groups and the unsaturations of the alkyd resin during film formation is reduced. Furthermore the examples given contain an organic solvent.

[0018] The object of the invention therefore is to provide a process for the manufacture of a hybrid of an auto-oxidatively crosslinkable polymer and an addition polymer that does not have at least one of the abovementioned disadvantages, in particular a process and resulting product that combines the good properties of both the AOC polymer and the addition polymer in a single composition but with a reduced phase segregation tendency both of the composition itself (storage stability) as well as on drying, resulting for example in better drying properties, low (no) volatile organic compounds and coatings having good chemical resistance, mechanical properties and optical appearance (high gloss) and good film forming properties.

BRIEF DESCRIPTION OF THE INVENTION

[0019] According to the invention there is provided a process for the manufacture of an auto-oxidatively cross-linking hybrid polymer comprising the step of reacting in a mini-emulsion process one or more ethylenically unsaturated monomers to form an addition polymer (also referred to as the vinyl polymer) in the presence of a modified auto-oxidatively crosslinkable (AOC) polymer which has been modified with terminal unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl wherein the modified AOC polymer is a hydrophobic polymer having an acid number between 5 to 30.

[0020] In a particularly preferred embodiment the modified AOC polymer is an alkyd resin comprising unsaturated fatty acids wherein preferably the terminal unsaturated group on the AOC polymer is a vinyl, acryloyl or methacryloyl group.

[0021] The hybrid polymer is preferably produced by addition polymerization of an aqueous dispersion of ethylenically unsaturated monomers in the presence of the modified oxidatively cross-linkable polymer. The most preferred process is a mini-emulsion polymerisation process comprising the steps of:

I. mixing:
   a) one or more modified auto-oxidatively crosslinkable polymers,
   b) one or more ethylenically unsaturated monomers,
   c) one or more surfactants
II. forming a mini-emulsion in water of the mixture obtained in step I),
III. adding a free radical initiator before, during and/or after step I), II) and/or IV),
IV. addition polymerizing the unsaturated monomers in the mini-emulsion to form a dispersion of hybrid particles of the auto-oxidatively crosslinkable polymer and the addition polymer,

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Amended claims dated June 5, 2012

CLAIM

1) A process for the manufacture of an auto-oxidatively cross-linking hybrid polymer comprising the step of reacting in a mini-emulsion process, in the presence of a radical initiator and a surfactant, one or more ethylenically unsaturated monomers to form an addition polymer (also referred to as the vinyl polymer) in the presence of a modified auto-oxidatively crosslinkable (AOC) polymer which is an alkyd resin comprising unsaturated fatty acids which has been modified with terminal unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl, prepared by reacting A) carboxylic acid or -anhydride or B) hydroxyl reactive groups on the AOC alkyd polymer with a compound comprising the terminal unsaturated group and respectively A1) epoxy or A2) hydroxyl reactive groups or B1) carboxylic acid or -ester or B2) isocyanate reactive groups and wherein the modified AOC alkyd polymer is a hydrophobic alkyd polymer having an acid number from 5 to 20 mg KOH/g and an oil length of the resin between 40 and 95%.

2) The process according to claim 1, wherein the terminal unsaturated group on the modified AOC polymer is a vinyl, acryloyl or methacryloyl group.

3) The process according to claims 1 to 2, wherein the modified AOC polymer is an alkyd comprising carboxylic acid reactive groups reacted with glycidyl ester of an acrylic or methacrylic acid.

4) The process according to claims 1 to 3, wherein the average amount of the terminal unsaturated groups per molecule of the modified AOC polymer is more than 1, preferably at least 1.2, more preferably at least 1.5 but preferably less than 2 and more preferably less than 1.7.

5) The process according to claims 1 to 4 comprising the steps of:

I. mixing:

a) one or more modified AOC polymers,
b) one or more ethylenically unsaturated monomers,
c) one or more surfactants

II. forming a mini-emulsion in water of the mixture obtained in step I),
III. adding a free radical initiator before, during and/or after step I), II) and/or IV),
IV. addition polymerizing the unsaturated monomers in the mini-emulsion to form a dispersion of hybrid particles of the auto-oxidatively crosslinkable polymer and the addition polymer,

wherein the AOC polymer has been modified by pending unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl.

6) The process according to claims 1 to 5 comprising the steps of:
I. mixing:
a) one or more modified AOC polymer in an amount of 10 to 90 wt % (wt % here and hereafter defined as the weight relative to the total weight of the mixture of the components in step (I) to (III)),
b) one or more ethylenically unsaturated monomers in an amount of 10 to 90 wt %,
c) one or more surfactants in an amount of 1 to 15 wt %,
II. forming a mini-emulsion in water of the mixture obtained in step I),
III. adding a free radical initiator before, during and/or after step I) , II) and/or IV), in an amount of 0.05 to 6 wt % (based on the weight of the unsaturated monomers),
IV. addition polymerizing the unsaturated monomers in the mini-emulsion forming a dispersion comprising 30 to 70 % by weight of solids.

7) The process according to anyone of claims 1 to 6, wherein the modified AOC polymer is a hydrophobic polymer having an acid number between 5 and 20 mg KOH/g and wherein in addition to the hydrophobic modified AOC polymer, the ethylenically unsaturated monomers comprise hydrophobic monomers, preferably lauryl of stearyl acrylate or methacrylate preferably in an amount between 2 to 10, more preferably between 3 and 5 mol% (relative to the total unsaturated monomer content)

8) The process according to anyone of claims 1 to 7, wherein the amount of modified AOC polymer (relative to the total of the modified AOC polymer and the vinyl polymer) is between 25 and 75 wt%, preferably between 30 and 70, more preferably between 40 and 60 wt%.

9) The process according to anyone of claims 1 to 8, wherein the molecular weight of the modified AOC polymer is between 1000 and 50,000 and the oil length of the resin is between 20 and 95%.

10) An aqueous hybrid polymer dispersion obtainable according to the process of claims 1 to 9 comprising 30 to 70 % by weight of solids of hybrid polymer comprising:
   a. 10 to 90 wt % of one or more modified AOC polymers having been modified by pending unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl at least partially grafted onto
   b. 10 to 90 wt % of an addition polymer.

11) The aqueous hybrid polymer dispersion according to claim 10, which is essentially free of volatile organic solvent.

12) Use of the aqueous hybrid polymer dispersion according to anyone of claims 10 or 11 for the manufacture of coating compositions, ink compositions or adhesives.

13) A coating composition comprising the hybrid polymer dispersion according to anyone of claims 10-11 as a binder.

14) A substrate coated with the aqueous hybrid polymer dispersion of claims 10 or 11 or the coating composition according to claim 13.

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groups and the unsaturations of the alkyd resin during film formation is reduced. Furthermore the examples given contain an organic solvent.

[0018] The object of the invention therefore is to provide a process for the manufacture of a hybrid of an auto-oxidatively crosslinkable polymer and an addition polymer that does not have at least one of the abovementioned disadvantages, in particular a process and resulting product that combines the good properties of both the AOC polymer and the addition polymer in a single composition but with a reduced phase segregation tendency both of the composition itself (storage stability) as well as on drying, resulting for example in better drying properties, low (no) volatile organic compounds and coatings having good chemical resistance, mechanical properties and optical appearance (high gloss) and good film forming properties.

BRIEF DESCRIPTION OF THE INVENTION

[0019] According to the invention there is provided a process for the manufacture of an auto-oxidatively cross-linking hybrid polymer comprising the step of reacting in a mini-emulsion process, in the presence of a radical initiator and a surfactant, one or more ethylenically unsaturated monomers to form an addition polymer (also referred to as the vinyl polymer) in the presence of a modified auto-oxidatively crosslinkable (AOC) polymer which is an alkyd resin comprising unsaturated fatty acids which has been modified with terminal unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl, prepared by reacting A) carboxylic acid or -anhydride or B) hydroxyl reactive groups on the AOC alkyd polymer with a compound comprising the terminal unsaturated group and respectively A1) epoxy or A2) hydroxyl reactive groups or B1) carboxylic acid or –ester or B2) isocyanate reactive groups and wherein the AOC alkyd polymer is a hydrophobic alkyd polymer having an acid number from 5 to 20 mg KOH/g and an oil length of the resin between 40 and 95%.

[0020] In a particularly preferred embodiment the modified AOC polymer is an alkyd resin comprising unsaturated fatty acids wherein preferably the terminal unsaturated group on the AOC polymer is a vinyl, acryloyl or methacryloyl group.

[0021] The hybrid polymer is preferably produced by addition polymerization of an aqueous dispersion of ethylenically unsaturated monomers in the presence of the modified oxidatively cross-linkable polymer. The most preferred process is a mini-emulsion polymerisation process comprising the steps of:

I. mixing:
    a) one or more modified auto-oxidatively crosslinkable polymers,
    b) one or more ethylenically unsaturated monomers,
    c) one or more surfactants
II. forming a mini-emulsion in water of the mixture obtained in step I),
III. adding a free radical initiator before, during and/or after step I), II) and/or IV),
IV. addition polymerizing the unsaturated monomers in the mini-emulsion to form a dispersion of hybrid particles of the auto-oxidatively crosslinkable polymer and the addition polymer,

CLAIMS

1) A process for the manufacture of an auto-oxidatively cross-linking hybrid polymer comprising the step of reacting in a mini-emulsion process, in the presence of a radical initiator and a surfactant, one or more ethylenically unsaturated monomers to form an addition polymer (also referred to as the vinyl polymer) in the presence of a modified auto-oxidatively crosslinkable (AOC) polymer which is an alkyd resin comprising unsaturated fatty acids which has been modified with terminal unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl, prepared by reacting A) carboxylic acid or -anhydride or B) hydroxyl reactive groups on the AOC alkyd polymer with a compound comprising the terminal unsaturated group and respectively A1) epoxy or A2) hydroxyl reactive groups or B1) carboxylic acid or –ester or B2) isocyanate reactive groups and wherein the AOC alkyd polymer is a hydrophobic alkyd polymer having an acid number from 5 to 20 mg KOH/g and an oil length of the resin between 40 and 95%.

2) The process according to claim 1, wherein the terminal unsaturated group on the modified AOC polymer is a vinyl, acryloyl or methacryloyl group.

3) The process according to claims 1 to 2, wherein the modified AOC polymer is an alkyd comprising carboxylic acid reactive groups reacted with glycidyl ester of an acrylic or methacrylic acid.

4) The process according to claims 1 to 3, wherein the average amount of the terminal unsaturated groups per molecule of the modified AOC polymer is more than 1, preferably at least 1.2, more preferably at least 1.5 but preferably less than 2 and more preferably less than 1.7.

5) The process according to claims 1 to 4 comprising the steps of:
   I. mixing:
      a) one or more modified AOC polymers,
      b) one or more ethylenically unsaturated monomers,
      c) one or more surfactants
   II. forming a mini-emulsion in water of the mixture obtained in step I),
   III. adding a free radical initiator before, during and/or after step I), II) and/or IV),
   IV. addition polymerizing the unsaturated monomers in the mini-emulsion to form a dispersion of hybrid particles of the auto-oxidatively crosslinkable polymer and the addition polymer,

wherein the AOC polymer has been modified by pending unsaturated groups of the formula – $C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl.

6) The process according to claims 1 to 5 comprising the steps of:
   I. mixing:
      a) one or more modified AOC polymer in an amount of 10 to 90 wt % (wt % here and hereafter defined as the weight relative to the total weight of the mixture of the components in step (I) to (III)),
      b) one or more ethylenically unsaturated monomers in an amount of 10 to 90 wt %,
      c) one or more surfactants in an amount of 1 to 15 wt %,
   II. forming a mini-emulsion in water of the mixture obtained in step I),

III. adding a free radical initiator before, during and/or after step I) , II) and/or IV), in an amount of 0.05 to 6 wt % (based on the weight of the unsaturated monomers),
IV. addition polymerizing the unsaturated monomers in the mini-emulsion forming a dispersion comprising 30 to 70 % by weight of solids.

7) The process according to anyone of claims 1 to 6, wherein the modified AOC polymer is a hydrophobic polymer having an acid number between 5 and 20 mg KOH/g and wherein in addition to the hydrophobic modified AOC polymer, the ethylenically unsaturated monomers comprise hydrophobic monomers, preferably lauryl of stearyl acrylate or methacrylate preferably in an amount between 2 to 10, more preferably between 3 and 5 mol% (relative to the total unsaturated monomer content)

8) The process according to anyone of claims 1 to 7, wherein the amount of modified AOC polymer (relative to the total of the modified AOC polymer and the vinyl polymer) is between 25 and 75 wt%, preferably between 30 and 70, more preferably between 40 and 60 wt%.

9) The process according to anyone of claims 1 to 8, wherein the molecular weight of the modified AOC polymer is between 1000 and 50,000 and the oil length of the resin is between 40 and 95%.

10) An aqueous hybrid polymer dispersion obtainable according to the process of claims 1 to 9 comprising 30 to 70 % by weight of solids of hybrid polymer comprising:
a. 10 to 90 wt % of one or more modified AOC polymers having been modified by pending unsaturated groups of the formula $-C(R_1)=CH_2$ wherein R_1 can be hydrogen, alkyl or aryl at least partially grafted onto
b. 10 to 90 wt % of an addition polymer.

11) The aqueous hybrid polymer dispersion according to claim 10, which is essentially free of volatile organic solvent.

12) Use of the aqueous hybrid polymer dispersion according to anyone of claims 10 or 11 for the manufacture of coating compositions, ink compositions or adhesives.

13) A coating composition comprising the hybrid polymer dispersion according to anyone of claims 10-11 as a binder.

14) A substrate coated with the aqueous hybrid polymer dispersion of claims 10 or 11 or the coating composition according to claim 13.