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(54) **Non-aqueous quinacridone dispersions using dispersion synergists**

Nichtwässerige Chinakridondispersionen unter Verwendung von Dispersionssynergisten

Dispersions de quinacridone non-aqueuses par utilisation de synergistes de dispersion

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US-B1- 6 451 103	**US-B1- 6 641 655**

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Description

Technical Field

[0001] The present invention relates to stable quinacridone dispersions and inkjet inks using specific dispersion synergists.

Background Art

[0002] Pigment dispersions are made using a dispersant. A dispersant is a substance for promoting the formation and stabilization of a dispersion of pigment particles in a dispersion medium. Dispersants are generally surface-active materials having an anionic, cationic or non-ionic structure. The presence of a dispersant substantially reduces the dispersing energy required. Dispersed pigment particles may have a tendency to re-agglomerate after the dispersing operation, due to mutual attraction forces. The use of dispersants also counteracts this re-agglomeration tendency of the pigment particles.

[0003] The dispersant has to meet particularly high requirements when used for inkjet inks. Inadequate dispersing manifests itself as increased viscosity in liquid systems, loss of brilliance and/or hue shifts. Moreover, particularly good dispersion of the pigment particles is required to ensure unimpeded passage of the pigment particles through the nozzles of the print head, which are usually only a few micrometers in diameter. In addition, pigment particle agglomeration and the associated blockage of the printer nozzles has to be avoided in the standby periods of the printer.

[0004] Polymeric dispersants contain in one part of the molecule so-called anchor groups, which adsorb onto the pigments to be dispersed. In a spatially separate part of the molecule, polymeric dispersants have polymer chains compatible with the dispersion medium, thus stabilizing the pigment particles in the dispersion medium. Typical polymeric dispersants include graft copolymer and block copolymer dispersants.

[0005] In aqueous inkjet inks, the polymeric dispersants generally contain hydrophobic anchor groups exhibiting a high affinity for the pigment surface and hydrophilic polymer chains for stabilizing the pigments in the aqueous dispersion medium.

[0006] The preparation of good thermally stable dispersions with submicron particles is more difficult for non-aqueous inkjet inks, such as solvent based, oil based and radiation curable inkjet inks. The pigments are especially difficult to disperse when they have a non-polar surface.

[0007] These problems have lead to the design of very specific polymeric dispersants wherein the anchor groups are pigment derivatives. For example, EP 0763378 A (TOYO INK) discloses a pigment composition comprising a non-aqueous type pigment dispersing agent having a portion which has a high affinity with a pigment and which has at least one type selected from the group consisting of an organic dye, anthraquinone and acridone only at a terminal end or at both terminal ends of at least one polymer selected from a linear urethane polymer and a linear acrylic polymer, and a pigment.

[0008] Another approach for dispersing pigments with non-polar surfaces in non-aqueous dispersion media is changing the surface to a more polar surface by addition of compounds known as dispersion synergists. A dispersion synergist is a compound that promotes the adsorption of the polymeric dispersant on the surface of the pigment. It is suggested that the synergist should possess the pigment structure substitued by one or more sulphonic acid groups or ammonium salts thereof.

[0009] US 4461647 (ICI) discloses a dispersion of a pigment in an organic liquid containing a water-insoluble asymmetric disazo compound comprising a central divalent group free from acidic and other ionic substituents linked through azo groups to two monovalent end groups characterized in that one end group, the first, is free from acidic and other ionic substituents and the other end group, the second, carries a single substituted ammonium-acid salt group.

[0010] US 4057436 (ICI) discloses pigment dispersions in organic liquids using polymeric or resinous dispersing agents in the presence of a substituted ammonium salt of a colored acid wherein there are between 16 and 60 carbon atoms contained in at least 3 chains attached to the N-atom of the substituted ammonium ion.

[0011] US 6641655 (AVECIA) discloses the use of a diquaternary ammonium salt of a coloured acid as fluidising agent wherein the diquaternary ammonium cation contains two or more nitrogen atoms.

[0012] Although these dispersion synergists work fine for some pigments, many other pigments can not be dispersed to an acceptable quality in a non-aqueous medium. This is the case for quinacridone pigments, for which it is difficult to obtain stable non-aqueous pigment dispersions, especially stable non-aqueous ink-jet inks.

[0013] Sulfonated quinacridone derivatives have been disclosed, for example, by US 6152968 (BASF). However, US 6152968 (BASF) is silent on their use in non-aqueous media.

[0014] US 6827775 (CIBA SPECIALTY CHEMICALS) discloses the use of a pigment and its sulfonation product in a solid solution, water and organic solvents such as xylene. However, US 6827775 (CIBA SPECIALTY CHEMICALS) is silent on the stability of non-aqueous dispersions of quinacridone type pigments and their sulfonation products.

[0015] US 4844742 (CIBA GEIGY) discloses the surface modification of quinacridone pigments, wherein the pigment is treated with a solvent-free, basic, nitrogen-containing copolymer of the polyurethane series and with a dispersion-improving quinacridone derivative resulting in compositions exhibiting enhanced performance in automative and other finish systems. The derivatives used are phthalimidomethyl or sulfonic acid derivatives of quinacridone. Again no details are given on the stability of non-aqueous dispersions of quinacridone type pigments.

[0016] WO02/064680 (CLARIANT) discloses pigment dispersants derived from an organic pigment selected from the group of the perinone, quinacridone, quinacridonequinone, anthanthrone, indanthrone, dioxazine, diketopyrrolopyrrole, indigo, thioindigo, thiazine indigo, isoindoline, isoindolinone, pyranthrone, isoviolanthrone, flavanthrone or anthrapyrimidine pigments; and also pigment preparations therewith.

[0017] DE 1619618 (DU PONT) discloses mixed crystals of quinacridone pigments;

[0018] US2005/0196697 A1 (KONICA MINOLTA) discloses an actinic ray curable composition containing a quinacridone pigment; a dispersant; a cationically polymerizable monomer; a photo acid generator; and a quinacridone derivative.

[0019] US6451103 (TOYO INK) discloses a self-dispersible aqueous pigment dispersion including watersoluble quinacridone derivatives.

[0020] For consistent image quality, inkjet inks require a dispersion stability capable of dealing with high temperatures (above 60°C) during transport of the ink to a customer, jetting at elevated temperatures and changes in the dispersion medium of the inkjet ink during use, for example, evaporation of solvent and increasing concentrations of humectants, penetrants and other additives.

[0021] Therefore, it is highly desirable to be able to manufacture pigmented inkjet inks using quinacridone pigments in a non-aqueous medium exhibiting a high dispersion quality and stability.

Objects of the invention

[0022] It is an object of the present invention to provide non-aqueous quinacridone dispersions with high dispersion quality and stability.

[0023] It is a further object of the present invention to provide non-aqueous quinacridone inkjet inks producing images of high image quality with a high optical density.

[0024] Further objects of the invention will become apparent from the description hereinafter.

Summary of the invention

[0025] It has been surprisingly found that non-aqueous quinacridone pigment dispersions of high dispersion quality and stability were obtained by using a quinacridone derivative containing a carboxylic acid group as dispersion synergist, whereas quinacridone derivatives containing only sulfonic acid groups or other compounds containing a carboxylic acid group failed.

[0026] Objects of the present invention have been realized with a non-aqueous pigment dispersion comprising a quinacridone pigment, a polymeric dispersant and a dispersion synergist in a dispersion medium characterized in that said dispersion synergist is a quinacridone derivative containing at least one carboxylic acid group or a salt thereof

[0027] Objects of the present invention have also been realized with a method for printing an ink-jet image comprising the steps of:

(a) providing a curable ink-jet ink set containing a curable ink-jet ink comprising a quinacridone pigment and a quinacridone derivative containing at least one carboxylic acid group or a salt thereof;
(b) printing an image with said curable ink-jet comprising a quinacridone pigment; and
(c) curing said printed image.

Disclosure of Invention

Definitions

[0028] The term "colorant", as used in disclosing the present invention, means dyes and pigments.

[0029] The term "dye", as used in disclosing the present invention, means a colorant having a solubility of 10 mg/L or more in the medium in which it is applied and under the ambient conditions pertaining.

[0030] The term "pigment" is defined in DIN 55943, herein incorporated by reference, as a colouring agent that is practically insoluble in the application medium under the pertaining ambient conditions, hence having a solubility of less than 10 mg/L therein.

[0031] The term "C.I." is used in disclosing the present application as an abbreviation for Colour Index.

[0032] The term "dispersion", as used in disclosing the present invention, means an intimate mixture of at least two substances, one of which, called the dispersed phase or colloid, is uniformly distributed in a finely divided state through the second substance, called the dispersion medium.

[0033] The term "non-aqueous pigment dispersion" as used in disclosing the present invention means a pigment dispersion containing no or almost no water, i.e. less than 5 wt% based on the pigment dispersion.

[0034] The term "actinic radiation" as used in disclosing the present invention, means electromagnetic radiation capable of initiating photochemical reactions.

[0035] The term "spectral separation factor" as used in disclosing the present invention means the value obtained by calculating the ratio of the maximum absorbance A_{max} (measured at wavelength λ_{max}) over the reference absorbance A_{ref} determined at a higher wavelength λ_{ref}.

[0036] The abbreviation "SSF" is used in disclosing the present invention for spectral separation factor.

[0037] The term "alkyl" means all variants possible for each number of carbon atoms in the alkyl group i.e. for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

[0038] The term "acyl group" means -(C=O)-aryl and -(C=O)-alkyl groups.

[0039] The term "aliphatic group" means saturated straight chain, branched chain and alicyclic hydrocarbon groups.

[0040] The term "unsaturated aliphatic group" means straight chain, branched chain and alicyclic hydrocarbon groups which contain at least one double or triple bond.

[0041] The term "aromatic group" as used in disclosing the present invention means an assemblage of cyclic conjugated carbon atoms, which are characterized by large resonance energies, e.g. benzene, naphthalene and anthracene.

[0042] The term "alicyclic hydrocarbon group" means an assemblage of cyclic carbon atoms, which do not form an aromatic group, e.g. cyclohexane.

[0043] The term "substituted" as used in disclosing this present invention means that one or more of the carbon atoms and/or hydrogen atoms of one or more of carbon atoms in an aliphatic group, an aromatic group or an alicyclic hydrocarbon group, are replaced by another atom, e.g. a halogen atom, an oxygen atom, a nitrogen atom, a silicon atom, a sulphur atom, a phosphorous atom, selenium atom or a tellurium atom. Such substituents include hydroxyl groups, ether groups, carboxylic acid groups, ester groups and amine groups.

[0044] The term "heteroaromatic group" means an aromatic group wherein at least one of the cyclic conjugated carbon atoms is replaced by a non-carbon atom such as a nitrogen atom, a sulphur atom, a phosphorous atom, selenium atom and a tellurium atom.

[0045] The term "heterocyclic group" means an alicyclic hydrocarbon group wherein at least one of the cyclic carbon atoms is replaced by an oxygen atom, a nitrogen atom, a phosphorous atom, a silicon atom, a sulphur atom, a selenium atom or a tellurium atom.

Pigment dispersions

[0046] The non-aqueous pigmented dispersion according to the present invention contains at least four components: (i) a colour pigment, (ii) a polymeric dispersant, (iii) a dispersion synergist and (iv) a dispersion medium.

[0047] The non-aqueous pigment dispersion according to the present invention may further also contain at least one surfactant.

[0048] The non-aqueous pigment dispersion according to the present invention may contain at least one humectant to prevent the clogging of the nozzle, due to its ability to slow down the evaporation rate of ink.

[0049] The non-aqueous pigment dispersion according to the present invention is preferably an inkjet ink selected from the group consisting of an organic solvent based, an oil based and a curable pigmented inkjet ink. The curable pigmented inkjet ink is preferably radiation curable. The viscosity of the pigmented inkjet ink is preferably lower than 100 mPa.s at 30°C. The viscosity of the pigmented inkjet ink is preferably lower than 30 mPa.s, more preferably lower than 15 mPa.s, and most preferably between 2 and 10 mPas at a shear rate of 100 s^{-1} and a jetting temperature between 10 and 70°C.

[0050] The curable pigment dispersion may contain as dispersion medium monomers, oligomers and/or prepolymers possessing different degrees of functionality. A mixture including combinations of mono-, di-, tri- and/or higher functionality monomers, oligomers or prepolymers may be used. A catalyst called an initiator for initiating the polymerization reaction may be included in the curable pigmented inkjet ink. The initiator can be a thermal initiator, but is preferably a photo-initiator. The photo-initiator requires less energy to activate than the monomers, oligomers and/or prepolymers to form the polymer. The photo-initiator suitable for use in the curable pigment dispersion may be a Norrish type I initiator, a Norrish type II initiator or a photo-acid generator.

Dispersion synergists

[0051] The non-aqueous pigment dispersion according to the present invention contains at least one dispersion synergist. A mixture of dispersion synergists may be used to obtain a better dispersion stability.

[0052] The dispersion synergist is a quinacridone derivative containing at least one carboxylic acid group or a salt thereof.

[0053] In a preferred embodiment the at least one carboxylic acid group or a salt thereof is located on one of the two nitrogen atoms of the quinacridone structure.

[0054] The at least one carboxylic acid group or a salt thereof may be an alkanoic acid group, an alicyclic acid group, a heterocyclic acid group, an aromatic acid group or salts thereof.

[0055] The aromatic acid group or a salt thereof is preferably a benzoic acid group or a salt therof.

[0056] The dispersion synergist may contain two or more carboxylic acid groups, preferably in a meta- or para-position on a phenyl ring. A preferred aromatic acid group or a salt thereof containing two carboxylic acid groups or salts thereof is a phtalic acid group or a salt thereof. Preferably the phtalic acid group is an isophtalic group.

[0057] A combination with other types of acid groups or salts thereof, such as sulphonic acid and phosphoric acid or salts thereof, may also be advantageously used.

[0058] The at least one carboxylic acid group or a salt thereof may be attached directly to the quinacridone structure or may be attached through a linking group containing 1 or more carbon atoms. The linking group contains preferably 1 to 20 carbon atoms, more preferably 1 to 12 and most preferably 1 to 6 carbon atoms. In a preferred embodiment the linking group is a straight chain of 1 or more carbon atoms, wherein some of the carbon atoms may be substituted by a heteroatom such as an oxygen atom, a nitrogen atom, a sulphur atom, a phosphorous atom, selenium atom and a tellurium atom. It is also possible that, if present, some of the hydrogen atoms attached to a carbon atom are substituted by a heteroatom such as an oxygen atom, a nitrogen atom, a sulphur atom, a halogen atom, a phosphorous atom, selenium atom and a tellurium atom.

[0059] In case that the dispersion synergist contains a salt of a carboxylic acid group, the charge of the carboxylate anion is compensated by a cation.

[0060] The cation may be an inorganic cation selected from the group consisting of the Ia and IIa metals in the table of Mendeleev. In a preferred embodiment the cation is Li^+.

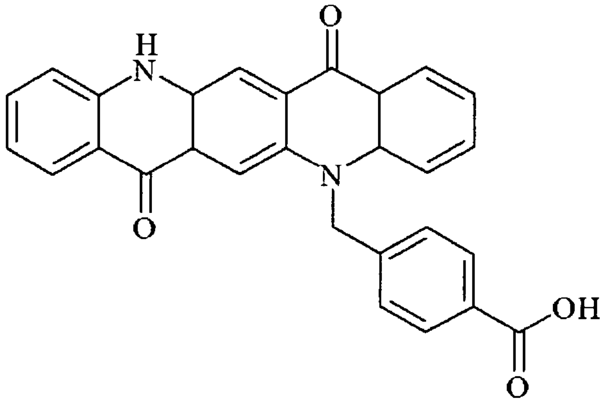
[0061] The cation may also be an organic cation. A preferred cation is an ammonium and a substituted ammonium group.

[0062] In a preferred embodiment the cation is selected from the substituted ammonium cations disclosed in US 4461647 (ICI), US 4057436 (ICI) and US 6641655 (AVECIA) incorporated herein by reference.

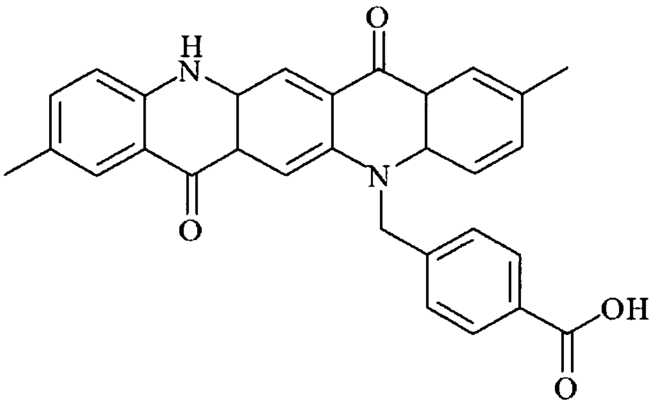
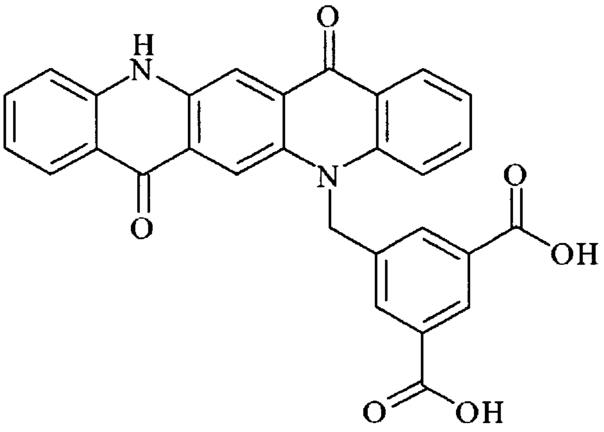
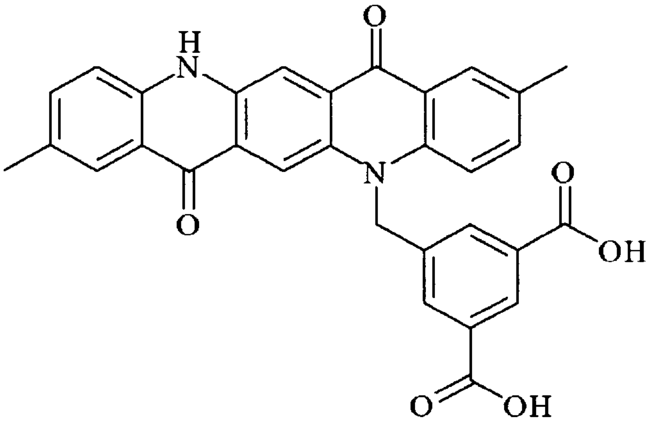
[0063] Particularly preferred cations include the substituted ammonium groups selected from the group consisting of $^+N(CH_3)_2(C_{18}H_{37})_2$, $^+NH(CH_3)_2(C_{18}H_{37})$, $^+N(CH_3)_2(C_{12}H_{25})_2$, $^+NH(CH_3)_2(C_{12}H_{25})$, $^+N(CH_3)_2(C_{10}H_{21})_2$, $^+NH(CH_3)_2(C_{10}H_{21})$, $^+N(CH_3)_2(C_8H_{17})_2$, $^+NH(CH_3)_2(C_8H_{17})$, $^+NH(C_8H_{17})_3$, $^+NH(C_{10}H_{21})_3$, $^+ NH(C_{12}H_{25})_3$ and $^+NH(C_{18}H_{35})_3$.

[0064] Suitable dispersion synergists include those disclosed in Table 1.

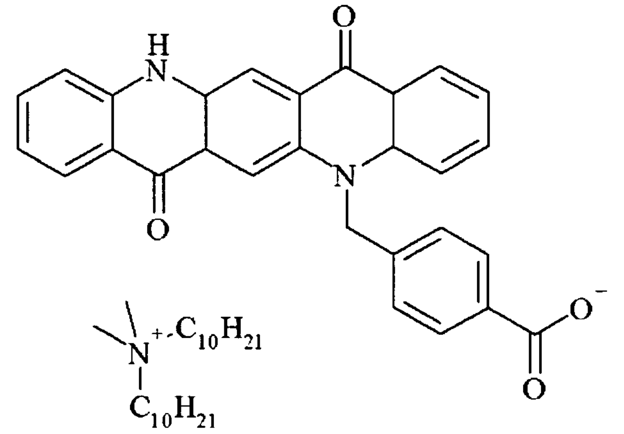
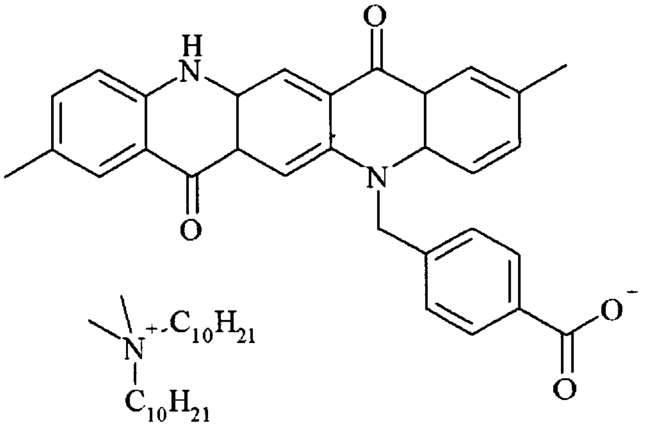
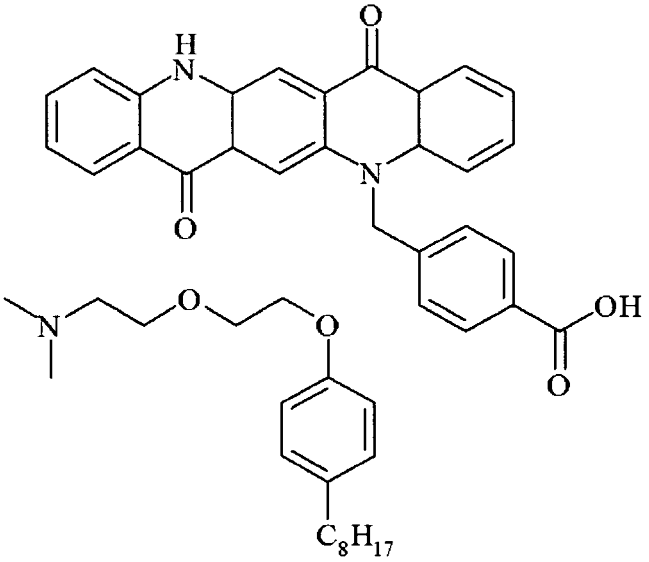
Table 1

Dispersion Synergist	Chemical Structure
QAD-1	

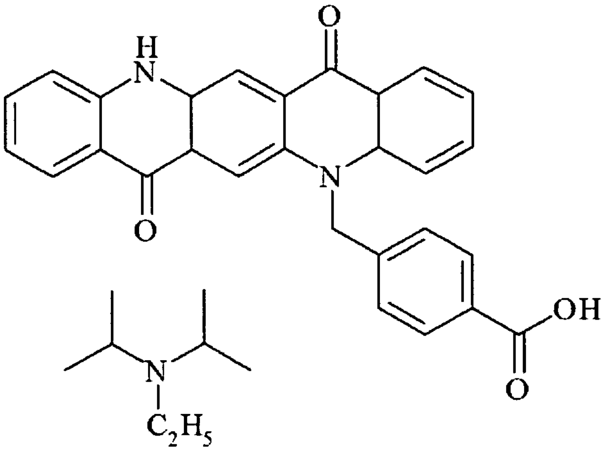
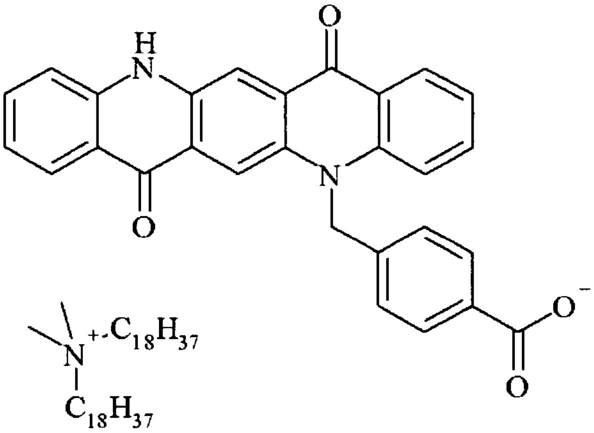
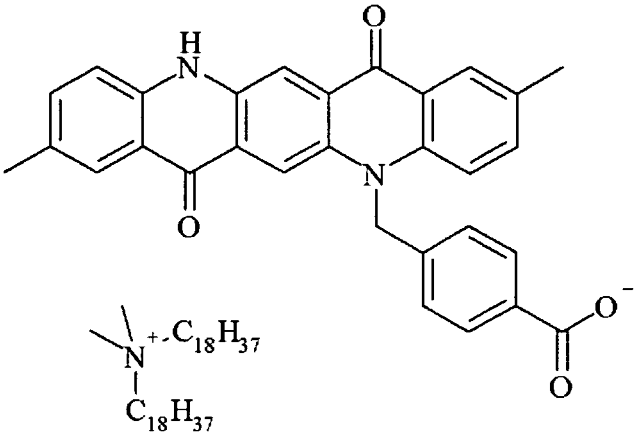
(continued)

Dispersion Synergist	Chemical Structure
QAD-2	
QAD-3	
QAD-4	

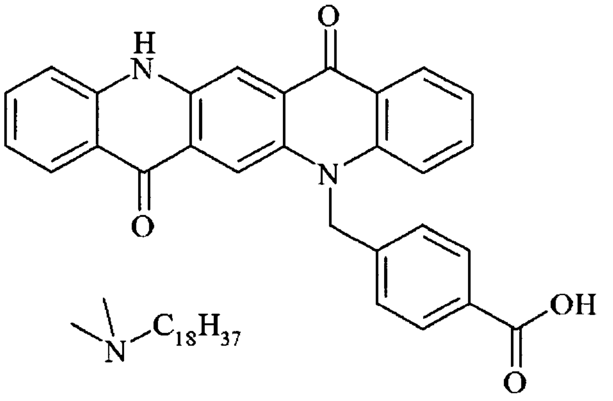
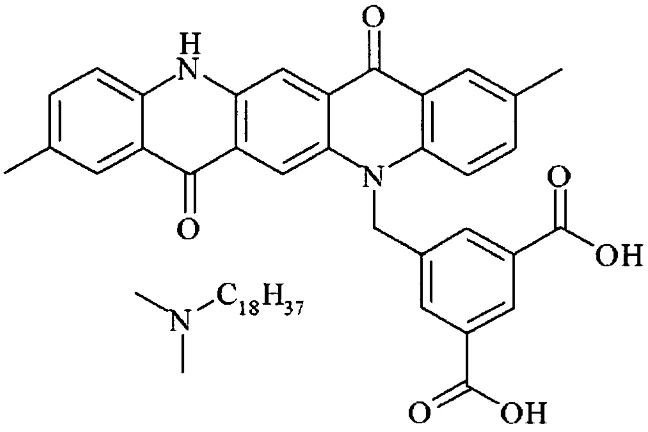
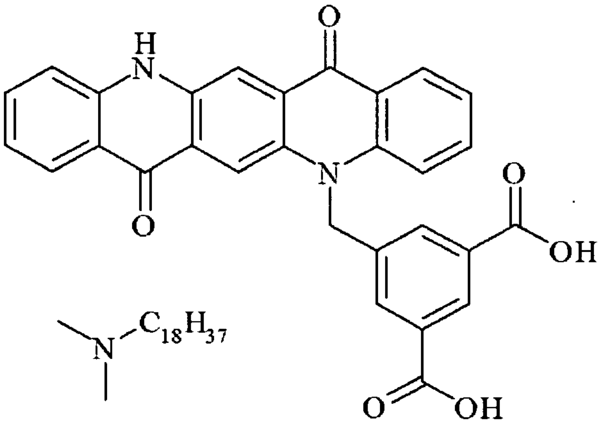
(continued)

Dispersion Synergist	Chemical Structure
QAD-5	
QAD-6	
QAD-7	

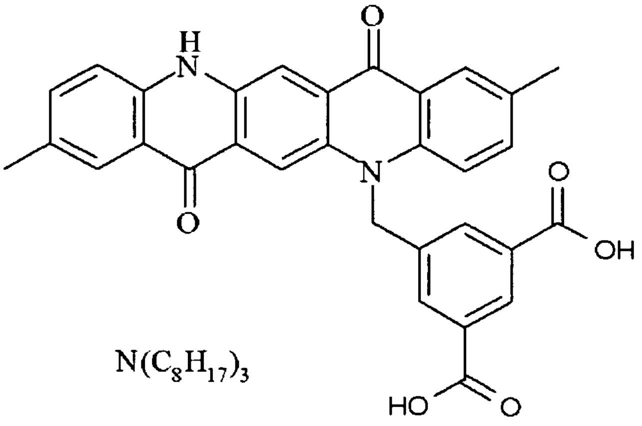
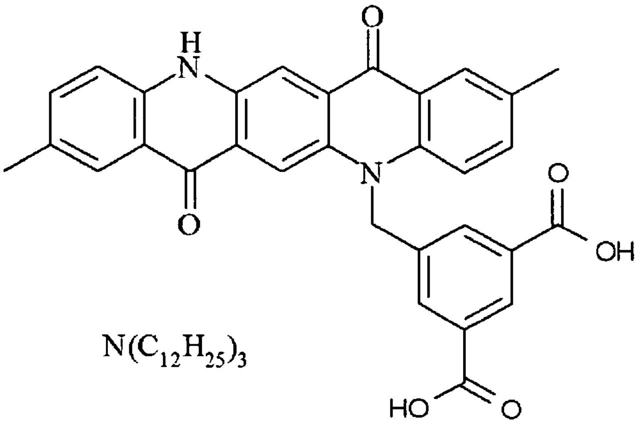
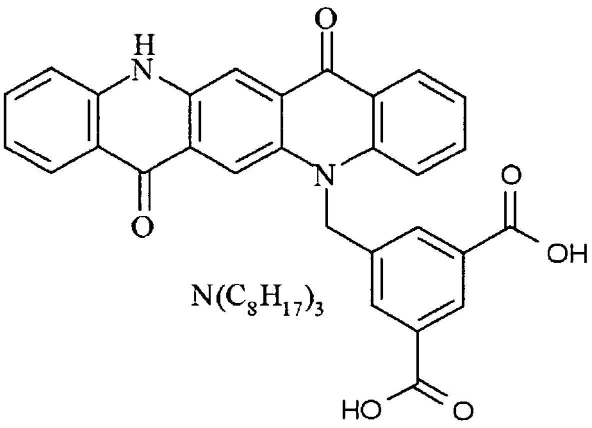
(continued)

Dispersion Synergist	Chemical Structure
QAD-8	
QAD-9	
QAD-10	

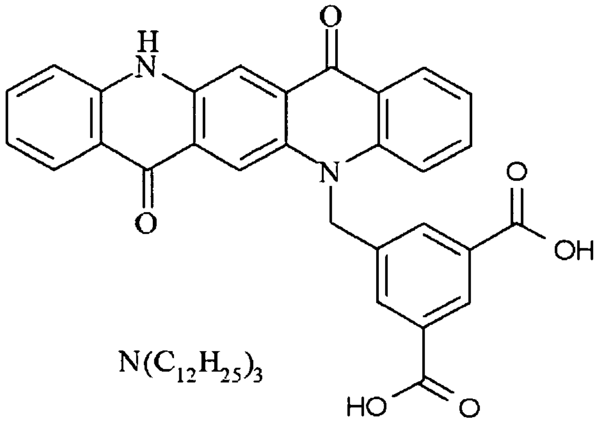
(continued)

Dispersion Synergist	Chemical Structure
QAD-11	
QAD-12	
QAD-13	

(continued)

Dispersion Synergist	Chemical Structure
QAD-14	 $N(C_8H_{17})_3$
QAD-15	 $N(C_{12}H_{25})_3$
QAD-16	 $N(C_8H_{17})_3$

(continued)

Dispersion Synergist	Chemical Structure
QAD-17	

[0065] The subsituted ammonium group can also be chemically represented as an amine with the hydrogen attached to the carboxylate anion. This is exemplified for the structures QAD-7, QAD-8 and QAD-11 to QAD-17 of Table 1.

[0066] The synergist should be additional to the amount of polymeric dispersant(s). The ratio of polymeric dispersant/dispersion synergist depends upon the pigment and should be determined experimentally. Typically the ratio wt% polymeric dispersant/wt% dispersion synergist is selected between 2:1 to 100:1, preferably between 2:1 and 20:1.

Quinacridone pigments

[0067] The quinacridone pigment may be chosen from those disclosed by HERBST, Willy, et al. Industrial Organic Pigments, Production, Properties, Applications. 3rd edition. Wiley - VCH , 2004. ISBN 3527305769.

[0068] Suitable pigments include C.I. Pigment Red 122, 192, 202, 207 and 209.

[0069] Particular preferred quinacridone pigments are C.I. Pigment Violet 19 and C.I. Pigment Red 122.

[0070] Suitable pigments include mixed crystals of the above particular preferred pigments. A commercially available example is Cinquasia Magenta RT-355-D from Ciba Specialty Chemicals. Preferably the quinacridone pigment is selected from the group consisting of C.I. Pigment Violet 19, C.I. Pigment Red 122, C.I. Pigment Red 202 and mixed crystals of quinacridone pigments.

[0071] Pigment particles in pigmented inkjet ink should be sufficiently small to permit free flow of the ink through the inkjet-printing device, especially at the ejecting nozzles. It is also desirable to use small particles for maximum colour strength and to slow down sedimentation.

[0072] The average particle size of the pigment in a pigmented inkjet ink should be between 0.005 and 15 μm. Preferably, the numeric average pigment particle size is between 0.005 and 5 μm, more preferably between 0.005 and 1 μm, particularly preferably between 0.005 and 0.3 μm and most preferably between 0.040 and 0.150 μm.

[0073] The quinacridone pigment is preferably used in the non-aqueous pigment dispersion in an amount of 0.1 to 20 wt%, preferably 1 to 10 wt% based on the total weight of the non-aqueous pigment dispersion.

Dispersants

[0074] The dispersant used in the non-aqueous pigment dispersion according to the present invention is preferably a polymeric dispersant.

[0075] Typical polymeric dispersants are copolymers of two monomers but may contain three, four, five or even more monomers. The properties of polymeric dispersants depend on both the nature of the monomers and their distribution in the polymer. Copolymeric dispersants suitable in pigment dispersions according to the present invention may have the following polymer compositions:

- randomly polymerized monomers (e.g. monomers A and B polymerized into ABBAABAB);
- alternating polymerized monomers (e.g. monomers A and B polymerized into ABABABAB);
- gradient (tapered) polymerized monomers (e.g. monomers A and B polymerized into AAABAABBABBB);
- block copolymers (e.g. monomers A and B polymerized into AAAAABBBBBB) wherein the block length of each of the blocks (2, 3, 4, 5 or even more) is important for the dispersion capability of the polymeric dispersant;

- graft copolymers (graft copolymers consist of a polymeric backbone with side chains attached to the backbone); and
- mixed forms of these polymers, e.g. blocky gradient copolymers.

[0076] Polymeric dispersants suitable in pigment dispersions according to the present invention may have different polymer architecture including linear, comb/branched, star, dendritic (including dendrimers and hyperbranched polymers). A general review on the architecture of polymers is given by ODIAN, George, Principles Of Polymerization, 4th edition, Wiley-Interscience, 2004, p. 1-18.

[0077] Comb/branched polymers have side branches of linked monomer molecules protruding from various central branch points along the main polymer chain (at least 3 branch points).

[0078] Star polymers are branched polymers in which three or more either similar or different linear homopolymers or copolymers are linked together to a single core.

[0079] Dendritic polymers comprise the classes of dendrimers and hyperbranched polymers. In dendrimers, with well-defined mono-disperse structures, all branch points are used (multi-step synthesis), while hyperbranched polymers have a plurality of branch points and multifunctional branches that lead to further branching with polymer growth (one-step polymerization process).

[0080] Polymeric dispersants suitable in pigment dispersions according to the present invention may be prepared via addition or condensation type polymerizations. Polymerization methods include those described by ODIAN, George, Principles Of Polymerization, 4th edition, Wiley-Interscience, 2004, p. 39-606.

[0081] Addition polymerization methods suitable for preparing polymeric dispersants for use in pigment dispersions according to the present invention include free radical polymerization (FRP) and controlled polymerization techniques. Suitable controlled radical polymerization methods include:

- RAFT: reversible addition-fragmentation chain transfer;
- ATRP: atom transfer radical polymerization
- MADIX: reversible addition-fragmentation chain transfer process, using a transfer active xanthate;
- Catalytic chain transfer (e.g. using cobalt complexes);
- Nitroxide (e.g. TEMPO) mediated polymerizations;

[0082] Other suitable controlled polymerization methods include:

- GTP: group transfer polymerization;
- Living cationic (ring-opening) polymerizations;
- Anionic co-ordination insertion ring-opening polymerization; and
- Living anionic (ring-opening) polymerization.

[0083] Reversible addition-fragmentation transfer (RAFT): controlled polymerization occurs via rapid chain transfer between growing polymer radicals and dormant polymer chains. A review article on RAFT synthesis of dispersants with different polymeric geometry is given in QUINN J.F. et al., Facile Synthesis of comb, star, and graft polymers via reversible addition-fragmentation chain transfer (RAFT) polymerization, Journal of Polymer Science, Part A: Polymer Chemistry, Vol.40, 2956-2966, 2002.

[0084] Group transfer polymerization (GTP): the method of GTP used for synthesis of AB block copolymers is disclosed by SPINELLI, Harry J, GTP and its use in water based pigment dispersants and emulsion stabilisers, Proc. of 20th Int.. Conf. Org. Coat. Sci. Technol., New Platz, N.Y., State Univ. N.Y., Inst. Mater. Sci. p. 511-518.

[0085] The synthesis of dendritic polymers is described in the literature. The synthesis of dendrimers in NEWCOME, G.R., et al. Dendritic Molecules: Concepts, Synthesis, Perspectives. VCH: WEINHEIM, 2001. Hyperbranching polymerization is described by BURCHARD, W.. Solution properties of branched macromolecules. Advances in Polymer Science. 1999, vol. 143, no.II, p. 113-194. Hyperbranched materials can be obtained by polyfunctional polycondensation as disclosed by FLORY,P.J.. Molecular size distribution in three-dimensional polymers. VI. Branched polymer containing A-R-Bf-1-type units. Journal of the American Chemical Society. 1952, vol.74, p. 2718-1723.

[0086] Living cationic polymerizations is e.g. used for the synthesis of polyvinyl ethers as disclosed in WO 2005012444 (CANON), US 20050197424 (CANON) and US 200501768454 (CANON). Anionic co-ordination ring-opening polymerization is e.g. used for the synthesis of polyesters based on lactones. Living anionic ring-opening polymerization is e.g. used for the synthesis of polyethylene oxide macromonomers.

[0087] Free radical Polymerization (FRP) proceeds via a chain mechanism, which basically consists of four different types of reactions involving free radicals: (1) radical generation from non-radical species (initiation), (2) radical addition to a substituted alkene (propagation), (3) atom transfer and atom abstraction reactions (chain transfer and termination by disproportionation), and (4) radical-radical recombination reactions (termination by combination).

[0088] Polymeric dispersants having several of the above polymer compositions are disclosed in US 6022908

(HEWLETT-PACKARD COMPANY), US 5302197 (DU PONT) and US 6528557 (XEROX CORPORATION).

[0089] Suitable random copolymeric dispersants are disclosed in US 5648405 (DU PONT), US 6245832 (FUJI XEROX), US 6262207 (3M INNOVATIVE PROPERTIES COMPANY), US 20050004262 (KAO CORPORATION) and US 6852777B1 (KAO CORPORATION).

[0090] Suitable alternating copolymeric dispersants are described in US 20030017271 (AKZO NOBEL N.V.).

[0091] Suitable block copolymeric dispersants have been described in numerous patents, especially block copolymeric dispersants containing hydrophobic and hydrophilic blocks. For example, US 5859113 (DU PONT) discloses AB block copolymers, US 6413306 (DU PONT) discloses ABC block copolymers.

[0092] Suitable graft copolymeric dispersants are described in CA 2157361 (DU PONT) (hydrophobic polymeric backbone and hydrophilic side chains); other graft copolymeric dispersants are disclosed in US 6652634 (LEXMARK), US 6521715 (DU PONT) and US 2004102541 (LEXMARK).

[0093] Suitable branched copolymeric dispersants are described in US 6005023 (DU PONT), US 6031019 (KAO CORPORATION), US 6127453 (EASTMAN KODAK).

[0094] Suitable dendritic copolymeric dispersants are described in e.g. US 6518370 (3M INNOVATIVE PROPERTIES COMPANY), US 6258896 (3M INNOVATIVE PROPERTIES COMPANY), WO 2000063305 (GEM GRAVURE CORPOPATION), US 6649138 (QUANTUM DOT CORPORATION), US 2002256230 (BASF), EP 1351759 (EFKA ADDITIVES), EP 1295919 (EASTMAN KODAK)

[0095] Suitable designs of polymeric dispersants for inkjet inks are disclosed in SPINELLI, Harry J., Polymeric Dispersants in Ink Jet technology, Advanced Materials, 1998, Vol. 10, no. 15, p. 1215-1218.

[0096] The monomers and/or oligomers used to prepare the polymeric dispersant can be any monomer and/or oligomer found in the Polymer Handbook Vol 1 + 2, 4th edition, edited by J. BRANDRUP et al., Wiley-Interscience, 1999.

[0097] Polymers useful as pigment dispersants include naturally occurring polymers, and specific examples thereof include: proteins, such as glue, gelatine, casein, and albumin; naturally occurring rubbers, such as gum arabic and tragacanth; glucosides such as saponin; alginic acid and alginic acid derivatives, such as propylene glycol alginate; and cellulose derivatives, such as methyl cellulose, carboxymethyl cellulose and ethylhydroxy cellulose; wool and silk, and synthetic polymers.

[0098] Suitable examples of monomers for synthesising polymeric dispersants include: acrylic acid, methacrylic acid, maleic acid (or there salts), maleic anhydride, alkyl(meth)acrylates (linear, branched and cycloalkyl) such as methyl (meth)acrylate, n-butyl(meth)acrylate, tert-butyl(meth)acrylate, cyclohexyl(meth)acrylate, and 2-ethylhexyl(meth)acrylate; aryl(meth)acrylates such as benzyl(meth)acrylate, and phenyl(meth)acrylate; hydroxyalkyl(meth)acrylates such as hydroxyethyl(meth)acrylate, and hydroxypropyl(meth)acrylate; (meth)acrylates with other types of functionalities (e.g. oxiranes, amino, fluoro, polyethylene oxide, phosphate substituted) such as glycidyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, trifluoroethyl acrylate, methoxypolyethyleneglycol (meth)acrylate, and tripropyleneglycol (meth)acrylate phosphate; allyl derivatives such as allyl glycidil ether; styrenics such as styrene, 4-methylstyrene, 4-hydroxystyrene, 4-acetostyrene, and styrenesulfonic acid; (meth)acrylonitrile; (meth)acrylamides (including N-mono and N,N-disubstituted) such as N-benzyl (meth)acrylamide; maleimides such as N-phenyl maleimide; vinyl derivatives such as vinylalcohol, vinylcaprolactam, vinylpyrrolidone, vinylimidazole, vinylnapthalene, and vinyl halides; vinylethers such as vinylmethyl ether; vinylesters of carboxylic acids such as vinylacetate, vinylbutyrate, and vinyl benzoate. Typical condensation type polymers include polyurethanes, polyamides, polycarbonates, polyethers, polyureas, polyimines, polyimides, polyketones, polyester, polysiloxane, phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, polysulfide, polyacetal or combinations thereof.

[0099] Suitable copolymeric dispersants are acrylic acid/acrylonitrile copolymer, vinyl acetate/acrylic ester copolymer, acrylic acid/acrylic ester copolymer, styrene/acrylic acid copolymer, styrene/methacrylic acid copolymer, styrene/methacrylic acid/acrylic ester copolymer, styrene/α-methylstyrene/acrylic acid copolymer, styrene/α-methylstyrene/acrylic acid/acrylic ester copolymer, styrene/maleic acid copolymer, styrene/maleic anhydride copolymer, vinylnaphthalene/acrylic acid copolymer, vinylnapthalene/maleic acid copolymer, vinyl acetate/ethylene copolymer, vinyl acetate/fatty acid/ethylene copolymer, vinyl acetate/maleic ester copolymer, vinyl acetate/crotonic acid copolymer, vinyl acetate/acrylic acid copolymer.

[0100] Suitable chemistries of copolymeric dispersants also include:

- Copolymers which are the product of a condensation process of poly(ethylene imine) with a carboxylic acid terminated polyester (made by addition polymerization); and
- Copolymers which are the product of a reaction of multifunctional isocyanate with a mono-substituted active H-containing compound like polyester, with a compound containing two active hydrogens (like a polyether) which serves as a crosslinker and the residual isocyanates being transformed to carbamates or urea with compounds containing active hydrogens and a N-containing ring.

[0101] A detailed list of suitable polymeric dispersants is disclosed by MC CUTCHEON, Functional Materials, North

American Edition, Glen Rock, N.J.: Manufacturing Confectioner Publishing Co., 1990, p. 110-129.

[0102] Suitable pigment stabilisers are also disclosed in DE 19636382 (BAYER), US 5720802 (XEROX), US 5713993 (DU PONT), PCT/GB95/02501, US 5085689 (BASF) and GB 2303376 (FUJITSU ISOTEC).

[0103] The pigmented dispersion can contain one polymeric dispersant or a mi xture of two or more polymeric dispersants to improve the dispersion stability further. Sometimes surfactants can also be used as pigment dispersants, thus a combination of a polymeric dispersant with a surfactant is also possible.

[0104] The polymeric dispersant can be non-ionic, anionic or cationic in nature; salts of the ionic dispersants can also be used.

[0105] The polymeric dispersant preferably has preferably a polymerization degree DP between 5 and 1000, more preferably between 10 and 500 and most preferably between 10 and 100.

[0106] The polymeric dispersant preferably has preferably a number average molecular weight Mn between 500 and 30000, more preferably between 1500 and 10000.

[0107] The polymeric dispersant preferably has preferably an average molecular weight Mw smaller than 100000, more preferably smaller than 50000 and most preferably smaller than 30000.

[0108] The polymeric dispersant has preferably a polymeric dispersity PD smaller than 2, more preferably smaller than 1.75 and most preferably smaller than 1.5.

[0109] Commercial examples of polymeric dispersants are the following:

- DISPERBYK™ dispersants available from BYK CHEMIE GMBH;
- SOLSPERSE™ dispersants available from NOVEON;
- TEGO™ DISPERS™ dispersants from DEGUSSA;
- EDAPLAN™ dispersants from MÜNZING CHEMIE;
- ETHACRYL™ dispersants from LYONDELL;
- GANEX™ dispersants from ISP;
- DISPEX™ and EFKA™ dispersants from CIBA SPECIALTY CHEMICALS INC;
- DISPONER™ dispersants from DEUCHEM; and
- JONCRYL™ dispersants from JOHNSON POLYMER.

[0110] Particularly preferred for non-aqueous ink jet inks include Solsperse™ dispersants from NOVEON, Efka™ dispersants from CIBA SPECIALTY CHEMICALS INC and Disperbyk™ dispersants rom BYK CHEMIE GMBH.

[0111] Particularly preferred dispersants for solvent based pigmented dispersions are Solsperse™ 32000 and 39000 from NOVEON.

[0112] Particularly preferred dispersants for oil based pigmented dispersions are Solsperse™ 11000, 11200, 13940, 16000, 17000 and 19000 from NOVEON.

[0113] Particularly preferred dispersants for UV-curable pigmented dispersions are Solsperse™ 32000 and 39000 dispersants from NOVEON.

[0114] The polymeric dispersant is preferably used in the pigmented dispersion in an amount of 2 to 600 wt%, more preferably 5 to 200 wt% based on the weight of the pigment.

Dispersion media

[0115] The dispersion medium used in the pigmented inkjet ink according to the present invention is a liquid.

[0116] In one embodiment the dispersion medium consists of organic solvent(s). Suitable organic solvents include alcohols, ketones, esters, ethers, glycols and polyglycols and derivatives thereof, lactones, N-containing solvents such as amides, saturated hydrocarbons and unsaturated hydrocarbons. Preferably mixtures of one or more of these solvents are used.

[0117] Examples of suitable alcohols include methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, heptyl alcohol, octyl alcohol, cyclohexyl alcohol, benzyl alcohol, phenylethyl alcohol, phenylpropyl alcohol, furfuryl alcohol, anise alcohol and fluoroalcohols.

[0118] Examples of suitable ketones include acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl isopropyl ketone, methyl n-butyl ketone, methyl isobutyl ketone, methyl n-amyl ketone, methyl isoamyl ketone, diethyl ketone, ethyl n-propyl ketone, ethyl isopropyl ketone, ethyl n-butyl ketone, ethyl isobutyl ketone, di-n-propyl ketone, diisobutyl ketone, cyclohexanone, methylcyclohexanone and isophorone, 2,4-pentanedione and hexafluoroacetone.

[0119] Examples of suitable esters include methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, hexyl acetate, octyl acetate, benzyl acetate, phenoxyethyl acetate, ethyl phenyl acetate, methyl lactate, ethyl lactate, propyl lactate, butyl lactate; methyl propionate, ethyl propionate, benzyl propionate, ethylene carbonate, propylene carbonate, amyl acetate, ethyl benzoate, butyl benzoate, butyl laurate, isopropyl myristate, isopropyl palmirate, triethyl phosphate, tributyl phosphate, diethyl phthalate, dibutyl phthalate, diethyl malonate, dipropyl malonate, diethyl succinate, dibutyl succinate, diethyl glutarate, diethyl adipate, dibutyl adipate and diethyl sebacate.

[0120] Examples of suitable ethers include butyl phenyl ether, benzyl ethyl ether, hexyl ether, diethyl ether, dipropyl ether, tetrahydrofuran and dioxane.

[0121] Examples of suitable glycols and polyglycols include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol and tripropylene glycol.

[0122] Examples of suitable glycol and polyglycol derivatives include ethers such as alkylene glycol mono alkyl ethers, alkylene glycol dialkyl ethers, polyalkylene glycol nono alkyl ethers, polyalkylene glycol dialkyl ethers and esters of the preceding glycol ethers such as acetate and propionate esters, in case of dialkyl ethers only one ether function (resulting in mixed ether/ester) or both ether functions can be esterized (resulting in dialkyl ester).

[0123] Examples of suitable alkylene glycol mono alkyl ethers include ethylene glycol mono methyl ether, ethylene glycol mono ethyl ether, ethylene glycol mono propyl ether, ethylene glycol mono butyl ether, ethylene glycol mono hexyl ether, ethylene glycol mono 2-ethyl-hexyl ether, ethylene glycol mono phenyl ether, propoylene glycol mono methyl ether, propylene glycol mono ethyl ether, propylene glycol mono n-propyl ether, propylene glycol mono n-butyl ether, propylene glycol mono iso-butyl ether, propylene glycol mono t-butyl ether and propylene glycol mono phenyl ether.

[0124] Examples of suitable alkylene glycol dialkyl ethers include ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol methyl ethyl ether, ethylene glycol dibutyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether and propylene glycol dibutyl ether.

[0125] Examples of suitable polyalkylene glycol mono alkyl ethers include diethylene glycol mono methyl ether, diethylene glycol mono ethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono n-butyl ether, diethylene glycol mono hexyl ether, triethylene glycol mono methyl ether, triethylene mono ethyl ether, triethylene glycol mono butyl ether, dipropylene mono methyl ether, dipropylene glycol mono ethyl ether, dipropylene glycol n-propyl ether, dipropylene glycol mono n-butyl ether, dipropylene mono t-butyl ether, tripropylene glycol mono methyl ether, tripropylene glycol mono ethyl ether, tripropylene glycol mono n-propyl ether and tripropylene glycol mono n-butyl ether.

[0126] Examples of suitable polyalkylene glycol dialkyl ethers include diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol diethyl ether, tetraethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, triethylene glycol methyl ethyl ether, tetraethylene glycol methyl ethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-iso-propyl ether, dipropylene glycol dimethyl ether, dipropylene glcyol diethyl ether, dipropylene di n-propyl ether, dipropylene di t-butyl ether, tripropylene glycol dimethyl ether and tripropylene glycol diethyl ether.

[0127] Examples of suitable glycol esters include ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether acetate and propylene glycol monomethyl ether propionate.

[0128] Suitable commercial glycol ether solvents include Cellosolve™ solvents and Carbitol™ solvents from UNION CARBIDE, Ektasolve™ solvents from EASTMAN, Dowanol™ solvents from DOW, Oxitoll™ solvents, Dioxitoll™ solvents, Proxitoll™ solvents and Diproxitoll™ solvents from SHELL CHEMICAL and Arcosolv™ solvents from LYONDELL.

[0129] Lactones are compounds having a ring structure formed by ester bonds and can be of the γ-lactone (5-membered ring structure), δ-lactone (6-membered ring structure) or ε-lactone (7-membered ring structure) types. Suitable examples of lactones include γ-butyrolactone, γ-valerolactone, γ-hexalactone, γ-heptalactone, γ-octalactone, γ-nonalactone, γ-decalactone, γ-undecalactone, δ-valerolactone, δ-hexalactone, δ-heptalactone, δ-octalactone, δ-nonalactone, δ-decalactone, δ-undecalactone and ε-caprolactone.

[0130] Suitable examples of N-containing organic solvents include 2-pyrrolidone, N-methylpyrrolidone, N,N-dimethylacetamid, N,N-dimethylformamid, acetonitril and N,N-dimethyldodecanamide.

[0131] Examples of suitable hydrocarbons include saturated hydrocarbons such as n-hexane, isohexane, n-nonane, isononane, dodecane and isododecane; unsaturated hydrocarbons such as 1-hexene, 1-heptene and 1-octene; cyclic saturated hydrocarbons such as cyclohexane, cycloheptane, cyclooctane, cyclodecane and decalin; cyclic unsaturated hydrocarbons such as cyclohexene, cycloheptene, cyclooctene, 1,1,3,5,7-cyclooctatetraene; and cyclododecene; and aromatic hydrocarbons such as benzene, toluene and xylene.

[0132] In another embodiment the dispersion medium comprises oil types of liquids, alone or in combination with organic solvent(s).

[0133] Suitable organic solvents include alcohols, ketones, esters, ethers, glycols and polyglycols and derivatives thereof, lactones, N-containing solvents such as amides, higher fatty acid ester and mixtures of one or more of the solvents as described above for solvent based dispersion media.

[0134] The amount of polar solvent is preferably lower than the amount of oil. The organic solvent has preferably a high boiling point, preferably above 200°C. Examples of suitable combinations are disclosed by EP 0808347 (XAAR TECHNOLOGY LTD) especially for the use of oleyl alcohol and EP 1157070 (VIDEOJET TECHNOLOGIES INC) for the combination of oil and volatile organic solvent.

[0135] Suitable oils include saturated hydrocarbons and unsaturated hydrocarbons, aromatic oils, paraffinic oils, extracted paraffinic oils, napthenic oils, extracted napthenic oils, hydrotreated light or heavy oils, vegetable oils, white oils, petroleum naptha oils, halogen-substituted hydrocarbons, silicones and derivatives and mixtures thereof.

[0136] Hydrocarbons may be selected from straight chain or branched chain aliphatic hydrocarbons, alicyclic hydrocarbons and aromatic hydrocarbons. Examples of hydrocarbons are saturated hydrocarbons such as n-hexane, isohexane, n-nonane, isononane, dodecane and isododecane; unsaturated hydrocarbons such as 1-hexene, 1-heptene and 1-octene; cyclic saturated hydrocarbons such as cyclohexane, cycloheptane, cyclooctane, cyclodecane and decalin; cyclic unsaturated hydrocarbons such as cyclohexene, cycloheptene, cyclooctene, 1,1,3,5,7-cyclooctatetraene; and cyclododecene; and aromatic hydrocarbons such as benzene, toluene, xylene, napthalene, phenanthrene, anthracene and derivatives thereof. In literature the term paraffinic oil is often used. Suitable Paraffinic oils can be normal paraffin type (octane and higher alkanes), isoparaffins (isooctane and higher iso-alkanes) and cycloparaffins (cyclooctane and higher cycloalkanes) and mixtures of paraffin oils. The term "liquid paraffin" is often used to refer to a mixture of mainly comprising three components of a normal paraffin, an isoparaffin and a monocyclic paraffin, which is obtained by highly refining a relatively volatile lubricating oil fraction through a sulphuric-acid washing or the like, as described in US 6730153 (SAKATA INX CORP.). Suitable hydrocarbons are also described as de-aromatized petroleum distillates.

[0137] Suitable examples of halogenated hydrocarbons include methylene dichloride, chloroform, carbon tetrachloromethane and methyl chloroform. Other suitable examples of halogen-substituted hydrocarbons include perfluoroalkanes, fluorine-based inert liquids and fluorocarbon iodides.

[0138] Suitable examples of silicone oils include dialklyl polysiloxane (e.g., hexanemethyl disiloxane, tetramethyl disiloxane, octamethyl trisiloxane, hexanemethyl trisiloxane, heptamethyl trisiloxane, decamethyl tetrasiloxane, trifluoropropyl heptamethyl trisiloxane, diethyl tetramethyl disiloxane), cyclic dialkyl polysiloxane (e.g., hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, tetramethyl cyclotetrasiloxane, tetra(trifluoropropyl)tetramethyl cyclotetrasiloxane), and methylphenyl silicone oil.

[0139] White oils is a term used for white mineral oils, which are highly refined mineral oils that consist of saturated aliphatic and alicyclic non-polar hydrocarbons. White oils are hydrophobic, colorless, tasteless, odourless, and do not change colour over time.

[0140] Vegetable oils include semi-drying oils such as soybean oil, cotton seed oil, sunflower oil, rape seed oil, mustard oil, sesame oil and corn oil; non-drying oils such as olive oil, peanut oil and tsubaki oil; and drying oils such as linseed oil and safflower oil, wherein these vegetable oils can be used alone or as a mixture thereof.

[0141] Examples of other suitable oils include petroleum oils, non-drying oils and semi-drying oils.

[0142] Commercially available suitable oils include the aliphatic hydrocarbons types such as the Isopar™ range (isoparaffins) and Varsol/Naphtha range from EXXON CHEMICAL, the Soltrol™ range and hydrocarbons from CHEVRON PHILLIPS CHEMICAL, and the Shellsol™ range from SHELL CHEMICALS.

[0143] Suitable commercial normal paraffins include the Norpar™ range from EXXON MOBIL CHEMICAL.

[0144] Suitable commercial napthenic hydrocarbons include the Nappar™ range from EXXON MOBIL CHEMICAL.

[0145] Suitable commercial de-aromatized petrolemum distillates include the Exxsol™ D types from EXXON MOBIL CHEMICAL

[0146] Suitable commercial fluoro-substituted hydrocarbons include fluorocarbons from DAIKIN INDUSTRIES LTD, Chemical Division.

[0147] Suitable commercial silicone oils include the silicone fluid ranges from SHIN-ETSU CHEMICAL, Silicone Division.

[0148] Suitable commercial white oils include Witco™ white oils from CROMPTON CORPORATION.

[0149] If the non-aqueous pigment dispersion is a curable pigment dispersion, the dispersion medium comprises one or more monomers and/or oligomers to obtain a liquid dispersion medium. Sometimes, it can be advantageous to add a small amount of an organic solvent to improve the dissolution of the dispersant. The content of organic solvent should be lower than 20 wt% based on the total weight of the pigmented inkjet ink. In other cases, it can be advantageous to add a small amount of water, for example, to improve the spreading of the inkjet ink on a hydrophilic surface, but preferably the ink-jet ink contains no water.

[0150] Preferred organic solvents include alcohols, aromatic hydrocarbons, ketones, esters, aliphatic hydrocarbons, higher fatty acids, carbitols, cellosolves, higher fatty acid esters. Suitable alcohols include, methanol, ethanol, propanol and 1-butanol, 1-pentanol, 2-butanol, t.-butanol. Suitable aromatic hydrocarbons include toluene, and xylene. Suitable ketones include methyl ethyl ketone, methyl isobutyl ketone, 2,4-pentanedione and hexafluoroacetone. Also glycol, glycolethers, N-methylpyrrolidone, N,N-dimethylacetamid, N, N-dimethylformamid may be used.

[0151] Suitable monomers and oligomers can be found in Polymer Handbook, Vol. 1 + 2. 4th edition. Edited by J. BRANDRUP, et al. Wiley-Interscience, 1999.

[0152] Suitable examples of monomers for curable pigmented inkjet inks include: acrylic acid, methacrylic acid, maleic acid (or their salts), maleic anhydride; alkyl(meth)acrylates (linear, branched and cycloalkyl) such as methyl(meth)acrylate, n-butyl(meth)acrylate, tert-butyl(meth)acrylate, cyclohexyl(meth)acrylate and 2-ethylhexyl(meth)acrylate; aryl (meth)acrylates such as benzyl(meth)acrylate and phenyl(meth)acrylate; hydroxyalkyl(meth)acrylates such as hydroxyethyl(meth)acrylate and hydroxypropyl(meth)acrylate; (meth)acrylates with other types of functionalities (e.g. oxirane, amino, fluoro, polyethylene oxide, phosphate-substituted) such as glycidyl (meth)acrylate, dimethylaminoethyl(meth) acrylate, trifluoroethyl acrylate, methoxypolyethyleneglycol (meth)acrylate and tripropyleneglycol(meth)acrylate phosphate; allyl derivatives such as allyl glycidyl ether; styrenics such as styrene, 4-methylstyrene, 4-hydroxystyrene, and 4-acetoxystyrene; (meth)acrylonitrile; (meth)acrylamides (including N-mono and N,N-disubstituted) such as N-benzyl (meth)acrylamide; maleimides such as N-phenyl maleimide, N-benzyl maleimide and N-ethyl maleimide; vinyl derivatives such as vinylcaprolactam, vinylpyrrolidone, vinylimidazole, vinyl naphthalene and vinyl halides; vinylethers such as vinylmethyl ether; and vinylesters of carboxylic acids such as vinylacetate and vinylbutyrate.

[0153] A combination of monomers, oligomers and/or prepolymers may also be used. The monomers, oligomers and/or prepolymers may possess different degrees of functionality, and a mixture including combinations of mono-, di-, tri-and higher functionality monomers, oligomers and/or prepolymers may be used.

Binders

[0154] Non-aqueous ink jet ink compositions preferably comprise a binder resin. The binder functions as a viscosity controlling agent and also provides fixability relative to the polymeric resin substrate, e.g. a polyvinyl chloride substrate, also called vinyl substrate. The binder must be selected to have a good solubility in the solvent(s).

[0155] Suitable examples of binder resins include acrylic resins, modified acrylic resins, styrene acrylic resins, acrylic copolymers, acrylate resins, aldehyde resins, rosins, rosin esters, modified rosins and modified rosin resins, acetyl polymers, acetal resins such as polyvinyl butyral, ketone resins, phenolic resins and modified phenolic resins, maleic resins and modified maleic resins, terpene resins, polyester resins, polyamide resins, polyurethane resins, epoxy resins, vinyl resins, vinyl chloride-vinyl acetate copolymer resins, cellulose type resins such as nitro cellulose, cellulose acetopropionate and cellulose acetate butyrate, and vinyl toluene-α-methylstylene copolymer resin. These binders may be used alone or in a mixture thereof. The binder is preferably a film-forming thermoplastic resin.

[0156] The amount of binder resin in ink jet ink is preferably in the range of 0.1 to 30 wt%, more preferably 1 to 20 wt%, most preferably 2 to 10 wt% based on the total weight of the ink jet ink.

Surfactants

[0157] The pigmented inkjet ink according to the present invention may contain at least one surfactant. The surfactant (s) can be anionic, cationic, non-ionic, or zwitter-ionic and are usually added in a total quantity less than 20 wt% based on the total weight of the pigmented inkjet ink and particularly in a total less than 10 wt% based on the total weight of the pigmented inkjet ink.

[0158] Suitable surfactants for the pigmented inkjet ink according to the present invention include fluorinated surfactants, fatty acid salts, ester salts of a higher alcohol, alkylbenzene sulphonate salts, sulphosuccinate ester salts and phosphate ester salts of a higher alcohol (for example, sodium dodecylbenzenesulphonate and sodium dioctylsulphosuccinate), ethylene oxide adducts of a higher alcohol, ethylene oxide adducts of an alkylphenol, ethylene oxide adducts of a polyhydric alcohol fatty acid ester, and acetylene glycol and ethylene oxide adducts thereof (for example, polyoxyethylene nonylphenyl ether, and SURFYNOL™ 104, 104H, 440, 465 and TG available from AIR PRODUCTS & CHEMICALS INC.).

Humectants/Penetrants

[0159] Suitable humectants include triacetin, N-methyl-2-pyrrolidone, glycerol, urea, thiourea, ethylene urea, alkyl urea, alkyl thiourea, dialkyl urea and dialkyl thiourea, diols, including ethanediols, propanediols, propanetriols, butanediols, pentanediols, and hexanediols; glycols, including propylene glycol, polypropylene glycol, ethylene glycol, polyethylene glycol, diethylene glycol, tetraethylene glycol, and mixtures and derivatives thereof. Preferred humectants are triethylene glycol mono butylether, glycerol and 1,2-hexanediol. The humectant is preferably added to the inkjet ink formulation in an amount of 0.1 to 40 wt% of the formulation, more preferably 0.1 to 10 wt% of the formulation, and most preferably approximately 4.0 to 6.0 wt%.

Preparation of a pigmented inkjet ink

[0160] The pigmented inkjet ink according to the present invention may be prepared by precipitating or milling the pigment in the dispersion medium in the presence of the dispersant.

[0161] Mixing apparatuses may include a pressure kneader, an open kneader, a planetary mixer, a dissolver, and a Dalton Universal Mixer. Suitable milling and dispersion apparatuses are a ball mill, a pearl mill, a colloid mill, a high-speed disperser, double rollers, a bead mill, a paint conditioner, and triple rollers. The dispersions may also be prepared using ultrasonic energy.

[0162] Many different types of materials may be used as milling media, such as glasses, ceramics, metals, and plastics. In a preferred embodiment, the grinding media can comprise particles, preferably substantially spherical in shape, e.g. beads consisting essentially of a polymeric resin or yttrium stabilized zirconium beads.

[0163] In the process of mixing, milling and dispersion, each process is preferably performed with cooling to prevent build up of heat.

[0164] In the process of mixing, milling and dispersion, each process is performed with cooling to prevent build up of heat, and for radiation curable inkjet inks as much as possible under light conditions in which actinic radiation has been substantially excluded.

[0165] The inkjet ink according to the present invention may contain more than one pigment, the inkjet ink may be prepared using separate dispersions for each pigment, or alternatively several pigments may be mixed and co-milled in preparing the dispersion.

[0166] The dispersion process can be carried out in a continuous, batch or semi-batch mode.

[0167] The preferred amounts and ratios of the ingredients of the mill grind will vary widely depending upon the specific materials and the intended applications. The contents of the milling mixture comprise the mill grind and the milling media. The mill grind comprises pigment, polymeric dispersant and a liquid carrier. For inkjet inks, the pigment is usually present in the mill grind at 1 to 50 wt%, excluding the milling media. The weight ratio of pigment over polymeric dispersant is 20:1 to 1:2.

[0168] The milling time can vary widely and depends upon the pigment, mechanical means and residence conditions selected, the initial and desired final particle size, etc. In the present invention pigment dispersions with an average particle size of less than 100 nm may be prepared.

[0169] After milling is completed, the milling media is separated from the milled particulate product (in either a dry or liquid dispersion form) using conventional separation techniques, such as by filtration, sieving through a mesh screen, and the like. Often the sieve is built into the mill, e.g. for a bead mill. The milled pigment concentrate is preferably separated from the milling media by filtration.

[0170] In general it is desirable to make the inkjet inks in the form of a concentrated mill grind, which is subsequently diluted to the appropriate concentration for use in the inkjet printing system. This technique permits preparation of a greater quantity of pigmented ink from the equipment. By dilution, the inkjet ink is adjusted to the desired viscosity, surface tension, colour, hue, saturation density, and print area coverage for the particular application.

Spectral Separation Factor

[0171] The spectral separation factor SSF was found to be an excellent measure to characterize a pigmented inkjet ink, as it takes into account properties related to light-absorption (e.g. wavelength of maximum absorbance λ_{max}, shape of the absorption spectrum and absorbance-value at λ_{max}) as well as properties related to the dispersion quality and stability.

[0172] A measurement of the absorbance at a higher wavelength gives an indication on the shape of the absorption spectrum. The dispersion quality can be evaluated based on the phenomenon of light scattering induced by solid particles in solutions. When measured in transmission, light scattering in pigment inks may be detected as an increased absorbance at higher wavelengths than the absorbance peak of the actual pigment. The dispersion stability can be evaluated by comparing the SSF before and after a heat treatment of e.g. a week at 80°C.

[0173] The spectral separation factor SSF of the ink is calculated by using the data of the recorded spectrum of an ink solution or a jetted image on a substrate and comparing the maximum absorbance to the absorbance at a higher reference wavelength λ_{ref}. The spectral separation factor is calculated as the ratio of the maximum absorbance A_{max} over the absorbance A_{ref} at a reference wavelength.

$$SSF = \frac{A_{max}}{A_{ref}}$$

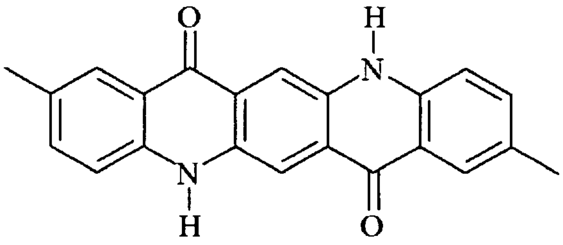
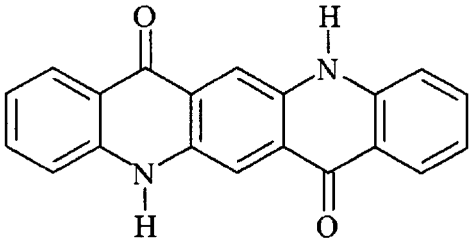
[0174] The SSF is an excellent tool to design inkjet ink sets with large colour gamut. Often inkjet ink sets are now commercialized, wherein the different inks are not sufficiently matched with each other. For example, the combined absorption of all inks does not give a complete absorption over the whole visible spectrum, e.g. "gaps" exist between the absorption spectra of the colorants. Another problem is that one ink might be absorbing in the range of another ink. The resulting colour gamut of these inkjet ink sets is low or mediocre.

EXAMPLES

Materials

[0175] All materials used in the following examples were readily available from standard sources such as Aldrich Chemical Co. (Belgium) and Acros (Belgium) unless otherwise specified.
DEGDEE is diethylene glycol diethylether from ACROS.
SOLSPERSE™ 32000 is a hyperdispersant from NOVEON.
SYN-1 is benzoic acid from ACROS.
SYN-2 is abietic acid from ACROS.
SYN-3 is 4-benzoylbenzoicacid from ACROS.
SYN-4 is 4-fluorenone-4-carboxylic acid from ALDRICH.
SYN-5 is 4-octylfenoxyethoxyethyl-dimethylamine.
SYN-6 is 3-amino benzoic acid from ACROS.
Potassium tert-butoxide from ACROS.
Methyl-4-(bromomethyl)benzoate from ACROS.
1,4-butanesultone from ACROS.
Tridodecylamine from ACROS.
Diethyl-5-(hydroxymethyl)isophtalate from ALDRICH.
Thionylchloride from ACROS.
N,N-dimethyl-N-octadecylamine from ACROS.
DPGDA™ is dipropylene glycol diacrylate available from CYTEC SURFACE "PECIALTIES.
PR122 is the abbreviation for C.I. Pigment Red 122 for Ink Jet Magenta™ E02VP2621 from CLARIANT was used.
PV19 is the abbreviation for C.I. Pigment Violet 19 for which Hostaperm Red™ E5B02 from CLARIANT was used.
The chemical structure of the quinacridone pigments used is listed in Table 2.

Table 2

PR122	
PV19	

Measurement methods

1. Measurement of SSF

[0176] The spectral separation factor SSF of the ink was calculated by using the data of the recorded spectrum of an ink solution and comparing the maximum absorbance to the absorbance at a reference wavelength.The reference wavelength chosen for a magenta inkjet ink was 650 nm.

[0177] The absorbance was determined in transmission with a Shimadzu UV-2101 PC double beam-spectrophotometer. The ink was diluted with ethyl acetate to have a pigment concentration of 0.005%. A spectrophotometric measurement of the UV-VIS-NIR absorption spectrum of the diluted ink was performed in transmission-mode with a double beam-spectrophotometer using the settings of Table 3. Quartz cells with a path length of 10 mm were used and ethyl acetate was chosen as a blank.

Table 3

Mode	Absorbance
Wavelength range	240-900 nm
Slit width	2.0 nm
Scan interval	1.0 nm
Scan speed	Fast (1165 nm/min)
Detector	photo-multiplier(UV-VIS)

[0178] Efficient pigmented inkjet inks exhibiting a narrow absorption spectrum and a high maximum absorbance have a value for SSF of at least 30.

2. Dispersion stability

[0179] The dispersion stability was evaluated by comparing the SSF before and after a heat treatment of one week at 80˚C. Pigmented inkjet inks exhibiting good dispersion stability have a SSF after heat treatment still larger than 30 and a loss in SSF of less than 35%.

3. Particle size

[0180] The particle size of pigment particles in pigmented inkjet ink was determined by photon correlation spectroscopy at a wavelength of 633 nm with a 4mW HeNe laser on a diluted sample of the pigmented inkjet ink. The particle size analyzer used was a Malvern™ nano-S available from Goffin-Meyvis.

[0181] The sample was prepared by addition of one drop of ink to a cuvet containing 1.5 mL ethyl acetate and mixed until a homogenous sample was obtained. The measured particle size is the average value of 3 consecutive measurements consisting of 6 runs of 20 seconds. For good ink jet characteristics (jetting characteristics and print quality) the average particle size of the dispersed particles is below 200 nm, preferably about 100 nm. The pigmented inkjet ink is considered to be a stable pigment dispersion if the particle size remained below 200 nm after a heat treatment of 7 days at 80˚C.

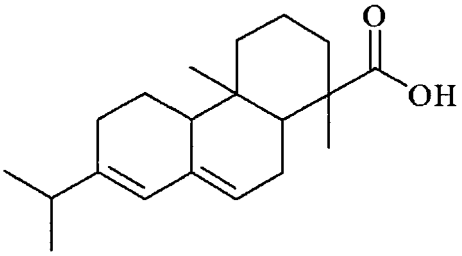
EXAMPLE 1

[0182] This example illustrates that non-aqueous C.I. Pigment Red 122 inkjet inks with high dispersion quality for producing high image quality are obtained when using quinacridone derivatives containing one or more carboxylic acid groups or salts thereof as dispersion synergists compared to dispersions lacking a quinacridone derivative or with other compounds having a carboxylic acid group.

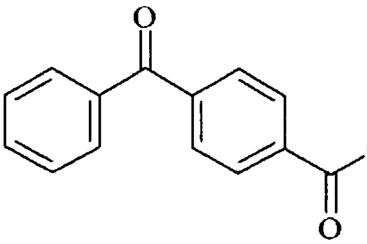
Dispersion synergists

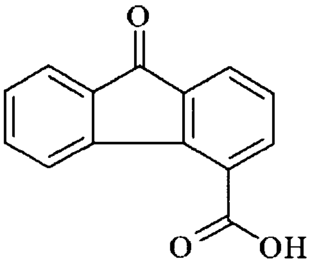
[0183] The compounds SYN-1 to SYN-4 were used as comparative dispersion synergists.

SYN-1 SYN-2



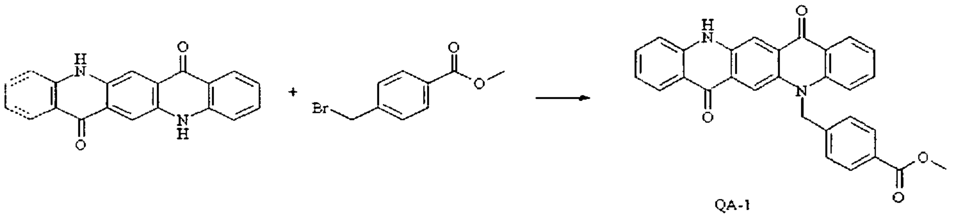
SYN-3 SYN-4



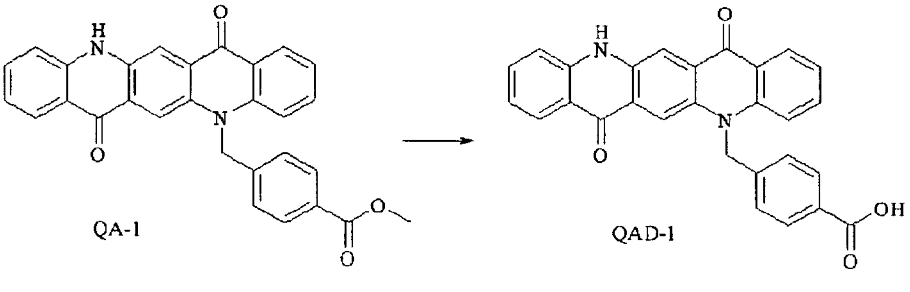


Dispersion synergist QAD-1

[0184] Synthesis of the dispersion synergist QAD-1 was accomplished according to the following synthesis scheme:



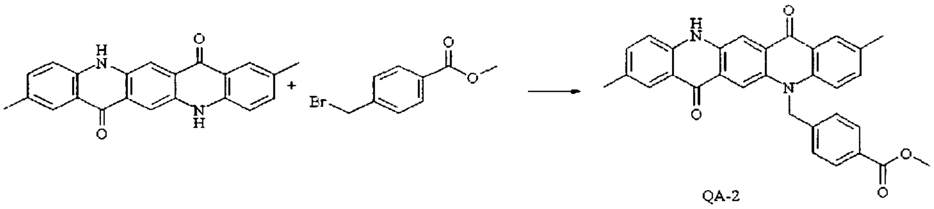
31.2 g (0.1 mol) of the pigment PV19 in 500 mL dimethylsulfoxide was dissolved by addition of 22.44 g (0.2 mol) of potassium tert-butoxide. The blue solution was heated to about 70°C and 22.8 g (0.1 mol) of methyl-4-(bromomethyl) benzoate was added. The mixture was cooled to roomtemperature after 2 hours and the compound QA-1 was precipitated, filtered and washed with methanol. The yield was 77%.



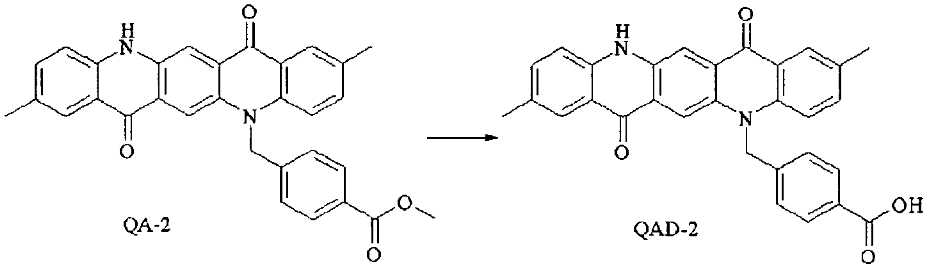
Formation of the dispersion synergist QAD-1 was accomplished by hydrolization of QA-1. This reaction took place during a reflux of 46 g (0.1 mol) of compound QA-1 in a mixture of ethanol and 50 mL (0.5 mol) of 29% sodiumhydroxide solution. After 1 hour the mixture was cooled down, the precipitate was filtered and washed with water. The precipitate was mixed in 1000 mL water and the acid form was made by the addition of 50 mL (0.6 mol) of concentrated hydrochloric acid. The dispersion synergist QAD-1 was filtered and washed with water and ethanol. The yield was 78%.

Dispersion synergist QAD-2

[0185] Synthesis of the dispersion synergist QAD-2 was accomplished according to the following synthesis scheme:



34 g (0.1 mol) of the pigment PR122 in 500 mL dimethylsulfoxide was dissolved by addition of 22.44 g (0.2 mol) of potassium tert-butoxide. The blue solution was heated to about 70˚C and 22.8 g (0.1 mol) of methyl-4-(bromomethyl) benzoate was added. The mixture was cooled after 2 hours and the product was precipitated, filtered and washed with methanol. The yield was 65%.



Formation of the dispersion synergist QAD-2 was accomplished by hydrolization of compound QA-2. This reaction takes place during a reflux of 48.8 g (0.1 mol) of compound QA-2 in a mixture of ethanol and 50 mL (0.5 mol) of 29% sodiumhydroxide solution. After 1 hour the mixture was cooled down, the precipitate was filtered and washed with water. The precipitate was taken up in 1 L of water and the acid form was made by the addition of 50 mL (0.6 mol) of concentrated hydrochloric acid. The dispersion synergist QAD-2 was filtered and washed with water and ethanol. The yield was 71 %.

Preparation and evaluation of ink-jet inks

[0186] All inkjet inks were prepared in the same manner to obtain a composition as described in Table 4, except that different dispersion synergists were used. In some examples, the ratio of polymeric dispersant over dispersion synergist was altered through replacement or addition of the organic solvent DEGDEE.

Table 4

Component	wt%
PR122	4.50
Dispersion synergist	0.50
Solsperse™ 32000	5.00
DEGDEE	90.00

[0187] An ink composition was made by mixing the pigment PR122, the polymeric dispersant Solsperse™ 32000, the dispersion synergist and the organic solvent DEGDEE with a dissolver and subsequently treating this mixture with a roller mill procedure using yttrium-stabilized zirconium oxide-beads of 0.4 mm diameter ("high wear resistant zirconia grinding media" from TOSOH Co.). A polyethylene flask of 60mL was filled to half its volume with grinding beads and 20 mL of the mixture. The flask was closed with a lit and put on the roller mill for three days. The speed was set at 150 rpm. After milling the dispersion was separated from the beads using a filter cloth.

[0188] Using the above method, the comparative inkjet inks COMP-1 to COMP-5 and the inventive inkjet inks INV-1 to INV-6 were prepared according to Table 5. The amount of synergist indicates how much dispersion synergist was used in wt% based on the polymeric dispersant. The spectral separation factor SSF was determined to evaluate the dispersion quality. The results are listed in Table 5.

Table 5

Inkjet ink	Dispersion Synergist		SSF
	Type	amount	
COMP-1	None	---	36
COMP-2	SYN-1	10%	45
COMP-3	SYN-2	10%	25
COMP-4	SYN-3	10%	30
COMP-5	SYN-4	10%	30
INV-1	QAD-1	5%	104
INV-2	QAD-1	10%	141
INV-3	QAD-1	20%	186
INV-4	QAD-2	5%	97
INV-5	QAD-2	10%	207
INV-6	QAD-2	20%	103

[0189] From Table 5, it should be clear that only the inventive inkjet inks INV-1 to INV-6 using quinacridone derivatives containing a carboxylic acid group as a dispersion synergist delivered pigmented inkjet inks of superior quality compared to the comparative inkjet inks COMP-2 to COMP-5 using comparative dispersion synergists with a carboxylic acid group or compared to the comparative inkjet ink COMP-1 lacking a dispersion synergist. The concentration of the dispersion synergist can be altered to maximize dispersion quality.

EXAMPLE 2

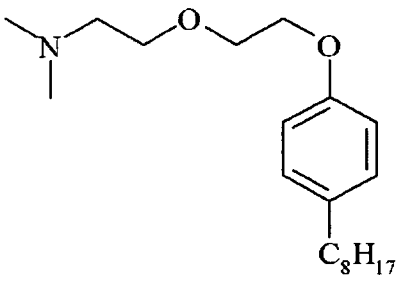
[0190] This example illustrates that stable C.I. Pigment Violet 19 dispersions were obtained using quinacridone derivatives containing one or more carboxylic acid groups or salts thereof as dispersion synergists.

Dispersion synergists

Dispersion synergist SYN-5

[0191] The compound SYN-5 was used as a comparative dispersion synergist.

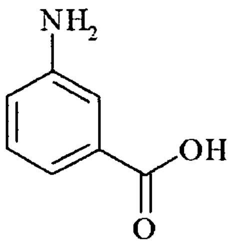
SYN-5



Dispersion synergist SYN-6

[0192] The compound SYN-6 was used as a comparative dispersion synergist.

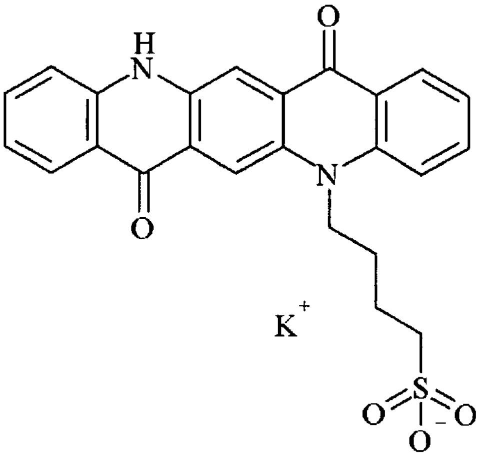
SYN-6



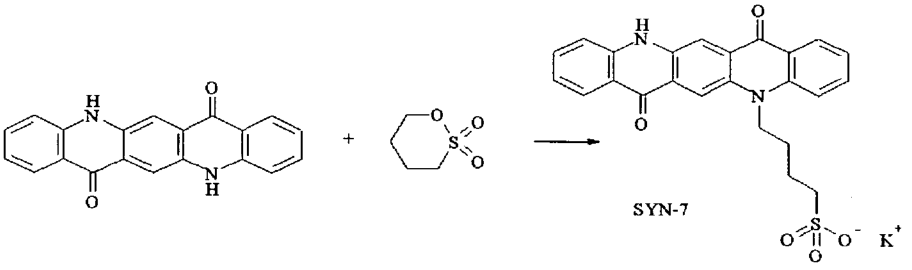
Dispersion synergist SYN-7

[0193] The compound SYN-7 having a quinacridone structure but a sulfonic acid salt group was used as a comparative dispersion synergist.

SYN-7



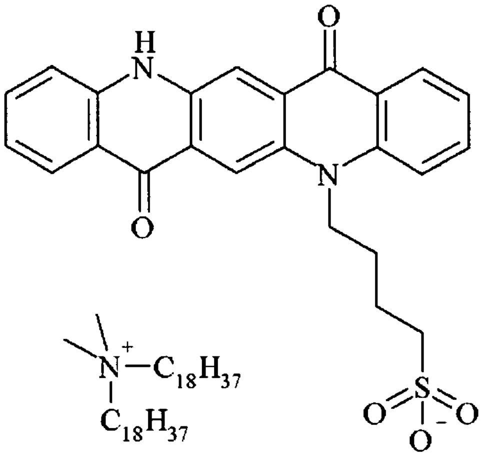
[0194] Synthesis of the dispersion synergist SYN-7 was accomplished according to the following synthesis scheme:



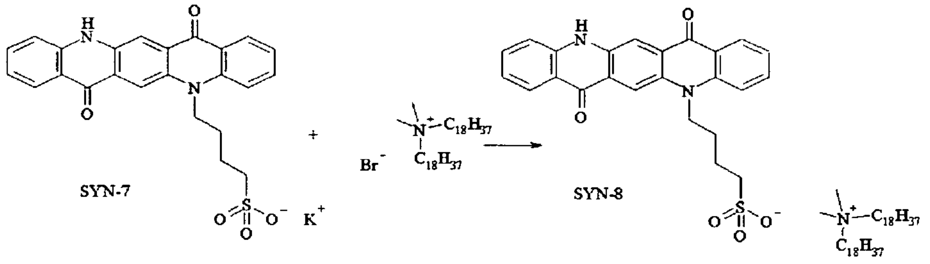
31.2 g (0.1 mol) of the pigment PV19 in 210 mL dimethylsulfoxide was heated to about 80°C. The magenta suspension was dissolved by addition of 22.44 g (0.2 mol) of potassium tert-butoxide.13.6 g (0.1 mol) of 1,4-butanesultone and 1; 7 g (0.01 mol) of potassium iodide are added to the blue solution and the mixture was heated during 4 hours. After cooling down the dispersion synergist SYN-7 was precipitated by adding 210 mL of methanol. The synergist was filtered and washed with methanol. The yield was 60%.

Dispersion synergist SYN-8

[0195] The compound SYN-8 having a quinacridone structure but a sulfonic acid



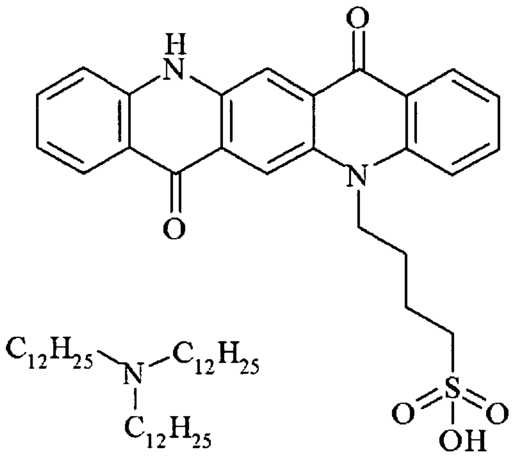
[0196] Synthesis of the dispersion synergist SYN-8 was accomplished according to the following synthesis scheme:



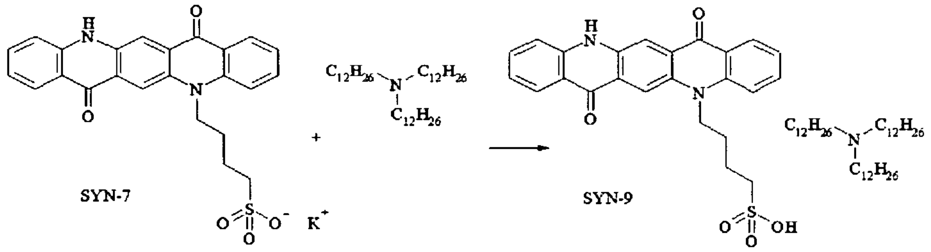
A solution of 48.7 g (0.1 mol) of dispersion synergist SYN-7 in 500 mL water was heated to about 70°C. 63 g (0.1 mol) of dimethyl dioctadecyl ammonium bromide was added to this solution and after 15 minutes a precipitate appeared. The mixture was cooled to roomtemperature and the precipitate was filtered and washed with methanol. The yield was 70%.

Dispersion synergist SYN-9

[0197] The compound SYN-9 having a quinacridone structure but a sulfonic acid



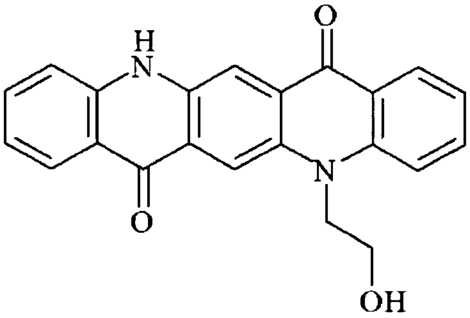
[0198] Synthesis of the dispersion synergist SYN-9 was accomplished according to the following synthesis scheme:



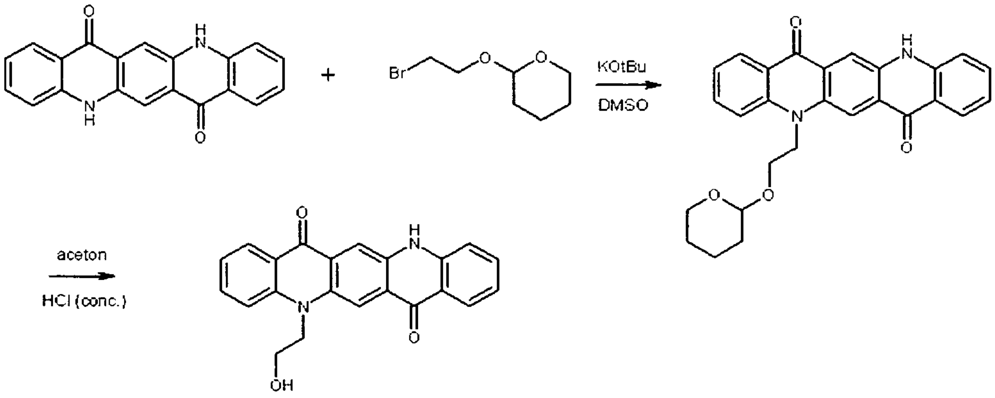
A solution of 48.7 g (0.1 mol) of dispersion synergist SYN-7 in 500 mL water was heated to about 70°C. 52.2 g (0.1 mol) of tridodecylamine was added and the mixture was heated during 15 minutes. After this period the mixture was cooled to roomtemperature and 41.6 mL (0.5 mol) of hydrochloric acid was dropwise added. The product was precipitated as an oil. During the night the oil was converted in a solid product. This synergist was filtered and washed with water. The yield was 61%.

Dispersion synergist SYN-1 0

[0199] The compound SYN-10 having a quinacridone structure but with a hydroxyethyl group was used as a comparative dispersion synergist.



[0200] Synthesis scheme of SYN-10:

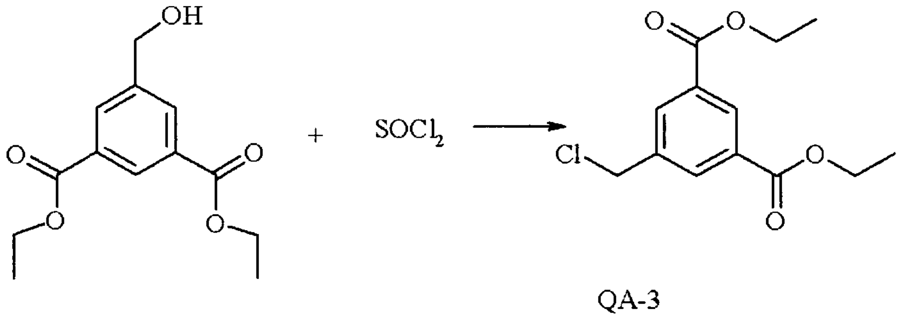


25 g (80 mmol) PV19 was suspended in 200 mL DMSO. 17.9 g (160 mmol) KOtBu was added and the suspension was heated to 70°C. 21.64 g (104 mmol) 2-(2-bromoethoxy)-tetrahydro-2H-pyran was added and the reaction was allowed to continue for 3 hours at 70°C. After cooling down to room temperature, 300 mL of water is added. The crude intermediate was isolated by filtration, washed with water and dried. The crude intermediate was suspended in 500 mL acetone. 8.0 mL HCl (conc.) was added and the reaction was allowed to continue for 1 hour at room temperature. N-hydroxyethyl-quinacridone was isolated by filtration, washed with aceton, resuspended in aceton, again isolated by filtration and dried.

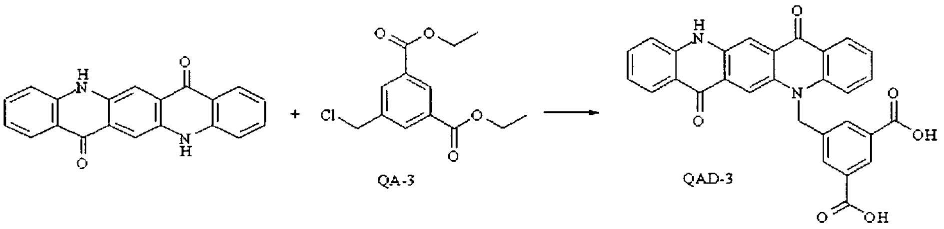
The crude product was used for polymer modification without further purification. The yield was 92 %.

Dispersion synergist QAD-3

[0201] Synthesis of the dispersion synergist QAD-3 was accomplished according



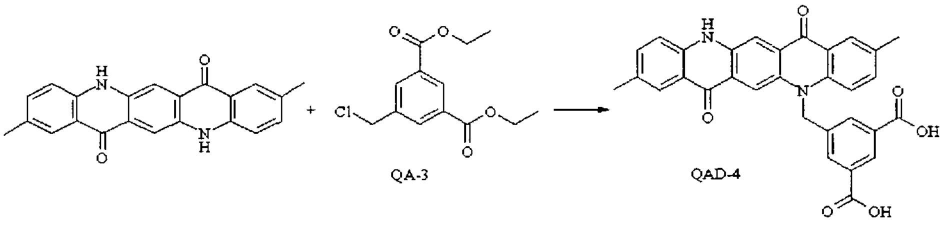
25 g (0.1 mol) of diethyl-5-hydroxymethyl)isophtalate was dissolved in a mixture of 100 mL of methylenechloride and 0.3 g dimethylacetamide (catalyst). 19.6 g (0.165 mol) of thionylchloride was dropwise added and the mixture was stirred during the night. After this period, the mixture was cooled in an ice bath and 150 mL of ethanol was added. While the methylenechloride was evaporated under reduced pressure a solid appeared. This solid product QA-3 was filtered and washed with a small volume of ethanol. The yield was 86%.



31.0 g (0.1 mol) of dried pigment PV 19 in 500 mL dimethylsulfoxide was dissolved by the addition of 22.44 g (0.2 mol) potassium tert-butoxide. The blue solution was heated to about 70°C and 27.1 g (0.1 mol) of compound QA-3 was added. The alkylation-step was done after 2 hours and the product was hydrolyzed by the addition of 72.4 g (0.4 mol) sodium-methylate and 200ml of water. After 1 hour the mixture was cooled to about 50°C and the pigment was precipitated with acetone (about 1000 mL). The precipitate was filtered and washed with acetone. This solid product was dissolved in 1000 mL of water and the acid form was precipitated by the addition of an excess of concentrated hydrochloric acid. The dispersion synergist QAD-3 was filtered and washed with water. The yield was 85%.

Dispersion synergist QAD-4

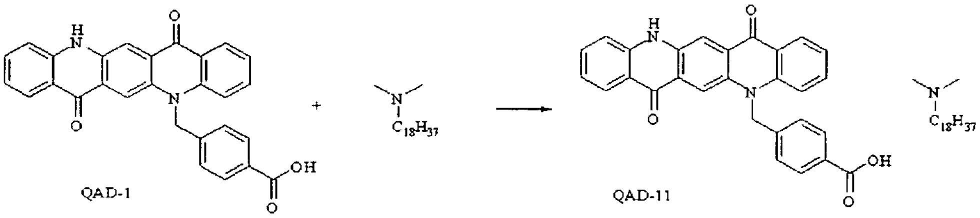
[0202] Synthesis of the dispersion synergist QAD-4 was accomplished according to the following synthesis scheme:



34.0 g (0.1 mol) of dried pigment PR122 in 500 mL dimethylsulfoxide was dissolved by the addition of 22.44 g (0.2 mol) potassium tert-butoxide. The blue solution was heated to about 70°C and 27.1 g (0.1 mol) of compound QA-3 was added. The alkylation-step was done after 2 hours and the product was hydrolyzed by the addition of 72.4 g (0.4 mol) sodium methylate and 200 mL of water. After 1 hour the mixture was cooled to about 50°C and the product was precipitated with acetone (about 1000 mL). The precipitate was filtered and washed with acetone. The solid product was dissolved in 1000 mL of water and the acid form was precipitated by the addition of an excess of concentrated hydrochloric acid. The dispersion synergist QAD-4 was filtered and washed with acetone. The yield was 85%.

Dispersion synergist QAD-11

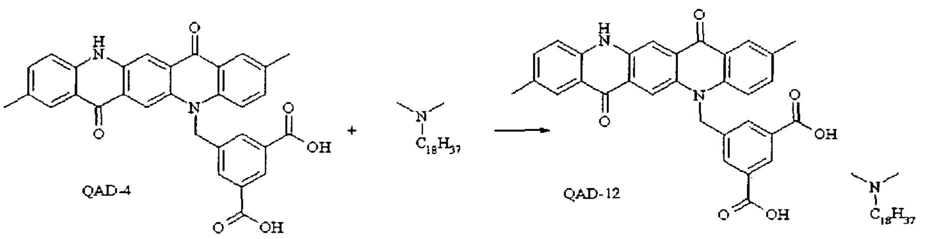
[0203] Synthesis of the dispersion synergist QAD-11 was accomplished according to the following synthesis scheme:



44.6 g (0.1 mol) of the dispersion synergist QAD-1 is suspended in a mixture of 200 mL methanol, 100 mL water and 200ml methylenechloride. 44.55 g (0.15 mol) of N,N-dimethyl-N-octadecylamine was added and the mixture was mixed during 2 days at roomtemperature. After 2 days the methylenechloride was evaporated and the dispersion synergist QAD-11 was filtered and washed with a mixture of water / methanol (1/1). The yield was 67%.

Dispersion synergist QAD-12

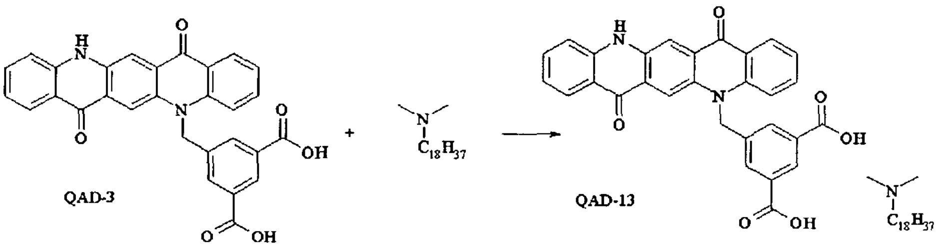
[0204] Synthesis of the dispersion synergist QAD-12 was accomplished according to the following synthesis scheme:



51.9 g (0.1 mol) of the dispersion synergist QAD-4 was suspended in a mixture of 200 mL methanol, 200 mL methylenechloride and 100 mL water. 74.25 (0.25 mol) of N,N-dimethyl-N-octadecylamine was added and the mixture was stirred during 3 days at roomtemperature. After 3 days the methylenechloride was evaporated under vacuum and the the dispersion synergist QAD-12 was filtered and washed with a mixture of water / m ethanol (1/1). The yield was 60%.

Dispersion synergist QAD-13

[0205] Synthesis of the dispersion synergist QAD-13 was accomplished according to the following synthesis scheme:



49 g (0.1 mol) of the dispersion synergist QAD-3 was suspended in a mixture of 200 mL methanol; 200 mL methylenechloride and 100 mL water. 29.7 g (0.25 mol) of dimethyldioctadecylammonium bromide was added and the mixture was stirred during 3 days at roomtemperature. After 3 days the methylenechloride was evaporated under vacuum and the dispersion synergist QAD-13 was filtered and washed with methanol. The yield was 68%.

Preparation and evaluation of ink-jet inks

[0206] All inkjet inks were prepared in the same manner as in EXAMPLE 1 to obtain a composition as described in Table 6, except that PV19 was used as a pigment. In some examples, the ratio of polymeric dispersant over dispersion synergist was altered through replacement or addition of the organic solvent DEGDEE.

[0207] Using the above method, the comparative inkjet inks COMP-6 to COMP-13 and the inventive inkjet inks INV-7 to INV-12 were prepared according to Table 6. The amount of synergist indicates how much dispersion synergist was used in wt% based on the polymeric dispersant Solsperse™ 32000. The particle size and the spectral separation factor SSF was determined to evaluate the dispersion quality and was determined again after a heat treatment of 7 days at 80°C. The particle sizes of comparative samples COMP-3 and COMP-4 were not measured after the heat treatment. The results are listed in Table 6.

Table 6

Sample	Dispersion Synergist		Particle size (nm)		SSF (no heat treatment)	Loss in SSF after 7d/80° C
	Type	Amount	Original	7d/80° C		
COMP-6	None	None	96	257	250	91%
COMP-7	SYN-5	10%	89	314	127	67%
COMP-8	SYN-6	5%	82	---	136	77%
COMP-9	SYN-6	20%	97	---	93	63%
COMP-10	SYN-7	10%	112	217	314	91%
COMP-11	SYN-8	10%	121	259	136	79%
COMP-12	SYN-9	10%	114	224	63	54%
COMP-13	SYN-10	10%	164	221	97	67%
INV-7	QAD-2	20%	74	112	114	26%
INV-8	QAD-3	10%	76	79	114	8%
INV-9	QAD-4	10%	80	78	122	7%
INV-10	QAD-11	10%	87	193	127	25%
INV-11	QAD-12	10%	83	85	100	6%
INV-12	QAD-13	10%	69	72	96	0%

[0208] Poor dispersion stability was observed for the comparative inkjet inks COMP-6 to COMP-13 illustrated by a sharp decrease in SSF and an increase in the particle size of the pigment. On the other hand the inventive inkjet inks INV-7 to INV-12 all exhibited improved dispersion stability.

EXAMPLE 3

[0209] This example illustrates that stable pigment dispersions of C.I. Pigment Violet 19 for use in radiation curable ink-jet inks were obtained when a quinacridone derivative containing two carboxylic acid groups was used as dispersion synergist.

Preparation and evaluation of pigment dispersions

[0210] All pigment dispersions were prepared in the same manner to obtain a composition as described in Table 7, except that different dispersion synergists were used. In some examples, the ratio of polymeric dispersant over dispersion synergist was altered through replacement or addition of the monomer DPGDA™.

Table 7

Component	wt%
PV19	4.50
Dispersion synergist	0.50
Solsperse™ 32000	5.00
DPGDA™	90.00

[0211] The pigment dispersion was made by mixing the pigment PV19, the polymeric dispersant Solsperse™ 32000, the dispersion synergist and the monomer DPGDA™ with a dissolver and subsequently treating this mixture with a roller mill procedure using yttrium-stabilized zirconium oxide-beads of 0.4 mm diameter ("high wear resistant zirconia grinding media" from TOSOH Co.). A polyethylene flask of 60mL was filled to half its volume with grinding beads and 20 mL of the mixture. The flask was closed with a lit and put on the roller mill for three days. The speed was set at 150 rpm. After milling the dispersion was separated from the beads using a filter cloth.

[0212] Using the above method, the comparative pigment dispersion COMP-14 and the inventive pigment dispersions INV-13 to INV-16 were prepared according to Table 8. The amount of synergist indicates how much dispersion synergist was used in wt% based on the polymeric dispersant. The particle size was determined before and after a heat treatment of 7 days at 80˚C to evaluate the dispersion stability. The results are listed in Table 8.

Table 8

Pigment dispersions	Dispersion synergist		Particle size (nm)	
	Type	Amount	Before 7d/80˚C	After 7d/80˚C
COMP-14	None	None	118	249
INV-13	QAD-3	10%	113	118
INV-14	QAD-4	10%	113	190
INV-15	QAD-12	10%	108	167
INV-16	QAD-13	10%	108	113

[0213] The comparative pigment dispersion COMP-14 exhibited a sharp increase in the particle size of the PV19 pigment after the heat treatment, while the inventive pigment dispersions INV-13 to INV-16 all exhibited improved dispersion stability.

Claims

1. A non-aqueous pigment dispersion comprising a quinacridone pigment, a polymeric dispersant and a dispersion synergist in a dispersion medium **characterized in that** the dispersion synergist is a quinacridone derivative containing at least one carboxylic acid group or a salt thereof wherein the at least one carboxylic acid group or a salt thereof is attached to one of the two nitrogen atoms of the quinacridone structure either directly or through a linking group containing 1 or more carbon atoms.

2. The non-aqueous pigment dispersion according to claim 1 wherein the at least one carboxylic acid group or a salt thereof is an aromatic acid group or a salt thereof.

3. The non-aqueous pigment dispersion according to claim 2 wherein the aromatic acid group or a salt thereof is a benzoic acid group, a phtalic acid group, an isophtalic acid group, a terephtalic acid group or salts thereof.

4. The non-aqueous pigment dispersion according to claim 1 wherein the at least one carboxylic acid group or a salt thereof is selected from the group consisting of an alkanoic acid group, an alicyclic acid group, a heterocyclic acid group and salts thereof.

5. The non-aqueous pigment dispersion according to any of claims 1 to 4 wherein the salt of the at least one carboxylic acid group is an ammonium acid salt group.

6. The non-aqueous pigment dispersion according to claim 5 wherein the ammonium acid salt group is a substituted ammonium group selected from the group consisting of $^+N(CH_3)_2(C_{18}H_{37})_2$, $^+NH(CH_3)_2(C_{18}H_{37})$, $^+N(CH_3)_2(C_{12}H_{25})_2$, $^+NH(CH_3)_2(C_{12}H_{25})$, $^+N(CH_3)_2(C_{10}H_{21})_2$, $^+NH(CH_3)_2(C_{10}H_{21})$, $^+N(CH_3)_2(C_8H_{17})_2$, $^+NH(CH_3)_2(C_8H_{17})$, $^+NH(C_8H_{17})_3$, $+NH(C_{10}H_{21})_3$, $^+NH(C_{12}H_{25})_3$ and $^+NH(C_{18}H_{35})_3$.

7. The non-aqueous pigment dispersion according to any of claims 1 to 6, wherein the pigment dispersion is a curable inkjet ink.

8. The non-aqueous pigment dispersion according to any of claims 1 to 7, wherein the pigment dispersion is a non-aqueous inkjet ink containing an organic solvent and/or oil.

9. The non-aqueous pigment dispersion according to any of claims 1 to 8, wherein the quinacridone pigment is selected from the group consisting of C.I. Pigment Violet 19, C.I. Pigment Red 122, C.I. Pigment Red 202 and mixed crystals of quinacridone pigments.

10. The non-aqueous pigment dispersion according to any of claims 1 to 9, wherein the pigment dispersion is a non-aqueous pigmented inkjet ink.

11. A method for printing an ink-jet image comprising the steps of:

(a) providing a curable ink-jet ink set containing a curable ink-jet ink comprising a quinacridone pigment and a quinacridone derivative containing at least one carboxylic acid group or a salt thereof;
(b) printing an image with the curable ink-jet comprising a quinacridone pigment; and
(c) curing the printed image.

Patentansprüche

1. Eine nicht-wässrige Pigmentdispersion, die ein Chinacridonpigment, ein polymeres Dispersionsmittel und einen Dispersionssynergisten in einem Dispersionsmedium enthält, **dadurch gekennzeichnet, dass** der Dispersionssynergist ein Chinacridon-Derivat ist, das zumindest eine Carbonsäuregruppe oder ein Salz davon enthält, wobei die zumindest eine Carbonsäuregruppe oder ein Salz davon entweder direkt oder aber über eine 1 oder mehr Kohlenstoffatome enthaltende Verbindungsgruppe an eines der zwei Stickstoffatome der Chinacridonstruktur gebunden ist.

2. Nicht-wässrige Pigmentdispersion nach Anspruch 1, **dadurch gekennzeichnet, dass** die zumindest eine Carbonsäuregruppe oder ein Salz davon eine aromatische Säuregruppe oder ein Salz davon ist.

3. Nicht-wässrige Pigmentdispersion nach Anspruch 2, **dadurch gekennzeichnet, dass** die aromatische Säuregruppe oder ein Salz davon eine Benzoesäuregruppe, eine Phthalsäuregruppe, eine Isophthalsäuregruppe, eine Terephthalsäuregruppe oder ein Salz davon ist.

4. Nicht-wässrige Pigmentdispersion nach Anspruch 1, **dadurch gekennzeichnet, dass** die zumindest eine Carbonsäuregruppe oder ein Salz davon aus der Gruppe bestehend aus einer Fettsäuregruppe, einer alicyclischen Säuregruppe, einer heterocyclischen Säuregruppe und Salzen derselben gewählt wird.

5. Nicht-wässrige Pigmentdispersion nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das Salz der zumindest einer Carbonsäuregruppe eine Ammoniumsäuresalzgruppe ist.

6. Nicht-wässrige Pigmentdispersion nach Anspruch 5, **dadurch gekennzeichnet, dass** die Ammoniumsäuresalzgruppe eine substituierte Ammoniumgruppe aus der Gruppe bestehend aus $^+N(CH_3)_2(C_{18}H_{37})_2$, $^+NH(CH_3)_2(C_{18}H_{37})$, $^+N(CH_3)_2(C_{12}H_{25})_2$, $^+NH(CH_3)_2(C_{12}H_{25})$, $^+N(CH_3)_2(C_{10}H_{21})_2$, $^+NH(CH_3)_2(C_{10}H_{21})$, $^+N(CH_3)_2(C_8H_{17})_2$, $^+NH(CH_3)_2(C_8H_{17})$, $^+NH(C_8H_{17})_3$, $^+NH(C_{10}H_{21})_3$, $^+NH(C_{12}H_{25})_3$ und $^+NH(C_{18}H_{35})_3$ ist.

7. Nicht-wässrige Pigmentdispersion nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Pigmentdispersion eine härtbare Tintenstrahltinte ist.

8. Nicht-wässrige Pigmentdispersion nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** die Pigmentdispersion eine nicht-wässrige Tintenstrahltinte ist, die ein organisches Lösungsmittel und/oder ein Öl enthält.

9. Nicht-wässrige Pigmentdispersion nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** das Chinacridonpigment aus der Gruppe bestehend aus C.I. Pigment Violet 19, C.I. Pigment Red 122, C.I. Pigment Red 202 und Mischkristallen von Chinacridonpigmenten gewählt wird.

10. Nicht-wässrige Pigmentdispersion nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** die Pigmentdispersion eine nicht-wässrige pigmentierte Tintenstrahltinte ist.

11. Ein die nachstehenden Schritte umfassendes Verfahren zum Drucken eines Tintenstrahlbildes :

(a) Bereitstellen eines Satzes härtbarer Tintenstrahltinten, enthaltend eine härtbare Tintenstrahltinte, die ein Chinacridonpigment und ein zumindest eine Carbonsäuregruppe oder ein Salz davon enthaltendes Chinacridon-Derivat enthält,
(b) Drucken eines Bildes unter Verwendung der härtbaren, ein Chinacridonpigment enthaltenden Tintenstrahltinte und
(c) Härtung des gedruckten Bildes.

Revendications

1. Une dispersion de pigment non aqueuse contenant un pigment de quinacridone, un agent de dispersion polymère et un synergiste de dispersion dans un milieu dispersant, **caractérisée en ce que** le synergiste de dispersion est un dérivé de quinacridone contenant au moins un groupe acide carboxylique ou un sel de celui-ci, ledit au moins un groupe acide carboxylique ou un sel de celui-ci étant lié à l'un des deux atomes d'azote de la structure de quinacridone par une liaison directe ou par un groupe de liaison comprenant au moins 1 atome de carbone.

2. Dispersion de pigment non aqueuse selon la revendication 1, **caractérisée en ce que** ledit au moins un groupe acide carboxylique ou un sel de celui-ci est un groupe acide aromatique ou un sel de celui-ci.

3. Dispersion de pigment non aqueuse selon la revendication 2, **caractérisée en ce que** le groupe acide aromatique ou un sel de celui-ci est un groupe acide benzoïque, un groupe acide phtalique, un groupe acide isophtalique, un groupe acide téréphtalique ou un sel de ceux-ci.

4. Dispersion de pigment non aqueuse selon la revendication 1, **caractérisée en ce que** ledit au moins un groupe acide carboxylique ou un sel de celui-ci est choisi parmi le groupe composé d'un groupe acide gras, d'un groupe acide alicyclique, d'un groupe acide hétérocyclique et de sels de ceux-ci.

5. Dispersion de pigment non aqueuse selon l'une quelconque des revendications 1 à 4, **caractérisée en ce que** le sel dudit au moins un groupe acide carboxylique est un groupe sel d'acide d'ammonium.

6. Dispersion de pigment non aqueuse selon la revendication 5, **caractérisée en ce que** le groupe sel d'acide d'ammonium est un groupe ammonium substitué choisi parmi le groupe composé de $^+N(CH_3)_2(C_{18}H_{37})_2$, $^+NH(CH_3)_2(C_{18}H_{37})$, $^+N(CH_3)_2(C_{12}H_{25})_2$, $^+NH(CH_3)_2(C_{12}H_{25})$, $^+N(CH_3)_2(C_{10}H_{21})_2$, $^+NH(CH_3)_2(C_{10}H_{21})$, $^+N(CH_3)_2(C_8H_{17})_2$, $^+NH(CH_3)_2(C_8H_{17})$, $^+NH(C_8H_{17})_3$, $^+NH(C_{10}H_{21})_3$, $^+NH(C_{12}H_{25})_3$ et $^+NH(C_{18}H_{35})_3$.

7. Dispersion de pigment non aqueuse selon l'une quelconque des revendications 1 à 6, **caractérisée en ce que** la dispersion de pigment est une encre pour jet d'encre durcissable.

8. Dispersion de pigment non aqueuse selon l'une quelconque des revendications 1 à 7, **caractérisée en ce que** la dispersion de pigment est une encre pour jet d'encre non aqueuse contenant un solvant organique et/ou une huile.

9. Dispersion de pigment non aqueuse selon l'une quelconque des revendications 1 à 8, **caractérisée en ce que** le pigment de quinacridone est choisi parmi le groupe composé de C.I. Pigment Violet 19, de C.I. Pigment Red 122, C.I. de Pigment Red 202 et de cristaux mixtes de pigments de quinacridone.

10. Dispersion de pigment non aqueuse selon l'une quelconque des revendications 1 à 9, **caractérisée en ce que** la dispersion de pigment est une encre pour jet d'encre non aqueuse pigmentée.

11. Un procédé pour l'impression d'une image formée par jet d'encre, comprenant les étapes ci-après :

(a) la mise à disposition d'un ensemble d'encres pour jet d'encre durcissables, comprenant une encre pour jet d'encre durcissable contenant un pigment de quinacridone et un dérive de quinacridone contenant au moins un groupe acide carboxylique ou un sel de celui-ci,
(b) l'impression d'une image en utilisant l'encre pour jet d'encre durcissable contenant un pigment de quinacridone et
(c) le durcissement de l'image imprimée.

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