barcodes, 2-dimensional barcodes, 3-dimensional barcodes, a data matrix~~. and the like~~. The application of markings is frequently carried out by a printing process which uses a printing ink with specific optical properties that are imparted to the ink by one or more substances contained therein such as, e.g., luminescent dyes and pigments and cholesteric liquid crystal compounds.

[0005] A class of compounds which is suitable for use in, e.g., printing inks for marking purposes are perylene dyes. The parent compound perylene displays fluorescence and there are many derivatives of perylene which are known and may theoretically be employed as colorants in compositions for marking such as printing inks~~ and the like~~. However, a drawback of perylene dyes is their often unsatisfactorily low solubility or dispersibility in liquid media such as those which are useful in printing inks. This low solubility/dispersibility limits the suitability of perylene dyes as colorants for liquid compositions in general. It would thus, be advantageous to be able to increase the solubility and/or dispersibility of perylene dyes in liquid media and in particular, liquid media for use in printing inks.

FR 2 850 651 and its corresponding application US 2004/0194665 A1 discloses pyrelene dyestuffs with sterically hindered stabilizing polymers. US 2002/0112297 A1 discloses fluorescent or non-fluorescent dye compounds having a terminal hydroxy, carboxylic acid/ester or amino group. US 5030697 A discloses polymer-bound dyes, a process for their production and their use for example as marker substances in analytical procedures.

SUMMARY OF THE INVENTION

[0006] The present invention provides a method of increasing the solubility and/or dispersibility of a perylene dye in a liquid medium such as, e.g., a liquid medium comprised in a printing ink composition. The

method comprises binding the perylene dye to a polymer which is soluble in the liquid medium.

[0007] In one aspect of the method, the liquid medium may be a polar liquid medium.

[0008] In another aspect, the perylene dye may be covalently bonded to the polymer. For example, the polymer may comprise at least one (recurring) monomer unit that comprises at least one polar group which

comprise one or two additional heteroatoms which are selected from O, N and S. The ring will usually have five or six ring members. Also, the ring will often comprise no additional heteroatom. Further, the ring may have one or two aromatic and/or heteroaromatic rings (e.g., benzene rings) fused to it and/or may be substituted with one or more (e.g., one, two, three, four~~, etc~~ or more.) substituents which are preferably selected from F, Cl, Br, and I, OH, -COOH (including partially or completely salified forms thereof), -SO_3H, cyano, nitro, alkoxy having from 1 to about 4 carbon atoms such as, e.g., methoxy and ethoxy, acyloxy having from 1 to about 4 carbon atoms such as, e.g., acetoxy and propionyloxy, aryloxy having from about 6 to about 10 carbon atoms such as, e.g., phenoxy, aroyloxy having from about 6 to about 10 carbon atoms such as, e.g., benzoyloxy, amino, monoalkylamino and dialkylamino wherein the alkyl groups have from 1 to about 6 carbon atoms, e.g., from 1 to about 4 carbon atoms, such as, e.g., methylamino, dimethylamino, ethylamino, diethylamino, propylamino and dipropylamino, acylamino having from 1 to about 8 carbon atoms such as, e.g., acetylamino and propionylamino, aminocarbonyl, monoalkylaminocarbonyl, diaminocarbonyl and alkoxycarbonyl having from 1 to about 4 carbon atoms in the alkyl groups such as, e.g., methoxycarbonyl and ethoxycarbonyl, optionally substituted acyl having from 2 to about 8 carbon atoms such as acetyl and propionyl, alkylsulfonyl, arylsulfonyl and alkylsulfonylamino, optionally substituted alkyl having from 1 to about 6 carbon atoms such as, e.g., methyl, ethyl, hydroxymethyl and hydroxyethyl, optionally substituted (hetero)aryl such as, e.g., phenyl, tolyl, xylyl, hydroxyphenyl, pyridinyl and pyrrolyl, and optionally substituted alkylaryl such as, e.g., benzyl. If more than one substituent is present, the substituents may be the same or different. Non-limiting examples of unsubstituted N-containing 5- to 7- membered rings include pyrrolyl, pyrrolidinyl, pyridinyl, pyrimidinyl, piperidinyl, morpholinyl, piperazinyl, thienyl, pyrazolyl, pyrazolidinyl, oxazolyl and oxazolidinyl.

slightly polar and aprotic organic solvents, such as, e.g., methyl ethyl ketone (MEK), acetone, ethyl acetate, ethyl 3-ethoxypropionate, toluene and mixtures of two or more thereof.

[0069] In particular if the printing ink composition of the present invention is to be applied by continuous inkjet printing the composition will usually also comprise at least one conductivity imparting agent (for example, a salt). The conductivity imparting agent will have a non-negligible solubility in the composition. Non-limiting examples of suitable conductivity imparting agents include salts such as, e.g., tetraalkyl ammonium salts (e.g., tetrabutyl ammonium nitrate, tetrabutyl ammonium perchlorate and tetrabutyl ammonium hexafluorophosphate), alkali metal thiocyanates such as potassium thiocyanate, akali potassium salts such as KPF_6 and alkali metal perchlorates such as lithium perchlorate. The conductivity imparting agent will be present in a concentration which is sufficient to provide the conductivity which is required or desirable. Of course, mixtures of two or more different conductivity imparting agents (salts) can be used. Often the one or more conductivity imparting agents will be present in a total concentration of from about 0.1 % to 2 % by weight, based on the total weight of the composition.

[0070] The printing ink composition according to the present invention may furthermore comprise one or more customary additives, such as, for example, fungicides, biocides, surfactants, sequestering agents, or pH adjusters~~, etc~~. in the amounts customary for these additives. Further, the printing ink composition may comprise one or more additional colorants and/or components which impart a specific optical property (i.e., components which are different from the polymer-bonded perylene dyes of the present invention). These additional components may be selected from, for example, conventional pigments and dyes, luminescent (e.g., fluorescent) pigments and dyes, and cholesteric and/or nematic liquid crystals. Examples of luminescent pigments include certain classes of inorganic compounds such as the sulphides, oxysulphides, phosphates,

Ink Formulation 2

Component	Function	% b.w.
Dynapol L411 (Polyester resin)	Binder resin	1.5
Lithium Perchlorate	Salt for conductivity	0.3
Polymer-bonded Perylene Dye	Dye	1.0
Black Microlith®	Pigment	1.2
Methyl ethyl ketone	Solvent	96

Ink Formulation 3

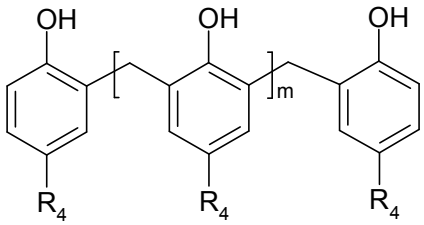
Component	Function	% b.w.
Dynapol L411 (Polyester resin)	Binder resin	1.5
Lithium Perchlorate	Salt for conductivity	0.3
Polymer-bonded Perylene Dye	Dye	2.2
Methyl ethyl ketone	Solvent	96

[0076] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to an exemplary embodiment, it is understood that the words which have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope ~~and spirit~~ of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the

CLAIMS

1. A method of increasing at least one of the solubility and dispersibility of a perylene dye in a liquid medium, wherein the method comprises binding the perylene dye to a polymer ~~which is soluble in the liquid medium.~~

~~2. The method of any one of claim 1,~~ wherein the polymer comprises a phenolic resin of formula



(IV)

wherein the groups R_4 may be the same or different, and may be in the meta- or para-position with respect to the OH group, and there may be more than one group R_4 (e.g., 2 or 3 groups R_4) present on a phenyl ring, R_4 is ~~and are~~ selected from alkyl groups having from 1 to about 10 carbon atoms and the average number of m is from about 1 to about 30, each of the phenyl group may comprise 1 or 2 additional substituents which may be the same of different and are selected within optionally substituted alkyl having 1 to 10 carbon atoms, halogen, OH, COOH and amino, which is soluble in the liquid medium.

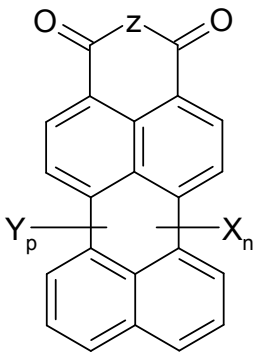
~~3.~~2. The method of claim 1, wherein the perylene dye comprises a compound of formula (A) or (B):

heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms and may also be combined to form, together with the N atom to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

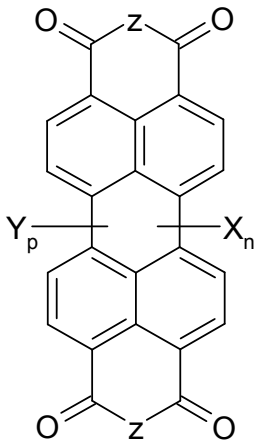
n and p each represent 0 or an integer of from 1 to 8, provided that (n+p) is not higher than 8 and further provided that for n = 0 at least one of R, R' and R" comprises at least one group X as substituent.

~~4.~~3. A perylene dye whose solubility or dispersibility in a polar liquid medium has been increased by the method of claim 1.

~~5.~~4. A polymer-bonded perylene dye of formulae (A) or (B):



(A)



(B)

wherein

the groups Z, the same or different from each other, represent O, S or N-R, provided that a unit -CO-Z-CO- may be replaced by –CS-Z-CO-, -CS-Z-CS-, or [–COOH HOOC-] and for Z = N-R a unit -CO-Z-CO- may be replaced by a unit –C(=NR')-NR-CO-;

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl,

alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

the groups X may be the same or different and represent halogen, isocyanate and COOH;

the groups Y may be the same or different and are selected from OH, NO_2, CN, groups of formula R", OR", COOR", OCOR", CONHR", $CON(R")_2$, OCONHR", $OCON(R")_2$, COR", SO_3H, $SO_3R"$, $SO_2NHR"$, $SO_2N(R")_2$, NHCOR", NRCOR", NHCOOR", NRCOOR", $NHSO_2R"$, $NRSO_2R"$, NHR", and $N(R")_2$, wherein the groups R" may be the same or different and represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms and may also be combined to form, together with the N atom to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

n and p each represent 0 or an integer of from 1 to 8, provided that (n+p) is not higher than 8 and further provided that for n = 0 at least one of R, R' and R" comprises at least one group X as substituent;

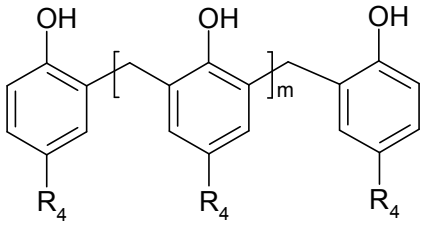
provided that at least one group X represents a group of formula –L-P wherein L represents a covalent bond or a bridging group and P represents a polymer molecule.

~~6.The polymer-bonded perylene dye of claim 5, wherein the perylene dye is a compound of formula (A).~~

~~7.The polymer-bonded perylene dye of claim 5, wherein the perylene dye is a compound of formula (B) wherein the groups Z may be the same or different and represent O or N-R.~~

~~8.The polymer-bonded perylene dye of claim 5, wherein L is selected from O, COO, OCO, CONH, and NHCOO.~~

~~9.The polymer-bonded perylene dye of claim 5, wherein the polymer P~~ comprise~~s~~ing a phenolic resin of formula



(IV)

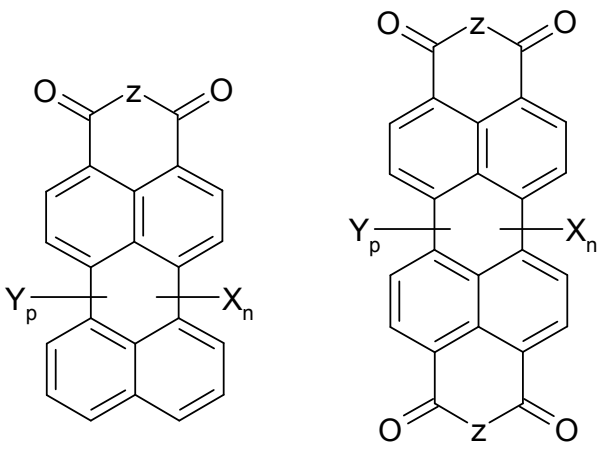
wherein the groups R_4 may be the same or different, and may be in the meta- or para-position with respect to the OH group, and there may be more than one group R_4 (e.g., 2 or 3 groups R_4) present on a phenyl ring, R_4 is~~are~~ selected from alkyl groups having from 1 to about 10 carbon atoms and the average number of m is from about 1 to about 30, each of the phenyl groups may comprise 1 or 2 additional substituents which may be the same of different and are selected within optionally substituted alkyl having 1 to 10 carbon atoms, halogen, OH, COOH and amino.

5. The polymer-bonded perylene dye of claim 4, wherein the perylene dye is a compound of formula (A).

6. The polymer-bonded perylene dye of claim 4, wherein the perylene dye is a compound of formula (B) wherein the groups Z may be the same or different and represent O or N-R.

7. The polymer-bonded perylene dye of claim 4, wherein L is selected from O, COO, OCO, CONH, and NHCOO.

~~10.~~8. A process for making a polymer-bonded perylene dye according to claim ~~5~~4, wherein the process comprises contacting a perylene dye of formula (A) or (B):



(A) (B)

wherein

the groups Z, the same or different from each other, represent O, S or N-R, provided that a unit -CO-Z-CO- may be replaced by –CS-

5

Z-CO-, -CS-Z-CS-, or [–COOH HOOC-] and for Z = N-R a unit -CO-Z-CO- may be replaced by a unit –C(=NR')-NR-CO-;

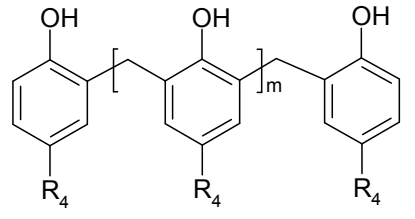
R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

the groups X may be the same or different and represent halogen, isocyanate and COOH;

the groups Y may be the same or different and are selected from OH, NO_2, CN, groups of formula R", OR", COOR", OCOR", CONHR", $CON(R")_2$, OCONHR", $OCON(R")_2$, COR", SO_3H, $SO_3R"$, $SO_2NHR"$, $SO_2N(R")_2$, NHCOR", NRCOR", NHCOOR", NRCOOR", $NHSO_2R"$, $NRSO_2R"$, NHR", and $N(R")_2$, wherein the groups R" may be the same or different and represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms and may also be combined to form, together with the N atom to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

n and p each represent 0 or an integer of from 1 to 8, provided that (n+p) is not higher than 8 and further provided that for n = 0 at least one of R, R' and R" comprises at least one group X as substituent;

with a polymer P ~~under conditions which cause a reaction of a group X of the perylene dye with a functional group of the polymer to covalently bind the polymer to the perylene dye.~~

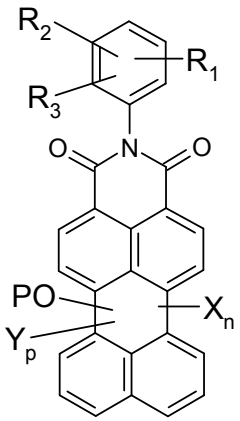


(IV)

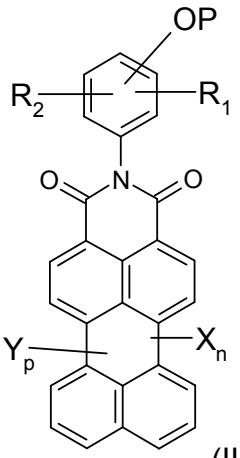
wherein the groups R_4 may be the same or different, and may be in the meta- or para-position with respect to the OH group, and there may be more than one group R_4 (e.g., 2 or 3 groups R_4) present on a phenyl ring, R_4 is selected from alkyl groups having from 1 to about 10 carbon atoms and the average number of m is from about 1 to about 30, each of the phenyl groups may comprise 1 or 2 additional substituents which may be the same or different and are selected within optionally substituted alkyl having 1 to 10 carbon atoms, halogen, OH, COOH and amino.

under conditions which cause a reaction of a group X of the perylene dye with a functional group of the polymer to covalently bind the polymer to the perylene dye.

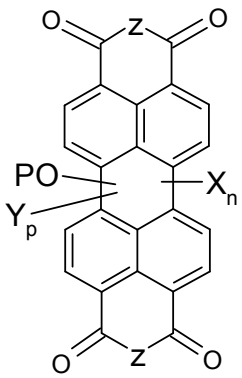
~~11.~~9. The polymer-bonded perylene dye of claim ~~5~~4, where the perylene dye comprises a dye of one of formulae (I) to (III):



(I), or



(II), or



(III),

wherein

the groups Z, the same or different from each other, represent O, S or N-R, provided that in the case of formula (III) one or both units -CO-Z-CO- may be replaced by –CS-Z-CO-, -CS-Z-CS-, or [–COOH HOOC-] and for Z = N-R a unit -CO-Z-CO- may be replaced by a unit –C(=NR')-NR-CO-;

R and R' independently represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms; and R and R' may be combined to form, together with the N atoms to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

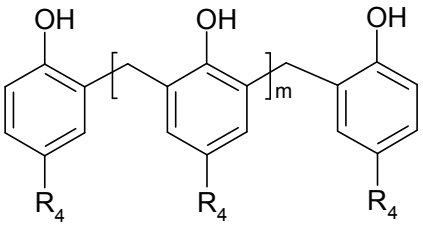
R_1, R_2 and R_3 are independently selected from hydrogen, C_1-C_4 alkyl, C_1-C_4 alkyl-COOH, C_1-C_4 alkyl-SO_3H, C_1-C_4 alkoxy, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, C_1-C_4 aminoalkyl, halogen, cyano, nitro, and SO_3H, the alkyl groups being optionally substituted;

the groups X may be the same or different and represent halogen, isocyanate and COOH;

the groups Y may be the same or different and are selected from OH, NO_2, CN, groups of formula R", OR", COOR", OCOR", CONHR", $CON(R")_2$, OCONHR", $OCON(R")_2$, COR", SO_3H, $SO_3R"$, $SO_2NHR"$, $SO_2N(R")_2$, NHCOR", NRCOR", NHCOOR", NRCOOR", $NHSO_2R"$, $NRSO_2R"$, NHR", and $N(R")_2$, wherein the groups R" may be the same or different and represent an optionally substituted aliphatic, cycloaliphatic, aromatic, heteroaromatic, alkylaryl, alkylheteroaryl, arylalkyl or heteroarylalkyl group having from 1 to about 20 carbon atoms and may also be combined to form, together with the N atom to which they are attached, an optionally substituted and/or fused 5- to 7-membered ring;

in the case of formula (II), n and p each represent 0 or an integer of from 1 to 8, provided that (n+p) is not higher than 8; and in the case of formulae (I) and (III) n and p each represent 0 or an integer of from 1 to 7, provided that (n+p) is not higher than 7; and

P represents a polymer molecule- comprising a phenolic resin of formula



(IV)

wherein the groups R_4 may be the same or different, and may be in the meta- or para-position with respect to the OH group, and there may be more than one group R_4 (e.g., 2 or 3 groups R_4) present on a phenyl ring, R_4 is selected from alkyl groups having from 1 to about 10 carbon atoms and the average number of m is from about 1 to about 30, each

of the phenyl group may comprise 1 or 2 additional substituents which may be the same or different and are selected within optionally substituted alkyl having 1 to 10 carbon atoms, halogen, OH, COOH and amino.

~~12.~~10. A printing ink composition, wherein the composition comprises a polar liquid medium and at least one polymer-bonded perylene dye according to claims ~~5~~4 to 9 dissolved or dispersed in the medium.

~~13.~~11. The printing ink composition of claim ~~12~~10, wherein the composition comprises from about 0.01 % to about 40 % by weight of the at least one polymer-bonded perylene dye based on a total weight of the composition.

~~14.~~12. A marking or security feature which is made with the printing ink composition of claim ~~12~~10.

~~15.~~13. A marking or security feature which comprises at least one polymer-bonded perylene dye of claim ~~5~~4.

~~16.~~14. The marking or security feature of claim ~~15~~13, wherein the marking or security feature comprises at least one of a thread, a label, a barcode, a 2D code, a pattern, indicia and a data matrix.

~~17.~~15. An article which comprises the marking or security feature of claim ~~15~~13.

~~18.~~16. A method of authenticating an article, wherein the method comprises providing the article with the marking or security feature of claim ~~15~~13.

~~19.~~17. A method of authenticating an article, wherein the method comprises applying onto the article the printing ink composition of claim ~~12~~10.

~~20.A dye-doped polymer, wherein at least about 0.1 % of the polymer molecules have bonded thereto a perylene dye and wherein the polymer is obtainable by the process of claim 10.~~