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(54) **METHOD OF MAKING NANOSIZED PARTICLES OF MONOAZO LAKED PIGMENT**

Related U.S. Application Data

(63) Continuation-in-part of application No. 11/759,913, filed on Jun. 7, 2007.

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(57) **ABSTRACT**

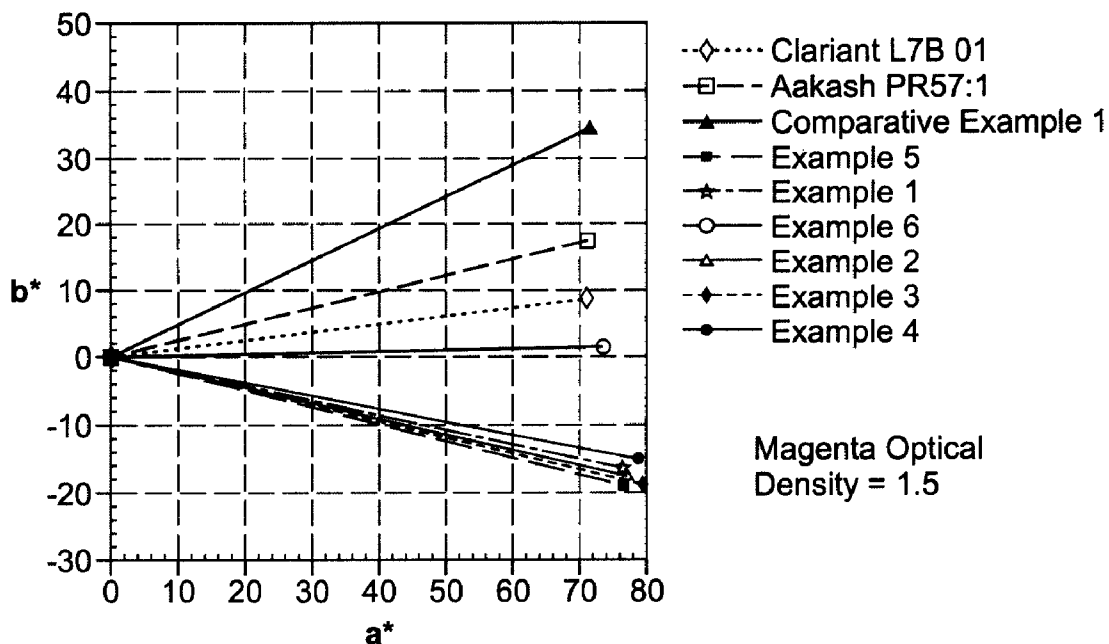
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A nanoscale pigment particle composition includes an organic monoazo laked pigment including at least one functional moiety, and a sterically bulky stabilizer compound including at least one functional group, wherein the functional moiety associates non-covalently with the functional group; and the presence of the associated stabilizer limits the extent of particle growth and aggregation, to afford nanoscale-sized pigment particles.

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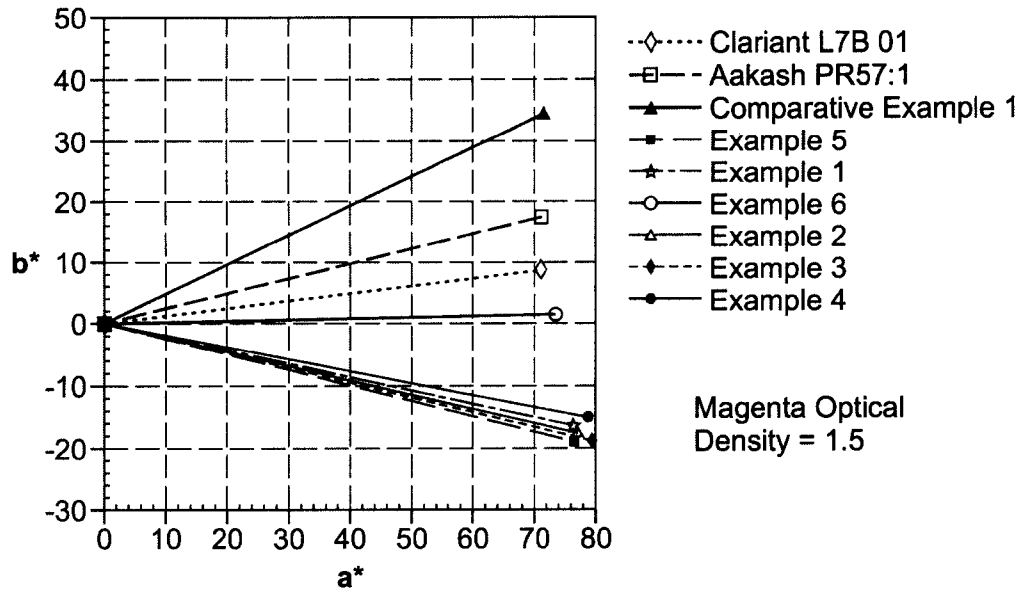


FIG. 1

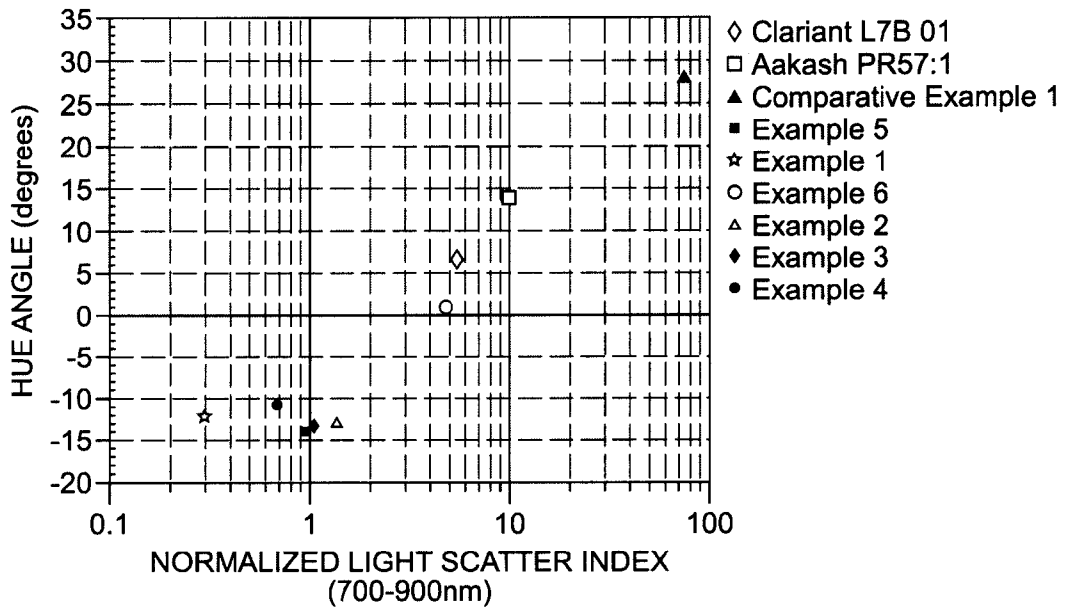


FIG. 2

METHOD OF MAKING NANOSIZED PARTICLES OF MONOAZO LAKED PIGMENT

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 11/759,913 to Rina Carlini et al. filed Jun. 7, 2007, the entire disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] This disclosure is generally directed to methods for producing nanoscale pigment particle compositions. More specifically, this disclosure is directed to methods of making organic mono-azo laked nanoscale pigments. Such particles are useful, for example, as nanoscopic colorants for such compositions as inks, toners and the like.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0003] Disclosed in commonly assigned U.S. patent application Ser. No. 11/759,913 to Rina Carlini et al. filed Jun. 7, 2007, is a nanoscale pigment particle composition, comprising: an organic monoazo laked pigment including at least one functional moiety, and a sterically bulky stabilizer compound including at least one functional group, wherein the functional moiety associates non-covalently with the functional group; and the presence of the associated stabilizer limits the extent of particle growth and aggregation, to afford nanoscale-sized pigment particles. Also disclosed is a process for preparing nanoscale-sized monoazo laked pigment particles, comprising: preparing a first reaction mixture comprising: (a) a diazonium salt including at least one functional moiety as a first precursor to the laked pigment and (b) a liquid medium containing diazotizing agents generated in situ from nitrous acid derivatives; and preparing a second reaction mixture comprising: (a) a coupling agent including at least one functional moiety as a second precursor to the laked pigment and (b) a sterically bulky stabilizer compound having one or more functional groups that associate non-covalently with the coupling agent; and (c) a liquid medium combining the first reaction mixture into the second reaction mixture to form a third solution and effecting a direct coupling reaction which forms a monoazo laked pigment composition wherein the functional moiety associates non-covalently with the functional group and having nanoscale particle size. Further disclosed is a process for preparing nanoscale monoazo laked pigment particles, comprising: providing a monoazo precursor dye to the monoazo laked pigment that includes at least one functional moiety; subjecting the monoazo precursor dye to an ion exchange reaction with a cation salt in the presence of a sterically bulky stabilizer compound having one or more functional groups; and precipitating the monoazo laked pigment as nanoscale particles, wherein the functional moiety of the pigment associates non-covalently with the functional group of the stabilizer and having nanoscale particle size.

[0004] Disclosed in commonly assigned U.S. patent application Ser. No. 11/759,906 to Maria Birau et al. filed Jun. 7, 2007, is a nanoscale pigment particle composition, comprising: a quinacridone pigment including at least one functional moiety, and a sterically bulky stabilizer compound including at least one functional group, wherein the functional moiety associates non-covalently with the functional group; and the

presence of the associated stabilizer limits the extent of particle growth and aggregation, to afford nanoscale-sized particles. Also disclosed is a process for preparing nanoscale quinacridone pigment particles, comprising: preparing a first solution comprising: (a) a crude quinacridone pigment or pigment precursor including at least one functional moiety and (b) a liquid medium; preparing a second solution comprising: (a) a sterically bulky stabilizer compound having one or more functional groups that associate non-covalently with the pigment functional moiety, and (b) a liquid medium; combining the first solution into the second solution to form a third reaction mixture which forms a quinacridone pigment composition of nanoscale particle size and wherein the functional moiety associates non-covalently with the functional group. Still further is disclosed a process for preparing nanoscale quinacridone pigment particles, comprising: preparing a first solution comprising a quinacridone pigment including at least one functional moiety in an acid; preparing a second solution comprising an liquid medium and a sterically bulky stabilizer compound having one or more functional groups that associate non-covalently with the functional moiety of the pigment; treating the second solution with the first solution to precipitate quinacridone pigment of nanoscale particle size, wherein the functional moiety associates non-covalently with the functional group.

[0005] The entire disclosure of the above-mentioned application is totally incorporated herein by reference.

BACKGROUND

[0006] A printing ink is generally formulated according to strict performance requirements demanded by the intended market application and required properties. Whether formulated for office printing or for production printing, a particular ink is expected to produce images that are robust and durable under stress conditions. In a typical design of a piezoelectric ink jet printing device, the image is applied by jetting appropriately colored inks during four to six rotations (incremental movements) of a substrate (an image receiving member or intermediate transfer member) with respect to the ink jetting head, i.e., there is a small translation of the printhead with respect to the substrate in between each rotation. This approach simplifies the printhead design, and the small movements ensure good droplet registration. At the jet operating temperature, droplets of liquid ink are ejected from the printing device and, when the ink droplets contact the surface of the recording substrate, either directly or via an intermediate heated transfer belt or drum, they quickly solidify to form a predetermined pattern of solidified ink drops.

[0007] Pigments are a class of colorants useful in a variety of applications such as, for example, paints, plastics and inks, including inkjet printing inks. Dyes have typically been the colorants of choice for inkjet printing inks because they are readily soluble colorants which enable jetting of the ink. Dyes have also offered superior and brilliant color quality with an expansive color gamut for inks, when compared to conventional pigments. However, since dyes are molecularly dissolved in the ink vehicle, they are often susceptible to unwanted interactions that lead to poor ink performance, for example photooxidation from light (will lead to poor light-fastness), dye diffusion from the ink into paper or other substrates (will lead to poor image quality and showthrough), and the ability for the dye to leach into another solvent that makes contact with the image (will lead to poor water-/solvent-fastness). In certain situations, pigments are the better alter-

native as colorants for inkjet printing inks since they are insoluble and cannot be molecularly dissolved within the ink matrix, and therefore do not experience colorant diffusion. Pigments can also be significantly less expensive than dyes, and so are attractive colorants for use in all printing inks.

[0008] Key challenges with using pigments for inkjet inks are their large particle sizes and wide particle size distribution, the combination of which can pose critical problems with reliable jetting of the ink (i.e. inkjet nozzles are easily blocked). Pigments are rarely obtained in the form of single crystal particles, but rather as large aggregates of crystals and with wide distribution of aggregate sizes. The color characteristics of the pigment aggregate can vary widely depending on the aggregate size and crystal morphology. Thus, an ideal colorant that is widely applicable in, for example, inks and toners, is one that possesses the best properties of both dyes and pigments, namely: 1) superior coloristic properties (large color gamut, brilliance, hues, vivid color); 2) color stability and durability (thermal, light, chemical and air-stable colorants); 3) minimal or no colorant migration; 4) processable colorants (easy to disperse and stabilize in a matrix); and 5) inexpensive material cost. Thus, there is a need addressed by embodiments of the present invention, for smaller nano-sized pigment particles that minimize or avoid the problems associated with conventional larger-sized pigment particles. There further remains a need for processes for making and using such improved nano-sized pigment particles as colorant materials. The present nanosized pigment particles are useful in, for example, paints, coatings and inks (e.g., inkjet printing inks) and other compositions where pigments can be used such as plastics, optoelectronic imaging components, photographic components, and cosmetics among others.

[0009] The following documents provide background information:

[0010] Hideki Maeta et al., "New Synthetic Method of Organic Pigment Nano Particle by Micro Reactor System," in an abstract available on at URL address: http://aiche.confex.com/aiche/s06/preliminaryprogram/abstract_40072.htm, which describes a new synthetic method of an organic pigment nanoparticle was realized by micro reactor. A flowing solution of an organic pigment, which dissolved in an alkaline aqueous organic solvent, mixed with a precipitation medium in a micro channel. Two types of micro reactor can be applied efficiently on this build-up procedure without blockage of the channel. The clear dispersion was extremely stable and had narrow size distribution, which were the features, difficult to realize by the conventional pulverizing method (breakdown procedure). These results proved the effectiveness of this process on micro reactor system.

[0011] U.S. Patent Application Publication No. 2005/0109240 describes a method of producing a fine particle of an organic pigment, containing the steps of: flowing a solution of an organic pigment dissolved in an alkaline or acidic aqueous medium, through a channel which provides a laminar flow; and changing a pH of the solution in the course of the laminar flow.

[0012] WO 2006/132443 A1 describes a method of producing organic pigment fine particles by allowing two or more solutions, at least one of which is an organic pigment solution in which an organic pigment is dissolved, to flow through a microchannel, the organic pigment solution flows through the microchannel in a non-laminar state. Accordingly, the contact area of solutions per unit time can be increased and the length of diffusion mixing can be shortened, and thus instantaneous

mixing of solutions becomes possible. As a result, nanometer-scale monodisperse organic pigment fine particles can be produced in a stable manner.

[0013] K. Balakrishnan et al., "Effect of Side-Chain Substituents on Self-Assembly of Perylene Diimide Molecules: Morphology Control," *J. Am. Chem. Soc.*, vol. 128, p. 7390-98 (2006) describes the use of covalently-linked aliphatic side-chain substituents that were functionalized onto perylene diimide molecules so as to modulate the self-assembly of molecules and generate distinct nanoparticle morphologies (nano-belts to nano-spheres), which in turn impacted the electronic properties of the material. The side-chain substituents studied were linear dodecyl chain, and a long branched nonyldecyl chain, the latter substituent leading to the more compact, spherical nanoparticle.

[0014] WO 2006/011467 discloses a pigment, which is used, for example, in color image display devices and can form a blue pixel capable of providing a high level of bright saturation, particularly a refined pigment, which has bright hue and is excellent in pigment properties such as lightfastness, solvent resistance and heat resistance, and a process for producing the same, a pigment dispersion using the pigment, and an ink for a color filter. The pigment is a subphthalocyanine pigment that is prepared by converting subphthalocyanine of the specified formula, to a pigment, has diffraction peaks at least at diffraction angles (2 θ) 7.0°, 12.3°, 20.4° and 23.4° in X-ray diffraction and an average particle diameter of 120 to 20 nm.

[0015] U.S. Patent Application Publication No. 2006/0063873 discloses a process for preparing nano water paint comprising the steps of: A. modifying the chemical property on the surface of nano particles by hydroxylation for forming hydroxyl groups at high density on the surface of the nano particles; B. forming self-assembly monolayers of low surface energy compounds on the nano particles by substituting the self-assembly monolayers for the hydroxyl groups on the nano particles for disintegrating the clusters of nano particles and for forming the self-assembly monolayers homogeneously on the surface of the nano particles; and C. blending or mixing the nano particles having self-assembly monolayers formed thereon with organic paint to form nano water paint.

[0016] WO 2006/024103 discloses nanopigments prepared from organic IR dye and Na-bentonite with CEC of 95 mmole Na per 100 g of bentonite, at room temperature, by dissolving the Na-bentonite in water and mixing for 2 hours, and mixing in the dye, dissolved in ethanol, for 18 hours. The precipitate is filtered, washed three times with water/ethanol mixture, dried at 105° C. for 10 hours, and milled in a kitchen miller for 2 mins. 0.3 parts of the nanopigments were mixed to 100 parts of pulverized SPG resin and processed in an extruder with a die temperature of 190° C. to form transparent, faintly green or grey colored extrudates which were used to press film of 0.4 mm thickness at 160° C. The films were used to prepare IR-active laminated glass. Near infrared absorption spectra of the glass structures were obtained in a Perkin-Elmer Spectrophotometer.

[0017] WO 2006/005521 discloses a photoprotective composition comprising, in a physiologically acceptable medium: a) at least one aqueous phase, b) at least hydrophilic metal oxide nanoparticles, c) at least one vinylpyrrolidone homopolymer. The reference also discloses the use of at least one vinylpyrrolidone homopolymer in a photoprotective composition comprising at least one aqueous phase and at

least hydrophilic metal oxide nanoparticles for the purpose of reducing the whitening and/or of improving the stability of the said composition. (dispersibility of the nanoparticles in the aqueous phase).

[0018] WO 2006/005536 discloses a method for producing nanoparticles, in particular, pigment particles. Said method consists of the following steps: (i) a raw substance is passed into the gas phase, (ii) particles are produced by cooling or reacting the gaseous raw substance and (iii) an electrical charge is applied to the particles during the production of the particles in step (ii), in a device for producing nanoparticles. The disclosure further relates to a device for producing nanoparticles, comprising a supply line, which is used to transport the gas flow into the device, a particle producing and charging area in order to produce and charge nanoparticles at essentially the same time, and an evacuation line which is used to transport the charged nanoparticles from the particle producing and charging area.

[0019] Japanese Patent Application Publication No. JP 2005238342 A2 discloses irradiating ultrashort pulsed laser to organic bulk crystals dispersed in poor solvents to induce ablation by nonlinear absorption for crushing the crystals and recovering the resulting dispersions of scattered particles. The particles with average size approximately 10 nm are obtained without dispersants or grinding agents for contamination prevention and are suitable for pigments, pharmaceuticals, etc.

[0020] U.S. Patent Application Publication No. 2003/0199608 discloses a functional material comprising fine coloring particles having an average primary particle diameter of 1 to 50 nm in a dried state, and having a BET specific surface area value of 30 to 500 m²/g and a light transmittance of not less than 80%. The functional material composed of fine coloring particles, exhibits not only an excellent transparency but also a high tinting strength and a clear hue.

[0021] U.S. Pat. No. 6,837,918 discloses a process and apparatus that collects pigment nanoparticles by forming a vapor of a pigment that is solid at room temperature, the vapor of the pigment being provided in an inert gaseous carrying medium. At least some of the pigment is solidified within the gaseous stream. The gaseous stream and pigment material is moved in a gaseous carrying environment into or through a dry mechanical pumping system. While the particles are within the dry mechanical pumping system or after the nanoparticles have moved through the dry pumping system, the pigment material and nanoparticles are contacted with an inert liquid collecting medium.

[0022] U.S. Pat. No. 6,537,364 discloses a process for the fine division of pigments which comprises dissolving coarsely crystalline crude pigments in a solvent and precipitating them with a liquid precipitation medium by spraying the pigment solution and the precipitation medium through nozzles to a point of conjoint collision in a reactor chamber enclosed by a housing in a microjet reactor, a gas or an evaporating liquid being passed into the reactor chamber through an opening in the housing for the purpose of maintaining a gas atmosphere in the reactor chamber, and the resulting pigment suspension and the gas or the evaporated liquid being removed from the reactor through a further opening in the housing by means of overpressure on the gas entry side or underpressure on the product and gas exit side.

[0023] U.S. Pat. No. 5,679,138 discloses a process for making ink jet inks, comprising the steps of: (A) providing an organic pigment dispersion containing a pigment, a carrier for

the pigment and a dispersant; (B) mixing the pigment dispersion with rigid milling media having an average particle size less than 100 μm ; (C) introducing the mixture of step (B) into a high speed mill; (D) milling the mixture from step (C) until a pigment particle size distribution is obtained wherein 90% by weight of the pigment particles have a size less than 100 nanometers (nm); (E) separating the milling media from the mixture milled in step (D); and (F) diluting the mixture from step (E) to obtain an ink jet ink having a pigment concentration suitable for ink jet printers.

[0024] Japanese Patent Application Publications Nos. JP 2007023168 and JP 2007023169 discloses providing a pigment dispersion compound excellent in dispersibility and flowability used for the color filter which has high contrast and weatherability. The solution of the organic material, for example, the organic pigment, dissolved in a good solvent under the existence of alkali soluble binder (A) which has an acidic group, and a poor solvent which makes the phase change to the solvent are mixed. The pigment nanoparticles dispersed compound re-decentralized in the organic solvent containing the alkali soluble binder (B) which concentrates the organic pigment nanoparticles which formed the organic pigment as the particles of particle size less than 1 μm , and further has the acidic group.

[0025] Kazuyuki Hayashi et al., "Uniformed nano-downsizing of organic pigments through core-shell structuring," Journal of Materials Chemistry, 17(6), 527-530 (2007) discloses that mechanical dry milling of organic pigments in the presence of mono-dispersed silica nanoparticles gave core-shell hybrid pigments with uniform size and shape reflecting those of the inorganic particles, in striking contrast to conventional milling as a breakdown process, which results in limited size reduction and wide size distribution.

[0026] U.S. Patent Application Publication No. 2007/0012221 describes a method of producing an organic pigment dispersion liquid, which has the steps of: providing an alkaline or acidic solution with an organic pigment dissolved therein and an aqueous medium, wherein a polymerizable compound is contained in at least one of the organic pigment solution and the aqueous medium; mixing the organic pigment solution and the aqueous medium; and thereby forming the pigment as fine particles; then polymerizing the polymerizable compound to form a polymer immobile from the pigment fine particles.

[0027] The appropriate components and process aspects of each of the foregoing may be selected for the present disclosure in embodiments thereof, and the entire disclosure of the above-mentioned references are totally incorporated herein by reference.

SUMMARY

[0028] The present disclosure addresses these and other needs, by providing methods for producing nanoscale pigment particle compositions.

[0029] In an embodiment, the present disclosure provides a process for preparing nanoscale-sized monoazo laked pigment particles, comprising:

[0030] preparing a first reaction mixture comprising: (a) a diazonium salt including at least one functional moiety as a first precursor to the laked pigment and (b) a liquid medium containing diazotizing agents; and

[0031] preparing a second reaction mixture comprising: (a) a coupling agent including at least one functional moiety as a second precursor to the laked pigment and (b) a sterically

bulky stabilizer compound having one or more functional groups that associate non-covalently with the coupling agent; and (c) a liquid medium

[0032] combining the first reaction mixture into the second reaction mixture to form a third solution and

[0033] effecting a direct coupling reaction which forms a monoazo laked pigment composition wherein the functional moiety associates non-covalently with the functional group and having nanoscale particle size.

[0034] In another embodiment, the present disclosure provides a process for preparing nanoscale-sized monoazo laked pigment particles, comprising: preparing a solution of a monoazo precursor dye to the monoazo laked pigment that includes at least one functional moiety, and dissolving it in a liquid medium;

[0035] subjecting the monoazo precursor dye to an ion exchange reaction with a metal cation salt in the presence of a sterically bulky stabilizer compound having one or more functional groups; and

[0036] precipitating the monoazo laked pigment as nanoscale particles, wherein the functional moiety of the pigment associates non-covalently with the functional group of the stabilizer and having nanoscale particle size.

BRIEF DESCRIPTION OF THE DRAWINGS

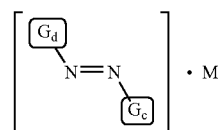
[0037] FIG. 1 shows a two-dimensional b*a* Gamut for pigmented coatings according to embodiments.

[0038] FIG. 2 shows a relationship between hue angle and normalized light scatter index (NLSI) for pigmented coatings prepared according to embodiments.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

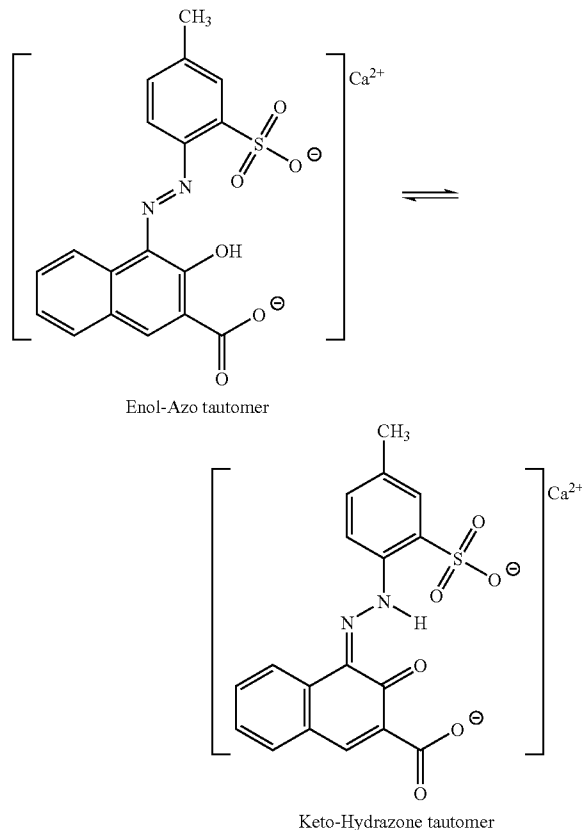
[0039] Embodiments of the present disclosure provide methods for producing nanoscale pigment particle compositions. The nanoscale pigment particle compositions generally comprise an organic monoazo laked pigment including at least one functional moiety that associates non-covalently with a functional group from a sterically bulky stabilizer compound. The presence of the associated stabilizer limits the extent of particle growth and aggregation, to afford nanoscale particles.

[0040] Organic monoazo “laked” pigments are the insoluble metal salt colorants of monoazo colorants which can include monoazo dyes or pigments, and in certain geographic regions these pigments have been referred to as either “toners” or “lakes”. The process of ion complexation with a metal salt, or “laking” process, provides decreased solubility of the non-ionic monoazo pigment, which can enhance the migration resistance and thermal stability properties of a monoazo pigment, and thereby enable the applications of such pigments for robust performance, such as colorizing plastics and heat-stable paints for outdoor use. Formula 1 depicts a general representation of monoazo laked pigments, which are ionic compounds that are structurally comprised of a diazo group (denoted G_d) and a nucleophilic coupling group (denoted as G_c) that are linked together with one azo ($N=N$) functional group, and a cation (M^{n+}) which is typically a metal salt. Either or both of the groups G_d and G_c can contain one or more ionic functional moieties (denoted as FM), such as sulfonate or carboxylate anions or the like.



Formula (1)

[0041] As an example, the organic monoazo laked pigment PR 57:1 (“PR” refers to Pigment Red) has two functional moieties of two different types, a sulfonate anion group (SO_3^-) and carboxylate anion group (CO_2^-) and a metal counter-cation M^{n+} that is chosen from Group 2 alkaline earth metals such as Ca^{2+} . Other monoazo laked pigment compositions also exist that have a counter-cation chosen from either Group 2 alkaline earth metals (Be, Mg, Ca, Sr, Ba), Group 3 metals (B, Al, Ga), Group 1 alkali metals (Li, Na, K, Cs), the transition metals such as Cr, Mn, Fe, Ni, Cu, Zn, or others non-metallic cations such as ammonium (NR_4^+), phosphonium (PR_4^+) wherein R-group can be H or alkyl group having from about 1 to about 12 carbons. Further, the azo group in the compounds can generally assume one or more tautomeric forms, such as the “azo” tautomer form which has the ($N=N$) linkage, and the “hydrazone” tautomer form which has the ($C=N-NH-$) linkage that is stabilized by an intramolecular hydrogen bond, where the hydrazone tautomer is known to be the preferred structural form for PR 57:1.



It is understood that formula (1) is understood to denote both such tautomer forms. Due to the structural nature of monoazo

laked pigments being ionic salts, it is possible to have compounds that associate non-covalently with the pigment, such as organic or inorganic ionic compounds that can associate directly through ionic or coordination-type bonding, and typically with the counter-cation group like M^{n+} . Such ionic compounds are included in a group of compounds which herein are referred to as “stabilizers”, and that function to reduce the surface tension of the pigment particle and neutralize attractive forces between two or more pigment particles or structures, thereby stabilizing the chemical and physical structure of the pigment.

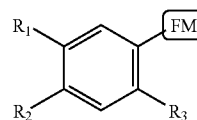
[0042] The term “complementary” as used in “complementary functional moiety” of the stabilizer indicates that the complementary functional moiety is capable of noncovalent chemical bonding with the functional moiety of the organic pigment and/or the functional moiety of a pigment precursor.

[0043] The term “precursor” as used in “precursor to the organic pigment” can be any chemical substance that is an advanced intermediate in the total synthesis of a compound (such as the organic pigment). In embodiments, the organic pigment and the precursor to the organic pigment may or may not have the same functional moiety. In embodiments, the precursor to the organic pigment may or may not be a colored compound. In still other embodiments, the precursor and the organic pigment can have different functional moieties. In embodiments, where the organic pigment and the precursor have a structural feature or characteristic in common, the phrase “organic pigment/pigment precursor” is used for convenience rather than repeating the same discussion for each of the organic pigment and the pigment precursor.

[0044] The functional moiety (denoted as FM) of the organic pigment/precursor can be any suitable moiety capable of non-covalent bonding with the complementary functional group of the stabilizer. Illustrative functional moieties of the organic pigment/precursor include (but are not limited to) the following: sulfonate/sulfonic acid, (thio)carboxylate/(thio)carboxylic acid, phosphonate/phosphonic acid, ammonium and substituted ammonium salts, phosphonium and substituted phosphonium salts, substituted carbonium salts, substituted arylum salts, alkyl/aryl (thio)carboxylate esters, thiol esters, primary or secondary amides, primary or secondary amines, hydroxyl, ketone, aldehyde, oxime, hydroxylamino, enamines (or Schiff base), porphyrins, (phthalocyanines, urethane or carbamate, substituted ureas, guanidines and guanidinium salts, pyridine and pyridinium salts, imidazolium and (benz)imidazolium salts, (benz)imidazolones, pyrrole, pyrimidine and pyrimidinium salts, pyridinone, piperidine and piperidinium salts, piperazine and piperazinium salts, triazolo, tetraazolo, oxazole, oxazolines and oxazolinium salts, indoles, indenones, and the like.

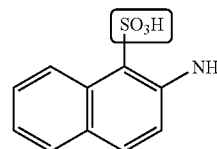
[0045] Pigment precursors for making monoazo laked nanoparticles consist of a substituted aniline precursor (denoted as “DC” in Table 1) which forms the diazo group G_d of Formula (1), a nucleophilic or basic coupling compound (denoted as “CC” in Tables 2-6) which leads to the coupling group G_c of Formula (1), and a cation salt which is preferably a metal (denoted as “M” as shown in Formula (1)). Representative examples of the aniline precursor of laked monoazo pigments that have the functional moiety capable of non-covalent bonding with a complementary functional group on the stabilizer, include (but are not limited to) the following structures (with the functional moiety “FM” denoted, if applicable).

[0046] In an embodiment, the substituted aniline precursor (DC) which leads to the diazonium group can be of the formula (2):



Formula (2)

where R_1 , R_2 , and R_3 independently represent H, a straight or branched alkyl group of from about 1 to about 10 carbon atoms (such as methyl, ethyl, propyl, butyl, and the like), halogen (such as Cl, Br, I), NH_2 , NO_2 , CO_2H , CH_2CH_3 , and the like; and functional moiety FM represents SO_3H , $-C(=O)-NH-Aryl-SO_3^-$ where the aryl group can be unsubstituted or substituted with either halogens (such as Cl, Br, I, F) or alkyl groups having from about 1 to about 10 carbons (such as methyl, ethyl, propyl, butyl and the like) CO_2H , halogen (such as Cl, Br, I), NH_2 , $-C(=O)-NH_2$, and the like. The substituted aniline precursor (DC) can be also be Tobias Acid, of the formula (3):



Formula (3)

Specific examples of types of aniline precursors (DC) that are used to make the diazo group G_d in the monoazo laked pigments include those of Table 1:

TABLE 1

Pre- cursor to Group G_d	Functional Moiety FM	R_1	R_2	R_3
DC1	SO_3H	CH_3	H	NH_2
DC2	SO_3H	CH_3	Cl	NH_2
DC3	SO_3H	Cl	CH_3	NH_2
DC4	SO_3H	Cl	CO_2H	NH_2
DC5	SO_3H	Cl	CH_2CH_3	NH_2
DC6	SO_3H	Cl	Cl	NH_2
DC7	SO_3H	H	NH_2	H
DC8	SO_3H	H	NH_2	CH_3
DC9	SO_3H	NH_2	H	Cl
DC10	SO_3H	H	H	NH_2
DC11	SO_3H	H	NH_2	H
DC12	SO_3H	NO_2	NH_2	H

DC13

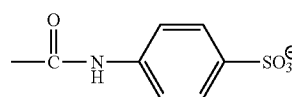
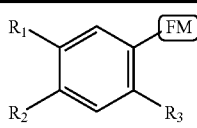
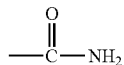
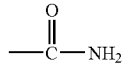
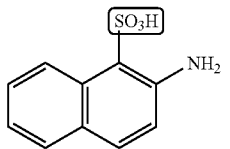
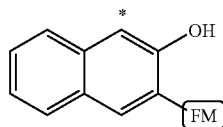


TABLE 1-continued

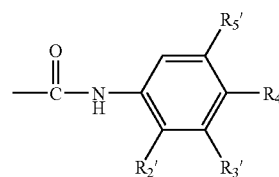
Pre-cursor to Group G _d	Functional Moiety FM	R ₁	R ₂	R ₃
				
DC14	CO ₂ H	H	H	NH ₂
DC15	Cl	H	H	NH ₂
DC16	NH ₂	CH ₃	H	H
DC17	NH ₂	H	CH ₃	H
DC18		NH ₂	CH ₃	H
DC19		H	NH ₂	H
DC20	NH ₂	H	H	H
DC21				

[0047] In an embodiment, the coupling group G_c of Formula (1) can include β-naphthol and derivatives of Formula (4), naphthalene sulfonic acid derivatives of Formulas (5) and (6), pyrazolone derivatives of Formula (7), acetoacetic arylide derivatives of Formula (8), and the like. In formulas (4)-(8), the asterisk "*" denotes the point of coupling or attachment to the monoazo (N=N) linkage.

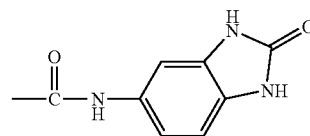


Formula (4)

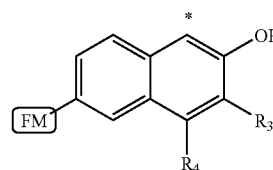
where FM represents H, CO₂H, SO₃H, —C(=O)—NH-Aryl-SO₃⁻ where the aryl group can be unsubstituted or substituted with either halogens (such as Cl, Br, I, F) or alkyl groups having from about 1 to about 10 carbons (such as methyl, ethyl, propyl, butyl and the like) CO₂H, halogen (such as Cl, Br, I), NH₂, —C(=O)—NH₂, substituted benzamides such as:



wherein groups R₂' R₃', R₄' and R₅' can independently be H, alkyl groups having from about 1 to 10 carbons (such as methyl, ethyl, propyl, butyl, and the like), alkoxy groups (such as OCH₃, OCH₂CH₃, and the like), hydroxyl or halogen (such as Cl, Br, I, F) or nitro NO₂; or benzimidazolone amides such as:

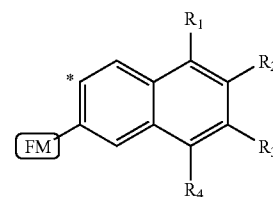


and the like.



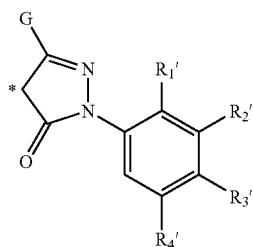
Formula (5)

where FM represents preferably SO₃H, but also can represent CO₂H, —C(=O)—NH-Aryl-SO₃⁻ where the aryl group can be unsubstituted or substituted with either halogens (such as Cl, Br, I, F) or alkyl groups having from about 1 to about 10 carbons (such as methyl, ethyl, propyl, butyl and the like) CO₂H, halogen (such as Cl, Br, I), NH₂, —C(=O)—NH₂ groups R₃ and R₄ independently represent H, SO₃H, and the like.



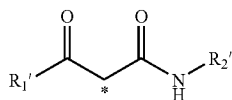
Formula (6)

where FM represents preferably SO₃H, but also can represent CO₂H, —C(=O)—NH-Aryl-SO₃⁻ where the aryl group can be unsubstituted or substituted with either halogens (such as Cl, Br, I, F) or alkyl groups having from about 1 to about 10 carbons (such as methyl, ethyl, propyl, butyl and the like) CO₂H, halogen (such as Cl, Br, I), NH₂, —C(=O)—NH₂; R₁, R₂, R₃ and R₄ independently represent H, SO₃H, —C(=O)—NH-Phenyl, and the like.



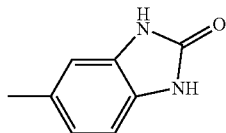
Formula (7)

where G represents CO₂H, straight or branched alkyl such as having from 1 to about 10 carbon atoms (such as methyl, ethyl, propyl, butyl, or the like), and the like; and R₁' , R₂' , R₃' and R₄' independently represent H, halogen (such as Cl, Br, I), SO₃H, nitro (NO₂) or alkoxy group such as OCH₃ or OCH₂CH₃ and the like.

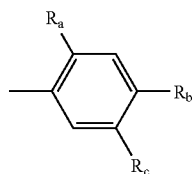


Formula (8)

where R₁' represents a straight or branched alkyl group having, for example, from 1 to about 10 carbon atoms (such as methyl, ethyl, propyl, butyl, and the like); R₂' represents a benzimidazolone group:



or a substituted aryl group



where each of R_a, R_b, and R_c independently represents H, a straight or branched alkyl group having, for example, from 1 to about 10 carbon atoms (such as methyl, ethyl, propyl,

butyl, and the like), alkoxy groups such as OCH₃ or OCH₂CH₃ and the like, halogen (such as Cl, Br, I), nitro NO₂, and the like.

[0048] Representative examples of the nucleophilic coupling component as a precursor of laked monoazo pigments which have the functional moiety that is capable of non-covalent bonding with a complementary functional group on the stabilizer, include (but are not limited to) the following structures shown in Tables 2-6 (with the functional moiety "FM" denoted, if applicable):

TABLE 2

Precursor to group G _c	Class of Coupling Component	Functional Moiety FM
CC1	β-Naphthol	H
CC2	β-oxynaphthoic acid ("BONA")	CO ₂ H
CC3	Naphthol AS derivatives	
CC6	Benzimidazolone	

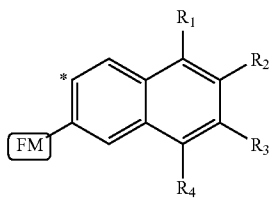
* = point of coupling to diazo component

TABLE 3

Precursor to group G _c	Class of Coupling Component	FM	R ₃	R ₄
CC4a	Naphthalene Sulfonic Acid derivatives	SO ₃ H	H	H
CC4b	Naphthalene Sulfonic Acid derivatives	SO ₃ H	SO ₃ H	H

* = point of coupling to diazo component

TABLE 4

Precursor to group G _c	Class of Coupling Component	FM	R ₁	R ₂	R ₃	R ₄
CC5	Naphthalene Sulfonic Acid derivatives	SO ₃ H		H	H	SO ₃ H

* = point of coupling to diazo component

TABLE 5

Precursor to group G _c	Class of Coupling Component	G	R ₁ '	R ₂ '	R ₃ '	R ₄ '
CC7	Pyrazolone deriv.	CO ₂ H	H	H	SO ₃ H	H
CC8	Pyrazolone deriv.	CH ₃	H	H	SO ₃ H	H

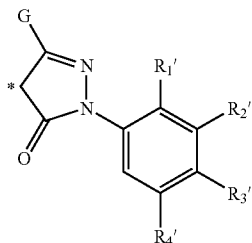
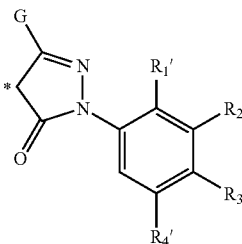


TABLE 5-continued

Precursor to group G _c	Class of Coupling Component	G	R ₁ '	R ₂ '	R ₃ '	R ₄ '
CC9	Pyrazolone deriv.	CH ₃	H	SO ₃ H	H	H
CC10	Pyrazolone deriv.	CH ₃	Cl	H	SO ₃ H	Cl



* = point of coupling to diazo component

TABLE 6

Precursor to group G _c	Class of Coupling Component	R ₁ '	R ₂ '	R _a	R _b	R _c
CC11	Acetoacetic arylyde	CH ₃	R _a	H	H	H

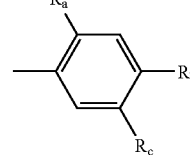
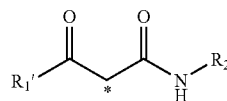
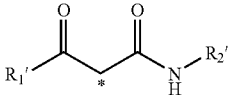
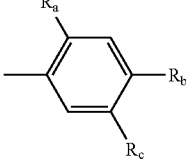
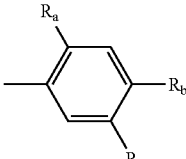
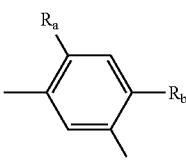
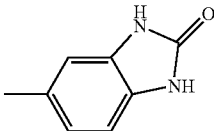


TABLE 6-continued

Precursor to group G _c	Class of Coupling Component					
		R ₁ '	R ₂ '	R _a	R _b	R _c
CC12	Acetoacetic arylide	CH ₃		CH ₃	H	H
CC13	Acetoacetic arylide	CH ₃		Cl	H	H
CC14	Acetoacetic arylide	CH ₃		H	OCH ₃	H
CC15	Acetoacetic benzimidazolone	CH ₃		—	—	—

* = point of coupling to diazo component

[0049] The organic pigment, and in some embodiments, the organic pigment precursor, also generally includes a counterion as part of the overall structure. Such counterions can be, for example, any suitable counterion including those that are well known in the art. Such counterions can be, for example, cations or anions of either metals or non-metals that include N, P, S and the like, or carbon-based cations or anions. Examples of suitable cations include ions of Ba, Ca, Cu, Mg, Sr, Li, Na, K, Cs, Mn, Cu, Cr, Fe, Ti, Ni, Co, Zn, V, B, Al, Ga, and other metal ions, as well as ammonium and phosphonium cations, mono-, di-, tri-, and tetra-substituted ammonium and

phosphonium cations, where the substituents can be aliphatic alkyl groups, such as methyl, ethyl, butyl, stearyl and the like, as well as aryl groups such as phenyl or benzyl and the like.

[0050] Representative examples of monoazo laked pigments comprised from a selection of substituted aniline precursors (denoted DC) which can also include Tobias Acid, nucleophilic coupling component (denoted as CC) and metal salts (denoted as M) to provide the counter-cation Mⁿ⁺ of formula (1) are listed in Table 7, and other laked pigment structures may arise from other combinations of DC and CC and metal cation salt (M) that are not shown in Table 7.

TABLE 7

Color Index # (C.I.)	Color Index (C.I.) Name	Laked Pigment Class	G _d precursor	G _c precursor	Metal Salt M
15500:1	Red 50:1	β-Naphthol Lakes	DC14	CC1	½ Ba
15510:1	Orange 17	β-Naphthol Lakes	DC7	CC1	Ba
15510:2	Orange 17:1	β-Naphthol Lakes	DC7	CC1	⅔ Al
15525	Red 68	β-Naphthol Lakes	DC4	CC1	2 Ca
15580	Red 51	β-Naphthol Lakes	DC8	CC1	Ba
15585	Red 53	β-Naphthol Lakes	DC3	CC1	2 Na
15585:1	Red 53:1	β-Naphthol Lakes	DC3	CC1	Ba
15585:3	Red 53:3	β-Naphthol Lakes	DC3	CC1	Sr
15602	Orange 46	β-Naphthol Lakes	DC5	CC1	Ba
15630	Red 49	β-Naphthol Lakes	DC21	CC1	2 Na
15630:1	Red 49:1	β-Naphthol Lakes	DC21	CC1	Ba
15630:2	Red 49:2	β-Naphthol Lakes	DC21	CC1	Ca
15630:3	Red 49:3	β-Naphthol Lakes	DC21	CC1	Sr
15800	Red 64	β-oxynaphthoic acid (BONA) Lakes	DC20	CC2	½ Ba
15800:1	Red 64:1	β-oxynaphthoic acid (BONA) Lakes	DC20	CC2	½ Ca
15800:2	Brown 5	β-oxynaphthoic acid (BONA) Lakes	DC20	CC2	½ Cu
15825:2	Red 58:2	β-oxynaphthoic acid (BONA) Lakes	DC9	CC2	Ca
15825:4	Red 58:4	β-oxynaphthoic acid (BONA) Lakes	DC9	CC2	Mn
15850:1	Red 57:1	β-oxynaphthoic acid (BONA) Lakes	DC1	CC2	Ca
15860:1	Red 52:1	β-oxynaphthoic acid (BONA) Lakes	DC3	CC2	Ca
15860:2	Red 52:2	β-oxynaphthoic acid (BONA) Lakes	DC3	CC2	Mn
15865:1	Red 48:1	β-oxynaphthoic acid (BONA) Lakes	DC2	CC2	Ba
15865:2	Red 48:2	β-oxynaphthoic acid (BONA) Lakes	DC2	CC2	Ca
15865:3	Red 48:3	β-oxynaphthoic acid (BONA) Lakes	DC2	CC2	Sr
15865:4	Red 48:4	β-oxynaphthoic acid (BONA) Lakes	DC2	CC2	Mn
15865:5	Red 48:5	β-oxynaphthoic acid (BONA) Lakes	DC2	CC2	Mg
15867	Red 200	β-oxynaphthoic acid (BONA) Lakes	DC5	CC2	Ca
15880:1	Red 63:1	β-oxynaphthoic acid (BONA) Lakes	DC21	CC2	Ca
15880:2	Red 63:2	β-oxynaphthoic acid (BONA) Lakes	DC21	CC2	Mn
15892	Red 151	Naphthol AS Lakes	DC10	CC3	Ba
				(R ₂ ' = H, R ₄ ' = SO ₃ H)	
15910	Red 243	Naphthol AS Lakes	DC2	CC3	½ Ba
				(R ₂ ' = OCH ₃ , R ₄ ' = H)	
15915	Red 247	Naphthol AS Lakes	DC13	CC3	Ca
				(R ₂ ' = H, R ₄ ' = OCH ₃)	
15985:1	Yellow 104	Naphthalene Sulfonic Acid Lakes	DC7	CC4a	⅔ Al
15990	Orange 19	Naphthalene Sulfonic Acid Lakes	DC15	CC4a	½ Ba
16105	Red 60	Naphthalene Sulfonic Acid Lakes	DC14	CC4b	⅔ Ba
18000:1	Red 66	Naphthalene Sulfonic Acid Lakes	DC16	CC5	½ Ba, Na

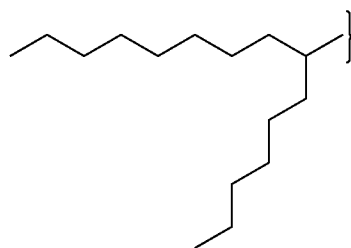
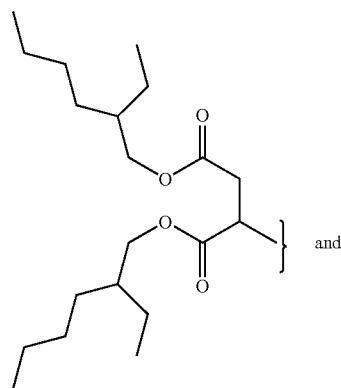
[0051] The complementary functional group of the stabilizer can be one or more of any suitable moiety capable of non-covalent bonding with the functional moiety of the stabilizer. Illustrative complementary functional groups on the stabilizer include the following: sulfonate/sulfonic acid, (thio)carboxylate/(thio)carboxylic acid, phosphonate/phosphonic acid, ammonium and substituted ammonium salts, phosphonium and substituted phosphonium salts, substituted carbonium salts, substituted arylum salts, alkyl/aryl (thio)carboxylate esters, thiol esters, primary or secondary amides, primary or secondary amines, hydroxyl, ketone, aldehyde, oxime, hydroxylamino, enamines (or Schiff base), porphyrins, (phthalocyanines, urethane or carbamate, substituted ureas, guanidines and guanidinium salts, pyridine and pyridinium salts, imidazolium and (benz)imidazolium salts, (benz)imidazolones, pyrrole, pyrimidine and pyrimidinium salts, pyridinone, piperidine and piperidinium salts, piperazine

and piperazinium salts, triazolo, tetraazolo, oxazole, oxazolines and oxazolium salts, indoles, indenones, and the like.

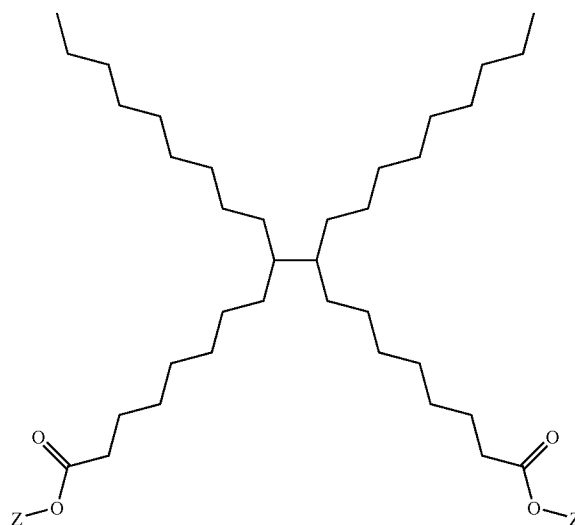
[0052] The stabilizer can be any compound that has the function of limiting the extent of pigment particle or molecular self-assembly so as to produce predominantly nanoscale-sized pigment particles. The stabilizer compound should have a hydrocarbon moiety that provides sufficient steric bulk to enable the function of the stabilizer to regulate pigment particle size. The hydrocarbon moiety in embodiments is predominantly aliphatic, but in other embodiments can also incorporate aromatic groups, and generally contains at least 6 carbon atoms, such as at least 12 carbons or at least 16 carbons, and not more than about 100 carbons, but the actual number of carbons can be outside of these ranges. The hydrocarbon moiety can be either linear, cyclic or branched, and in embodiments is desirably branched, and may or may not contain cyclic moieties such as cycloalkyl rings or aromatic

rings. The aliphatic branches are long with at least 2 carbons in each branch, such as at least 6 carbons in each branch, and not more than about 100 carbons.

[0053] It is understood that the term “steric bulk” is a relative term, based on comparison with the size of the pigment or pigment precursor to which it becomes non-covalently associated. In embodiments, the phrase “steric bulk” refers to the situation when the hydrocarbon moiety of the stabilizer compound that is coordinated to the pigment/precursor surface, occupies a 3-dimensional spatial volume that effectively prevents the approach or association of other chemical entities (e.g. colorant molecules, primary pigment particles or small pigment aggregate) toward the pigment/precursor surface. Thus, the stabilizer should have its hydrocarbon moiety large enough so that as several stabilizer molecules become non-covalently associated with the chemical entity (pigment or precursor), the stabilizer molecules act as surface barrier agents for the primary pigment particles and effectively encapsulates them, and thereby limits the growth of the pigment particles and affording only nanoparticles of the pigment. For example, for the pigment precursor Lithol Rubine and for the organic pigment Pigment Red 57:1, the following illustrative groups on a stabilizer are considered to have adequate “steric bulk” so as to enable the stabilizer to limit the extent of pigment self-assembly or aggregation and mainly produce pigment nano-sized particles:

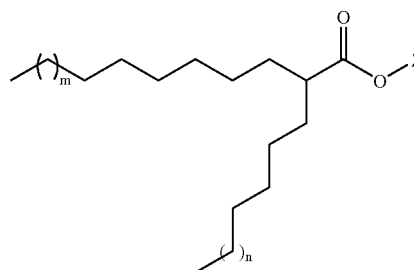


[0054] Representative examples of stabilizer compounds that have both the functional group that non-covalently associates with the pigment and the sterically bulky hydrocarbon moiety, include (but are not limited to) the following compounds:

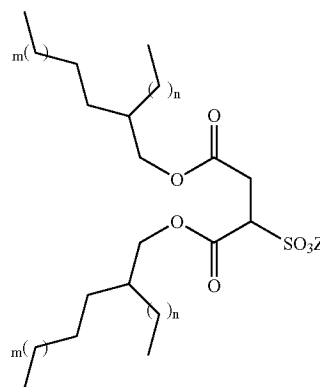


C36 Dimer Diacid

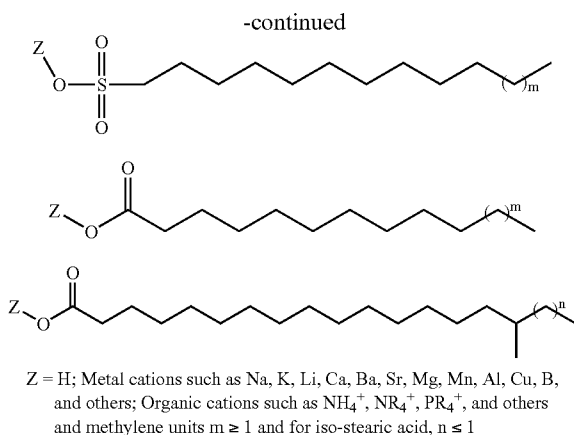
Z = H; Metal cations such as Na, K, Li, Ca, Ba, Sr, Mg, Mn, Al, Cu, B, and others; Organic cations such as NH_4^+ , NR_4^+ , PR_4^+ , and others



Z = H; Metal cations such as Na, K, Li, Ca, Ba, Sr, Mg, Mn, Al, Cu, B, and others; Organic cations such as NH_4^+ , NR_4^+ , PR_4^+ , and others and methylene units $(m + n) > 1$



Z = H; Metal cations such as Na, K, Li, Ca, Ba, Sr, Mg, Mn, Al, Cu, B, and others; Organic cations such as NH_4^+ , NR_4^+ , PR_4^+ , and others and methylene units $(m + n) > 1$ per branch



wherein m and n denotes the number of repeated methylene units, and where m can range between 1 and 50, and n can range between 1 and 5, however the values can also be outside these ranges.

[0055] In additional embodiments, other stabilizer compounds having different structures than those described previously may be used in addition to sterically bulky stabilizer compounds, to function as surface active agents (or surfactants) that either prevent or limit the degree of pigment particle aggregation. Representative examples of such surface active agents include, but are not limited to, rosin natural products such as abietic acid, dehydroabietic acid, pimaric acid, rosin soaps (such as the sodium salt of the rosin acids), hydrogenated derivatives of rosins and their alkyl ester derivatives made from glycerol or pentaerythritol or other such hydrocarbon alcohols, acrylic-based polymers such as poly(acrylic acid), poly(methyl methacrylate), styrene-based copolymers such as poly(styrene sodio-sulfonate) and poly(styrene)-co-poly(alkyl (meth)acrylate), copolymers of α -olefins such as 1-hexadecene, 1-octadecene, 1-eicosene, 1-triacontene and the like, copolymers of 4-vinyl pyridine, vinyl imidazole, and vinyl pyrrolidinone, polyester copolymers, polyamide copolymers, copolymers of acetals and acetates, such as the copolymer poly(vinylbutyral)-co-(vinyl alcohol)-co-(vinyl acetate).

[0056] The types of non-covalent chemical bonding that can occur between the functional moiety of the precursor/pigment and the complementary functional group of the stabilizer are, for example, van der Waals' forces, ionic or coordination bonding, hydrogen bonding, and/or aromatic pi-stacking bonding. In embodiments, the non-covalent bonding is predominately ionic bonding, but can include hydrogen bonding and aromatic pi-stacking bonding as additional or alternative types of non-covalent bonding between the functional moieties of the stabilizer compounds and the precursor/pigment.

[0057] The "average" pigment particle size, which is typically represented as d_{50} , is defined as the median particle size value at the 50th percentile of the particle size distribution, wherein 50% of the particles in the distribution are greater than the d_{50} particle size value and the other 50% of the particles in the distribution are less than the d_{50} value. Average particle size can be measured by methods that use light scattering technology to infer particle size, such as Dynamic Light Scattering. The term "particle diameter" as used herein

refers to the length of the pigment particle at the longest dimension (in the case of acicular shaped particles) as derived from images of the particles generated by Transmission Electron Microscopy (TEM). The term "nano-sized", "nanoscale", "nanoscopic", or "nano-sized pigment particles" refers to for instance, an average particle size, d_{50} , or an average particle diameter of less than about 150 nm, such as of about 1 nm to about 100 nm, or about 10 nm to about 80 nm. Geometric standard deviation is a dimensionless number that typically estimates a population's dispersion of a given attribute (for instance, particle size) about the median value of the population and is derived from the exponentiated value of the standard deviation of the log-transformed values. If the geometric mean (or median) of a set of numbers $\{A_1, A_2, \dots, A_n\}$ is denoted as μ_g , then the geometric standard deviation is calculated as:

$$\sigma_g = \exp \sqrt{\frac{\sum_{i=1}^n (\ln A_i - \ln \mu_g)^2}{n}}$$

[0058] The method of making nano-sized particles of the monoazo laked pigments such as those listed in Table 7 is a process that involves at least one or more reaction steps. A diazotization reaction is a key reaction step for synthesis of the monoazo laked pigment, whereby a suitably substituted aniline precursor (denoted as diazo component DC) such as those listed in Table 1, and Formulas (2) and (3), is either directly or indirectly converted first to a diazonium salt using standard procedures, such as that which includes treatment with an effective diazotizing agent such as nitrous acid HNO_2 (which is generated in situ by mixing sodium nitrite with dilute protic acid solution such as hydrochloric acid), or nitrosyl sulfuric acid (NSA), which is commercially available or can be prepared by mixing sodium nitrite in concentrated sulfuric acid. Initially, it may be necessary to first dissolve the precursor substituted aniline in alkaline solution (such as aqueous potassium hydroxide solution, or ammonia water) followed by treatment with the diazotizing agent and acid solution, so as to generate the diazonium salt. The diazotization procedure is typically carried out at cold temperatures so as to keep the diazonium salt stable, and the resulting reaction mixture will comprise mainly the diazonium salt either dissolved or suspended as a precipitate in acidic medium. If desired and effective, an aqueous solution of the metal salt (M^{n+}) can be optionally added that will define the specific composition of the desired monoazo laked pigment product, such as those listed in Table 7. A second solution or suspension is prepared by dissolving or suspending the nucleophilic coupling component (denoted as CC, such as those shown in Tables 2-6, and Formulas (4)-(8)) mainly into water, which may optionally contain another liquid such as an organic solvent (for example, iso-propanol, tetrahydrofuran, methanol, or other), and either acids or bases to render the coupling component into solution or a fine suspension and aid reaction with the diazonium salt solution, and additionally any buffers or surface active agents including the sterically bulky stabilizer compounds such as those described previously.

[0059] The reaction mixture containing the dissolved or suspended diazonium salt is then transferred into the solution or suspension of the desired nucleophilic coupling component, and the temperature of the mixture can range from about

10° C. to about 75° C., in order to produce a solid colorant material suspended as a precipitate in an aqueous slurry.

[0060] The solid colorant material may be the desired monoazo laked pigment product formed as nano-sized particles, or it may be an advanced synthetic intermediate for making the monoazo laked pigment product. In the case of the latter, a two-step process is required for preparing the nano-sized particles of monoazo laked pigment, whereby the second step involves rendering the advanced synthetic intermediate of the first step above (the pigment precursor) into homogeneous liquid solution by treatment with either strong acid or alkaline base, then treating this solution with one or more surface active agents in addition to the sterically bulky stabilizer compounds, as described previously, followed lastly by treatment with the required metal salt solution to provide the desired laked monoazopigment composition as a solid precipitate, said metal salt solution effectively functioning as a pigment precipitating agent. There are several chemical as well as physical processing factors can affect the final particle size and distribution of the monoazo laked pigment nanoparticles, including stoichiometries of the DC and CC starting reactants, metal salt, surface active agents, and stabilizer compounds, the concentrations of chemical species in the liquid medium, pH of liquid medium, temperature, addition rate, order of addition, agitation rate, post-reaction treatments such as heating, isolation and washing of particles, and drying conditions.

[0061] In embodiments is disclosed a two-step method of making nano-sized monoazo laked red pigments, for example Pigment Red 57:1, wherein the advanced pigment precursor Lithol Rubine is first synthesized as a potassium salt and is a water-soluble orange dye. The first step involves the diazotization of 2-amino-5-methyl-benzenesulfonic acid (DC1 in Table 1) by first dissolving the DC in dilute aqueous potassium hydroxide solution (0.5 mol/L) and cooling to a temperature anywhere in the range of about -5° C. to about 5° C., and then treating the solution with an aqueous solution of sodium nitrite (20 wt %), following with slow addition of concentrated hydrochloric acid at a rate that maintains the internal reaction temperature between -5° C. and +5° C. The resulting suspension that forms is stirred for additional time so as to ensure completeness of diazotization, and then the suspension is carefully transferred to a second solution containing 3-hydroxy-2-naphthoic acid dissolved in dilute alkaline solution (0.5 mol/L potassium hydroxide), using vigorous agitation as the colorant product is produced in the aqueous slurry. After stirring for additional time of at least 1 hour at room temperature, the colorant product (Lithol Rubine-potassium salt) is isolated by filtration as an orange dyestuff and washed with deionized water to remove excess salt by-products.

[0062] The second step of the process involves redispersing the orange Lithol Rubine-potassium salt dyestuff in deionized water to a concentration that can range from about 0.5 wt % to about 20 wt %, such as from about 1.5 wt % to about 10 wt % or from about 3.5 wt % to about 8 wt %, but the concentrations can also be outside of these ranges. The colorant solids in the slurry is then dissolved completely into liquid solution by treatment with aqueous alkaline base, such as sodium hydroxide or potassium hydroxide or ammonium hydroxide solution, until the pH level is high, such as above pH 8.0 or above pH 9.0 or above pH 10.0. To this alkaline solution of dissolved Lithol Rubine colorant can be optionally added a surface active agent as described previously, in

particular embodiments surface active agent such as rosin soaps, delivered as an aqueous solution in the amount ranging from 0.1 wt % to 20 wt % based on colorant solids, such as in an amount ranging from 0.5 wt % to about 10 wt %, or in an amount ranging from 1.0 wt % to about 8.0 wt % based on colorant solids, but the amount used can also be outside of these ranges.

[0063] In embodiments, the preparation of ultrafine and nanosized particles of the monoazo laked Pigment Red 57:1 was only enabled by the additional use of a sterically bulky stabilizer compound having a functional group that could non-covalently bond to the complementary functional moiety of the pigment as well as branched aliphatic functional groups that could provide steric bulk to the pigment particle surface. In embodiments, particularly suitable sterically bulky stabilizer compounds are branched hydrocarbons with either carboxylate or sulfonate functional groups, compounds such as di[2-ethylhexyl]-3-sulfosuccinate sodium or sodium 2-hexyldecanoate, and the like. The stabilizer compound is introduced as a solution or suspension in a liquid that is predominantly aqueous but may optionally contain a water-miscible organic solvent such as THF, iso-propanol, NMP, Dowanol and the like, to aid dissolution of the stabilizer compound, in an amount relative to colorant moles ranging from about 5 mole-percent to about 100 mole-percent, such as from about 20 mole-percent to about 80 mole-percent, or from about 30 mole-percent to about 70 mole-percent, but the concentrations used can also be outside these ranges and in large excess relative to moles of colorant.

[0064] Lastly, the metal cation salt is added to transform the pigment precursor (Lithol Rubine-potassium salt in embodiments) into the desired monoazo laked pigment (Pigment Red 57:1 in embodiments), precipitated as nano-sized pigment particles. The aqueous solution of metal salt (calcium chloride in embodiments) with concentration ranging anywhere from 0.1 mol/L to about 2 mol/L, is slowly added dropwise in nearly stoichiometric quantities such as amounts ranging from 1.0 molar equivalents relative to about 2.0 molar equivalents, or from 1.1 to about 1.5 molar equivalents, or from 1.2 to about 1.4 molar equivalents relative to moles of colorant, however the amounts used can also be outside of these ranges and in large excess.

[0065] The type of metal salt can have an impact on the extent of forming nano-sized pigment particles of monoazo laked pigments, in particular the type of ligand that is coordinated to the metal cation and the relative ease with which it is displaced by a competing ligand from either the pigment functional moiety or the complementary functional moiety of the stabilizer compound, or both. In embodiments for monoazo laked Pigment Red 57:1, the nano-sized particles are formed using calcium (II) salts with ligands such as chloride, sulfate, acetate, and hydroxide; however a particularly desirable metal salt is calcium chloride for fastest reactivity.

[0066] The rates of addition of metal salt solution can also vary. For example, the slower the rate of addition, the more controlled is the rate of pigment crystal formation and particle aggregation, and therefore the smaller in size the pigment particles become.

[0067] Also important is the agitation rate and mixing pattern as the pigment formation/precipitation step is occurring. The higher the agitation rate and the more dynamic or complex is the mixing pattern (i.e. with baffles to prevent dead mixing zones), the smaller is the average particle diameter and the more narrow is the particle size distribution, as

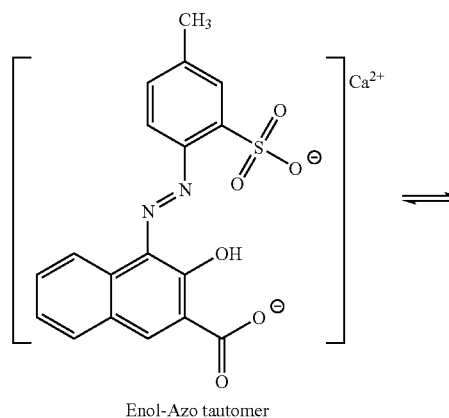
observable by Transmission Electron Microscopy (TEM) imaging. Agitation can be made more effective by using high-shear mixers such as homogenizers, attritors, or even the use of ultrasonic probes.

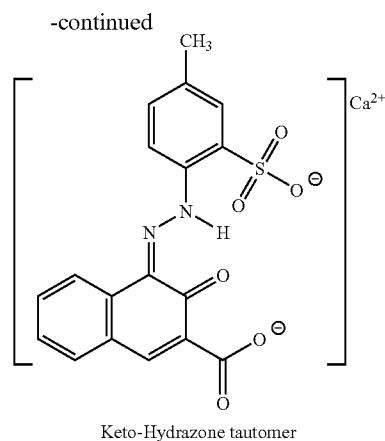
[0068] Temperature during the pigment precipitation step using the metal salt solution is also important. In embodiments, lower temperatures are desired, such as from about 10° C. to about 50° C., or from about 15° C. to about 30° C., but the temperature can also be outside of these ranges.

[0069] In another embodiment is disclosed a one-step method of making nano-sized monoazo laked red pigments, for example Pigment Red 57:1. The process involves preparing a first reaction mixture by dissolving the desired aniline precursor (for example, 2-amino-5-methyl-benzenesulfonic acid which is denoted as DC1 in Table 1) into aqueous ammonia solution (30% ammonium hydroxide) and cooling to a temperature anywhere in the range of about -5° C. to about 5° C., then treating the solution with an aqueous solution of sodium nitrite (20 wt %), following with slow addition of concentrated hydrochloric acid at a rate that maintains the internal reaction temperature between -5° C. and +5° C. The resulting suspension that forms is stirred for additional time so as to ensure completeness of diazotization. To the suspension is added the metal salt as either an aqueous solution or as a neat solid (for precipitating the pigment lake after coupling occurs). A second solution is prepared by dissolving or suspending the nucleophilic coupling component (denoted as CC, such as those shown in Tables 2-6, and Formulas (4)-(8)) mainly into water, which may optionally contain another liquid such as an organic solvent (for example, isopropanol, tetrahydrofuran, methanol, or other), and preferably alkaline base, for example aqueous ammonia, to render the coupling component into solution and aid reaction with the diazonium salt solution, and additionally buffers, and in particular embodiments surface active agent such as rosin soaps delivered as an aqueous solution in the amount ranging from 0.1 wt % to 20 wt % based on colorant solids, such as in an amount ranging from 0.5 wt % to about 10 wt %, or in an amount ranging from 1.0 wt % to about 8.0 wt % based on colorant solids, but the amount used can also be outside of these ranges. Further, in particular embodiments is also included the sterically bulky stabilizer compounds such as those described previously, delivered as an aqueous solution in the amount relative to colorant moles ranging from about 5 mole-percent to about 100 mole-percent, such as from about 20 mole-percent to about 80 mole-percent, or from about 30 mole-percent to about 70 mole-percent, but the concentrations used can also be outside these ranges and in large excess relative to moles of colorant. The first reaction mixture containing the dissolved or suspended diazonium salt is then transferred slowly into the second solution or suspension of the desired nucleophilic coupling component, using vigorous agitation such as for example a high-speed mixer, and the temperature of the mixture can range from about 15° C. to about 75° C., in order to produce the laked monoazo pigment material suspended as a fine precipitate in an aqueous slurry. The pigment particles are isolated by either vacuum-filtration or centrifugal separation and washed with deionized water to remove excess salt by-products.

[0070] In embodiments, the slurry of pigment nanoparticles is not treated nor processed any further, such as performing additional heating which is often practiced by pigment manufacturers, but instead is isolated by vacuum filtration or centrifugal separation processes. The pigment solids can be washed copiously with deionized water to remove excess salts or additives that are not highly associated or bonded with the pigment particle surface. The pigment solids can be dried by freeze-drying under high vacuum, or alternatively, they can be pre-rinsed with a water-miscible solvent such as isopropanol or acetonitrile to remove excess water and then vacuum-oven dried. The resulting nano-size pigment particles are generally non-aggregated and of high quality, which when imaged by TEM (Transmission Electron Microscopy), exhibit primary pigment particles and small aggregates ranging in diameters from about 30 nm to about 150 nm, and predominantly from about 50 nm to about 125 nm. (Here, it is noted that average particle size d_{50} and particle size distributions are measured by Dynamic Light Scattering, an optical measurement technique that estimates the hydrodynamic radius of non-spherical pigment particles gyrating and translating in a liquid dispersion via Brownian motion, by measuring the intensity of the incident light scattered from the moving particles. As such, the d_{50} particle size metric obtained by DLS technique is always a larger number than the actual particle diameters observed by TEM imaging.)

[0071] Characterization of the chemical composition of washed and dried nano-sized pigment particles are performed by NMR spectroscopy and elemental analysis. In embodiments, the composition of the monoazo laked pigment Red 57:1 indicated that the nano-sized particles prepared by the methods described above, particularly when using di[2-ethylhexyl]-3-sulfosuccinate sodium as the sterically bulky stabilizer, retained at least 80% of the sterically bulky stabilizer that was loaded into the process of making the nanoparticles, even after copious washing with deionized water to remove excess salts. Solid state ^1H - and ^{13}C -NMR spectroscopic analyses indicated that the steric stabilizer compound was associated non-covalently with the pigment as a calcium salt, and the chemical structure of the pigment adopted the hydrazone tautomer form, as shown in Figure below.





[0072] Pigment particles of monoazo laked pigments such as PR 57:1 that have smaller particle sizes could also be prepared by the above two-step method in the absence of using sterically bulky stabilizers and with the use of surface active agents alone (for example, only rosin-type surface agents), depending on the concentrations and process conditions employed, but the pigment product did not predominantly exhibit nano-sized particles nor did the particles exhibit regular morphologies. In the absence of using the sterically bulky stabilizer compound, either the one-step or the two-step methods described above typically produced rod-like particle aggregates, ranging in average particle diameter from 200-700 nm and with wide particle distribution, and such particles were difficult to disperse into a polymer coating matrix and generally gave poor coloristic properties. In embodiments, the combined use of a suitable sterically bulky stabilizer compound, such as branched alkanesulfonates or alkylcarboxylates, with a minor amount of suitable surface active agent such as derivatives of rosin-type surfactants, using either of the synthesis methods described previously would afford the smallest fine pigment particles having nanometer-scale diameters, more narrow particle size distribution, and low aspect ratio. Various combinations of these compounds, in addition to variations with process parameters such as stoichiometry of reactants, concentration, addition rate, temperature, agitation rate, reaction time, and post-reaction product recovery processes, enables the formation of pigment particles with tunable average particle size (d_{50}) from nanoscale sizes (about 1 to about 100 nm) to mesoscale sizes (about 100 to about 500 nm) or larger. The dispersion ability and coloristic properties (L^* , a^* , b^* , chroma, hue angle, light scatter index) of the pigment particles in a thin polymer binder coating were directly correlated to the average pigment particle size, which in turn was impacted by both the structural composition and amount of sterically bulky stabilizer compound (relative to molar amount of pigment) that was employed within the synthesis process.

[0073] The advantages of this process include the ability to tune particle size and composition for the intended end-use application of the monoazo laked pigment, such as toners and inks and coatings, which include phase-change, gel-based and radiation-curable inks, solid and non-polar liquid inks, solvent-based inks and aqueous inks and ink dispersions. For the end-use application in piezoelectric inkjet printing, nano-sized particles are advantageous to ensure reliable inkjet

printing and prevent blockage of jets due to pigment particle agglomeration. In addition, nano-sized pigment particles are advantageous for offering enhanced color properties in printed images, since in embodiments the color properties of nano-sized particles of monoazo laked pigment Red 57:1 were tunable with particle size, whereby as average particle size was decreased to nanometer-scale, the hue angles were shifted from yellowish-red hues to bluish-red hues by an amount ranging from about 5 to about 350 in the color gamut space.

[0074] In embodiments, the nano-sized pigment particles that were obtained for monoazo laked pigments can range in the average particle size, d_{50} , or in the average particle diameter, from about 10 nm to about 250 nm, such as from about 25 nm to about 175 nm, or from about 50 nm to about 150 nm, as measured by either dynamic light scattering method or from TEM images. In embodiments, the particle size distributions can range such that the geometric standard deviation (denoted as GSD) can range from about 1.1 to about 1.9, or from about 1.2 to about 1.7, as measured by dynamic light scattering method. The shape of the nano-sized pigment particles can be one or more of several morphologies, including rods, platelets, needles, prisms or nearly spherical, and the aspect ratio of the nanosize pigment particles can range from 1:1 to about 10:1, such as having aspect ratio between 1:1 and 5:1; however the actual metric can lie outside of these ranges.

[0075] The color of the nanosized pigment particles have the same general hue as is found with larger pigment particles. However, in embodiments, is disclosed coloristic properties of thin coatings of the nano-sized pigment particles of red monoazo laked pigments dispersed in a polymer binder (such as of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate)), that exhibited a significant shift to lower hue angle and lower b^* values that revealed more bluish magenta hues, and having either no change or a small enhancement of a^* value. In embodiments, the hue angles of the coatings dispersed with the nano-sized particles of monoazo laked pigment such as Pigment Red 57:1 measured in the range from about 345° to about 5° on the 2-dimensional b^*a^* color gamut space, as compared with hue angles ranging from about 0° to about 20° for similarly prepared polymer coatings dispersed with conventional larger sized particles of Pigment Red 57:1. In embodiments is disclosed the coloristic properties (hue angle, a^* , b^* , and NLSI as measure of specular reflectivity) of nano-sized pigment particles, particularly of monoazo laked red pigment, that are directly correlated and tunable with the average pigment particle size, measured by either Dynamic Light Scattering or electron microscopy imaging techniques, as well as pigment composition with the non-covalently associated stabilizer, the latter which enables the control of particle size during pigment synthesis, and also enables enhanced dispersability within certain polymer binders for coating or other applications.

[0076] Additionally, the specular reflectivity of the coatings of the nano-sized monoazo laked red pigment was significantly enhanced from coatings produced with conventional larger sized pigment particles, which is an indicator of having very small particles being well-dispersed within the coating. Specular reflectivity was quantified as the degree of light scattering for the pigmented coating, a property that is dependent on the size and shape distributions of the pigment particles and their relative dispersability within the coating binder. The Normalized Light Scatter Index (NLSI) was quantified by measuring the spectral absorbance of the coat-

ing in a region where there is no absorbance from the chromogen of the monoazo laked pigment, but only absorbance due to light scattered from large aggregates and/or agglomerated pigment particles dispersed in the coating binder. The light scattering absorbance data is then normalized to a lambda-max optical density of 1.5, resulting in the NLSI value, in order to directly compare the light scattering indices of several pigmented coatings. The lower is the NLSI value, the smaller is the pigment particle size within the dispersed coating matrix. In embodiments, the NLSI value of the nano-sized monoazo laked red pigments can range from about 0.1 to about 3.0, such as from about 0.1 to about 1.0, as compared to the NLSI values observed with similarly prepared coatings containing larger sized monoazo laked red pigments that range anywhere from about 3.0 to about 75 (a very poorly dispersed coating).

[0077] The formed nanoscale pigment particle compositions can be used, for example, as coloring agents in a variety of compositions, such as in liquid (aqueous or non-aqueous) ink vehicles, including inks used in conventional pens, markers, and the like, liquid ink jet ink compositions, solid or phase change ink compositions, and the like. For example, the colored nanoparticles can be formulated into a variety of ink vehicles, including "low energy" solid inks with melt temperatures of about 60 to about 130° C., solvent-based liquid inks or radiation-curable such as UV-curable liquid inks comprised of alkyoxylated monomers, and even aqueous inks.

[0078] Examples are set forth herein below and are illustrative of different compositions and conditions that can be utilized in practicing the disclosure. All proportions are by weight unless otherwise indicated. It will be apparent, however, that the disclosure can be practiced with many types of compositions and can have many different uses in accordance with the disclosure above and as pointed out hereinafter.

EXAMPLES

Examples of Compositions and Methods of Making Nano-Sized Monoazo Laked Red Pigment

Comparative Example 1

Synthesis of Pigment Red 57:1 Using a Two-Step Method

[0079] **Step 1: Diazotization and Coupling:** Into a 500 mL round bottom flask equipped with a mechanical stirrer, thermometer, and addition funnel was dissolved 2-amino-5-methylbenzenesulfonic acid (8.82 g) into 0.5M KOH aqueous solution (97.0 mL). The resulting brown solution was cooled to 0° C. A 20 wt % aqueous solution of sodium nitrite (NaNO₂; 3.28 g dissolved into 25 mL water) was added slowly to the first solution while maintaining the temperature below 3° C. To the red-brown homogeneous mixture was added dropwise concentrated HCl (10M, 14.15 mL) over 1 hour, maintaining the internal temperature below 2° C. The mixture formed a pale brown suspension, and following complete addition of conc. HCl, the suspension was stirred an additional 30 min.

[0080] In a separate 2-L resin kettle was dissolved 3-hydroxy-2-naphthoic acid (8.86 g) into an aqueous solution of KOH (8.72 g) in water (100 mL). An additional 250 mL of water was added, and the light-brown solution was then cooled to 15° C. while stirring vigorously. The cold suspension of the diazonium salt suspension was then added slowly to the coupling solution while mixing vigorously. The color

changed initially to a dark red solution, and ultimately to a yellowish-red (orange) slurry of precipitated dyestuff. The mixture was stirred for 2 hours while warming up to room temp, then filtered and diluted with about 500 mL of deionized water to produce an orange aqueous slurry of Lithol Rubine-Potassium salt dye (a synthetic precursor of Pigment Red 57:1) having solids content of about 1.6 wt %.

Step 2: Laking Step to Produce Pigment Red 57:1 Particles

[0081] Into a 500 mL round bottom flask equipped with mechanical stirrer and condenser was charged 126 g of aqueous slurry of Lithol Rubine-Potassium salt dye precursor from above having about 1.6% wt solids content. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 13 mL) was added dropwise to the slurry while stirring vigorously. A red precipitate formed immediately, and after addition was completed, the slurry was stirred for an additional 1 hour. The red slurry was then heated to about 75° C. for 20 min, then cooled to room temp. The slurry was filtered under high vacuum through a 1.2 μm acrylic polymer membrane, then reslurried twice with 200 mL portions of deionized water. The pH and conductivity of the filtrates after each filtration were measured and recorded, with the final wash filtrate having nearly neutral pH of 6.2 and conductivity of about 13.5 μS/cm, indicating low residual salts. The red pigment filtercake was reslurried into about 200 mL of DIW and freeze-dried for 48 hours, to afford a red colored powder (1.95 grams). TEM microscopy revealed long rod-like particles and aggregates, with particle diameters ranging from about 200 nm to about 700 nm, and large aspect ratios ranging from about 4:1 to about 10:1.

Comparative Example 2

Synthesis of Pigment Red 57:1 Using a One-Step Method

[0082] **Diazotization Mixture:** Into a 100 mL round bottom flask equipped with a mechanical stirrer, thermometer, and addition funnel was added 2-amino-5-methylbenzenesulfonic acid (2.2 g), deionized water (22 mL) and concentrated ammonia (30 wt %; 1.5 g). The resulting light brown solution was cooled to -2° C. An aqueous solution of sodium nitrite (NaNO₂; 0.82 g dissolved into 3 mL water) was added slowly to the first solution while maintaining the temperature below 2° C. To the reddish-brown homogeneous mixture was added dropwise concentrated HCl (3.6 g) so as to maintain the internal temperature below 2° C. The mixture formed a pale brown suspension, and following complete addition of conc. HCl, the suspension was stirred an additional 30 min. A solution of calcium chloride dehydrate (2.6 g) dissolved into deionized water (5 mL) was added to the diazo suspension

[0083] **Coupling Mixture:** In a separate 500 mL flask equipped with high-speed mechanical stirrer, thermometer and dropping funnel was added 3-hydroxy-2-naphthoic acid (2.3 g), deionized water (60 mL), and concentrated ammonia (30 wt %, 1.5 g). After stirring to dissolution, an aqueous solution of 5 wt % Dresinate-X rosin surfactant (10 mL) was added and the mixture stirred to dissolution.

[0084] The cold suspension of the diazonium salt suspension was then added slowly to the coupling solution under vigorous mixing. The color changed to a red slurry of precipitated pigment particles. The mixture was stirred for 30

minutes, then vacuum-filtered through a 0.8 μm acrylic polymer membrane, reslurried once with 300 mL of DIW and filtered again. The red pigment 57:1 filtercake was reslurried into about 250 mL of DIW for a final time, and freeze-dried for 48 hours to afford a red powder (3.55 grams). TEM micrograph images showed a distribution of long platelet-like particles with diameters ranging from 200 to 500 nm, and large aspect ratios ranging from about 4:1 to about 10:1.

Example 1

Synthesis of Nano-Sized Particles of Pigment Red 57:1 by a Two-Step Method

[0085] Step 1: Diazotization and Coupling: Into a 500 mL round bottom flask equipped with a mechanical stirrer, thermometer, and addition funnel was dissolved 2-amino-5-methylbenzenesulfonic acid (8.82 g) into 0.5M KOH aqueous solution (97.0 mL). The resulting brown solution was cooled to 0° C. A 20 wt % aqueous solution of sodium nitrite (NaNO_2 ; 3.28 g dissolved into 25 mL water) was added slowly to the first solution while maintaining the temperature below 3° C. To the red-brown homogeneous mixture was added dropwise concentrated HCl (10M, 14.15 mL) over 1 hour, maintaining the internal temperature below 2° C. The mixture formed a pale brown suspension, and following complete addition of conc. HCl, the suspension was stirred an additional 30 min.

[0086] In a separate 2-L resin kettle was dissolved 3-hydroxy-2-naphthoic acid (8.86 g) into an aqueous solution of KOH (8.72 g) in water (100 mL). An additional 250 mL of water was added, and the light-brown solution was then cooled to 15° C. while stirring vigorously. The cold suspension of the diazonium salt suspension was then added slowly to the coupling solution while mixing vigorously. The color changed immediately to a dark red solution, and ultimately to a yellowish-red (orange) slurry of precipitated dyestuff. The mixture was stirred for 2 hours while warming up to room temp, then filtered and reslurried with about 500 mL of deionized water to produce an orange aqueous slurry of Lithol Rubine-Potassium salt dye having solids content of about 1.6 wt %.

Step 2: Laking Step to Produce Pigment Red 57:1 Particles:

[0087] Into a 500 mL round bottom flask equipped with mechanical stirrer and condenser was charged 126 g of aqueous slurry of Lithol Rubine-Potassium salt dye from above (Example 1, Step 1) having about 1.6% wt solids content. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (4.0 mL) was added, followed by a solution containing sodium dioctyl sulfosuccinate (0.96 g) dissolved in 100 mL of 90:10 deionized water/THF mixture. No visible change was observed. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 13 mL) was added dropwise to the slurry while stirring vigorously. A red precipitate formed immediately, and after complete addition of the calcium chloride solution, the slurry was stirred for an additional 1 hour. The red slurry was then heated to about 75° C. for 20 min, then cooled to room temp. The slurry was filtered under high vacuum through a 0.45 μm Nylon membrane cloth, then reslurried twice with 75 mL portions of DIW. The pH and conductivity of the final wash filtrate was 7.4 and about 110 $\mu\text{S}/\text{cm}$, respectively, indicating that residual acids and salt

by-products were removed. The red pigment filtercake was reslurried in about 250 mL of DIW and freeze-dried for 48 hours to afford a dark red colored powder (2.65 grams). Transmission electron microscopy images of the powder revealed platelet-like particles with particle diameters ranging from 30-150 nm, and aspect ratios that were less than 3:1. $^1\text{H-NMR}$ spectroscopy analysis (300 MHz, DMSO-d_6) of the pigment indicated that the pigment adopted the hydrazone tautomer form, and that the dioctyl sulfosuccinate stabilizer compound was present at approximately 40 mol % (representing about 80% remaining of actual loading) and was associated with a calcium cation (determined by ICP spectroscopy).

Example 2

Synthesis of Nano-Sized Particles of Pigment Red 57:1 by a Two-Step Method

[0088] The procedure of Step 1 of Example 1 above was reproduced.

Step 2: Laking

[0089] Into a 500 mL round bottom flask equipped with mechanical stirrer and condenser was charged 126 g of aqueous slurry of Lithol Rubine-Potassium salt dye from above (Example 1) having about 1.6% wt solids content. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (4.0 mL) was added, followed by a solution containing sodium dioctyl sulfosuccinate (0.96 g) dissolved in 100 mL of 90:10 deionized water/THF mixture. No visible change was observed. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 13 mL) was added dropwise to the slurry while stirring vigorously. A red precipitate formed immediately, and after complete addition of the calcium chloride solution, the slurry was stirred for an additional 1 hour. The red slurry was then heated to about 75° C. for 20 min, then cooled to room temp. The slurry was filtered under high vacuum through a 0.45 μm Nylon membrane cloth, then reslurried twice with 75 mL portions of DIW. The pH and conductivity of the final wash filtrate was 7.15 and about 155 $\mu\text{S}/\text{cm}$, respectively. The red pigment filtercake was reslurried in about 250 mL of DIW and freeze-dried for 48 hours to afford a dark red-colored powder (2.62 grams). Transmission electron microscopy images of the powder revealed platelet-like particles with particle diameters ranging from 50-175 nm, and aspect ratios equal to or less than 3:1

Example 3

Synthesis of Nano-Sized Particles of Pigment Red 57:1 by a Two-Step Method

[0090] Step 1: Diazotization and Coupling: Into a 500 mL round bottom flask equipped with a mechanical stirrer, thermometer, and addition funnel was dissolved 2-amino-5-methylbenzenesulfonic acid (12.15 g) into 0.5M KOH aqueous solution (135 mL). The resulting brown solution was cooled to 0° C. A 20 wt % aqueous solution of sodium nitrite (NaNO_2 ; 4.52 g dissolved into 30 mL water) was added slowly to the first solution while maintaining the temperature below -2° C. Concentrated HCl (10M, 19.5 mL) was then slowly added dropwise over 1 hour while maintaining the internal temperature below 0° C. The mixture formed a pale

brown suspension and following complete addition of conc. HCl, the suspension was stirred an additional 30 min.

[0091] In a separate 2-L resin kettle was dissolved 3-hydroxy-2-naphthoic acid (12.2 g) into an aqueous solution of KOH (12.0 g) in water (130 mL). An additional 370 mL of water was added, and the pale brown solution was then cooled to about 15° C. while stirring. The cold suspension of the diazonium salt solution was then added slowly to the coupling solution while mixing vigorously. The color change was immediate to dark black-red solution, and ultimately to a yellowish-red (orange) slurry of precipitated dyestuff. The mixture was stirred for at least 2 hours while warming up to room temp, then filtered and reslurried with about 600 mL of deionized water to produce an orange-colored slurry of Lithol Rubine-Potassium salt dye having solids content of 3.75%-wt.

Step 2: Laking step to produced nano-sized particles of Pigment Red 57:1

[0092] Into a 1-L resin kettle equipped with mechanical stirrer and condenser was charged 265 g of aqueous slurry of Lithol Rubine-Potassium salt dye prepared from Step 1 of Example 2 above, having approximately 3.75%-wt solids content). The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (20.0 mL) was added while stirring, followed by a solution containing sodium dioctyl sulfosuccinate (4.8 g) dissolved in 220 mL of 90:10 deionized water/THF mixture was slowly added to the mixture with stirring. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 65 mL) was added dropwise to the slurry while stirring vigorously. A red precipitate formed immediately, and after complete addition of the calcium chloride solution, the slurry was stirred for an additional 1 hour. The red slurry was then heated to about 60° C. for 30 min, then cooled immediately in a cold water bath. The slurry was filtered under high vacuum through a 0.8 micron Versapor membrane cloth (obtained from PALL Corp.), then reslurried twice with about 750 mL portions of DIW, and filtered once more. The pH and conductivity of the final wash filtrate was 7.5 and about 208 μ S/cm, respectively. The red pigment filtercake was reslurried in about 600 mL of deionized water and freeze-dried for 48 hours, to afford a dark red-colored powder (12.75 grams). Transmission electron microscopy images of the powder revealed predominantly platelet-like particles with particle diameters ranging from 50-150 nm, and aspect ratios that were equal to or less than about 3:1

Example 4

Preparation of Nano-Sized Particles of Pigment Red 57:1 Using the Two-Step Method

[0093] Into a 250 mL round bottom flask equipped with mechanical stirrer and condenser was charged 10 g of aqueous slurry of Lithol Rubine-Potassium salt dye precursor prepared as in Step 1 of Example 3, except that the solids concentration in the aqueous slurry was about 10.0 wt %. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (1.0 mL) was added, followed by a 0.05 mol/L solution (34.5 mL) containing sodium dioctyl sulfosuccinate dissolved in 90:10 deionized water/THF. No visible change was observed. An aqueous solution of calcium chloride dihydrate (1.0 M solu-

tion, 2.15 mL) was added dropwise by syringe pump to the slurry while stirring vigorously. A red precipitate formed immediately, and then the slurry was stirred at room temperature for an additional 30 min. The red slurry was then filtered under high vacuum through a 0.8 μ m Versapor membrane cloth (obtained from PALL Corp.), then reslurried twice with 50 mL portions of deionized water and filtered each time after reslurrying. The pH and conductivity of the final wash filtrate was 7.5 and about 135 μ S/cm, respectively, indicating that residual acids and salt by-products were removed. The red pigment filtercake was reslurried in about 30 mL of deionized water and freeze-dried for 48 hours to afford a dark red colored powder (1.32 grams). Transmission electron microscopy images of the powder revealed very small platelet-like particles with particle diameters ranging from 50-175 nm, and aspect ratios were equal to or less than about 3:1. ¹H-NMR spectroscopy analysis (300 MHz, DMSO-d₆) of the material indicated that the pigment adopted the hydrazone tautomer form, and that the dioctyl sulfosuccinate stabilizer compound was present at a level ranging from approximately 50-75 mol %.

Example 5

Preparation of Fine and Nano-Sized Particles of Pigment Red 57:1 Using the Two-Step Method

[0094] Into a 500 mL round bottom flask equipped with mechanical stirrer and condenser was charged 126 g of aqueous slurry of Lithol Rubine-Potassium salt dye precursor (prepared as in Step 1 of Example 1) having about 1.6% wt solids content. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (4.0 mL) was added, followed by a solution containing sodium dioctyl sulfosuccinate (1.92 g) dissolved in 100 mL of 90:10 deionized water/THF mixture. No visible change was observed. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 13 mL) was added dropwise to the slurry while stirring vigorously. A red precipitate formed immediately, and after complete addition of the calcium chloride solution, the slurry was stirred for an additional 1 hour. The red slurry was then heated to about 75° C. for 20 min, then cooled to room temp. The slurry was filtered under high vacuum through a 0.45 μ m Nylon membrane cloth, then reslurried twice with 75 mL portions of DIW. The pH and conductivity of the final wash filtrate was 7.75 and conductivity of about 500 μ S/cm. The red pigment filtercake was reslurried in about 250 mL of DIW and freeze-dried for 48 hours to afford a dark red-colored powder (2.73 grams). Transmission electron microscopy images of the powder showed a distribution of particle sizes, with diameter ranging from 50 to 400 nm and having particle morphologies that were predominantly platelets.

Example 6

Preparation of Fine and Nanosized Particles of Pigment Red 57:1 Using a Two-Step Method

[0095] The sterically bulky stabilizer compound used was potassium salt of 2-hexyldecanoic acid, prepared by treatment of 2-hexyldecanoic acid with potassium hydroxide dissolved in THF, after which the THF solvent was removed. Into a 500-mL round-bottom flask equipped with condenser and mechanical stirrer was charged 126 g of aqueous slurry of

Lithol Rubine-Potassium salt (prepared as in Step 1 of Example 1) having about 1.6% wt solids content. The pH of the slurry was adjusted to at least 9.0 or higher by addition of 0.5 M KOH solution, after which the dyestuff was fully dissolved. An aqueous solution 5 wt % Dresinate X (4.0 mL) was added, followed by a solution containing potassium 2-hexyldecanoate (1.28 g) dissolved in 100 mL of 80:20 deionized water/THF mixture, added dropwise while stirring vigorously. An aqueous solution of calcium chloride dihydrate (0.5 M solution, 13 mL) was added to the slurry while stirring vigorously causing a bluish-red pigment precipitate to form. The slurry was stirred for 1 hour, heated to about 75° C. for 20 min, then cooled to room temperature. The slurry was filtered under high vacuum through a 0.8 µm Nylon membrane cloth, then reslurried once with 150 mL of DIW and filtered again. The pH and conductivity of the final wash filtrate was pH 8.38 and conductivity of about 63 µS/cm. The red pigment 57:1 filtercake was reslurried into about 150 mL of DIW and freeze-dried for 48 hours to afford a red powder (2.95 grams). TEM micrograph images showed a distribution of particle sizes, with diameters ranging from 50 to about 400 nm and having particle morphologies that included platelets as well as rods.

Example 7

Synthesis of Nano-Sized Particles of Pigment Red 57:1 by a One-Step Procedure

[0096] Diazotization Mixture: Into a 100 mL round bottom flask equipped with a mechanical stirrer, thermometer, and addition funnel was added 2-amino-5-methylbenzenesulfonic acid (4.4 g), deionized water (45 mL) and concentrated ammonia (30 wt %; 3.0 g). The resulting light brown solution was cooled to -2° C. An aqueous solution of sodium nitrite (NaNO₂; 1.64 g dissolved into 6 mL water) was added slowly to the first solution while maintaining the temperature below 3° C. To the reddish-brown homogeneous mixture was added dropwise concentrated HCl (7.2 g) so as to maintain the internal temperature below 2° C. The mixture formed a pale brown suspension, and following complete addition of conc. HCl, the suspension was stirred an additional 30 min. A solution of calcium chloride dehydrate (5.20 g) dissolved into deionized water (10 mL) was added to the diazo suspension

[0097] Coupling Mixture: In a separate 500 mL flask equipped with high-speed mechanical stirrer, thermometer and dropping funnel was added 3-hydroxy-2-naphthoic acid (4.60 g), deionized water (120 mL), and concentrated ammonia (30 wt %, 3.0 g). After stirring to dissolution, an aqueous solution of 5 wt % Dresinate-X rosin soap surfactant (20 mL) was added, followed with a prepared solution containing sodium dioctyl sulfosuccinate (5.25 g) dissolved in 56 mL of 90:10 deionized water/THF mixture.

[0098] The cold suspension of the diazonium salt suspension was then added slowly to the coupling solution under vigorous mixing. The color changed immediately to a dark red solution, and ultimately to a bluish-red slurry of precipitated pigment particles. The mixture was heated at 50° C. for 15 minutes, then cooled to room temperature. The slurry was filtered under high vacuum through a 0.8 µm acrylic membrane cloth, then reslurried once with 400 mL of DIW and filtered again. The red pigment 57:1 filtercake was reslurried into about 200 mL of DIW and freeze-dried for 48 hours to afford a red powder (8.73 grams). TEM micrograph images showed a distribution of particles with diameters ranging

from 50 to 300 nm, the majority of which were less than 200 nm in diameter, and having particle morphologies that were generally platelets, and having aspect ratio that were equal to or less than about 3:1.

Examples of Liquid Dispersions Containing Nano-Sized Pigments and Color Properties

Example 8

Preparation of Liquid Dispersions and of Polymer Coatings

[0099] A series of liquid, non-aqueous dispersions were prepared using a polymeric dispersant and the nano-sized PR 57:1 pigments from Examples 1, 2,3,4,5 and 6; the larger-sized pigment particles prepared as described in the Comparative Example 1; as well as two commercial sources of PR 57:1 obtained from Clariant (lot #L7B01) and Aakash. Coatings on clear Mylar film were prepared from these liquid dispersions, and evaluated in the following manner: Into a 30 mL amber bottle was added 0.22 g of pigment, 0.094 g polyvinylbutyral (B30HH obtained from Hoescht), 7.13 g n-butyl acetate (glass-distilled grade, obtained from Caledon Laboratories) and 70.0 g of 1/8" stainless steel shot (Grade 25 440C obtained from Hoover Precision Products). The bottles were transferred to a jar mill and were allowed to gently mill for 4 days at 100 RPM. Two draw-down coatings were obtained for each dispersion using an 8-path gap on clear Mylar film such that the wet thicknesses for each coating comprised of PR 57:1 pigment sample were 0.5 and 1 mil. The air-dried coatings on clear Mylar film were then dried in a horizontal forced-air oven at 100° C. for 20 minutes.

Example 9

Evaluation of Coatings Prepared from Liquid Pigment Dispersions

[0100] The coatings on clear Mylar film prepared as described in Example 7 were assessed for coloristic and light scattering properties in the following manner: The UV/VIS/NIR transmittance spectra of each coating were obtained using a Shimadzu UV160 spectrophotometer, and the results showed dramatically reduced light scattering and remarkable specular reflectivity for the nano-sized PR 57:1 pigment samples described herein, compared with the spectra of coatings prepared with commercial PR 57:1 pigment samples obtained from Clariant and Aakash. The degree of light scattering in a coating is dependent on both the size and shape distributions of the pigment particles and their relative dispersability within the coating matrix, and the Normalized Light Scatter Index (NLSI) method was developed to be a measure of this characteristic for the pigmented coatings. NLSI is quantified by first measuring the spectral absorbance of the coating in a region where there is no absorbance from the chromogen of the monoazo laked pigment (for PR 57:1, a suitable region is 700-900 nm), but only absorbance due to light scattered from large aggregates and/or agglomerated pigment particles dispersed in the coating binder. The Normalized Light Scatter Index (NLSI) is then obtained by normalizing each of the samples' light scattering indices (from 700 to 900 nm) to a lambda-max optical density=1.5. In this way, the degree of light scattering for each pigmented coating could be compared directly against each other. The lower the NLSI value, the smaller the inferred particle size of the dispersed pigment in the coating. A relationship between

decreasing average particle size and decreasing NLSI value was found to exist with the coatings prepared from the example pigments shown in Table 8. In particular, the nano-sized monoazo laked pigment PR 57:1 of Example 3 had by far the lowest degree of light scattering, with an NLSI value of 0.3. The coloristic properties of the Mylar coatings were determined using an X-RITE 938 spectrodensitometer. $L^*a^*b^*$ and optical density (O.D.) values were obtained for each of the samples, and the $L^*a^*b^*$ were normalized to an optical density of 1.5, and used to calculate the hue angle and chroma (c^*), as listed in Table 8.

systems or applications. Also that various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims.

1. A process for preparing nanoscale particles of monoazo laked pigments, comprising:

providing an organic pigment precursor to a monoazo laked pigment that contains at least one functional moiety,

TABLE 8

Metric	Normalized Light Scatter Indices (NLSI) and Coloristic properties of example PR 57:1 pigments, normalized to O.D. = 1.5								
	Clariant L7B01	Aakash PR57:1	Comparative Example 1	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
L^*	47.9	48.0	44.8	50.8	50.6	51.7	53.0	49.9	49.6
a^*	71.1	71.2	71.5	76.5	77.2	79.4	78.8	76.7	73.6
b^*	8.7	17.5	34.8	-16.4	-17.4	-18.8	-15.0	-18.9	1.4
Hue Angle (°)	6.6	13.8	28.1	347.9	347.1	346.6	349.2	346.1	0.9
C^*	72.6	73.4	78.1	78.6	77.5	81.3	80.5	78.9	73.9
Normalized Light Scatter Index	5.5	9.9	74.1	0.3	1.3	1.0	0.7	0.9	4.8

Example 10

b^*a^* Coloristic Properties of Coatings Prepared from Liquid Pigment Dispersions

[0101] The graphs in FIGS. 1 and 2 visually illustrate the significant shifts in b^*a^* gamut observed with coatings prepared with the nano-sized PR 57:1 pigments from Examples 1, 2, 3, 4 and 5, in addition to the extended c^* chroma for the nano-sized pigment examples. Furthermore, the graph in FIG. 1 shows a clear blue-shifting of hue that directly corresponds to decreasing particle size/particle diameters of the example PR 57:1 pigments, a relationship which is also inferred from the Normalized Light Scatter Index (NLSI) values of Table 8. (Note: For ease of generating the graph, the b^* vertical axis shows "negative" hue angles, which represent the number of degrees < 360 degrees.) The light scattering and coloristic data accumulated provide evidence for the ability to tune color properties and specular reflectivity of pigmented coatings with tunable particle size of surface-enhanced fine particles of monoazo laked red pigments, in particular Pigment Red 57:1. This is achieved by using the methods of making such nano-sized pigments of PR 57:1 as described herein, in particular using the two-step process which uses sterically bulky stabilizer compounds to limit particle aggregation and thereby limit particle size as well as enhance dispersion and color characteristics of the nano-sized pigment particles. Furthermore, the ability to easily tune color properties of such monoazo laked pigments provides a means to control the color quality so that inexpensive azo laked pigments like PR 57:1 can be used to obtain magenta color that are normally exhibited by higher cost red pigments, such as the quinacridone-type Pigment Red 122 and Pigment Red 202.

[0102] It will be appreciated that various of the above-disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different

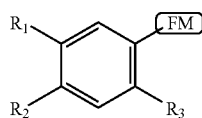
providing a sterically bulky stabilizer compound that contains at least one functional group, and carrying out a chemical reaction to form a monoazo laked pigment composition, whereby the functional moiety found on the pigment precursor is incorporated within the monoazo laked pigment and non-covalently associated with the functional group of the stabilizer, so as to allow the formation of nanoscale-sized pigment particles.

2. The process of claim 1, wherein the nanoscale-sized pigment particles have an average particle diameter as derived from transmission electron microscopy imaging, of less than about 150 nm.

3. The process of claim 1, wherein the at least one functional moiety of the organic monoazo laked pigment is selected from the group consisting of sulfonate/sulfonic acid, (thio)carboxylate/(thio)carboxylic acid, phosphonate/phosphonic acid, ammonium and substituted ammonium salts, phosphonium and substituted phosphonium salts, substituted carbonium salts, substituted arylum salts, alkyl/aryl (thio) carboxylate esters, thiol esters, primary and secondary amides, primary and secondary amines, hydroxyl, ketone, aldehyde, oxime, hydroxylamino, enamines, porphyrins, (phthalocyanines, urethane, carbamate, substituted ureas, guanidines and guanidinium salts, pyridine and pyridinium salts, imidazolium and (benz)imidazolium salts, (benz)imidazolones, pyrrole, pyrimidine and pyrimidinium salts, pyridinone, piperidine and piperidinium salts, piperazine and piperazinium salts, triazolo, tetraazolo, oxazole, oxazolines and oxazolinium salts, indoles, indenones, and mixtures thereof.

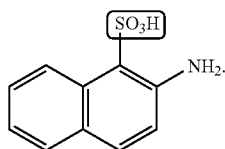
4. The process of claim 1, wherein the organic monoazo laked pigment comprises a diazonium component linked to a coupling component through an azo or hydrazone group, with a counterion.

5. The process of claim 4, wherein a precursor to the diazonium component of the monoazo laked pigment is a compound of Formula (2):



Formula (2)

where R_1 , R_2 , and R_3 independently represent H, a straight or branched alkyl group of from about 1 to about 10 carbon atoms, halogen, NH_2 , NO_2 , CO_2H , or CH_2CH_3 ; and FM represents SO_3H , $-C(=O)-NH-Aryl-SO_3^-$ (where the aryl group can be unsubstituted or substituted with either halogens or alkyl groups having from about 1 to about 10 carbons), CO_2H , halogen, NH_2 , or $-C(=O)-NH_2$, or is a compound of Formula (3):

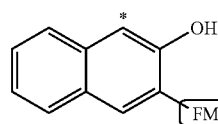


6. The process of claim 5, wherein a precursor to the diazonium component is selected from the group consisting of the following compounds of Formula (2) wherein:

- FM is SO_3H , R_1 is CH_3 , R_2 is H, and R_3 is NH_2 ,
- FM is SO_3H , R_1 is CH_3 , R_2 is Cl, and R_3 is NH_2 ,
- FM is SO_3H , R_1 is Cl, R_2 is CH_3 , and R_3 is NH_2 ,
- FM is SO_3H , R_1 is Cl, R_2 is CO_2H , and R_3 is NH_2 ,
- FM is SO_3H , R_1 is Cl, R_2 is CH_2CH_3 , and R_3 is NH_2 ,
- FM is SO_3H , R_1 is Cl, R_2 is Cl, and R_3 is NH_2 ,
- FM is SO_3H , R_1 is H, R_2 is NH_2 , and R_3 is H,
- FM is SO_3H , R_1 is H, R_2 is NH_2 , and R_3 is CH_3 ,
- FM is SO_3H , R_1 is NH_2 , R_2 is H, and R_3 is Cl,
- FM is SO_3H , R_1 is H, R_2 is H, and R_3 is NH_2 ,
- FM is SO_3H , R_1 is H, R_2 is NH_2 , and R_3 is H,
- FM is SO_3H , R_1 is NO_2 , R_2 is NH_2 , and R_3 is H,
- FM is $-C(=O)-NH-Phenyl-SO_3-$, R_1 is NH_2 , R_2 is CH_3 , and R_3 is H,
- FM is CO_2H , R_1 is H, R_2 is H, and R_3 is NH_2 ,
- FM is Cl, R_1 is H, R_2 is H, and R_3 is NH_2 ,
- FM is NH_2 , R_1 is CH_3 , R_2 is H, and R_3 is H,
- FM is NH_2 , R_1 is H, R_2 is CH_3 , and R_3 is H,
- FM is $-C(=O)NH_2$, R_1 is NH_2 , R_2 is CH_3 , and R_3 is H,
- FM is $-C(=O)NH_2$, R_1 is H, R_2 is NH_2 , and R_3 is H,
- FM is NH_2 , R_1 is H, R_2 is H, and R_3 is H.

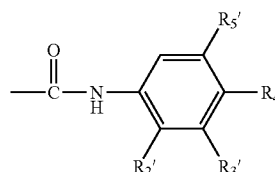
7. The process of claim 4, wherein a precursor to the coupling component of the monoazo laked pigment is selected from the group consisting of β -naphthol and derivatives thereof, naphthalene sulfonic acid derivatives, pyrazolone derivatives, and acetoacetic arylide derivatives.

8. The process of claim 4, wherein a precursor to the coupling component is selected from the group consisting of compounds of Formulas (4)-(8), wherein * denotes a point of coupling or attachment to the azo or hydrazone group:

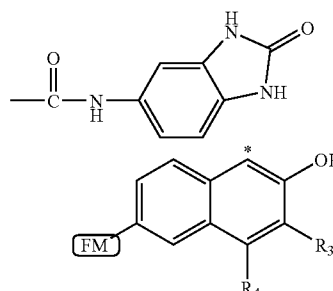


Formula (4)

where FM represents H, CO_2H , SO_3H , $-C(=O)-NH-Aryl-SO_3^-$ where the aryl group can be unsubstituted or substituted with either halogens, or alkyl groups having from about 1 to about 10 carbons, CO_2H , halogen, NH_2 , $-C(=O)-NH_2$, substituted benzamides of the formula:

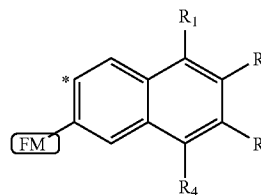


wherein groups R_2' , R_3' , R_4' and R_5' can independently be H, alkyl groups having from about 1 to 10 carbons, alkoxy groups, hydroxyl or halogens, or NO_2 ; or benzimidazolone amides of the formula:



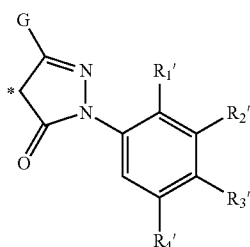
Formula (5)

where FM represents SO_3H , CO_2H , $-C(=O)-NH-Aryl-SO_3^-$ where the aryl group can be unsubstituted or substituted with either halogens, or alkyl groups having from about 1 to about 10 carbons, CO_2H , halogens, NH_2 , $-C(=O)-NH_2$ groups R_3 and R_4 independently represent H, SO_3H ;



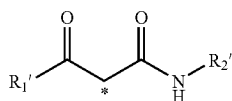
Formula (6)

where FM represents SO_3H , CO_2H , $-C(=O)-NH-Aryl-SO_3^-$ where the aryl group can be unsubstituted or substituted with either halogens, or alkyl groups having from about 1 to about 10 carbons, CO_2H , halogens, NH_2 , $-C(=O)-NH_2$; R_1 , R_2 , R_3 and R_4 independently represent H, SO_3H , $-C(=O)-NH-Phenyl$,



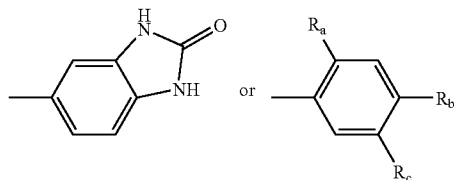
Formula (7)

where G represents CO₂H, straight or branched alkyl having from 1 to about 10 carbon atoms; and R₁', R₂', R₃' and R₄' independently represent H, halogens, SO₃H, NO₂ or alkoxy groups;



Formula (8)

where R₁' represents a straight or branched alkyl group having from 1 to about 10 carbon atoms, R₂' represents



where each of R_a, R_b, and R_c independently represents H, a straight or branched alkyl group having from 1 to about 10 carbon atoms, OCH₃, or halogens.

9. The process of claim 4, wherein the counterion is selected from the group consisting of metals, non-metals, and cations or anions based on either carbon, nitrogen or phosphorus.

10. The process of claim 1, wherein the at least one functional group of the sterically bulky stabilizer is selected from the group consisting of sulfonate/sulfonic acid, (thio)carboxylate/(thio)carboxylic acid, phosphonate/phosphonic acid, ammonium and substituted ammonium salts, phosphonium and substituted phosphonium salts, substituted carbonium salts, substituted arylum salts, alkyl/aryl (thio)carboxylate esters, thiol esters, primary and secondary amides, primary and secondary amines, hydroxyl, ketone, aldehyde, oxime, hydroxylamino, enamines, porphyrins, (phthalocyanines, urethane, carbamate, substituted ureas, guanidines and guanidinium salts, pyridine and pyridinium salts, imidazolium and (benz)imidazolium salts, (benz)imidazolones, pyrrole, pyrimidine and pyrimidinium salts, pyridinone, piperidine and piperidinium salts, piperazine and piperazinium salts, triazolo, tetraazolo, oxazole, oxazolines and oxazolium salts, indoles, indenones, and mixtures thereof.

11. The process of claim 1, wherein the sterically bulky stabilizer comprises at least one aliphatic hydrocarbon moiety.

12. (canceled)

13. The process of claim 1, further comprising adding a surfactant selected from the group consisting of rosin compounds; acrylic-based polymers; styrene-based copolymers; copolymers of α -olefins; copolymers of vinyl pyridine, vinyl imidazole, and vinyl pyrrolidinone; polyester copolymers; polyamide copolymers; and copolymers of acetals and acetates.

14. The process of claim 1, wherein the non-covalent association between the organic monoazo laked pigment and the sterically bulky stabilizer compound is at least one of van der Waals' forces, ionic bonding, coordination bonding, hydrogen bonding, and aromatic pi-stacking bonding.

15. The process of claim 1, wherein presence of the associated stabilizer limits an extent of particle growth and aggregation, to afford nanoscale-sized particles of monoazo laked pigments.

16. The process of claim 1, wherein the nanoscale-sized pigment particles have coloristic properties that are changeable as a function of particle size of the nanoscale-sized pigment particles.

17. The process of claim 1, comprising:

preparing a first reaction mixture comprising: (a) a diazonium salt having at least one functional moiety as a first precursor to the laked pigment and (b) a liquid medium containing diazotizing agents; and

preparing a second reaction mixture comprising: (a) a coupling agent having at least one functional moiety as a second precursor to the laked pigment and (b) a sterically bulky stabilizer compound having one or more functional groups that associate non-covalently with the coupling agent; and (c) a liquid medium

combining the first reaction mixture into the second reaction mixture to form a solution and

effecting a direct coupling reaction which forms a monoazo laked pigment composition wherein the functional moiety associates non-covalently with the functional group and having nanoscale particle size.

18. The process of claim 17, wherein the second reaction mixture further comprises one or more additives selected from the group consisting of inorganic and organic buffers, alkaline bases, and acids.

19. The process of claim 17, wherein the combining is conducted at ambient temperature with stirring.

20. The process of claim 1, comprising:

providing a monoazo precursor dye to the monoazo laked pigment that has at least one functional moiety;

subjecting the monoazo precursor dye to an ion exchange reaction with a metal cation salt in the presence of a sterically bulky stabilizer compound having one or more functional groups; and

precipitating the monoazo laked pigment as nanoscale particles, wherein the functional moiety of the pigment associates non-covalently with the functional group of the stabilizer and having nanoscale particle size.

21. A process for preparing nanoscale-sized monoazo laked pigment particles, comprising:

preparing a first reaction mixture comprising: (a) a diazonium salt having at least one functional moiety as a first precursor to the laked pigment and (b) a liquid medium containing diazotizing agents; and

preparing a second reaction mixture comprising: (a) a coupling agent having at least one functional moiety as a second precursor to the laked pigment and (b) a sterically bulky stabilizer compound having one or more functional groups that associate non-covalently with the coupling agent; and (c) a liquid medium

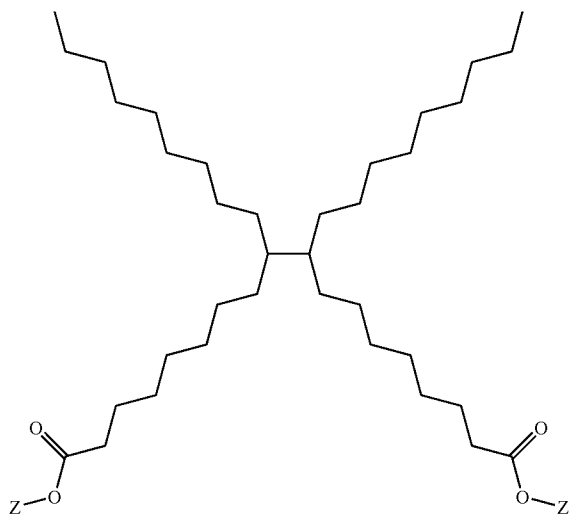
cally bulky stabilizer compound having one or more functional groups that associate non-covalently with the coupling agent; and (c) a liquid medium combining the first reaction mixture into the second reaction mixture to form a solution and effecting a direct coupling reaction which forms a monoazo laked pigment composition having nanoscale particle size, and wherein a functional moiety of the pigment associates non-covalently with the functional group of the stabilizer.

22. A process for preparing nanoscale monoazo laked pigment particles, comprising:

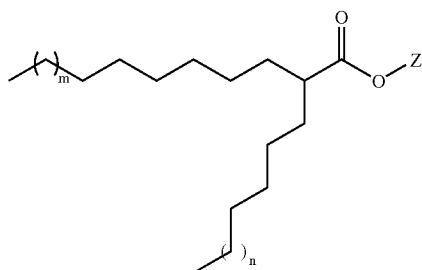
providing a monoazo precursor dye to the monoazo laked pigment that has at least one functional moiety; subjecting the monoazo precursor dye to an ion exchange reaction with a cation in the presence of a sterically bulky stabilizer compound having one or more functional groups; and

precipitating the monoazo laked pigment having nanoscale particle size, wherein the functional moiety of the pigment associates non-covalently with the functional group of sterically bulky stabilizer compound.

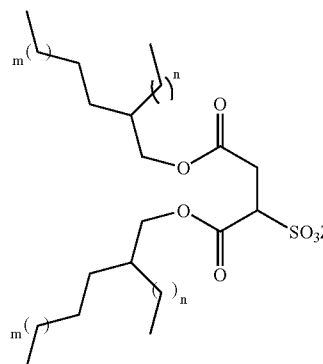
23. The process of claim 1, wherein the sterically bulky stabilizer is selected from the group consisting of the following compounds:



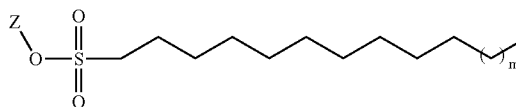
wherein Z is H, a metal cation, or an organic cation;



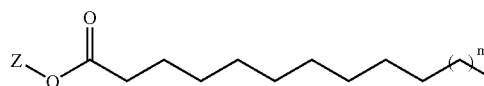
wherein Z is H, a metal cation, or an organic cation, and $m+n>1$;



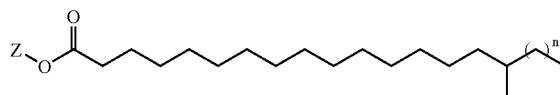
wherein Z is H, a metal cation, or an organic cation, and $m+n>1$ per branch;



wherein Z is H, a metal cation, or an organic cation, and $m \geq 1$;



wherein Z is H, a metal cation, or an organic cation, and $m \geq 1$; and



wherein Z is H, a metal cation, or an organic cation, and $n \leq 1$.

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