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(54) **Title**: LASER REACTIVE WATER-BASED INKS MANUFACTURED FROM WATER-BASED MASTERBATCH CONCENTRATES

(57) **Abstract**: The present invention relates to the formulation of a water-based masterbatch concentrate for the manufacture of coating and ink compositions for laser imaging substrates, particularly substrates typically used in the packaging industry, including flexible substrates. The masterbatch can be simply mixed with different water-based technical varnishes in order to obtain laser-reactive finished inks with the final physical properties as required.

LASER REACTIVE WATER-BASED INKS MANUFACTURED FROM WATER-BASED MASTERBATCH CONCENTRATES

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/047,110, filed September 8, 2014, which is hereby incorporated herein in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to the formulation of a water-based masterbatch concentrate for the manufacture of coating and ink compositions for laser imaging substrates, particularly substrates typically used in the packaging industry, including flexible substrates. The masterbatch can be simply mixed with different water-based technical varnishes in order to obtain laser-reactive finished inks with the final physical properties as required.

BACKGROUND OF THE INVENTION

[0003] Substrates produced on production lines, especially for the packaging industry of which paper, board, and polymeric films are examples, are usually marked with information such as logos, bar codes, expiration dates, and batch numbers.

[0004] Traditionally, the marking of these substrates has been achieved by various printing techniques, for example ink-jet and thermal transfer printing.

[0005] These printing techniques are being replaced more and more by laser marking, as this method of marking is cheaper in terms of overall economics, and also shows performance benefits such as high speed and contact free marking. Different logos, dates, and batch numbers can be easily and readily changed when required.

[0006] The substrates to be marked typically have laser markable patches to be imaged. When clear polymeric filmic substrates are to be imaged, these patches can be imaged either from the top surface or through the film.

[0007] Laser markable patches can be formed by printing of an area with an ink or coating containing a pigment that changes color when exposed to a laser beam (color changing pigments). Color changing pigments include dyes known as leuco dyes. These color changing pigments, particularly leuco dyes, are generally not stably dispersed in water-based systems, and can be included in the ink or coating composition only in low concentrations. Therefore, only finished ink or coating compositions, ready for printing, have generally been available. Thus, it has been necessary to buy and/or store separate compositions specific to each print job (i.e. for each type of printing method on different substrates).

[0008] WO 2013/192307 discloses solvent-based laser-reactive masterbatch concentrates. The laser-reactive masterbatch concentrate comprises one or more laser-reactive pigment systems; one or more solvents wherein at least one is a linear high chain alcohol with at least 3 carbon atoms; and one or more resins.

[0009] US 2012/0045624 describes laser-sensitive aqueous compositions comprising a color former, a developer, and a binder. The color former generally comprises an electron donating leuco dye and an electron accepting developer. Compositions may contain latent activator which can be either an acid derivative or a salt of an acid and an amine.

[00010] US 2011/0065576 discloses laser-sensitive coating compositions comprising titanium dioxide in the anatase form, or polymeric particles comprising a polymeric matrix comprising one or more water-insoluble polymers of titanium dioxide in the anatase form encapsulated in the polymeric matrix; and a polymeric binder. Compositions may include additional components such as IR absorbers, catalysts, pigments, etc.

[00011] US 2010/0233447 discloses polymeric particles comprising a polymeric matrix comprising one or more water-insoluble polymers and a laser-sensitive system

encapsulated in the polymeric matrix. Also described is the use of the polymeric particles in ink compositions.

[00012] US 8,105,506 describes coating compositions comprising an oxyanion of a multivalent metal, for example ammonium octamolybdate (AOM), a binder which is typically polymeric, and a solvent such as water or ethanol, and a conductive polymer that absorbs infrared (IR) radiation. Also listed is the addition of a color former and electron-donating dye precursor. Numerous separate individual formulations are listed.

[00013] US 5,413,629 discloses a method for marking information on a thermosensitive marking material by laser marking. A thermosensitive color forming layer is formed by printing with a printing ink containing a leuco dye as a color former, and an acidic substance as a color developer.

[00014] US 8,101,545 describes coating compositions comprising a color former, an amine salt of an organic metal compound, a binder, a solvent, and optional additional components. Several specific amine salts of silicon and boron are described.

[00015] US 8,101,544 describes coating compositions for making substrates comprising a color former, a metal salt of a carboxylic acid, a binder, and an organic solvent. Many individual binders are described as separate examples.

[00016] US 7,485,403 and US 8,048,605 disclose a laser markable coating composition comprising a binder and an oxyanion of a multivalent metal, such as ammonium octamolybdate (AOM). Coatings can be effectively imaged using a CO_2 laser, undergoing a color change upon exposure.

[00017] US 8,048,608 describes the use of reduced Indium Tin Oxide (r-ITO) in AOM based ink formulations. The r-ITO is a non-stoichiometric compound; the ITO being reduced bestows near-infrared (NIR) absorption properties. Individual ink formulations which are fiber laser reactive are listed.

[00018] US 7,270,919 discloses imageable coatings comprising an aqueous solution or dispersion, or a solution in an organic solvent, of amines of transition metal compounds, which change color when subjected to a laser. The coatings also contain a thermoplastic polymer or a photopolymerizable monomer.

[00019] WO 2005/012442 describes a laser-markable composition comprising a pigment, a solvent, and a conductive polymer. Amine molybdates are used as color developers, with color formers (e.g. color changing pigments).

[00020] US 8,083,973 discloses polychromic compounds that undergo a color change upon irradiation. The polychromic compounds are derivatives of carboxylic acids. Inks are described which contain the polychromic carboxylic acid derivatives and other substances capable of changing color.

[00021] US 8,173,253 describes secondary package labeling applications. One is a tape coated with a laser markable ink composition and a layer of adhesive. Another is a laser-imageable composition being applied as a spray.

[00022] US 8,178,277 describes electromagnetic radiation or thermally sensitive coating compositions for making substrates comprising a compound containing a carbonyl group, and a nucleophile compound; or a compound containing a free carbonyl group that is substituted with one or more nucleophilic groups. Preferred carbonyl compounds are reducing carbohydrates, and preferred nucleophiles are amines.

[00023] EP1560715 (WO 2004/045857) discloses a process for the laser marking of thin, flexible plastic films. A layer or layers of a laser-sensitive material and an ink are printed. The laser-sensitive material and ink may be separate layers, or the laser-sensitive material and ink may be combined in a single layer.

[00024] The creation of a water-based laser-reactive masterbatch concentrate system would be advantageous to end users (i.e. printers, manufacturers, etc.) who can quickly and easily blend a technical varnish with a laser-reactive masterbatch concentrate to produce finished laser-reactive inks and coatings for many different applications. Using one masterbatch concentrate, the end user has the flexibility to choose from a number of different technical varnishes to impart the necessary performance properties (adhesion, resistance, printability, etc.) for a wide range of printing applications.

SUMMARY OF THE INVENTION

[00025] The present invention provides a masterbatch concentrate for laser reactive water-based inks comprising:

a) a thermochromic leuco dye;
b) a blocked/latent acid;
c) an alkali/amine compound; and
d) water;

wherein the masterbatch concentrate can be combined with a technical varnish to form a laser reactive water-based ink.

[00026] The present invention also provides a masterbatch concentrate for laser reactive water-based inks comprising wherein the leuco dye is present in an amount of from about 10 wt% to about 30 wt%; the blocked/latent acid is present in an amount of from about 15 wt% to about 50 wt%; the alkali/amine is present in an amount of 1 wt% to about 10 wt%; and the water is present in an amount of about 15 wt% to about 50 wt%.

[00027] The present invention also provides a method of making a laser masterbatch concentrate comprising combining:

a) a thermochromic leuco dye;
b) a blocked/latent acid;
c) an alkali/amine compound; and
d) water;

wherein the masterbatch concentrate can be combined with a technical varnish to form a laser reactive water-based ink.

[00028] The present invention also provides a thermochromic leuco dye concentrate comprising:

a) 40 wt% to 70 wt% leuco dye;
b) 1 wt% to10 wt% alkali amine; and
c) 15 wt% to 40 wt% water.

[00029] The present invention also provides a blocked/latent acid concentrate comprising:

a) 40 wt% to 70 wt% blocked/latent acid;
b) 1 wt% to 10 wt% alkali amine; and
c) 15 wt% to 40 wt% water.

[00030] The present invention also provides a method of preparing a laser masterbatch concentrate by combining a thermochromic leuco dye concentrate and a blocked/latent acid concentrate.

[00031] The present invention also provides a laser reactive water-based ink comprising a masterbatch concentrate and a technical varnish.

[00032] The present invention also provides a method of making a laser reactive water-based ink comprising blending a masterbatch concentrate with a technical varnish, to form a finished water-based laser reactive ink.

[00033] The present invention also provides a method of making a laser reactive water-based ink, comprising:

a) blending a thermochromic leuco dye concentrate with a technical varnish;
b) blending a blocked/latent acid concentrate with a technical varnish; and
c) combining (a) and (b) to form a laser reactive water-based ink.

[00034] The present invention also provides a printed article comprising a laser reactive water-based ink made from a masterbatch concentrate and a technical varnish.

[00035] Other objects and advantages of the present invention will become apparent from the following description and claims.

DETAILED DESCRIPTION

[00036] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of any subject matter claimed.

[00037] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which the inventions belong. All patents, patent applications, published applications and publications, websites and other published materials referred to throughout the entire disclosure herein, unless noted otherwise, are incorporated by reference in their entirety for any purpose.

DEFINITIONS

[00038] In this application, the use of the singular includes the plural unless specifically stated otherwise. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[00039] In this application, the use of "or" means "and/or" unless stated otherwise.

[00040] As used herein, the terms "comprises" and/or "comprising" specify the presence of the stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Furthermore, to the extent that the terms "includes," "having," "has," "with," "composed," "comprised" or variants

thereof are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term "comprising."

[00041] As used herein, ranges and amounts can be expressed as "about" a particular value or range. "About" is intended to also include the exact amount. Hence "about 5 percent" means "about 5 percent" and also "5 percent." "About" means within typical experimental error for the application or purpose intended.

[00042] Throughout this disclosure, all parts and percentages are by weight (wt% or mass% based on the total weight) and all temperatures are in °C unless otherwise indicated.

[00043] As used herein, the terms "dispersing aid," "dispersant," and "surfactant" are used interchangeably.

[00044] As used herein, "technical varnish" refers to the vehicle used to let down (dilute) the masterbatch concentrate millbase to prepare the finished inks. Technical varnishes generally comprise polymer resins, solvents, oils (such as drying oils), and other additives.

MASTERBATCH CONCENTRATES

[00045] The present invention relates to the formulation of a water-based masterbatch concentrate for the manufacture of coating and ink compositions for laser imaging substrates, particularly substrates typically used in the packaging industry, including flexible substrates. The masterbatch can be simply mixed with different water-based technical varnishes in order to obtain laser-reactive finished inks with the final physical properties as required.

[00046] The masterbatch concentrate can be combined with numerous technical varnishes to obtain coating/ink compositions for laser imaging onto various substrates and end-use applications. One of the main areas of application would be flexible

substrates primarily used in the packaging industry, including polymeric types. A partial list of other substrates includes glass, paper, wood, metallics etc., or any other substrate that could be receptive to laser imaging inks.

[00047] Any suitable technical varnish can be used, and the choice will depend on the end use requirements of the finished laser-reactive ink or coating. For example, varnishes based on any suitable polymer resin can be used. These polymer resins include, but are not limited to acrylic and methacrylic resins, and polyurethane resins. Polymer resins suitable for use in the technical varnishes include, but are not limited to, Induprint 2622, Noncryl 90, Lucidene 605, Joncryl 535, Joncryl 1665, Neorez R650, and Joncryl 8050.

[00048] Inks and coatings made from the masterbatch can be applied by printing techniques commonly used in the flexible packaging industry, for example flexographic and gravure printing. The inks made using the masterbatch concept of the present invention could also be applied using other printing processes (e.g. screen, litho, digital, etc.).

[00049] Laser sensitive inks for CO_2 lasers (9400-10600nm), fiber lasers (1060-1600nm) and YAG (neodymium-doped yttrium aluminum garnet) laser imaging can be produced using the masterbatch route.

[00050] This system can be used either by the ink manufacturer or by ink users (printers) who can mix the 'masterbatch' with the appropriate technical varnish as and when required. When using this masterbatch method of producing finished inks, good mixing, without additional milling, will suffice, as the materials that require milling will be pre-milled during the manufacture of the masterbatch. This gives the user greater versatility when printing onto a variety of substrates, e.g. paper/board and various polymeric films.

[00051] The present invention refers specifically to the formulation of a water-based masterbatch concentrate for the manufacture of coating/ink compositions for laser imaging substrates primarily used in the packaging industry. This masterbatch can be simply mixed with different technical water-based varnishes in order to obtain the final physical properties as required. This masterbatch concentrate enables certain water-based inks to be used for both paper/board and filmic substrates. The inks are based on leuco dye/blocked acid technology, for laser imaging.

[00052] The masterbatches can contain either of the combinations – leuco dye or blocked/latent acid alone, or a mixture/combination of leuco dye and blocked/latent acid. For example, a leuco dye concentrate masterbatch can be prepared, and a separate blocked/latent acid concentrate masterbatch can be prepared. Each of these separate masterbatches will be incorporated into the finished laser-reactive. Alternatively, a single masterbatch, containing both the leuco dye and blocked/latent acid can be prepared. The single masterbatch would then be used to prepare the finished laser-reactive ink.

[00053] If a white ink is required, a white masterbatch can also be added to form a white laser imaging ink.

[00054] The milled masterbatch can be added, by simple mixing, to various technical varnishes either at the ink user (printer) or ink manufacturer.

[00055] As previously described, prior laser-sensitive coatings/inks are generally based on individual specific formulations. The systems described are based on a color former/leuco dye and the salt of a carboxylic acid. All these change color when subjected to the relevant lasers.

[00056] All the systems described change color when irradiated with a CO_2 laser, while only the systems incorporating an IR absorber change color with a fiber laser.

[00057] Typical pigments/systems used comprise a blocked/latent acid (e.g. carboxylic acid salt) or color developer, leuco dye, and, optionally, an infrared heat absorber (for any laser require an infrared absorbing component, e.g. fiber lasers, YAG lasers, etc.).

[00058] Examples of leucodye materials are described and listed in various publications, and can be incorporated herein to produce masterbatches. Such systems include those described in patents US 2012/0045624; US 8,101,545; and US 8,101,544, but are not only limited to these.

[00059] The color former (leuco dye) can be any suitable color former, including, but not limited to, xanthene leuco dyes, thioxanthene leuco dyes, acridine leuco dyes, phenoxazine leuco dyes, phenazine leuco dyes, merocyanine leuco dyes, thiazine leuco dyes, oxazine leuco dyes, azine leuco dyes, methine leuco dyes, azo leuco dyes, pyrazoline leuco dyes, stilbene leuco dyes, coumarin leuco dyes, triarylmethane leuco dyes, spiropyran leuco dyes, phthalide leuco dyes, fluoran leuco dyes, acylleucoazine dyes, leucoauramine dyes, rhodaminelactam leuco dyes, chromene leuco dyes, quinine leuco dyes, aminohydrocinnamic acid leuco dyes, 2-(*p*-hydroxyphenyl)-4,5-diphenylimidazole leuco dyes, indanone leuco dyes, indamine leuco dyes, hydrozine leuco dyes, indigoid leuco dyes, amino-2,3-dihydroanthraquinone leuco dyes, tetrahalo-*p,p'*-biphenol leuco dyes, phenethylaniline leuco dyes, and mixtures thereof.

[00060] Suitable leuco dyes include, but are not limited to, 2-phenylamino-3-methyl-6-diethylaminofluorane (WinCon-1), 3-di-*n*-butylamino-6-methyl-7-phenylaminofluorane (WinCon-2), 2-(2',4'-dimethyl phenylamino-3-methyl-6-diethylaminofluorane) (WinCon-15), 3-(*N*-ethyl-*N*-isopentylamino)-6-methyl-7-anilinofluorane (WinCon-205), 2-di(phenylmethyl)amine-6'- diethylaminospiro(isobenzofuran)- 1-(3*H*), 9'-[9*H*] xanthen-3-one (WinCon-Green), 3-diethylaminobenzofluorane (WinCon-R3), 7- (4-(diethylamino)-2-ethoxyphenyl)-7-(1-ethyl-2-methyl-1*H*-indol-3-yl)furo(3,4-*b*)pyridin-5(7*H*)-one (WinCon-Blue 63), and 3,3-bis(*p*-(dimethylamino)phenyl)-6-(dimethylamino)phthalide (Crystal Violet Lactone), all available from Connect Chemicals; and 6-dimethylamino-3,3-bis(4-dimethylaminophenyl)-2-benzofuran-1-one-

6-dimethylamino-3,3-bis(4-dimethylaminophenyl)phthalide (Pergascript Blue I 2R), 3,3'-bis(1-*n*-octyl-2-methylindol-3-yl)phthalide (Pergascript Red 16), 2-anilino-3-methyl-6-(di-*n*-butylamino)fluoran (Pergascript Black 2C), and 2-anilino-3-methyl-6-diethylaminofluoran (Pergascript Black 1C), all from BASF; and 2'-anilino-6'-[ethyl(*p*-tolyl)amino]-3'- methylspiro[isobenzofuran-1(3*H*),9'-[9*H*]xanthene]-3-one; and combinations thereof.

[00061] The leuco dye is present in the masterbatch concentrate in an amount of from about 10 wt% to about 30 wt%. In certain embodiments, the leuco dye is present in the masterbatch concentrate in an amount of from about 10 wt% to about 20 wt%; or 12 wt% to about 28 wt%; or from about 15 wt% to about 25 wt%; or from about 18 wt% to about 23 wt%; or from about 19 wt% to about 22 wt%. For example, the leuco dye may be present in an amount of from 10 wt5 to about 20 wt%; or from about 10 wt% to about 15 wt%; or from about 15 wt% to about 30 wt%; or from about 20 wt% to about 30 wt%.

[00062] Blocked/latent acids that can be used in the masterbatch concentrate include, but are not limited to, a carboxylic acid salt, a sulfonic acid salt, a phosphonic acid salt, and mixtures thereof. Preferably, the blocked/latent acid is a carboxylic acid salt.

[00063] Suitable carboxylic acid salts include, but are not limited to, tri-n-butylammonium borodisalicylate (this component may be formed in situ from an acid and a suitably basic blocking agent as described in US 5,413,629), phenylacetic acid, *p*-tolylacetic acid, mandelic acid, sorbic acid, succinic acid, lactic acid, 4-biphenylacetic acid, and trans-styrylacetic acid.

[00064] Blocked/latent acids are present in the masterbatch in an amount from about 15 wt% to about 50 wt%. In certain embodiments, the blocked/latent acid may be present in the masterbatch in an amount from about 18 wt% to about 45 wt%; or from about 20 wt% to about 40 wt%; or from about 25 wt% to about 35 wt%; or from about 20 wt% to about 30 wt%. For example, the blocked/latent acid may be present in an amount of from about

15 wt% to about 30 wt%; from about 20 wt% to about 40 wt%; or from about 40 wt% to about 50 wt%.

[00065] Suitable infrared radiation/heat (IR) absorbers include, but are not limited to, r-ITO (reduced indium tin oxide); Iriotec 8800 (potassium aluminum silicate) and Iriotec 8825 (mica coated with antimony-doped tin oxide (from Merck); antimony-doped tin oxide pigment (Mark-it available from BASF); mica based metal-oxide layer-substrate pigments (Laserflair pigments available from BASF); copper (II) hydroxyl phosphate (Fabulase 322 available from Budenheim); 3,4-polyethylenedioxythiophene-polystyrenesulfonate; carbon blacks; and a conductive polymer (Baytron P available from HC Starck). When present, IR absorbers are present in the masterbatch in an amount of from about 1wt% to about 15 wt%. In certain embodiments, the IR absorbers are present in the masterbatch in an amount from about 2 wt% to about 12 wt%; or from about 3 wt% to about 10 wt%; or from about 5 wt% to about 8 wt%.

[00066] Preferably, the masterbatch concentrates of the invention contain an alkali/amine compound. Suitable alkali/amine compounds include, but are not limited to, monoethanolamine, ammonia, sodium hydroxide, potassium hydroxide, triethanolamine, amine propyl alcohol, and mixtures thereof.

[00067] The alkali/amine is present in the masterbatch in an amount of from about 1 wt% to about 10 wt%. In certain embodiments, the alkali/amine may be present in an amount of from about 2 wt% to about 8 wt%; or from about 3 wt% to about 6 wt%; or from about 4 wt% to about 5 wt%. For example, the alkali/amine may be present in an amount of from about 1 wt% to about 4 wt%; from about 2 wt% to about 6 wt%; or from about 5 wt% to about 10 wt%.

[00068] The systems are considered to be 'transparent'. However the inks may be colored without any deterioration to the laser image.

[00069] It may be possible to tint the masterbatch or finished inks made from the masterbatch by incorporating traditional colorants. These colorants may be incorporated as color concentrates, flushes, liquid dyes, powders, etc. Colorants and/or white pigment can be added by the addition of a concentrate to obtain the desired color if necessary. Colorants and/or white pigment would preferably be incorporated as either a pre-dispersed concentrate or in a form that can be dispersed into the finished ink by means of mixing, without the need for milling. But it would also be possible to incorporate colorants that require milling by adding them and them subjecting the ink to further milling.

[00070] Suitable colorants include, but are not limited to organic or inorganic pigments and dyes. The dyes include, but are not limited to, azo dyes, anthraquinone dyes, xanthene dyes, azine dyes, combinations thereof and the like. Organic pigments may be one pigment or a combination of pigments, such as for instance Pigment Yellow Numbers 12, 13, 14, 17, 74, 83, 114, 126, 127, 174, 188; Pigment Red Numbers 2, 22, 23, 48:1, 48:2, 52, 52:1, 53, 57:1, 112, 122, 166, 170, 184, 202, 266, 269; Pigment Orange Numbers 5, 16, 34, 36; Pigment Blue Numbers 15, 15:3, 15:4; Pigment Violet Numbers 3, 23, 27; and/or Pigment Green Number 7. Inorganic pigments may be one of the following non-limiting pigments: iron oxides, titanium dioxides, chromium oxides, ferric ammonium ferrocyanides, ferric oxide blacks, Pigment Black Number 7 and/or Pigment White Numbers 6 and 7. Other organic and inorganic pigments and dyes can also be employed, as well as combinations that achieve the colors desired. If used, it is preferred that colorants be incorporated in relatively small amounts (e.g. <10%, more preferably <5%).

[00071] Optical brighteners (UV additives), such as UV fluorescers, can also be added to the masterbatch concentrate. This is useful to show where a transparent laser-reactive finished ink has been printed. Suitable optical brighteners include, but are not limited to, Tinopal NFW, Tinopal SFP, and Uvitex OB (all from BASF); and combinations thereof.

[00072] The addition of a dispersing aid to this system (dispersants and surfactants) can greatly improve the dispersion by reducing the viscosity and improving the flow significantly, which can reduce the milling time. These dispersants and surfactants are well known in printing inks, especially for flexible packaging, offering improved pigment dispersion in liquid organic media. Suitable dispersing aids include, but are not limited to, Disperbyk 190, 199 and 2010 (from Byk); TegoDispers 760W, 755W, and 757W (from Evonik); Orotan 850 and 731 (from Dow); Silcosperse HLD-11 (from Siltech); Edaplan 492 (from Munzing); and combinations thereof. Dispersing aids are typically present in the masterbatch concentrate in an amount of from about 0 wt% to about 5 wt%. For example, the dispersing aid may be present in an amount of from about 1 wt% to about 5 wt%; or from about 1 wt% to about 3 wt%; or from about 1 wt% to about 4 wt%; or from about 2 wt% to about 4 wt%; or from about 3 wt% to about 5 wt%.

[00073] In a preferred embodiment, polyethylene glycols with M_w ranging from 200 to 8,000, more preferably between 200 to 2,000 are selected, as these exhibit good properties as dispersing aids in the manufacture of the masterbatch concentrate. The benefit of these is that they are easier to disperse, there is a greater availability, lower cost, and they are approved by regulatory agencies.

[00074] Binders, such as acrylic resins and polyurethane resins, are typically included in the masterbatch concentrates. Suitable binders include, but are not limited to, Joncryl 671, 674, 678, 682, and 694; Induprint SR10; and NeoRez R650. When present, binders are generally present in an amount of from about 5 wt% to about 30 wt%. In certain embodiments, the binders may be present in the masterbatch in an amount of from about 8 wt% to about 25 wt%; or from about 10 wt% to about 20 wt%; or from about 15 wt% to about 18 wt%. For example, binders may be present in an amount of from about 5 wt% to about 20 wt%; or from about 5 wt% to about 15 wt%; or from about 10 wt% to about 30 wt%.

[00075] Although binders are typically included in the masterbatch concentrate, a masterbatch can also be made without a binder. In this case, the dispersing aid/surfactant

would be used as the milling medium. A masterbatch concentrate without binder resin typically contains from about 10 wt% to about 30 wt% leuco dye; from about 0 wt% to about 3 wt% defoamer; about 35 wt% to about 70 wt% blocked/latent acid; about 30 wt% to about 50 wt% water; and about 5 wt% to about 20 wt% dispersing aid/surfactant.

[00076] Adhesion promoters may be used in either the masterbatch or finished inks made from the masterbatch. Suitable adhesion promoters include, but are not limited to: organic titanates, such as Tyzor LA (from Dorf Ketal); chlorinated polyolefins, such as CP310W, 347W, and 349W, all from Eastman; silanes, such as Addid 900 and 906 from Evonik; zinc oxides; and zirconium proponiates; and combinations thereof. When present, adhesion promoters are present in an amount of from about 0 wt% to about 3 wt%, for example from about 1 wt% to about 2 wt%.

[00077] As with most printing inks, other additives, alone or in combination may be employed, including but not limited to, waxes, ammonia, defoamers, stabilizers, silicones, rheological modifiers, plasticizers and the like. Suitable defoamers include, but are not limited to, Byk 017, Byk 1740, B 094, (from Byk); Fluxair 85 SGR (from Nymco); Tego Foamex 3062, and Tego Foamex 1488 (from Evonik); and combinations thereof. Defoamers are typically present in an amount of from about 0 wt% to about 3 wt%, for example from about 1 wt% to about 2 wt%.

[00078] Water is typically present in the masterbatch concentrate in an amount of from about 15 wt% to about 50 wt%. In certain embodiments, the water may be present in the masterbatch in an amount of from about 18 wt% to about 45 wt%; or from about 20 wt% to about 40 wt%; or from about 25 wt% to about 35 wt%; or from about 20 wt% to about 30 wt%. For example, water may be present in an amount of from about 15 wt% to about 30 wt%; from about 20 wt% to about 40 wt%; or from about 40 wt% to about 50 wt%.

[00079] The masterbatch concentrate can be prepared with the leuco dye and the blocked/latent acid in a single composition, which can then be mixed with the relevant technical varnish. Alternatively, if separate individual masterbatch concentrates are

required of the leuco dye and blocked acid, once these are prepared, they can either be added together before mixing with the relevant technical varnish or added separately. That is, separate leuco dye and blocked/acid concentrates can be prepared, these concentrates mixed to produce a final masterbatch concentrate, and the final masterbatch concentrate blended into an ink or technical varnish, with or without colorant. Alternatively, leuco dye concentrate and the blocked/latent acid concentrate can be blended individually into the ink or technical varnish, with or without colorant.

[00080] In a further embodiment, a masterbatch concentrate could be created by first forming the blocked acid solution component and subsequently adding and mixing in the leuco dye component and the other materials. Conversely, the leuco dye solution component could be formed and subsequently the blocked acid component and other materials could be added and mixed together to form a finished masterbatch concentrate.

[00081] A leuco dye masterbatch concentrate typically contains leuco dye, a binder, an alkali/amine, water, a dispersing aid/surfactant, and a defoamer. Typical amounts of each are given below.

[00082] The leuco dye is generally present in the leuco dye concentrate in an amount of from about 40 wt% to about 70 wt%. In certain embodiments, the leuco dye may present in an amount of from about 35 wt% to about 65 wt%; or from about 30 wt% to about 60 wt%; or from about 40 wt% to about 50 wt%. For example, the leuco dye may be present in an amount of from about 40 wt% to about 60 wt%; or from about 45 wt% to about 70 wt%; or from about 50 wt% to about 65 wt%.

[00083] The binder is generally present in the leuco dye concentrate in an amount of from about 5 wt% to about 30 wt%. In certain embodiments, the binder is present in an amount of from about 8 wt% to about 25 wt%; or from about 10 wt% to about 20 wt%; or from about 15 wt% to about 18 wt%. For example, the binder may be present in an amount of from about 5 wt% to about 25 wt%; or from about 5 wt% to about 20 wt%; or from about 5 wt% to about 15 wt%; or from about 10 wt% to about 20 wt%.

[00084] The alkali/amine is generally present in the leuco dye concentrate in an amount of from about 1 wt% to about 10 wt%. In certain embodiments, the alkali/amine is present in an amount of from about 2 wt% to about 8 wt%; or from about 3 wt% to about 6 wt%; or from about 4 wt% to about 5 wt%. For example, the alkali/amine may be present in an amount of from about 1 wt% to about 8 wt%; or from about 2 wt% to about 10 wt%; or from about 3 wt% to about 6 wt%.

[00085] The water is generally present in the leuco dye concentrate in an amount of from about 15 wt% to about 40 wt%. In certain embodiments, the water is present in an amount of from about 20 wt% to about 35 wt%; or from about 25 wt% to about 30 wt%; or from about 20 wt% to about 25 wt%. For example, the water may be present in an amount of from about 15 wt% to about 30 wt%; or from about 20 wt% to about 40 wt%; or from about 15 wt% to about 25 wt%.

[00086] The dispersing aid/surfactant is generally present in the leuco dye concentrate in an amount of from about 0 wt% to about 5 wt%. In certain embodiments, the dispersing aid/surfactant may be present in an amount of from about 1 wt% to about 4 wt%; or from about 2 wt% to about 3 wt%. For example, the dispersing aid may be present in an amount of from about 1 wt% to about 5 wt%; or from about 2 wt% to about 5 wt%; or from about 2 wt% to about 4 wt%; or from about 3 wt% to about 5 wt%.

[00087] The defoamer is generally present in the leuco dye concentrate in an amount of from about 0 wt% to about 3 wt%. For example, the defoamer may be present in an amount of from about 1 wt% to about 3 wt%; or from about 1.5 wt% to about 3 wt%; or from about 0.5 wt% to about 2 wt%.

[00088] A blocked/latent acid concentrate typically contains a blocked/latent acid, a binder, an alkali/amine, water, a dispersing aid/surfactant, and a defoamer. Typical amounts are given below.

[00089] The blocked/latent acid is generally present in the blocked/latent acid concentrate in an amount of from about 40 wt% to about 70 wt%. In certain embodiments, the blocked/latent acid is present in an amount of from about 35 wt% to about 65 wt%; or from about 30 wt% to about 60 wt%; or from about 40 wt% to about 50 wt%. For example, the blocked/latent acid may be present in an amount of from about 40 wt% to about 60 wt%; or from about 45 wt% to about 70 wt%; or from about 50 wt% to about 65 wt%.

[00090] The binder is generally present in the blocked/latent acid concentrate in an amount of from about 5 wt% to about 30 wt%. In certain embodiments, the binder may be present in an amount of from about 8 wt% to about 25 wt%; or from about 10 wt% to about 20 wt%; or from about 15 wt% to about 18 wt%. For example, the binder may be present in an amount of from about 5 wt% to about 25 wt%; or from about 5 wt% to about 20 wt%; or from about 5 wt% to about 15 wt%; or from about 10 wt% to about 20 wt%.

[00091] The alkali/amine is generally present in the blocked/latent acid concentrate in an amount of from about 1 wt% to about 10 wt%. In certain embodiments, the alkali/amine may be present in an amount of from about 2 wt% to about 8 wt%; or from about 3 wt% to about 6 wt%; or from about 4 wt% to about 5 wt%. For example, the alkali/amine may be present in an amount of from about 1 wt% to about 8 wt%; or from about 2 wt% to about 10 wt%; or from about 3 wt% to about 6 wt%.

[00092] The water is generally present in the blocked/latent acid concentrate in an amount of from about 15 wt% to about 40 wt%. In certain embodiments, the water is present in an amount of from about 20 wt% to about 35 wt%; or from about 25 wt% to about 30 wt%; or from about 20 wt% to about 25 wt%. For example, the water may be present in an amount of from about 15 wt% to about 30 wt%; or from about 20 wt% to about 40 wt%; or from about 15 wt% to about 25 wt%.

[00093] The dispersing aid/surfactant is typically present in the blocked/latent acid concentrate in an amount of from about 0 wt% to about 5 wt%. In certain embodiments, the dispersing aid/surfactant may be present in an amount of from about 1 wt% to about 4 wt%; or from about 2 wt% to about 3 wt%. For example, the dispersing aid may be present in an amount of from about 1 wt% to about 5 wt%; or from about 2 wt% to about 5 wt%; or from about 2 wt% to about 4 wt%; or from about 3 wt% to about 5 wt%.

[00094] The defoamer is typically present in the blocked/latent acid concentrate in an amount of from about 0 wt% to about 3 wt%. For example, the defoamer may be present in an amount of from about 1 wt% to about 3 wt%; or from about 1.5 wt% to about 3 wt%; or from about 0.5 wt% to about 2 wt%.

[00095] When separate leuco dye concentrate and blocked/latent acid concentrates are used, they are typically mixed in a ratio of leuco dye:blocked/latent acid of 1:99 to 99:1. The ratio is dependent on the end use requirements.

[00096] The raw materials in the masterbatch concentrate formulation are mixed using a high shear mixer (for example a Silverson). Preferably, the acrylic resin is first mixed with water and the alkali/amine. The other constituents are then added and milled until the particle size is preferably less than 5mm as tested on a Hegman grind gauge. At this stage, optical brightener (UV tracer), preferably at about 0 to 20% can optionally be added for registration and QC determination. Optical brightener is added in order to see where and how much ink has been printed, as the ink is primarily clear. This is particularly useful when printing on white paper/board, and clear and white films.

[00097] If a white ink is required, a white masterbatch can be accommodated in the final ink. Certain customers require a white patch in their design. This is typical for a date or batch number which is sometimes situated in a printed box. A typical formulation for a finished white ink may be 50 wt% masterbatch concentrate, 25 wt% technical varnish, and 25 wt% white concentrate. However, it is to be understood that the amounts may be varied according to the required end use.

[00098] A white concentrate generally contains white pigment, binder, an alkali/amine, water, dispersing aid, and defoamer. The white concentrate may also contain a UV additive.

[00099] The white pigment is present in an amount of from about 30 wt% to about 50 wt%. In certain embodiments, the white pigment may be present in an amount of from about 35 wt% to about 45 wt%; or from about 30 wt% to about 40 wt%. For example, the white pigment may be present in an amount of from about 30 wt% to about 40 wt%; or from about 35 wt% to about 50 wt%; or from about 40 wt% to about 50 wt%.

[000100] The binder is generally present in the white concentrate in an amount of from about 10 wt% to about 30 wt%. In certain embodiments, the binder is present in an amount of from about 12 to about 28 wt%; or from about 15 wt% to about 25 wt%; or from about 18 wt % to about 23 wt%; or from about 19 wt% to about 22 wt%. For example, the binder may be present in amount of from about 10 wt% to about 25 wt%; or from about 15 wt% to about 30 wt%; or from about 15 wt% to about 25 wt%.

[000101] The alkali/amine is generally present in the white concentrate in an amount of from about 0.5 wt% to about 10 wt%. In certain embodiments, the alkali/amine is present in an amount of from about 1 wt% to about 10 wt%; or from about 2 wt% to about 8 wt%; or from about 3 wt% to about 6 wt%; or from about 4 wt% to about 5 wt%. For example, the alkali/amine may be present in an amount of from about 0.5 wt% to about 5 wt%; or from about 1 wt% to about 10 wt%; or from about 1 wt% to about 5 wt%; or from about 0.5 wt% to about 3 wt%; or from about 0.5 wt% to about 1 wt%.

[000102] The water is generally present in the white concentrate in an amount of from about 30 wt% to about 50 wt%. In certain embodiments, the water may be present in an amount of from about 35 wt% to about 45 wt%; or from about 30 wt% to about 40 wt%. For example, the water may be present in an amount of from about 30 wt% to about 45

wt%; or from about 30 wt% to about 40 wt%; or from 35 wt% to about to about 50 wt%; or from about 40 wt% to about 50 wt%.

[000103] The dispersing aid is generally present in the white concentrate in an amount of from about 0 wt% to about 5 wt%. In certain embodiments, the dispersing aid/surfactant may be present in an amount of from about 1 wt% to about 4 wt%; or from about 2 wt% to about 3 wt%. For example, the dispersing aid may be present in an amount of from about 1 wt% to about 5 wt%; or from about 2 wt% to about 5 wt%; or from about 2 wt% to about 4 wt%; or from about 3 wt% to about 5 wt%.

[000104] The defoamer is generally present in the white concentrate in an amount of from about 0 wt% to about 3 wt%. For example, the defoamer may be present in an amount of from about 1 wt% to about 3 wt%; or from about 1.5 wt% to about 3 wt%; or from about 0.5 wt% to about 2 wt%.

[000105] When present, a UV additive is typically present in the white concentrate in an amount of approximately 5 wt%. For example, the UV additive may be present in an amount of from about 1 wt% to about 5 wt%; or from about 1 wt% to about 3 wt%; or from about 2 wt% to about 4 wt%.

[000106] When imaging with a fibre laser, an IR absorber is preferably added. Reduced indium tin oxide would preferably be added to the formulation when imaging with a fibre laser is used.

[000107] Although the masterbatch can be used for all substrates, for specific substrates different masterbatch formulations are recommended. The difference is in the alkali/amine addition. In general MEA (monoethanolamine) is used for paper and corrugated boards, while ammonia is used for films and foils end use.

[000108] Once the masterbatch is made, preferably only simple mixing of the masterbatch and technical varnish is required (no milling). The white masterbatch can also preferably be added using simple mixing.

[000109] Finished ink formulations can be made by mixing masterbatch concentrate, technical varnish, and water. When a finished colored ink is required, this can be achieved by mixing masterbatch concentrate, technical varnish, colorant, and water. Typical amounts are shown in Tables A to C.

Table A. General formulation of finished ink

Material	%
Masterbatch Concentrate	30 - 80
Technical Varnish	10 - 70
Water	0 - 10

Table B. Preferred general formulation of finished ink

Material	%
Masterbatch Concentrate	40 - 60
Technical Varnish	40 - 60
Water	0 - 10

Table C. General formulation for finished ink with colorant and/or white pigment

Material	%
Masterbatch Concentrate	15 - 80
Colorant/white pigment	0 - 35
Technical Varnish	10 - 55
Water	0 - 10

[000110] Colorants and/or white pigment can be added by the addition of a concentrate to obtain the desired color. Colorants and/or white pigment would preferably be incorporated as either a pre-dispersed concentrate, or in a form that can be dispersed into

the finished ink by means of mixing, without the need for milling. But it would also be possible to incorporate colorants that require milling by adding them and then subjecting the ink to further milling.

[000111] All inks produced by the 'masterbatch' approach can be lasered by the appropriate laser, producing the required images. As previously described, the inks made for the fiber laser can also be laser imaged with a CO_2 laser. Any technical varnish that is compatible with the masterbatch could be utilized and depends on the end-use application of the ink or coating.

[000112] All inks produced using the masterbatch concentrates of the present invention can be printed using flexographic or gravure printing. The inks can be printed either as a surface print or as a reverse print. The performance properties of the inks are comparable among all of the print processes, and the data shown in the examples can be extrapolated to each of these print processes.

EXAMPLES

[000113] The following examples illustrate specific aspects of the present invention and are not intended to limit the scope thereof in any respect and should not be so construed.

[000114] Two coats of the finished laser-reactive inks were applied by hand proofer (Flexi-Proofer, from Weller Patents), using a 140# Anilox roller/blue rubber roller, onto the appropriate substrates.

[000115] The prints were allowed to dry, and then tested as described below. All tests were rated on a scale of 0 (worst) to 5 (best). A score of 0 means 100% ink removal, and a score of 5 means no ink removal or print surface damage.

Tape Adhesion

[000116] Adhesive strength of the printed finished laser-reactive inks to film substrates was tested using a tape adhesion test. Adhesive Tape (Scapa tape – ref: 1112) was stuck

on top of a proof print of the ink and was then pulled off. The level of ink removal was evaluated.

Scratch Resistance

[000117] The proof print was laid print-side up on a hard surface and the back of the index fingernail was scratched across the surface. The print was evaluated for level of ink removal.

Wrinkle Test

[000118] The proof print was grasped with thumb and forefinger at either side of the print, hands approximately 1 inch apart, and rotated vigorously for 20 cycles to simulate repeated flexing of the print. The level of ink removal and/or damage to the print surface was assessed. Only film substrates were tested using the wrinkle test.

SATRA Dry Rub

[000119] Using a SATRA rub tester (Model STM 461), a dry felt pad (25mm OD) under a specified load (1.8 Kg) was rotated on the surface of the print for 100 complete cycles. The print was examined for signs of ink removal and/or surface damage.

SATRA Wet Rub

[000120] Using a SATRA rub tester (Model STM 461), a water-soaked pad (25mm OD) under a specified load (1.8 Kg) was rotated on the surface of the print for 30 complete cycles. The print was examined for signs of ink removal and/or surface damage.

SATRA Oil Rub Test

[000121] A few drops of oil were placed under a dry felt pad. Using a SATRA rub tester (Model STM 461), the oil treated pad (25mm OD) under a specified load (1.8 Kg) was rotated on the surface of the print for 30 complete cycles. The print was examined for signs of ink removal and/or surface damage.

Example 1 – Masterbatch Concentrate 1 (MB1)

[000122] A laser-reactive masterbatch concentrate was made according to the formulation in Table 1.

Table 1. Masterbatch Concentrate 1 (MB1)

Material	**%**
Byk 017 Antifoam	0.2
Leuco Dye (WinCon, Connect Chemicals)	19.0
Blocked acid (SaBoTBA, Datalase)	31.0
Binder (Joncryl 678 acrylic resin, BASF)	15.3
Alkali/Amine – Monoethanolamine	4.0
Water	28.5
Disperbyk 190 Surfactant	2.0
Total	**100.0**

Example 2 – Masterbatch Concentrate 2 (MB2) made from Masterbatch Concentrates for both the Leuco Dye and Blocked/Latent Acid

[000123] A leuco dye masterbatch concentrate was prepared according to the formulation in Table 2A below. A blocked/latent acid masterbatch concentrate was prepared according to the formulation in Table 2B below. The concentrates of 2A and 2B were blended to produce the masterbatch concentrate (MB2) according to the formulation given in Table 2C below.

Table 2A. For the leuco dye masterbatch concentrate

Material	**%**
Byk 017 Antifoam	0.2
Leuco Dye (Wincon 1)	55.0
[1]Binder - Acrylic resin (Joncryl 678)	13.1
Alkali/Amine – Monoethanolamine (MEA)	3.5
Water	26.2
Surfactant – Disperbyk 190	2.0
Total	**100.0**

Table 2B. For the blocked acid masterbatch concentrate

Material	%
Antifoam	0.2
Blocked Acid	53.0
[1]Binder - Acrylic resin	13.8
Alkali/Amine	3.6
Water	27.4
Surfactant	2.0
Total	**100.0**

Table 2C: Blending of 2A and 2B to produce a masterbatch concentrate 2 (MB2)

Material	Ratio	%
Leuco dye masterbatch (2A)	1.0	37
Blocked acid masterbatch (2B)	1.7	63
Total	**-**	**100**

Example 3: Masterbatch Concentrate 3 (MB3) made without binder resin

[000124] A masterbatch concentrate 3 (MB3), without a binder resin, was made according to the formulation in Table 3 below. The surfactant was used as the milling medium.

Table 3. Masterbatch concentrate 3 without binder resin (MB3)

Material	Amounts
Leuco dye	19
Antifoam	0.2
Blocked Acid	31
Water	41.8
Surfactant	8.0
Total	**100.0**

Example 4. Finished laser-reactive white ink

[000125] A finished white ink was made according to the formulation in Table 4.

Table 4. Finished laser-reactive white ink

Material	%
Masterbatch	50
Technical Varnish	25

Material	%
White concentrate	25

[000126] The formulation of the white concentrate used to prepare the laser-reactive finished white ink described above is given in Table 5.

Table 5. White concentrate

Material	Amounts
Antifoam	0.2
White pigment (TiO_2)	42.1
Binder – Acrylic resin	15.0
Alkali/Amine	1.6
Water	40.7
Surfactant	0.4
Total	**100.0**

Example 5. Technical varnishes used to prepared finished laser-reactive inks

[000127] The formulations of the technical varnishes used to prepare finished laser-reactive inks are given in Tables 6 and 7 below.

Table 6: Formulations for technical varnishes 1 to 4 (V1 to V4)

Material	V1	V2	V3	V4
Main Resin	Induprint 2622 34.0	Joncryl 90 26.0	Lucidene 605 70.1	Joncryl 535 94.5
Water	61.8	42.8	12.7	
Antifoam Tegofoamex 1488	0.5	0.7	0.3	
Surfactant Disperbyk 190	0.6	0.2		
Monoethanolamine	3.1	0.8		
PE wax Aquacer 531		7.2	4.0	3.0
Thickener - Rheolate 278				1.5
Acrylic - Joncryl 678		8.0	3.7	
Acrylic - Joncryl 652		10.5		
Ammonia		1.9	0.9	

Material	V1	V2	V3	V4
Coalescent – glycol ethers (Dowanol DPM)		1.9	2.5	
Wetting aid : N-Propanol			4.3	
Silicone - Worleeadd			1.5	1.0
Total	**100.0**	**100.0**	**100.0**	**100.0**
Tg (°C)	40-80	>80	<0	0-40

Table 7: Formulations for technical varnishes 5 to 8 (V5 to V8)

Material	V5	V6	V7	V8
Main Resin	Joncryl 1665 58.8	Joncryl 1665 61.6	Neorez R650 78.1	Joncryl 8050 57.2
Water	4.5	13.5		21.0
Antifoam Tegofoamex 1488	0.5	0.6	0.4	0.5
Surfactant Disperbyk 190				1.0
Acrylic – Joncryl 678				3.5
PE wax Aquacer 531	10.3			
Styrene maleic anhydride	5.0	5.4		
Acrylic - Joncryl 90			20.0	
Acrylic - Joncryl 8050	10.3	10.7		
Ammonia				0.8
Coalescent – glycol ethers (Dowanol DPM)				6.0
Wetting aid : N-Propanol	7.6	8.2		6.0
Silicone - Worleeadd	3.0		1.5	4.0
Total	**100.0**	**100.0**	**100.0**	**100.0**
Tg (°C)	<0	<0	n/a	<0

Example 6. Performance of finished laser-reactive inks prepared with MB1

[000128] Masterbatch concentrate 1 (MB1) was combined with technical varnishes V1 to V8, according to the ratios given in Table 8 below. The properties of the finished inks are shown in Table 8.

Table 8. Properties of finished inks prepared using MB1

Varnish	Ratio	Substrate		Resistance Properties					
	MB:V	FS	PS	T	S	W	DR	WR	OR
V1	50:50		✓	-	-	-	3		
V2	50:50		✓	-	-	-	3		
V3	40:60	✓	✓	5	5	-	5	5	1
V4	50:50		✓	-	-	-	5	4	4
V5	40:60	✓	✓	5	5	5	5	4	4
V6	40:60	✓		5	5	3	5	4	3
V7	40:60	✓		5	5	5	3	-	-
V8	40:60	✓		5	5	4	5	4	2

All tests were rated on a scale of 0 (worst) to 5 (best). A score of 0 means 100% ink removal, and a score of 5 means no ink removal or print surface damage.
Substrate: film (FS), paper (PS).
Resistance Properties: tape adhesion (T), scratch (S), wrinkle (W), dry rub (DR), wet rub (WR), oil rub (OR).

Example 7. Performance of finished laser-reactive inks prepared with MB2

[000129] Masterbatch concentrate 2 (MB2) was combined with technical varnishes V2, V5 and V7, according to the ratios given in Table 9 below. The properties of the finished inks are shown in Table 9.

Table 9. Properties of finished inks prepared using MB2

Varnish	Ratio	Substrate		Resistance Properties					
	MB:V	FS	PS	T	S	W	DR	WR	OR
V2	50:50		✓	-	-	-	3		
V5	40:60	✓	✓	5	5	5	5	4	4
V7	40:60	✓		5	5	5	3	-	-

All tests were rated on a scale of 0 (worst) to 5 (best). A score of 0 means 100% ink removal, and a score of 5 means no ink removal or print surface damage.
Substrate: film (FS), paper (PS).
Resistance Properties: tape adhesion (T), scratch (S), wrinkle (W), dry rub (DR), wet rub (WR), oil rub (OR).

[000130] The results in Tables 8 and 9 show that finished laser-reactive inks prepared from masterbatch concentrates of the present invention have good resistance properties. The masterbatch concentrates are therefore useful to prepare laser-reactive inks suitable for a range of substrates, including paper and flexible film substrates often used in packaging.

[000131] As discussed above, the finished laser-reactive inks prepared from masterbatch concentrates of the present invention are suitable for flexographic and gravure printing, and can either be printed as a surface print or a reverse print. Suitable print processes are shown below, in Table 10.

Table 10. Suitable printing processes for finished laser-reactive inks

Varnish	Ratio	Substrate		Print Process				Note
	MB:V	FS	PS	FP	GP	SP	RP	
V1	50:50		✓	✓		✓		1
V2	50:50		✓	✓	✓	✓		1

Varnish	Ratio	Substrate		Print Process				Note
	MB:V	FS	PS	FP	GP	SP	RP	
V3	40:60	✓	✓	✓		✓	✓	2
V4	50:50		✓	✓		✓	✓	3
V5	40:60	✓	✓	✓	✓	✓	✓	4
V6	40:60	✓		✓	✓	✓		5
V7	40:60	✓		✓	✓	✓	✓	6
V8	40:60	✓		✓	✓		✓	7

Substrate: film (FS), paper (PS).
Print Process: flexographic printing (FP), gravure printing (GP), surface printing (SP), and reverse printing (RP).
Note (other properties): low cost/paper (1), PE film (2), tissue (3), OPP film (4), foil (5), lamination (6), and shrinksleeves (7).

[000132] The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on this invention that fall within the scope and spirit of the invention.

CLAIMS

What is claimed is:

1. A masterbatch concentrate for laser reactive water-based inks comprising:
   a) a thermochromic leuco dye;
   b) a blocked/latent acid;
   c) an alkali/amine compound; and
   d) water;

wherein the masterbatch concentrate can be combined with a technical varnish to form a laser reactive water-based ink.

2. The masterbatch concentrate of claim 1, wherein:
   a) the thermochromic leuco dye is present in an amount of 10 wt% to 30 wt%;
   b) the blocked/latent acid is present in an amount of 15 wt% to 50 wt%;
   c) the alkali amine is present in an amount of 1 wt% to 10 wt%; and
   d) the water is present in an amount of 15 wt% to 50 wt%.

3. The masterbatch concentrate of any one of claims 1 or 2, wherein the blocked/latent acid is selected from the group consisting of a carboxylic acid salt, a sulfonic acid salt, a phosphonic acid salt, and mixtures thereof.

4. The masterbatch concentrate of claim 3, wherein the blocked/latent acid is a carboxylic acid salt.

5. The masterbatch concentrate of claim 4, wherein the carboxylic acid salt is selected from the group consisting of tri-*n*-butylammonium borodisalicylate, phenylacetic acid, *p*-tolylacetic acid, mandelic acid, sorbic acid, succinic acid, lactic acid, 4-biphenylacetic acid, and trans-styrylacetic acid.

6. The masterbatch concentrate of claim 5, wherein the carboxylic acid salt is tri-*n*-butylammonium borodisalicylate.

7. The masterbatch concentrate of any one of claims 1 to 6, wherein the leuco dye is selected from xanthene leuco dyes, thioxanthene leuco dyes, acridine leuco dyes, phenoxazine leuco dyes, phenazine leuco dyes, merocyanine leuco dyes, thiazine leuco dyes, oxazine leuco dyes, azine leuco dyes, methine leuco dyes, azo leuco dyes, pyrazoline leuco dyes, stilbene leuco dyes, coumarin leuco dyes, triarylmethane leuco dyes, spiropyran leuco dyes, phthalide leuco dyes, fluoran leuco dyes, acylleucoazine dyes, leucoauramine dyes, rhodaminelactam leuco dyes, chromene leuco dyes, quinine leuco dyes, aminohydrocinnamic acid leuco dyes, 2-(*p*-hydroxyphenyl)-4,5-diphenylimidazole leuco dyes, indanone leuco dyes, indamine leuco dyes, hydrozine leuco dyes, indigoid leuco dyes, amino-2,3-dihydroanthraquinone leuco dyes, tetrahalo-*p,p'*-biphenol leuco dyes, phenethylaniline leuco dyes, and mixtures thereof.

8. The masterbatch concentrate of claim 7, wherein the leuco dye is selected from the group consisting of: 2-phenylamino-3-methyl-6-diethylaminofluorane; 3-di-*n*-butylamino-6-methyl-7-phenylaminofluorane; 2-(2',4'-dimethyl phenylamino-3-methyl-6-diethylaminofluorane); 3-(*N*-ethyl-*N*-isopentylamino)-6-methyl-7-anilinofluorane; 2-di(phenylmethyl)amine-6'- diethylaminospiro(isobenzofuran-1(3*H*), 9'-[9*H*] xanthen-3-one; 3-diethylaminobenzofluorane; 7- (4-(diethylamino)-2-ethoxyphenyl)-7-(1-ethyl-2-methyl-1*H*-indol-3-yl)furo(3,4-*b*)pyridin-5(7*H*)-one; 3,3-bis(*p*-(dimethylamino)phenyl)-6-(dimethylamino)phthalide (Crystal Violet Lactone); 6-dimethylamino-3,3-bis(4-dimethylaminophenyl)-2-benzofuran-1-one-6-dimethylamino-3,3-bis(4-dimethylaminophenyl)phthalide; 3,3'-Bis(1-*n*-octyl-2-methylindol-3-yl)phthalide; 2-anilino-3-methyl-6-(di-*n*-butylamino)fluoran; 2-anilino-3-methyl-6-diethylaminofluoran; and 2'-anilino-6'-[ethyl(*p*-tolyl)amino]-3'-methylspiro[isobenzofuran-1(3*H*),9'-[9*H*]xanthene]-3-one.

9. The masterbatch concentrate of claim 8, wherein the leuco dye is 2'-anilino-6'-[ethyl(*p*-tolyl)amino]-3'-methylspiro[isobenzofuran-1(3*H*),9'-[9*H*]xanthene]-3-one.

10. The masterbatch concentrate of any one of claims 1 to 9, wherein the alkali/amine compound is selected from the group consisting of monoethanolamine, ammonia, sodium hydroxide, potassium hydroxide, triethanolamine, amine propyl alcohol, and mixtures thereof.

11. The masterbatch concentrate of claim 10, wherein the alkali/amine is monoethanolamine.

12. The masterbatch concentrate of any of claims 1 to 11, further comprising one or more of a resin, an infrared (IR) heat absorber, an adhesion promoter, a UV fluorescer, a dispersing aid, or a colorant.

13. The masterbatch concentrate of any one of claims 1 to 12, further comprising one or more of waxes, defoamers, stabilizers, silicones, rheological modifiers, or plasticizers.

14. The masterbatch concentrate of claim 13, wherein the IR heat absorber is selected from the group consisting of: r-ITO (reduced indium tin oxide); antimony-doped tin oxide pigment; mica based metal-oxide layer-substrate pigments; copper (II) hydroxyl phosphate; 3,4-polyethylenedioxythiophene-polystyrenesulfonate; carbon blacks; potassium aluminum silicate; and mica coated with antimony-doped tin oxide; and a conductive polymer.

15. The masterbatch concentrate of claim 14, wherein the IR heat absorber is a reduced indium tin.

16. The masterbatch concentrate of claim 13, wherein the adhesion promoter is based on zirconium propionate.

17. The masterbatch concentrate of any one of claims 1 to 16, wherein the leuco dye, once activated, appears as a color selected from the group consisting of black, blue, red, green, and yellow.

18. The masterbatch concentrate of any one of claims 1 to 17, wherein the leuco dye is present in an amount of 12 wt% to 28 wt%.

19. The masterbatch concentrate of any one of claims 1 to 17, wherein the leuco dye is present in an amount of 15 wt% to 25 wt%.

20. The masterbatch concentrate of any one of claims 1 to 17, wherein the leuco dye is present in an amount of 18 wt% to 23 wt%.

21. The masterbatch concentrate of any one of claims 1 to 17, wherein the leuco dye is present in an amount of 19 wt% to 22 wt%.

22. The masterbatch concentrate of any one of claims 1 to 20, wherein the blocked/latent acid is present in an amount of 18 wt% to 45 wt%.

23. The masterbatch concentrate of any one of claims 1 to 20, wherein the blocked/latent acid is present in an amount of 20 wt% to 40 wt%.

24. The masterbatch concentrate of any one of claims 1 to 20, wherein the blocked/latent acid is present in an amount of 25 wt% to 35 wt%.

25. The masterbatch concentrate of any one of claims 1 to 23, wherein the alkali amine is present in an amount of 2 wt% to 8 wt%.

26. The masterbatch concentrate of any one of claims 1 to 23, wherein the alkali amine is present in an amount of 3 wt% to 6 wt%.

27. The masterbatch concentrate of any one of claims 1 to 23, wherein the alkali amine is present in an amount of 3 wt% to 5 wt%.

28. The masterbatch concentrate of any one of claims 1 to 26, wherein the water is present in an amount of 18 wt% to 45 wt%.

29. The masterbatch concentrate of any one of claims 1 to 26, wherein the water is present in an amount of 20 wt% to 40 wt%.

30. The masterbatch concentrate of any one of claims 1 to 26, wherein the water is present in an amount of 25 wt% to 35 wt%.

31. A method of preparing a masterbatch concentrate comprising combining:
    a) a thermochromic leuco dye;
    b) a blocked/latent acid;
    c) an alkali/amine compound; and
    d) water;

wherein the masterbatch concentrate can be combined with a technical varnish to form a laser reactive water-based ink.

32. A thermochromic leuco dye concentrate comprising:
    a) 40 wt% to 70 wt% leuco dye;
    b) 1 wt% to 10 wt% alkali amine; and
    c) 15 wt% to 40 wt% water.

33. A blocked/latent acid concentrate comprising:
    a) 40 wt% to 70 wt% blocked/latent acid;
    b) 1 wt% to 10 wt% alkali amine; and

c) 15 wt% to 40 wt% water.

34. The leuco dye concentrate of claim 32, further comprising one or more of a resin, an IR heat absorber, a dispersant, an adhesion promoter, a UV fluorescer, a dispersing aid, a colorant, waxes, defoamers, stabilizers, silicones, rheological modifiers, and plasticizers.

35. The blocked/latent acid concentrate of claim 33, further comprising one or more of a resin, an IR heat absorber, a dispersant, an adhesion promoter, a UV fluorescer, a dispersing aid, a colorant, waxes, defoamers, stabilizers, silicones, rheological modifiers, or plasticizers.

36. A masterbatch concentrate prepared by blending the leuco dye concentrate of any one of claims 32 or 34 with the blocked/latent acid concentrate of any one of claims 33 or 35.

37. A laser reactive water-based ink comprising the masterbatch concentrate of any one of claims 1 to 30 and 36, and a technical varnish.

38. A method of making a laser reactive water-based ink comprising blending the masterbatch concentrate of any one of claims 1 to 30 and 36, with a technical varnish, to form a finished water-based laser reactive ink.

39. A method of making a laser reactive water-based ink, comprising:
    a) blending the thermochromic leuco dye concentrate of any one of claims 32 or 34 with a technical varnish;
    b) blending the blocked/latent acid concentrate of any one of claims 33 or 35 with a technical varnish; and
    c) combining (a) and (b) to form a laser reactive water-based ink.

40. A printed article comprising the laser reactive water-based ink of claim 37.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/46001

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B41M 5/323; C09D 11/037, 11/101 (2015.01)
CPC - B41M 5/323; C09D 11/037, 11/101
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
-***-Continued Within the Next Supplemental Box-***-

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; ProQuest; IP.com: laser, reactive, water, ink, acid, amine, alkali, leuco dye, masterbatch, thermochromic, carboxylic, ammonia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/192307 A1 (SUN CHEMICAL CORPORATION) 27 December 2013; paragraphs [000015], [000025]-[000027], [000047], [000060], [000064], claim 4	1-2, 3/1, 3/2, 4/3/1, 4/3/2, 5/4/3/1, 5/4/3/2, 6/5/4/3/1, 6/5/4/3/2, 31
Y	US 2012/0045624 A1 (CAMPBELL, J et al.) 23 February 2012; paragraphs [0027], [0079], [0090], [0102], [0109], [0146], [0148]-[0149]	1-2, 3/1, 3/2, 4/3/1, 4/3/2, 5/4/3/1, 5/4/3/2, 6/5/4/3/1, 6/5/4/3/2, 31
A	US 5,611,818 A (DOMINGO, MJ) 18 March 1997; entire document	1-2, 3/1, 3/2, 4/3/1, 4/3/2, 5/4/3/1, 5/4/3/2, 6/5/4/3/1, 6/5/4/3/2, 31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 October 2015 (09.10.2015)	29 DEC 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/46001

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 7-30 and 36-40
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
-***-Please See Supplemental Page-***-

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6, 31

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US15/46001

-***-Continued from Box No. III: Observations where unity of invention is lacking-***-

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-6 and 31 are directed toward a masterbatch concentrate for laser reactive water-based inks.
Group II: Claims 32 and 34 are directed toward a thermochromic leuco dye concentrate.
Group III: Claims 33 and 35 are directed toward a blocked/latent acid concentrate.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical features of Group I include a masterbatch concentrate for laser reactive water-based inks which can be combined with a technical varnish to form a laser reactive water-based ink, which includes both of a thermochromic leuco dye and a blocked/latent acid, which is not present in groups II and III; and the special technical features of Group II include a thermochromic leuco dye concentrate comprising 40 weight percent to 70 weight percent leuco dye, which is not present in groups I and III; and the special technical features of Group II include a blocked/latent acid concentrate comprising 40 weight percent to 70 weight percent blocked/latent acid which is not present in groups I and II.

The common technical feature of Groups I, II, and III, common technical feature of Groups I and III, and common technical feature of Groups II and III are disclosed by US 2004/0151742 A1 to Beilfuss, et al. (hereinafter 'Beilfuss'). Beilfuss discloses a composition comprising 1 weight percent to 10 weight percent alkali/amine; and 15 weight percent to 40 weight percent water (liquid concentrate comprises 0.225 to 4.5 percent by weight of potassium (alkali) hydroxide and 35.5 to 64.275 percent by weight of water; paragraph [0042]). Beilfuss also discloses a composition comprising a blocked/latent acid; an alkali/amine compound; and water (liquid concentrate comprises sodium benzoate, potassium sorbate, and hydroxycarboxylic acids (blocked/latent acids), potassium (alkali) hydroxide, and water; paragraph [0042]).

The common technical feature of Groups I and II is disclosed by US 5,611,818 A (DOMINGO). Domingo discloses a composition comprising leuco dye (sulphur dies are reduced to leuco dyes with an excess of alkali metal hydroxide; column 2, lines 32-37; column 4, lines 41-67); alkali/amine; and water (after reaction and purification, the filter cake (leuco dye) is mixed with 50 percent sodium hydroxide and water solution; column 9, lines 65-67).

Since the common technical features are previously disclosed by Beilfuss and Domingo, these common features are not special and so Groups I-III lack unity.

-***-Continued from Box B. FIELDS SEARCHED -***-

IPC(8): B41M 5/00, 5/26, 5/28, 5/30, 5/323, 5/34; C09D 11/00, 11/02, 11/037, 11/101, 11/107, 11/32, 11/50, 11/54 (2015.01)

CPC: B41M 5/00, 5/26, 5/28, 5/282, 5/30, 5/323, 5/3275, 5/34; C09D 11/00, 11/005, 11/02, 11/037, 11/101, 11/107, 11/32, 11/50, 11/54