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 DISCLOSUREINVENTION

[0019] According to the disclosureinvention 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,

wherein the auto-oxidatively cross-linkable 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.

[0022] We have found that the process according to the disclosure~~invention~~ results in aqueous hybrid polymer dispersions having improved coating compositions and no longer presenting one or more disadvantages of the prior art. In the mini-emulsion polymerisation process, the modified AOC polymer is a hydrophobic polymer wherein the acid value is low, preferably even close to zero. Such that the AOC polymer will act as a hydrophobe in forming the mini-emulsion resulting in a stable mini-emulsion. The auto-oxidatively crosslinkable polymer and the addition polymer are homogeneously distributed in the particles of the aqueous hybrid polymer dispersion, which has better coating properties. The aqueous hybrid polymer dispersions have very low residual ethylenically unsaturated monomer content by achieving a high if not full conversion of the ethylenically unsaturated monomers at the end of the polymerization.

[0023] This hybrid polymer has, compared to both a blend of corresponding composition and to a hybrid polymer formed by polymerizing ethylenically unsaturated monomers in the presence of an auto-oxidatively crosslinkable polymer devoid of said terminal unsaturated groups, the advantage of improved storage stability of the dispersion, a reduced tendency to phase segregate upon film-formation and accordingly better coating properties.

[0024] Without wishing to be bound by theory it is considered that the improved properties relate to the presence of two different types of unsaturated groups in the modified AOC polymer: internal unsaturated groups in the AOC polymer before modification and terminal unsaturated groups introduced by the modification. In particular, in case of an alkyd, the polymer before modification contains unsaturated moieties originating from fatty acids or oils used in the synthesis of AOC polymer. Fatty acids are long-chained molecules having a methyl group at one end and a carboxylic acid group at the other end; the unsaturated group(s) are in the chain (internal) and not at the end (terminal $-C(R_1)=CH_2$). The terminal unsaturated groups are more reactive and will preferentially react during addition polymerization. It is believed that as a result the fatty acid unsaturated groups inhibit the addition polymerisation to a lesser extent resulting in less unreacted monomer. Further, the addition polymerisation does not or to a lesser degree reduce the amount of internal unsaturated groups of the alkyd resulting in better drying properties. More importantly, the degree of grafting between the OAC polymer and the addition polymer is significantly increased leading to less phase segregation.

[0024a] In one aspect, there is provided an aqueous hybrid polymer dispersion obtainable as defined herein 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.

[0024b] In one aspect, there is provided the use of the aqueous hybrid polymer dispersion as defined herein for the manufacture of coating compositions, ink compositions or adhesives.

[0024c] In one aspect, there is provided a coating composition comprising the hybrid polymer dispersion as defined herein as a binder.

[0024d] In one aspect, there is provided a substrate coated with the aqueous hybrid polymer dispersion as defined herein or the coating composition as defined herein.

DETAILED DESCRIPTION OF THE INVENTION

A: The modified auto-oxidatively crosslinkable polymer