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(54) Title: NON-AQUEOUS PIGMENT DISPERSIONS USING DISPERSION SYNERGISTS

(57) Abstract: Non-aqueous pigment dispersions exhibiting improved dispersion quality and/or stability were prepared for a specific selection of quinacridone pigments, diketopyrrolo-pyrrole pigments and azo pigments by using specific naphthol AS dispersion synergists. The non-aqueous pigment dispersions can be advantageously used in inkjet inks inkjet printing methods.

Description

NON-AQUEOUS PIGMENT DISPERSIONS USING DISPERSION SYNERGISTS

Technical Field

[0001] The present invention relates to pigmented dispersions and inkjet inks comprising colour pigments that are stabilized by polymeric dispersants in a non-aqueous medium using specific dispersion synergists.

Background Art

[0002] A dispersant is a substance for promoting the formation and stabilization of a dispersion of pigment particles in a dispersion medium and for substantially reducing 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 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 quality is required to ensure unimpeded passage of pigment particles through the nozzles of a 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 typically 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 pigment dispersions, 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, WO 2007/006635 (AGFA GRAPHICS) discloses pigment dispersions comprising a colour pigment and a polymeric dispersant having via a linking group covalently linked to its polymeric backbone at least one pending chromophore group which has a molecular weight smaller than 90% of the molecular weight of the colour pigment. A disadvantage is that the pending chromophore group must bear some similarity to the chemical formula of the pigment in order to obtain effective dispersion, which as a consequence results in different polymeric dispersants for the different pigments used in an ink set containing yellow, magenta and cyan inks.

[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. To be efficient, the synergist should bear some similarity to the pigment. Examples of these dispersion synergists are given in, for example, WO 2007/060254 (AGFA GRAPHICS)), EP 1790697 A (AGFA GRAPHICS) , EP 1790698 A (AGFA GRAPHICS) and WO 2007/060255 (AGFA GRAPHICS) .

[0009] However, both approaches lead to a considerable higher cost in composing non-aqueous pigment dispersions for inkjet ink sets, because the pigment dispersions require anchor groups on the polymeric dispersant or dispersion synergists which chemically resemble the pigments.

[0010] 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.

[0011] Therefore, it is highly desirable to manufacture low cost non-aqueous pigment dispersions, especially pigmented inkjet inks, exhibiting a high dispersion quality and stability using the same polymeric dispersant in all inks of an ink set.

Summary of invention

[0012] In order to overcome the problems described above, it has been surprisingly found that non-aqueous pigment dispersions, especially non-aqueous inkjet inks, of high dispersion quality and stability were obtained by a combination of a specific napthol AS dispersion synergist and a specific azo pigment, a diketopyrrolo-pyrrole pigments or a quinacridone pigment by using specific naphthol AS dispersion synergists as defined by claim 1. The magenta colour of A napthol AS dispersion had no negative effect on the colour of yellow pigment dispersions. CMYK inkjet ink sets could be made using the same magenta napthol AS dispersion synergist and polymeric dispersant in the yellow and magenta inkjet inks.

[0013] It is a further object of the present invention to produce images of high image quality with non-aqueous pigment dispersions, especially with non-aqueous inkjet inks.

[0014] Other features, elements, steps, characteristics and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the present invention hereinafter.

Definitions

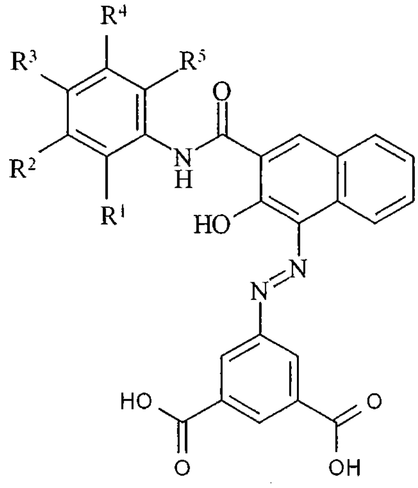
[0015] The term “C.I.” is used in disclosing the present application as an abbreviation for Colour Index.

[0016] 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.

Non-Aqueous Pigment Dispersions and Inkjet Inks

[0017] The non-aqueous pigment dispersion according to the present invention includes a non-aqueous dispersion medium, a polymeric dispersant, a pigment and a dispersion synergist,

wherein the dispersion synergist is represented by Formula (I):



Formula (I),

with R^1, R^2, R^3, R^4 and R^5 are each independently selected from the group consisting of hydrogen, methyl, ethyl, halogen, methoxy, ethoxy, -CONH-phenyl and $-NO_2$; and

wherein the pigment is selected from the group consisting of an azo pigment containing a benzimidazolone group, an azo pigment containing a quinoxalinedione group, a diketopyrrolo-pyrrole pigment, unsubstituted quinacridone, dichloro substituted quinacridone and mixed crystals thereof, with the proviso that the mixed crystal of unsubstituted quinacridone and/or dichloro substituted quinacridone does not contain dimethyl substituted quinacridone.

[0018] In one embodiment, the non-aqueous pigment dispersion according to the present invention includes a non-aqueous dispersion medium consisting of organic solvents.

[0019] The non-aqueous pigment dispersion can be advantageously used in paints, lacquers, e.g. automotive lacquers, and printing inks for applications in inkjet, offset, flexography and the like. The non-aqueous pigment dispersion is preferably curable by UV radiation or e-beam.

[0020] In one preferred embodiment, the non-aqueous pigment dispersion is an inkjet ink, more preferably an inkjet ink curable by UV radiation or e-beam.

[0021] In a preferred embodiment, the non-aqueous inkjet ink is part of an inkjet ink set, preferably an inkjet ink set including two or more inkjet inks in accordance with the invention. Preferably the inkjet ink set contains a yellow inkjet ink and a magenta inkjet ink in accordance with the present invention.

[0022] The non-aqueous inkjet ink forms preferably part of a non-aqueous CMY(K) inkjet ink set. The non-aqueous CMY(K) inkjet ink set may also be extended with extra inks such as red, green, blue, and/or orange to further enlarge the colour gamut of the image. The CMY(K) ink set may also be extended by the combination of full density and light density inks of both colour inks and/or black inks to improve the image quality by lowered graininess. The preferred pigments in a cyan ink are C.I. Pigment Blue 15:3 and 15:4. The preferred pigment in a black ink is carbon black.

[0023] The non-aqueous pigmented dispersion according to the present invention may further also contain at least one surfactant to control the homogenous spreading of the pigment dispersion on a substrate. For a non-aqueous pigmented inkjet ink, the surfactant is important to control the dot size of the ink droplet on a substrate.

[0024] In a preferred embodiment the non-aqueous pigmented dispersion is a non-aqueous inkjet ink containing at least one humectant to prevent the clogging of the nozzle, due to its ability to slow down the evaporation rate of ink.

[0025] The viscosity of an inkjet ink is preferably lower than 30 mPa.s, more preferably lower than 15 mPa.s, and most preferably between 2 and 10 mPa.s at a shear rate of 100 s^{-1} and a jetting temperature between 10 and 70°C.

[0026] The inkjet ink can be advantageously used in an inkjet printing method comprising the steps:

a) providing an inkjet ink according to the present invention; and

b) jetting the inkjet ink onto an ink-receiver. In a more preferred embodiment, the inkjet printing method uses a yellow inkjet ink and a magenta inkjet ink both according to the present inventions.

Pigments

[0027] The pigment used in the present invention is selected from the group consisting of an azo pigment containing a benzimidazolone group, an azo pigment containing a quinoxalinedione group, a diketopyrrolo-pyrrole pigment, unsubstituted quinacridone, dichloro substituted quinacridone and mixed crystals thereof, with the proviso that the mixed crystal of unsubstituted quinacridone and/or dichloro substituted quinacridone does not contain dimethyl substituted quinacridone.

[0028] In a preferred embodiment, the pigment is selected from the group consisting of C.I. Pigment Yellow 180, C.I. Pigment Yellow 194 and C.I. Pigment Yellow 213 and mixed crystals thereof.

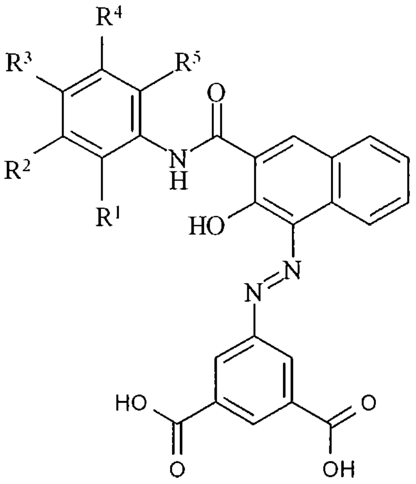
[0029] In a preferred embodiment, the diketopyrrolo-pyrrole pigment is selected from the group consisting of C.I. Pigment Red 254, C.I. Pigment Orange 71 and mixed crystals thereof.

[0030] The pigments are preferably present in the range of 0.05 to 20 %, more preferably in the range of 0.1 to 10 % by weight and most preferably in the range of 1 to 6 % by weight, each based on the total weight of the pigment dispersion or inkjet ink.

Dispersion Synergists

[0031] The dispersion synergists used in the non-aqueous pigment dispersions are known from WO 2007/060255 (AGFA GRAPHICS) for dispersing quinacridone pigments having a similar chemical structure. The synthesis of these dispersion synergists is described in WO 2007/060255 (AGFA GRAPHICS) , which therefore is incorporated herein as a specific reference.

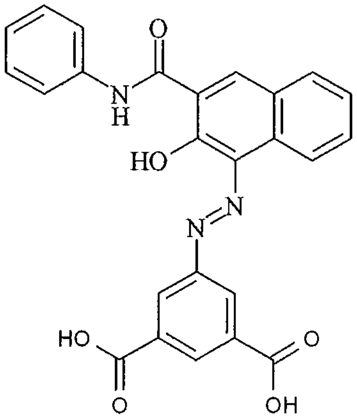
[0032] The dispersion synergist used in the present invention is represented by Formula (I):



Formula (I),

with R^1, R^2, R^3, R^4 and R^5 are each independently selected from the group consisting of hydrogen, methyl, ethyl, halogen, methoxy, ethoxy, -CONH-phenyl and $-NO_2$.

[0033] In a preferred embodiment, the dispersion synergist is represented by Formula (II):



Formula (II).

[0034] The dispersion synergist in accordance with the present invention is used to improve the dispersion quality and stability of a pigment selected from the group consisting of an azo pigment containing a benzimidazolone group, an azo pigment containing a quinoxalinedione group, a diketopyrrolo-pyrrole pigment, unsubstituted quinacridone, dichloro substituted quinacridone and mixed crystals thereof, with the proviso that the mixed crystal of unsubstituted quinacridone and/or dichloro substituted quinacridone does not contain dimethyl substituted quinacridone.

[0035] More preferably, the dispersion synergist in accordance with the present invention is used to improve the dispersion quality and stability of a pigment selected from the group consisting of C.I. Pigment Yellow 180, C.I. Pigment Yellow 194 and C.I. Pigment Yellow 213 and mixed crystals thereof.

[0036] More preferably, the dispersion synergist in accordance with the present invention is used to improve the dispersion quality and stability of a pigment selected from the group consisting of C.I. Pigment Red 254, C.I. Pigment Orange 71 and mixed crystals thereof.

[0037] 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.

Non-Aqueous Dispersion Media

[0038] The dispersion medium used in the pigment dispersion according to the present invention is a non-aqueous liquid. The dispersion medium may consist of organic solvent(s), but may also be a radiation curable liquid which can be cured by UV-radiation or e-beam.

[0039] Suitable 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.

[0040] Suitable examples of organic solvents are disclosed in [0133] to [0146] of EP 1857510 A (AGFA GRAPHICS) .

[0041] If the pigment dispersion is a curable pigment dispersion or inkjet ink, organic solvent(s) are preferably fully replaced by one or more monomers and/or oligomers to obtain the 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%, more preferably lower than 5 wt% based on the total weight of the pigmented inkjet ink and most preferably the curable pigment dispersion doesn't include any organic solvent.

[0042] For oil based pigment dispersions and inkjet inks, the dispersion medium can be any suitable oil including aromatic oils, paraffinic oils, extracted paraffinic oils, naphthenic oils, extracted napthenic oils, hydrotreated light or heavy oils, vegetable oils and derivatives and mixtures thereof. Paraffinic oils can be normal paraffin types (octane and higher alkanes), isoparaffins (isooctane and higher iso-alkanes) and cycloparaffins (cyclooctane and higher cyclo-alkanes) and mixtures of paraffin oils.

[0043] Suitable examples of oils are disclosed in [0151] to [0164] of EP 1857510 A (AGFA GRAPHICS) .

Monomers and Oligomers

[0044] The monomers and oligomers used in radiation curable pigment dispersions and inks, especially for food packaging applications, are preferably purified compounds having no or almost no impurities, more particularly no toxic or carcinogenic impurities. The impurities are usually derivative compounds obtained during synthesis of the polymerizable compound. Sometimes, however, some compounds may be added deliberately to pure polymerizable compounds in harmless amounts, for example, polymerization inhibitors or stabilizers.

[0045] Any monomer or oligomer capable of free radical polymerization may be used as polymerizable compound. 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. The viscosity of the radiation curable compositions and inks can be adjusted by varying the ratio between the monomers and oligomers.

[0046] Particularly preferred monomers and oligomers are those listed in [0106] to [0115] in EP 1911814 A (AGFA GRAPHICS) incorporated herein as a specific reference.

[0047] A preferred class of monomers and oligomers are vinyl ether acrylates such as those described in US 6310115 (AGFA) , incorporated herein by reference. Particularly preferred compounds are 2- (2-vinyloxyethoxy)ethyl (meth)acrylate, most preferably the compound is 2- (2-vinyloxyethoxy)ethyl acrylate.

Polymeric dispersants

[0048] 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 preferably have the following polymer compositions:

- statistically 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 polymeric side chains attached to the backbone); and
- mixed forms of these polymers, e.g. blocky gradient copolymers.

[0049] Suitable polymeric dispersants are listed in the section on “Dispersants”, more specifically [0064] to [0070] and [0074] to [0077], in EP 1911814 A (AGFA GRAPHICS) incorporated herein as a specific reference.

[0050] The polymeric dispersant has preferably a number average molecular weight Mn between 500 and 30000, more preferably between 1500 and 10000.

[0051] The polymeric dispersant has preferably a weight average molecular weight Mw smaller than 100,000, more preferably smaller than 50,000 and most preferably smaller than 30,000.

[0052] The polymeric dispersant has preferably a polydispersity PD smaller than 2, more preferably smaller than 1.75 and most preferably smaller than 1.5.

[0053] Commercial examples of polymeric dispersants are the following:

- DISPERBYK™ dispersants available from BYK CHEMIE GMBH;
- SOLSPERSE™ dispersants available from NOVEON;
- TEGO™ DISPERS™ dispersants from EVONIK;
- 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.

[0054] Particularly preferred polymeric dispersants include Solsperse™ dispersants from NOVEON, Efka™ dispersants from CIBA SPECIALTY CHEMICALS INC and Disperbyk™ dispersants from BYK CHEMIE GMBH. Particularly preferred dispersants are Solsperse™ 32000, 35000 and 39000 dispersants from NOVEON.

[0055] The polymeric dispersant is preferably used in an amount of 2 to 600 wt%, more preferably 5 to 200 wt%, most preferably 50 to 90 wt% based on the weight of the pigment.

Photoinitiators

[0056] If the pigment dispersion or ink is radiation curable, preferably one or more photoinitiators are present in the pigment dispersion or ink.

[0057] The photoinitiator is preferably a free radical initiator. A free radical photoinitiator is a chemical compound that initiates a polymerization of monomers and oligomers when exposed to actinic radiation by the formation of a free radical.

[0058] Two types of free radical photoinitiators can be distinguished and used in the pigment dispersion or ink of the present invention. A Norrish Type I initiator is an initiator which cleaves after excitation, yielding the initiating radical immediately. A Norrish type II-initiator is a photoinitiator which is activated by actinic radiation and forms free radicals by hydrogen abstraction from a second compound that becomes the actual initiating free radical. This second compound is called a polymerization synergist or co-initiator. Both type I and type II photoinitiators can be used in the present invention, alone or in combination.

[0059] Suitable photo-initiators are disclosed in CRIVELLO, J.V., et al. VOLUME III: Photoinitiators for Free Radical Cationic . 2nd edition. Edited by BRADLEY, G.. London,UK: John Wiley and Sons Ltd, 1998. p.287-294.

[0060] Specific examples of photo-initiators may include, but are not limited to, the following compounds or combinations thereof: benzophenone and substituted benzophenones, 1-hydroxycyclohexyl phenyl ketone, thioxanthones such as isopropylthioxanthone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-benzyl-2-dimethylamino- (4-morpholinophenyl) butan-1-one, benzil dimethylketal, bis (2,6- dimethylbenzoyl) -2,4, 4-trimethylpentylphosphine oxide, 2,4,6trimethylbenzoyldiphenylphosphine oxide, 2-methyl-1- [4- (methylthio) phenyl] -2-morpholinopropan-1-one, 2,2-dimethoxy-1, 2-diphenylethan-1-one or 5,7-diiodo-3- butoxy-6-fluorone, diphenyliodonium fluoride and triphenylsulfonium hexafluophosphate.

[0061] Suitable commercial photo-initiators include Irgacure™ 184, Irgacure™ 500, Irgacure™ 907, Irgacure™ 369, Irgacure™ 1700, Irgacure™ 651, Irgacure™ 819, Irgacure™ 1000, Irgacure™ 1300, Irgacure™ 1870, Darocur™ 1173, Darocur™ 2959, Darocur™ 4265 and Darocur™ ITX available from CIBA SPECIALTY CHEMICALS, Lucerin™ TPO available from BASF AG, Esacure™ KT046, Esacure™ KIP150, Esacure™ KT37 and Esacure™ EDB available from LAMBERTI, H-Nu™ 470 and H-Nu™ 470X available from SPECTRA GROUP Ltd..

[0062] Suitable cationic photo-initiators include compounds, which form aprotic acids or Bronstead acids upon exposure to ultraviolet and/or visible light sufficient to initiate polymerization. The photo-initiator used may be a single compound, a mixture of two or more active compounds, or a combination of two or more different compounds, i.e. co-initiators. Non-limiting examples of suitable cationic photo-initiators are aryldiazonium salts, diaryliodonium salts, triarylsulfonium salts, triarylselenonium salts and the like.

[0063] However for safety reasons, in particular for food packaging applications, the photoinitiator is preferably a so-called diffusion hindered photoinitiator. A diffusion hindered photoinitiator is a photoinitiator which exhibits a much lower mobility in a cured layer of the curable liquid or ink than a monofunctional photoinitiator, such as benzophenone. Several methods can be used to lower the mobility of the photoinitiator. One way is to increase the molecular weight of the photoinitiator so that the diffusion speed is reduced, e.g. difunctional photoinitiators or polymeric photoinitiators. Another way is to increase its reactivity so that it is built into the polymerizing network, e.g. multifunctional photoinitiators and polymerizable photoinitiators. The diffusion hindered photoinitiator is preferably selected from the group consisting of non-polymeric di- or multifunctional photoinitiators, oligomeric or polymeric photoinitiators and polymerizable photoinitiators. Non-polymeric di- or multifunctional photoinitiators are considered to have a molecular weight between 300 and 900 Dalton. Non-polymerizable monofunctional photoinitiators with a molecular weight in that range are not diffusion hindered photoinitiators. Most preferably the diffusion hindered photoinitiator is a polymerizable initiator.

[0064] A suitable diffusion hindered photoinitiator may contain one or more photoinitiating functional groups derived from a Norrish type I-photoinitiator selected from the group consisting of benzoinethers, benzil ketals, α,α-dialkoxyacetophenones, α-hydroxyalkylphenones, α-aminoalkylphenones, acylphosphine oxides, acylphosphine sulfides, α-haloketones, α-halosulfones and phenylglyoxalates.

[0065] A suitable diffusion hindered photoinitiator may contain one or more photoinitiating functional groups derived from a Norrish type II-initiator selected from the group consisting of benzophenones, thioxanthones, 1,2-diketones and anthraquinones.

[0066] Suitable diffusion hindered photoinitiators are also those disclosed in EP 2053101 A (AGFA GRAPHICS) in paragraphs [0074] and [0075] for difunctional and multifunctional photoinitiators, in paragraphs [0077] to [0080] for polymeric photoinitiators and in paragraphs [0081] to [0083] for polymerizable photoinitiators.

[0067] A preferred amount of photoinitiator is 0 - 50 wt%, more preferably 0.1 - 20 wt%, and most preferably 0.3 – 15 wt% of the total weight of the curable pigment dispersion or ink.

[0068] In order to increase the photosensitivity further, the curable pigment dispersion or ink may additionally contain co-initiators. Suitable examples of co-initiators can be categorized in 4 groups:

(1) tertiary aliphatic amines such as methyldiethanolamine, dimethylethanolamine, triethanolamine, triethylamine and N-methylmorpholine;

(2) aromatic amines such as amylparadimethylaminobenzoate, 2-n-butoxyethyl-4-(dimethylamino) benzoate, 2-(dimethylamino)ethylbenzoate, ethyl-4-(dimethylamino)benzoate, and 2-ethylhexyl-4-(dimethylamino)benzoate; and

(3) (meth)acrylated amines such as dialkylamino alkyl(meth)acrylates (e.g., diethylaminoethylacrylate) or N-morpholinoalkyl-(meth)acrylates (e.g., N-morpholinoethyl-acrylate).

The preferred co-initiators are aminobenzoates.

[0069] When one or more co-initiators are included into the curable pigment dispersion or ink according to the present invention, preferably these co-initiators are diffusion hindered for safety reasons, in particular for food packaging applications.

[0070] A diffusion hindered co-initiator is preferably selected from the group consisting of non-polymeric di- or multifunctional co-initiators, oligomeric or polymeric co-initiators and polymerizable co-initiators. More preferably the diffusion hindered co-initiator is selected from the group consisting of polymeric co-initiators and polymerizable co-initiators. Most preferably the diffusion hindered co-initiator is a polymerizable co-initiator having at least one (meth)acrylate group, more preferably having at least one acrylate group.

[0071] Preferred diffusion hindered co-initiators are the polymerizable co-initiators disclosed in **EP 2053101 A** (AGFA GRAPHICS) in paragraphs [0088] and [0097].

[0072] Preferred diffusion hindered co-initiators include a polymeric co-initiator having a dendritic polymeric architecture, more preferably a hyperbranched polymeric architecture. Preferred hyperbranched polymeric co-initiators are those disclosed in **US 2006014848** (AGFA) incorporated herein as a specific reference.

[0073] The curable pigment dispersion or ink preferably comprises the diffusion hindered co-initiator in an amount of 0.1 to 50 wt%, more preferably in an amount of 0.5 to 25 wt%, most preferably in an amount of 1 to 10 wt% of the total weight of the ink.

Polymerization inhibitors

[0074] The curable pigment dispersion may contain a polymerization inhibitor. Suitable polymerization inhibitors include phenol type antioxidants, hindered amine light stabilizers, phosphor type antioxidants, hydroquinone monomethyl ether commonly used in (meth)acrylate monomers, and hydroquinone, t-butylcatechol, pyrogallol may also be used.

[0075] Suitable commercial inhibitors are, for example, Sumilizer™ GA-80, Sumilizer™ GM and Sumilizer™ GS produced by Sumitomo Chemical Co. Ltd.; Genorad™ 16, Genorad™ 18 and Genorad™ 20 from Rahn AG; Irgastab™ UV10 and Irgastab™ UV22, Tinuvin™ 460 and CGS20 from Ciba Specialty Chemicals; Floorstab™ UV range (UV-1, UV-2, UV-5 and UV-8) from Kromachem Ltd, Additol™ S range (S100, S110, S120 and S130) from Cytec Surface Specialties.

[0076] Since excessive addition of these polymerization inhibitors will lower the ink sensitivity to curing, it is preferred that the amount capable of preventing polymerization is determined prior to blending. The amount of a polymerization inhibitor is preferably lower than 2 wt% of the total pigment dispersion or ink.

Binders

[0077] Non-aqueous pigment dispersions based on organic solvents or oils preferably include 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).

[0078] 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.

[0079] The amount of binder resin in a pigment dispersion or 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 pigment dispersion or ink.

Surfactants

[0080] The pigment dispersion or ink 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 inkjet ink and particularly in a total less than 10 wt% based on the total weight of the pigment dispersion or ink.

[0081] Suitable surfactants include fluorinated surfactants, fatty acid salts, ester salts of a higher alcohol, alkylbenzene sulfonate salts, sulfosuccinate ester salts and phosphate ester salts of a higher alcohol (for example, sodium dodecylbenzenesulfonate and sodium dioctylsulfosuccinate), 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.).

[0082] For non-aqueous inkjet inks preferred surfactants are selected from fluoro surfactants (such as fluorinated hydrocarbons) and silicone surfactants. The silicones are typically siloxanes and can be alkoxylated, polyether modified, polyether modified hydroxy functional, amine modified, epoxy modified and other modifications or combinations thereof. Preferred siloxanes are polymeric, for example polydimethylsiloxanes.

[0083] In a curable inkjet ink a fluorinated or silicone compound as disclosed above may be used as a surfactant, but preferably a cross-linkable surfactant is used. Polymerizable monomers having surface-active effects include silicone modified acrylates, silicone modified methacrylates, acrylated siloxanes, polyether modified acrylic modified siloxanes, fluorinated acrylates, and fluorinated methacrylates. Polymerizable monomers having surface-active effects can be mono-, di-, tri- or higher functional (meth)acrylates or mixtures thereof.

Humectants/Penetrants

[0084] 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.

[0085] 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 Pigment Dispersions and Inks

[0086] Pigment dispersions may be prepared by precipitating or milling the pigment in the dispersion medium in the presence of the dispersant.

[0087] 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.

[0088] 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.

[0089] In the process of mixing, milling and dispersion, each process is performed with cooling to prevent build up of heat, and for radiation curable pigment dispersions as much as possible under light conditions in which actinic radiation has been substantially excluded.

[0090] The pigment dispersion may contain more than one pigment, the pigment dispersion or ink may be prepared using separate dispersions for each pigment, or alternatively several pigments may be mixed and co-milled in preparing the dispersion.

[0091] The dispersion process can be carried out in a continuous, batch or semi-batch mode.

[0092] 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.

[0093] The milling time can vary widely and depends upon the pigment, the selected mechanical means and residence conditions, 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.

[0094] 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.

[0095] In general it is desirable to make 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

[0096] 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.

[0097] 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.

[0098] 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.

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

[0099] 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

[0100] 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.

[0101] PY155 is the abbreviation for C.I. Pigment Yellow 155 for which Ink jet Yellow 4G VP 2532 New from CLARIANT was used.

PY180 is the abbreviation for C.I. Pigment Yellow 180 for which Toner™ Yellow HG from CLARIANT was used.

PY194 is the abbreviation for C.I. Pigment Yellow 194 for which Novoperm™ yellow F2G from CLARIANT was used.

PY213 is the abbreviation for C.I. Pigment Yellow 213 for which Ink jet H5G LP3033 from CLARIANT was used.

PR122 is Chromofine™ Magenta 6878 which is a C.I. Pigment Red 122 pigment available from CLARIANT.

PV19 is Ink Jet Red™ E5B02 VP2984 which is a C.I. Pigment Violet 19 pigment available from CLARIANT.

PR202 is Cinquasia™ Magenta RT235D which is a C.I. Pigment Red 202 pigment available from CLARIANT.

PR209 is Hostaperm™ Red EG Transparant which is a C.I. Pigment Red 209 pigment available from CLARIANT.

PR282 is Irgazin™ Magenta 2012 which is a C.I. Pigment Red 282 pigment available from CIBA-GEIGY.

PV19/PR202 is Cromophtal™ Jet Magenta 2BC which is a mixed crystal of C.I. Pigment Violet 19 and C.I. Pigment Red 122 available from CIBA-

GEIGY.

PR254 is Irgazin™ DPP Red BTR which is a C.I. Pigment Red 254 pigment available from CIBA-GEIGY.

PO71 is Cromophtal™ DPP Orange TR which is a C.I. Pigment Orange 71 pigment available from CIBA-GEIGY.

S39000 is Solsperse™ 39000, a polyethyleneimine core grafted with polyester-hyperdispersant from LUBRIZOL.

DEGDEE is diethylene glycol diethyl ether.

DS is the dispersion synergist according to Formula (II) and was synthesized in the same manner as described in **WO 2007/060255** (AGFA GRAPHICS) for the synergist NAC-1 (see Example 1).

Measurement methods

1. SSF

[0102] 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 is dependent on the pigment(s) used:

- if the colour ink has a maximum absorbance A_{max} between 400 and 500 nm then the absorbance A_{ref} must be determined at a reference wavelength of 600 nm,
- If the colour ink has a maximum absorbance A_{max} between 500 and 600 nm then the absorbance A_{ref} must be determined at a reference wavelength of 650 nm,
- If the colour ink has a maximum absorbance A_{max} between 600 and 700 nm then the absorbance A_{ref} must be determined at a reference wavelength of 830 nm.

[0103] The absorbance was determined in transmission with a Shimadzu UV-2101 PC double beam-spectrophotometer. The inks were diluted with ethyl acetate to have a pigment concentration of 0.002 wt% based on the total weight of the ink. Quinacridone containing pigments were measured at a dilution of 0.005 wt% based on the total weight of the ink due to their lower extinction.

[0104] 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 1. Quartz cells with a path length of 10 mm were used and ethyl acetate was chosen as a blank.

Table 1

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)

[0105] Efficient pigmented inkjet inks exhibiting a narrow absorption spectrum and a high maximum absorbance have a value for SSF of at least 30.

2. Average particle size

[0106] 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.

[0107] The sample was prepared by addition of one drop of ink to a cuvette 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 between 70 and 150 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

[0108] This example illustrates how the dispersion quality and stability of a specific selection of pigments can be improved by a synergist having a totally different chemical structure than the pigments.

Preparation and Evaluation of Non-Aqueous Inkjet inks

[0109] All inkjet inks were prepared in the same manner to obtain a composition A or B as described in Table 2, depending on whether or not a dispersion synergist was used.

Table 2

wt% of component	Formulation A	Formulation B
Pigment	5.00	4.50
Dispersion synergist DS	---	0.50
S39000	5.00	5.00
DEGDEE	90.00	90.00

[0110] A pigment dispersion was made by mixing the pigment, the polymeric dispersant S39000, optionally 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.

[0111] The inkjet inks Ink-1 to Ink-24 were prepared according to Table 3 . The average particle size and the spectral separation factor SSF were determined to evaluate the dispersion quality and the average particle size was determined again after a heat treatment of 1 week at 80°C for evaluating the dispersion stability. The results are also listed in Table 3.

Table 3

Ink	Pigment	DS	Dispersion quality		Dispersion stability
			SSF	Size (nm)	Size (nm)
Ink-1	PY155	No	9	922	734
Ink-2	PY155	Yes	31	407	491
Ink-3	PY180	No	92	108	199

Ink-4	PY180	Yes	79	114	121
Ink-5	PY194	No	169	85	110
Ink-6	PY194	Yes	121	93	100
Ink-7	PY213	No	56	168	292
Ink-8	PY213	Yes	84	101	111
Ink-9	PR122	No	23	382	866
Ink-10	PR122	Yes	51	158	286
Ink-11	PV19	No	91	85	234
Ink-12	PV19	Yes	118	80	214
Ink-13	PR202	No	30	291	446
Ink-14	PR202	Yes	85	86	208
Ink-15	PR209	No	130	70	245
Ink-16	PR209	Yes	170	67	127
Ink-17	PR282	No	21	554	682
Ink-18	PR282	Yes	47	191	263
Ink-19	PV19/PR202	No	105	87	234
Ink-20	PV19/PR202	Yes	155	60	141
Ink-21	PR254	No	26	336	364
Ink-22	PR254	Yes	121	91	104
Ink-23	PO71	No	92	119	323
Ink-24	PO71	Yes	102	76	82

[0112] From Table 3, it should be clear that the dispersion synergist DS is capable to improve the dispersion quality and stability of the yellow azo pigments containing a benzimidazolone group or a quinoxalinedione group. The disazo pigment PY155, bearing some resemblance to the disazo pigment PY180 and the monoazo pigment PY213 but lacking a benzimidazolone group or a quinoxalinedione group, could not be dispersed to an acceptable level.

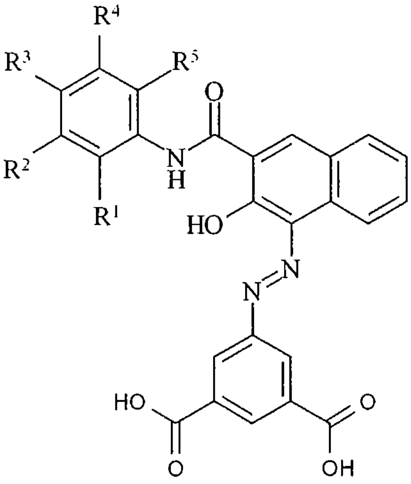
[0113] Similarly, the dispersion synergist DS improved the dispersion quality and stability of the unsubstituted quinacridone PV19, the dichloro substituted quinacridones PR202 and PR209 and a mixed crystal thereof, but not of the dimethyl substituted quinacridone PR122 or the mixed crystal PR282 containing a substantial amount of dimethyl substituted quinacridone.

[0114] The dispersion synergist DS also improved the dispersion quality and stability of the diketopyrrolo-pyrrole pigments C.I. Pigment Red 254 and C.I. Pigment Orange.

[0115] Printed samples of the yellow inks with or without the magenta dispersion synergist DS did not show any visible difference in colour.

Claims

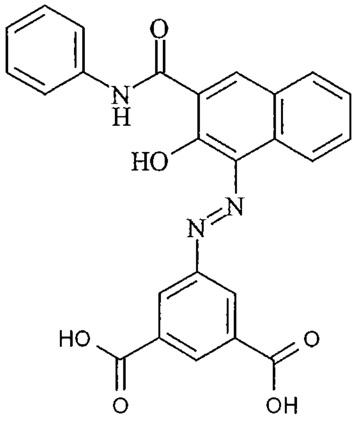
1. A non-aqueous pigment dispersion comprising a non-aqueous dispersion medium, a polymeric dispersant, a pigment and a dispersion synergist, wherein the dispersion synergist is represented by Formula (I):



Formula (I),

with R^1, R^2, R^3, R^4 and R^5 are each independently selected from the group consisting of hydrogen, methyl, ethyl, halogen, methoxy, ethoxy, -CONH-phenyl and $-NO_2$; and wherein the pigment is selected from the group consisting of an azo pigment containing a benzimidazolone group, an azo pigment containing a quinoxalinedione group, a diketopyrrolo-pyrrole pigment, unsubstituted quinacridone, dichloro substituted quinacridone and mixed crystals thereof, with the proviso that the mixed crystal of unsubstituted quinacridone and/or dichloro substituted quinacridone does not contain dimethyl substituted quinacridone.

2. The non-aqueous pigment dispersion according to claim 1 wherein the dispersion synergist is represented by Formula (II):



Formula (II).

3. The non-aqueous pigment dispersion according to claim 1 or 2 wherein the pigment is selected from the group consisting of C.I. Pigment Yellow 180, C.I. Pigment Yellow 194 and C.I. Pigment Yellow 213 and mixed crystals thereof.
4. The non-aqueous pigment dispersion according to claim 1 or 2 wherein the diketopyrrolo-pyrrole pigment is selected from the group consisting of C.I. Pigment Red 254, C.I. Pigment Orange 71 and mixed crystals thereof.
5. The non-aqueous pigment dispersion according to any one of claims 1 to 4 wherein the non-aqueous dispersion medium consists of organic solvents.
6. The non-aqueous pigment dispersion according to any one of claims 1 to 4 is a radiation curable liquid which can be cured by UV-radiation or e-beam.
7. An inkjet ink comprising the non-aqueous pigment dispersion according to any one of claims 1 to 6.
8. An inkjet ink set comprising one or more inkjet inks as defined by claim 7.
9. An inkjet printing method comprising the steps:
   a) providing an inkjet ink as defined by claim 7; and
   b) jetting the inkjet ink onto an ink-receiver.
10. The inkjet printing method according to claim 9 wherein in step a) a yellow inkjet ink and a magenta inkjet ink both as defined by claim 6 are provided.
11. Use of a dispersion synergist as defined by claim 1 or 2 to improve the dispersion quality and stability of a pigment selected from the group consisting of an azo pigment containing a benzimidazolone group, an azo pigment containing a quinoxalinedione group, a diketopyrrolo-pyrrole pigment,

unsubstituted quinacridone, dichloro substituted quinacridone and mixed crystals thereof, with the proviso that the mixed crystal of unsubstituted quinacridone and/or dichloro substituted quinacridone does not contain dimethyl substituted quinacridone.

12. The use according to claim 11 wherein the pigment is selected from the group consisting of C.I. Pigment Yellow 180, C.I. Pigment Yellow 194 and C.I. Pigment Yellow 213 and mixed crystals thereof.
13. The use according to claim 11 wherein the diketopyrrolo-pyrrole pigment is selected from the group consisting of C.I. Pigment Red 254, C.I. Pigment Orange 71 and mixed crystals thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/065711

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09B67/00 C09D11/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/060255 A2 (AGFA GRAPHICS NV [BE]; DEROOVER GEERT [BE]) 31 May 2007 (2007-05-31) cited in the application examples inv1,inv2,inv4,inv6,inv8 -----	1-13
A	EP 1 790 697 A1 (AGFA GRAPHICS NV [BE]) 30 May 2007 (2007-05-30) cited in the application examples inv1-inv7,inv12-inv15; table 5 examples inv1-inv6,inv13-inv18; table 6 -----	1-13
A	EP 1 790 698 A1 (AGFA GRAPHICS NV [BE]) 30 May 2007 (2007-05-30) cited in the application examples -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search 10 January 2011	Date of mailing of the international search report 20/01/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ketterer, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/065711

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