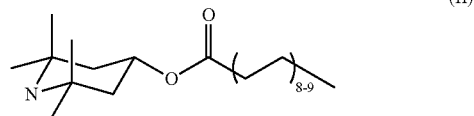
[0078] A compound of the formula (I) is used as component C of the molding compositions of the invention:



[0079] This sterically hindered amine (CAS number 52829-07-9) and production thereof are known to the person skilled in the art and are described in the literature (see by way of example U.S. Pat. No. 4,396,769 and the references cited therein). It is marketed as Tinuvin® 770 by BASF SE.

Component D:

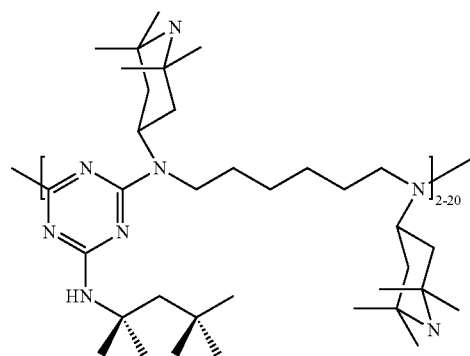
[0080] A compound of the formula (II) is used as component D of the molding compositions of the invention:



[0081] This sterically hindered amine (CAS number 167078-06-0) and production thereof are known to the person skilled in the art and described in the literature (Carlsson et al., Can. Journal of Polymer Science, Polymer Chemistry Edition (1982), 20(2), 575-82). It is marketed as Cyasorb® 3853 by Cytec Industries.

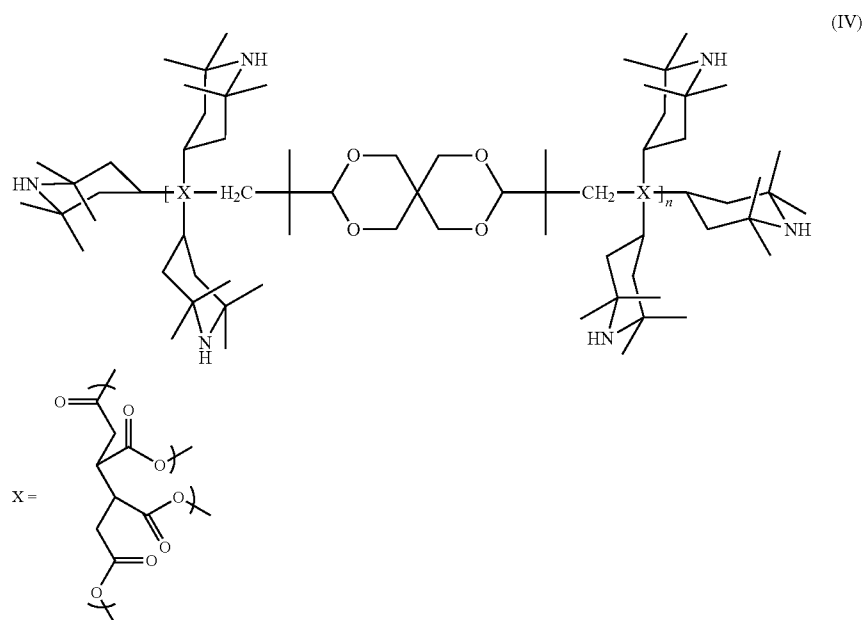
Component E:

[0082] A compound of the formula (III) can be used as component E of the molding compositions of the invention:



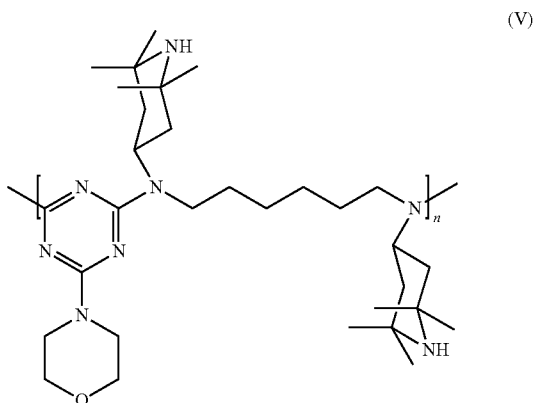
[0083] This sterically hindered amine (CAS number 71878-19-8) and production thereof are known to the person skilled in the art and are described in the literature (see by way of example EP-A-93 693 and the references cited therein). It is marketed as Chimassorb® 944 by BASF SE.

[0084] A compound of the formula (IV) can be used as further component E of the molding compositions of the invention:



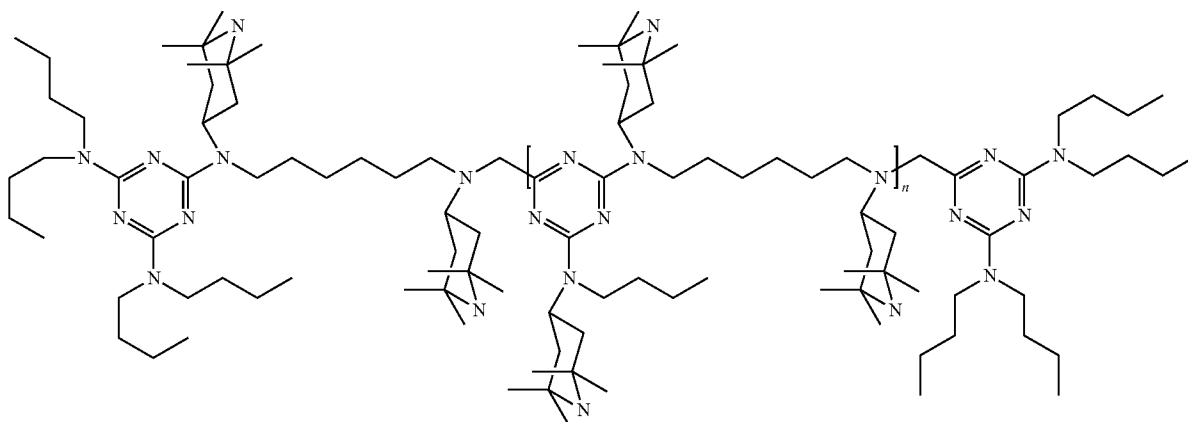
[0085] This sterically hindered amine (CAS number 101357-37-3) and production thereof are known to the person skilled in the art and are described in the literature (see by way of example U.S. Pat. No. 5,208,132 and the references cited therein). It is marketed as Adeka Stab® LA-68 by ADEKA.

[0086] A compound of the formula (V) can be used as further component E of the molding compositions of the invention:



[0087] This sterically hindered amine (CAS number 82451-48-7) and production thereof are known to the person skilled in the art and are described in the literature (see by way of example U.S. Pat. No. 4,331,586 and the references cited therein). It is marketed as Cyasorb® UV-3346 by Cytec Industries.

[0088] A compound of the formula (VI) can be used as further component E of the molding compositions of the invention:



[0089] This sterically hindered amine (CAS number 192268-64-7) and production thereof are known to the person skilled in the art and are described in the literature (see by way of example EP-A-782 994 and the references cited therein). It is marketed as Chimassorb® 2020 by BASF.

Component F:

[0090] The molding compositions of the invention can comprise, alongside components A, B, C, D, and E, one or more additives which are typical for, and commonly used in, plastics mixtures, and which differ from components C, D, and E.

[0091] Examples that may be mentioned of these additives are dyes, pigments, colorants, antistatic agents, antioxidants, stabilizers for improving thermal stability, for increasing lightfastness, and for raising hydrolysis resistance and chemicals resistance, agents to counteract decomposition by heat, and in particular the lubricants which are advantageous for producing moldings. These further additives can be metered into the material at any stage of the production process, but preferably at an early juncture, in order to utilize the stabilizing effects (or other specific effects) of the additive at an early juncture. Heat stabilizers or oxidation retarders are usually metal halides (chlorides, bromides, iodides) deriving from metals of group I of the Periodic Table of the Elements (e.g. Li, Na, K, Cu).

[0092] Stabilizers suitable as component E are the conventional hindered phenols, and also "vitamin E" and compounds of analogous structure. Other suitable compounds are benzophenones, resorcinols, salicylates, benzotriazoles, and others. The amounts of these usually used (based on the total weight of the molding compositions of the invention) are usually from 0 to 2% by weight, preferably from 0.01 to 2% by weight.

[0093] Suitable lubricants and mold-release agents are stearic acids, stearyl alcohol, stearic esters, and generally higher fatty acids, derivatives of these, and corresponding fatty acid mixtures having from 12 to 30 carbon atoms. The amounts of said additions—insofar as they are present—are in the range from 0.05 to 1% by weight (based on the total weight of the molding compositions of the invention).

[0094] Other additives that can be used are silicone oils, oligomeric isobutylene, or similar substances, and the conventional amounts—if these are present—are from 0.05 to 5% by weight (based on the total weight of the molding compositions of the invention). It is equally possible to use

pigments, dyes, optical brighteners, such as ultramarine blue, phthalocyanines, titanium dioxide, cadmium sulfides, and derivatives of perylenetetracarboxylic acid.

[0095] The amounts usually used of processing aids and stabilizers, lubricants, and antistatic agents are from 0 to 4% by weight, preferably from 0.01 to 4% by weight (based on the total weight of the molding compositions of the invention).

Component G:

[0096] The molding compositions of the invention comprise, as component G, fibrous or particulate fillers which

differ from components C, D, E, and F, or a mixture of these fillers. These are preferably commercially available products, for example carbon fibers and glass fibers. Glass fibers that can be used can be those made of E, A, or C glass, and have preferably been equipped with a size and with an adhesion promoter. Their diameter is generally from 6 to 20 μm . It is possible to use either continuous-filament fibers or chopped glass fibers (staple) or rovings with length from 1 to 10 mm, preferably from 3 to 6 mm.

[0097] It is also possible to add fillers or reinforcing materials such as glass beads, mineral fibers, whiskers, aluminum oxide fibers, mica, powdered quartz, and wollastonite.

[0098] The molding compositions of the invention can comprise further polymers alongside components A, B, C, D and optionally E and F.

[0099] The molding compositions of the invention can be produced from the components in any desired manner by any of the known methods. However, it is preferable that the components are blended by mixing in the melt, for example by extruding, kneading or rolling of the components together, e.g. at temperatures in the range from 160 to 400° C., preferably from 180 to 280° C., and in one preferred embodiment here the components have been to some extent or completely isolated in advance from the reaction mixtures obtained during the respective steps of production. By way of example, the graft copolymers B can be mixed in the form of moist crumb with granules of the vinylaromatic copolymer A, whereupon the full drying to give the graft copolymers described then takes place during the mixing process. The components can be introduced in respectively pure form into suitable mixing apparatuses, in particular extruders, preferably twin-screw extruders. However, it is also possible to begin by premixing individual components, for example A and B, and then to mix these with further components A or B or with other components, e.g. C and D. Component A here can be used in the form of component separately produced previously; however it is also possible to add the acrylate rubber and the vinylaromatic copolymer independently of one another. In one embodiment, a concentrate is first produced, for example, from components B and C in component A (these being known as additive batches or masterbatches), and is then mixed with the desired amounts of the remaining components. The molding compositions can be processed by processes known to the person skilled in the art by way of example to give granules, or else directly to give, for example, moldings.

[0100] The molding compositions of the invention can be processed to give foils, moldings or fibers. Said foils, moldings or fibers are particularly suitable for use outdoors, i.e. with exposure to weathering.

[0101] Said foils, moldings or fibers can be produced from the molding compositions of the invention by the known methods of thermoplastic processing. In particular, the production method used can be thermoforming, extrusion, injection molding, calendaring, blow molding, compression molding, pressure sintering or any other type of sintering, preferably injection molding.

[0102] When the molding compositions of the invention are compared with the known stabilized molding compositions, they exhibit a further improvement in weathering resistance, i.e. a further improvement in resistance to heat, to light, and/or to oxygen.

[0103] The examples below provide further explanation of the invention.

EXAMPLES

Test Methods:

[0104] To give a measure of weathering resistance, Xenotest weathering was carried out to ISO 4892/2, Method

A, external, on test specimens (60×60×2 mm, produced to ISO 294 in a mold family at a melt temperature of 260° C. and at a mold temperature of 60° C.). The surface gloss of all of the specimens was measured to DIN 67530 at an observation angle of 60° after the weathering times specified in Table 1.

[0105] Another measure of weathering resistance was the change within the color space ΔE to DIN 52 336 calculated from ΔL , ΔA , and ΔB to DIN 6174.

Starting Materials

[0106] Components or products with prefix “comp-” are not of the invention and serve for comparison.

[0107] Components A and B (and comp-A for comparison) used were:

[0108] AB-i: a butadiene-rubber-modified styrene-acrylonitrile copolymer (ABS) with swelling index 9 in toluene for A6 on repetition of example 11 from DE 197 28 629 A1. Instead of component B1, a styrene-acrylonitrile copolymer with intrinsic viscosity 81 and molecular weight 141 000, measured with the aid of SEC-MALLS, (Chi-san Wu, Handbook of size exclusion chromatography and related techniques, page 19) was used.

[0109] comp-AB-ii: a butadiene-rubber-modified styrene-acrylonitrile copolymer (ABS) with a swelling index of 23.1 in toluene in modification of example 11 of DE 197 28 629 A1, prepared using 40% more tert-dodecyl mercaptan in K4. Instead of component B1, a styrene-acrylonitrile copolymer with intrinsic viscosity 81 and molecular weight 141 000, measured with the aid of SEC-MALLS, (Chi-san Wu, Handbook of size exclusion chromatography and related techniques, page 19) was used.

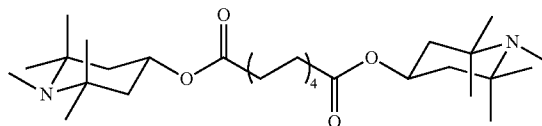
[0110] comp-AB-iii: a polystyrene marketed by BASF SE as polystyrene 158K.

[0111] Component C (and comp-C for comparison) used was:

[0112] C-i: a compound of the formula (I), marketed by BASF SE as Tinuvin® 770.

[0113] comp-C-ii: a compound of the formula (VII), marketed by BASF SE as Tinuvin® 765.

(VII)



[0114] Component D (and comp-D for comparison) used was:

[0115] D-i: a compound of the formula (II), marketed by Cytec Industries as Cyasorb® 3853.

[0116] Component E (and comp-E for comparison) used was:

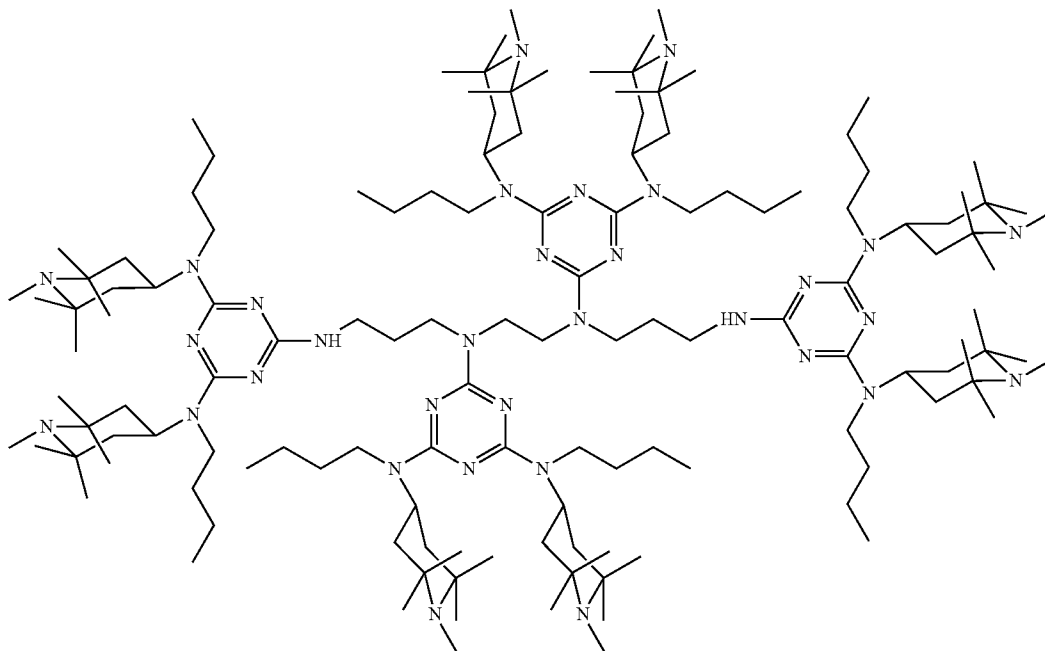
[0117] E-i: a compound of the formula (III), marketed by BASF SE as Chimassorb® 944.

[0118] E-ii: a compound of the formula (IV), marketed by Adeka as Adeka Stab® LA-68.

[0119] E-iii: a compound of the formula (V), marketed by Cytec Industries as Cyasorb® UV-3346.

[0120] comp-E-iiii: a high-molecular-weight sterically hindered amine, CAS number 106990-43-6, marketed by SABO S.p.A. as Sabostab® 119.

(VIII)



[0121] Component F (and comp-F for comparison) used was:

[0122] F-i: Black Pearls 880 carbon black, marketed by Cabot Corporation

Production of the Molding Compositions and Moldings:

[0123] Components A, B, C, and D (see Table 1 for respective parts by weight) were homogenized in a ZSK30 twin-

screw extruder from Werner & Pfleiderer at 250° C., and extruded into a water bath. The extrudates were granulated and dried. The granules were used in an injection-molding machine at a melt temperature of 260° C. and a mold surface temperature of 60° C. to produce test specimens, and the properties specified in Table 1 were determined.

TABLE 1

| Constitution and properties of molding compositions (prefix comp: for comparison) | | | | | | | | | |
|--|-----|------|------|------|------------|------------|------------|------------|------------|
| Example | 1 | 2 | 3 | 4 | comp- 5 | comp- 6 | comp- 7 | comp- 8 | comp- 9 |
| Constitution | | | | | | | | | |
| AB-i | 97 | 97 | 97 | 97 | — | — | — | 97 | 97 |
| comp-AB-ii | — | — | — | — | 97 | 99.75 | — | — | — |
| comp-AB-iii | — | — | — | — | — | — | 99.8 | — | — |
| C-i | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.05 | 0.1 | — | 0.5 |
| comp-C-ii | — | — | — | — | — | — | — | 0.5 | — |
| D-i | 0.5 | 0.25 | 0.25 | 0.25 | 0.25 | 0.05 | — | 0.25 | — |
| E-i | — | 0.25 | — | — | 0.25 | 0.1 | 0.1 | 0.25 | — |
| E-ii | — | — | 0.25 | — | — | — | — | — | — |
| E-iii | — | — | — | 0.25 | — | — | — | — | — |
| comp-E-iv | — | — | — | — | — | — | — | — | 0.5 |
| F-i | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Properties | | | | | | | | | |
| Gloss after | | | | | | | | | |
| 0 h of WT | 97 | 96 | 98 | 96 | 83 | 89 | 102 | 98 | 96 |
| 500 h of WT | 83 | 88 | 87 | 87 | 71 | 65 | 101 | 78 | 74 |
| 1000 h of WT | 27 | 32 | 35 | 33 | 11 | 5 | 7 | 3 | 2 |

TABLE 1-continued

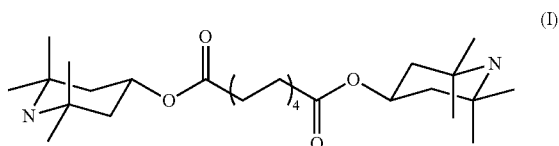
| Constitution and properties of molding compositions (prefix comp: for comparison) | | | | | | | | | |
|--|-----|-----|-----|-----|------------|------------|------------|------------|------------|
| Example | 1 | 2 | 3 | 4 | comp- 5 | comp- 6 | comp- 7 | comp- 8 | comp- 9 |
| <u>ΔE after</u> | | | | | | | | | |
| 0 h of WT | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 500 h of WT | 0.3 | 0.2 | 0.3 | 0.3 | 1.1 | 1.4 | 1.2 | 1.4 | 1.8 |
| 1000 h of WT | 0.8 | 0.6 | 0.7 | 0.6 | 1.7 | 2.3 | 3.8 | 3.8 | 4.2 |

[0124] The examples provide evidence that when the molding compositions of the invention are compared with the known stabilized molding compositions they exhibit a further improvement in weathering resistance, i.e. a further improvement in resistance to heat, to light, and/or to oxygen. Constitution has been given in parts by weight, and the abbreviation WT means weathering time.

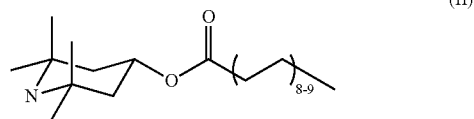
1-13. (canceled)

14. A thermoplastic molding composition comprising:

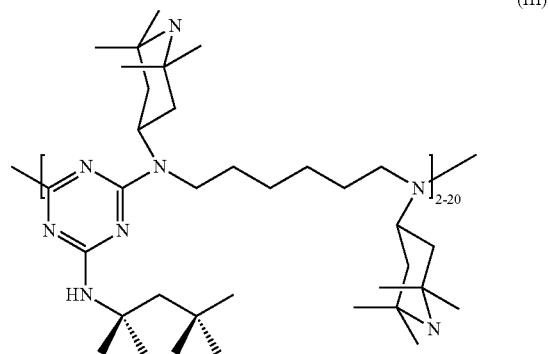
- from 3 to 94.6% by weight of one or more styrene copolymers as component A
- from 5 to 95.2% by weight of one or more impact-modifying graft rubbers having an olefinic double bond in the rubber phase as component B
- from 0.2 to 0.9% by weight of a compound of the formula (I) as component C:



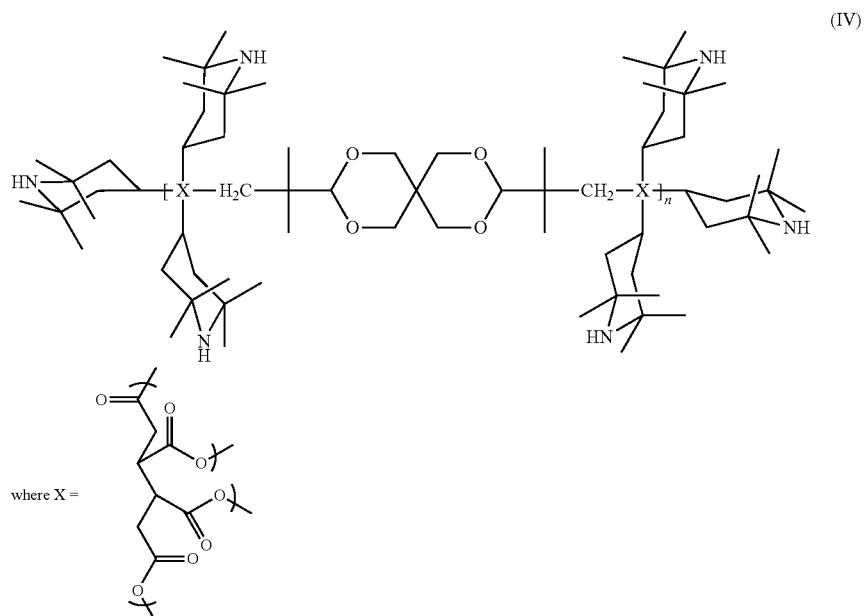
- from 0 to 0.9% by weight of a mixture of the formula (II) as component D:



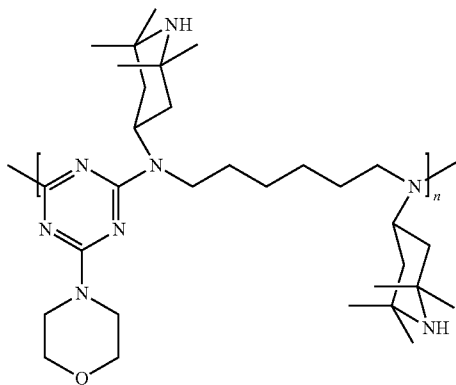
- from 0 to 0.5% by weight of a compound of the formula (III) as component E:



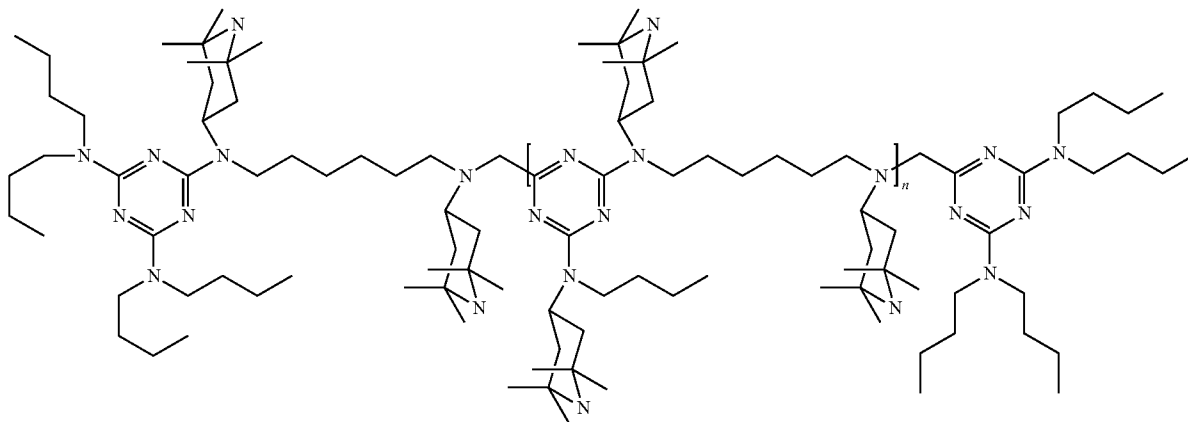
- from 0 to 0.5% by weight of a compound of the formula (IV):



or from 0 to 0.5% by weight of a compound of the formula (V):



or from 0 to 0.5% by weight of a compound of the formula (VI):



f) from 0 to 10% by weight of one or more additives, where these differ from components C, D, and E, as component F, and

g) from 0 to 40% by weight of fibrous or particulate fillers as component G,

with the proviso that if the amount of component D is 0% by weight the amount of component E is from 0.01 to 0.5% by weight of one or more of the compounds III, IV, V, or VI, where each of the % by weight values is based on the sum weight of components A to G, and the sum of these values does not exceed 100% by weight.

15. The thermoplastic molding composition according to claim 14, wherein the proviso that if the amount of component D is 0% by weight the amount of component E is from 0.1 to 0.5% by weight, of one or more of the compounds III, IV, V, or VI, where each of the % by weight values is based on the sum weight of components A to G, and the sum of these values is 100% by weight.

16. The thermoplastic molding composition according to claim 14, wherein the proviso that if the amount of compo-

nent D is 0% by weight the amount of component E is from 0.2 to 0.5% by weight, of one or more of the compounds III, IV, V, or VI, where each of the % by weight values is based on the sum weight of components A to G, and the sum of these values is 100% by weight.

17. The thermoplastic molding composition according to claim 14, wherein the swelling index of component B is from 5 to 20.

18. The thermoplastic molding composition according to claim 14, wherein component A used comprises a copolymer made of acrylonitrile, styrene, and/or α -methylstyrene, phenylmaleimide, methyl methacrylate, or a mixture of these.

19. The thermoplastic molding composition according to claim 16, wherein the swelling index of component B is from 5 to 20 and component A used comprises a copolymer made of acrylonitrile, styrene, and/or α -methylstyrene, phenylmaleimide, methyl methacrylate, or a mixture of these.

20. The thermoplastic molding composition according to claim 14, wherein component B used comprises a mixture made of an acrylonitrile-butadiene-styrene (ABS) graft polymer which comprises

from 50 to 80% by weight, based on B, of an elastomerically crosslinked butadiene polymer B1 and from 50 to 20% by weight, based on B, of a graft shell B2 made of a vinylaromatic monomer and made of one or more polar, copolymerizable, ethylenically unsaturated monomers, and optionally made of a further copolymerizable, ethylenically unsaturated monomer, in a ratio by weight of from 85:15 to 75:25.

21. The thermoplastic molding composition according to claim 19, wherein component B used comprises a mixture made of an acrylonitrile-butadiene-styrene (ABS) graft polymer which comprises

from 50 to 80% by weight, based on B, of an elastomerically crosslinked butadiene polymer B1 and from 50 to 20% by weight, based on B, of a graft shell B2 made of a vinylaromatic monomer and made of one or more polar, copolymerizable, ethylenically unsaturated monomers, and optionally made of a further copolymerizable, ethylenically unsaturated monomer, in a ratio by weight of from 85:15 to 75:25.

22. The thermoplastic molding composition according to claim 14, wherein the average particle diameter of component B is from 50 to 800 nm.

23. The thermoplastic molding composition according to claim 14, which uses components C and D in a ratio by weight of from 3:1 to 1:1 and components D and E in a ratio by weight of from 2:1 to 0.5:1.

24. The thermoplastic molding composition according to claim 21, which uses components C and D in a ratio by weight of from 3:1 to 1:1 and components D and E in a ratio by weight of from 2:1 to 0.5:1 and the average particle diameter of component B is from 50 to 800 nm.

25. The thermoplastic molding composition according to claim 14, which uses styrene or α -methylstyrene as vinylaromatic component in B2.

26. The thermoplastic molding composition according to claim 14, which uses, as ethylenically unsaturated component

in B2, acrylonitrile and/or alkyl methacrylates and/or alkyl acrylates having C₁-C₈-alkyl radicals.

27. The thermoplastic molding composition according to claim 14, which uses component B in bimodal form.

28. A process for producing a thermoplastic molding composition according claim 14, which comprises mixing components A to F with one another at temperatures of from 100 to 300° C. and at a pressure of from 1 to 50 bar in any desired sequence, and then kneading and extruding the material.

29. A process for producing a molding, a foil or a fiber which comprises utilizing the thermoplastic molding composition according to claim 14.

30. The process as claimed in claim 29, wherein a molding is produced for motor-vehicle components or for parts of electronic equipment.

31. A molding, fiber, or foil made of a thermoplastic molding composition according to claim 14.

* * * * *