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(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center
Saint Paul, Minnesota 55101(US)

(72) Inventor: **Sher, Frank T. c/o Minnesota Mining and**
Manufacturing Comp. 2501 Hudson Road
P.O.Box 33427
St. Paul Minnesota 55133-3427(US)
Inventor: **LeMire, Verna J. c/o Minnesota Mining and**
Manufacturing Comp. 2501 Hudson Road
P.O.Box 33427
St. Paul Minnesota 55133-3427(US)
Inventor: **Chang, Jeffrey C. c/o Minnesota Mining and**
Manufacturing Comp. 2501 Hudson Road
P.O.Box 33427
St. Paul Minnesota 55133-3427(US)

(74) Representative: **Bowman, Paul Alan et al**
LLOYD WISE, TREGEAR & CO. Norman House 105-109 Strand
London WC2R OAE(GB)

(54) Light sensitive element.

(57) A light sensitive, dry processing imaging material comprising imaging material which is substantially free of photosensitive silver compounds as an imaging component of the sheet; said material containing at least one image forming component selected from the group consisting of leuco dyes, bleachable dyes, and coupling compounds. Said imaging system comprising a true dispersion of active particles in a binder. Single layer, single sheet, color imaging elements may be formed by combinations of the particles. The individual particles may be spectrally sensitized to portions of the electromagnetic spectrum including the ultraviolet, visible and infrared regions.

LIGHT SENSITIVE ELEMENT

The present invention relates to light sensitive, dry processing imaging material comprising imaging material which is substantially free of silver as an imaging component of the sheet, said material containing (1) at least one image forming component selected from the group consisting of leuco dyes, bleachable dyes, and coupling compounds, and (2) a separate light absorbing, light sensitive component. Said imaging system comprises a true dispersion of active particles in a binder. Single layer, single sheet, color elements may be formed by combinations of the particles.

The present invention relates to imageable materials, particularly particulate binders containing imaging materials, and to imageable elements containing those particulate materials.

Light sensitive, dry processable materials containing leuco dyes have been known in the art for many years. These imaging systems basically comprise a leuco dye, a nitrate salt, an organic acid, and sensitizing dyes in combination with diaryl-iodonium salts or sensitizing dyes in combination with photolyzable organic halogen compounds, or diazonium salts, and a binder. Leuco dye imaging systems are well known in the literature. Leuco dyes in their reduced leuco form, when properly chosen, can form the basis of color image forming systems. Such leuco dye systems are discussed in "The Theory of the Photographic Process", 3rd edition, Mees and James, pp. 283-4, 390-1, Macmillion Co., N.Y.; and Kosar's "Light Sensitive Systems", pp. 367, 370-380, 406, (1965), Wiley and Son, Inc.,N.Y..

U.S. Patent No. 4,450,227 discloses a light sensitive system comprising a tetra(hydrocarbyl)borate and a dye used in the form of a dispersion, with the light sensitive borate and dye in one phase dispersed within a second phase. Because the dye-borate system combines the spectrally sensitive element and the image forming element at a molecular level, a multiplicity of colored dyes may be used (e.g. cyan, yellow, magenta in the same or different layers or in dispersed particles or droplets. The dye borate system is carried in one distinct phase, usually dissolved therein, and then that phase is dispersed as droplets or particles within the second distinct phase. U.S. Patent No. 4,450,227; also discusses the use of a spray drying technique (use of a spray gun atomizer) to form particles. (column 7, example 2, lines 67-68).

U.S. Patent No. 4,017,313 uses an imaging system comprising a combination of a photosensitive leuco dye, a photosensitizer for the dye, an aromatic aldehyde and a secondary or tertiary amine.

U.S. Patent Nos. 3,390,997, 2,884,326, and 2,772,284 discuss other photosensitive systems using leuco dyes.

U.S. Patent No. 4,460,677 discloses a thermally developable imaging system comprising leuco dye, nitrate ion, and a spectrally sensitized organic compound having photolyzable halogen atoms.

U.S. Patent No. 4,394,433 discloses a light sensitive, heat developable layer comprising a polymeric binder, a leuco dye, and a photosensitive diazonium salt.

U.S. Patent No. 4,386,154 discloses a thermally developable imaging system comprising a leuco dye, nitrate ion, and a spectrally sensitized compound selected from (1) aromatic iodonium salts, and (2) compounds of photolyzable halogen atoms.

U.S. Patent No. 4,370,401 discloses an imageable layer comprising a polymeric binder, a bleachable dye or a leuco dye, a nitrate salt, and a photosensitive diazonium salt, the nitrate salt in the imageable layer being capable of liberating HNO_3, NO, NO_2 or N_2O_4 in oxidizing amounts when the layer is heated to no more than 200 °C for 60 seconds. Mixtures of dyes in a single layer of this system would not produce color differentiation since the diazo absorbs substantially only UV radiation.

U.S. Patent No. 4,336,323 discloses a light insensitive imageable layer comprising a synthetic binder, a dye, a nitrate salt, and an acid.

Japanese published patent JP 77-025330 discusses photosensitive anthracene derivatives with leuco dye and an oxidizing agent.

Japanese published KOKAI (unexamined patent) JP 51-00941 discusses a photosensitive element containing aromatic nitro or carbonyl compounds as the photosensitive component, a nitrate salt, and a leuco dye.

Photoimaging chemistry is placed in a polymeric binder, and particles containing the chemistry in the binder are produced. The particles are then dispersed in a solution of a second binder, coated and dried to form the second binder (herein referred to as the "layer binder"). The particles are differentially spectrally sensitized, contained in a single layer, producing a multi-color element. The color images may be retained in the original element or transferred.

A dispersion of particles containing light sensitive, dry processable imaging chemistry is formed within a polymeric binder. The dispersion is not what is termed a dispersion in the photographic art, which is actually an emulsion of a liquid medium dispersed within a solid carrier phase. The dispersion of the present invention is a configuration wherein solid particles exist within a solid binder layer. The size of the useful particles is generally between 0.01 and 100 microns, and preferably between .1 and 20 microns. The construction may consist of one or more layers of both black and white and/or color dry processable light sensitive particles.

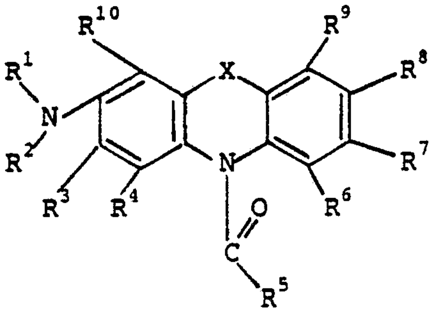
The light sensitive imaging chemistry and a binder are prepared as a homogenously mixed composition or single homogeneous composition, and particles are formed in any manner which does not affect activation, nor result in "predevelopment" of the chemistry. The particles can be formed by grinding, ball milling, spray drying, etc. It has been found to be preferred to spray dry the composition so that dried particles are formed in conventional spray drying equipment used in polymer particle processes.

Chemistry of the present invention is disclosed, for example, in U.S. Patent Nos. 4,370,401, 4,394,433, 4,386,154, and 4,460,677. Herein, the chemistry is comprised of a leuco dye, a nitrate ion, and sensitizing dyes in combination with diaryliodonium salts or photolyzable organic halogen compounds, or light sensitive diazonium salts, an organic acid, a dye or leuco dye, and a binder. Some of the compositions act as a reactive negative or positive image forming system. In addition to the active materials, a material which supplies hydrogen ion, such as an acid material, is a desirable ingredient. After exposure to light, the application of heat will develop the image by oxidizing leuco dye to a colored dye more rapidly in either exposed or unexposed regions.

Different groups of individual particles when used in the instant invention are individually sensitized to different portions of the electromagnetic spectrum and are associated with different color forming or color losing materials.

Examples of leuco dyes generally useful in the practice of the present invention are described in U.S. Patent Nos. 4,370,401, 4,394,433, 4,386,154, and 4,460,677. Leuco dyes are well known in the art. These are colorless compounds which when subjected to an oxidation reaction form a colored dye. These leuco dyes are known in the art (e.g. "The Theory Of The Photographic Process", 3rd Edition, Mees and James, pp. 283-4, 390-1, MacMillion Co., N.Y.; and "Light Sensitive Systems", Kosar, pp. 367, 370-380, 406, (1965) Wiley and Sons, Inc., N.Y.). Leuco dyes which can be converted to colored dyes by oxidation are useful in the practice of the present invention. Acid or base sensitive dyes such as phenolphthalein and other indicator dyes are not useful in the present invention unless they are also oxidizable to a colored state. Indicator dyes would only form transient images or would be too sensitive to changes in the environment.

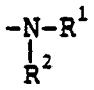
Preferred leuco dyes are comprised of acylated leuco azine, phenoxazine, and phenothiazine dyes and may in part be represented by the structure formula:



wherein
X is selected from O, S, and

N-R^{11}

R^1 and R^2 are independently selected from H and substituted or unsubstituted alkyl groups of 1 to 4 carbon atoms,
R^3, R^4, R^6 and R^7 are independently selected from H and alkyl groups of 1 to 4 carbon atoms,
R^5 is selected from alkyl groups of 1 to 16 carbon atoms, and aryl or substituted aryl groups of up to 16 carbon atoms,
R^8 is selected from



$$-N(R^2)-R^1$$

H, alkyl groups of 1 to 4 carbon atoms wherein R^1 and R^2 are independently selected and defined as above, R^9 and R^{10} are independently selected from H, and alkyl groups of 1 to 4 carbon atoms, and R^{11} is selected from alkyl groups of 1 to 4 carbon atoms and aryl groups of up to 11 carbon atoms.

The leuco dye should be present as at least 0.3% by weight of the particle, and preferably at least 4% by weight of the dried particle, and may be present as up to 10% or more (e.g. 20-30%) of the dried particle weight.

The leuco dyes of the present invention become colored due to oxidation, that is, they have absorbance after coloration in the visible portion of the electromagnetic spectrum (approximately 400 to 700 nm). The leuco dye should be present as at least about .03% by weight of the imageable layer, preferably at least 1.0% by weight, and most preferably at least 1% to 10% or more by weight of the dry weight of the imageable layer.

In forming the imageable layer containing the leuco dye, or coating of the dye particle layer binder onto a substrate, temperature should, of course, not be used during manufacture which would colorize the particle or binder layer or decompose the salts. Some slight coloration is tolerable, with the initial leuco dye concentrations chosen so as to allow for anticipated colorization. It is preferred, however, that little or no leuco dye be colorized during forming or coating. Depending on the anticipated development temperature, the coating or forming temperature can be varied. Therefore, if the anticipated development temperature were, for example, 350°F (167°C), the drying temperature could be 280°F (138°C), and it would not be desirable for the coating layer to gain 20% of its optical density at the drying temperature in less than 4-5 minutes. Such a gain would be tolerable by correspondingly increasing the amount of leuco dye.

The nitrate salts used in the preferred embodiment are disclosed in U.S. Patent Nos. 4,370,401, 4,394,433, 4,3861,154, and 4,460,677, and the previously referenced Kojin patents.

Nitrates themselves are well known, they may be supplied as various chemical compounds, but are desirably provided as a metal salt, and most preferably as a hydrated metal salt. Other ions which are ordinarily good oxidizing ions such as nitrite, chlorate, iodate, perchlorate, periodate, and persulfate, do not provide comparable results. Extremely active oxidizing agents such as iodate, even used in relatively smaller proportions to prevent complete and immediate oxidation or colorization of dyes do not perform nearly as well as nitrate ion compositions. The performance of nitrate is superior to any other ions, and it is preferred in the practice of the present invention.

Most means of supplying the nitrate salt into the particle composition are satisfactory. E.g. organic salts, metal salts, acid salts, mixtures of acids and salts, and other means of supplying the ion are useful. For example, nitrates of zinc, cadmium, potassium, calcium, zirconyl (ZrO_2), nickel, aluminum, chromium, iron, copper, magnesium, lead, and cobalt, ammonium nitrate, and cerous ammonium nitrate have been used.

The nitrate salt component of the present invention is desirably present in a form within the imaging particle so that oxidizing quantities of HNO_3, NO_2, or N_2O will be provided within the particle when it is heated in the layer binder to a temperature no greater than 200°C for 60 seconds and preferably no greater than 160°C for 60 or most preferably 30 seconds. This may be accomplished with many different types of salts, both organic and inorganic, and in variously different types of constructions.

The most convenient way of providing such thermal oxidant providing nitrate salts is to provide a hydrated nitrate salt such as aluminum nitrate nonahydrate ($Al(-NO_3)\bullet 9H_2O$).

In addition to inorganic nitrate salts generally described above, organic nitrate salts in an acidic environment are also capable of providing the oxidizing capability necessary for the practice of the present invention. Examples include ammonium nitrate, pyridinium nitrate, and guanidinium nitrate.

Another consideration should be given in the selection of the nitrate salt and that is the choice of a salt in which the cation is non-reactive with the dye. Non-reactive salts are defined in the practice of the present invention as those salts the cations of which do not spontaneously oxidize the dyes that they are associated with at room temperature. This may be readily determined in a number of fashions. For example, the dye and a non-nitrate (preferably halide) salt of the cation may be co-dissolved in a solution. If the salt oxidizes the dye spontaneously (within two minutes) at room temperature, it is a reactive salt. Such salts as silver nitrate, in which the cation is itself a strong oxidizing agent, is a reactive salt. Ceric nitrate is also reactive, while hydrated cerous nitrate is not.

Preferred salts are the hydrated metal salts such as the nickel nitrate hexahydrate, magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, ferric nitrate nonahydrate, cupric nitrate trihydrate, zinc nitrate hexahydrate, cadmium nitrate tetrahydrate, bismuth nitrate pentahydrate, thorium nitrate tetrahydrate, cobalt nitrate hexahydrate, gadolinium or lanthanum nitrate nonahydrate, mixtures of these hydrated nitrates and the like. Nonhydrated or organic nitrates may be admixed therewith.

It is preferred to have the nitrate salt present in the particle. It is preferred to have at least 0.10 moles of the nitrate ion per mole of the leuco dye. It is more preferred to have at least 0.30 to 0.50 moles of the ion per mole of the dye. Amounts of 1.0 moles or greater of the nitrate ion per mole of the dye have been found useful in the practice of the prsent invention. It is preferable to have .5% to 40 % by weight of the imaging layer.

When aqueous coatable layer binders are used (e.g. gelatin, polyvinyl alcohol), the nitrate is generally contained therein. The nitrate salt ordinarily constitutes from 0.5% to 40 % by weight of the imaging layer or particle, and most preferably 1% to 15% by weight of the imaging layer. Higher percentages are generally used with aqueous coatable layer binders.

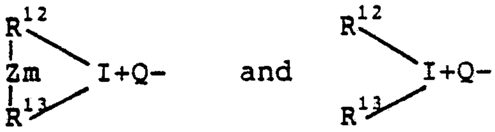
In the nitrate oxidizable leuco dye system of the present invention, inorganic or preferably organic acids are optionally added with the nitrate. Specific acids used in the present invention are disclosed in U. S. Patent Nos. 4,370,401, 4,386,154 and 4,460,677.

Acids may be added to the layer binder, in particular when aqueous coated layer binders are used. Inorganic acids are preferably chosen as the acid.

The acid may be present from 0 to 10% by weight, preferably from 0.01 to 5% by weight, and most preferably from 0.1 to 1% by weight of the imageable layer.

The image forming chemistry which contains colorizable or decolorizable imaging forming components is made sensitive to light by the use of separate light sensitive compounds. Light sensitve compounds useful in the present invention are disclosed in U.S. Patent Nos. 4,370,401, 4,386,154, 4,394,433, and 4,460,677. Preferred light sensitive compounds of the present invention are sensitizing dyes in combination with diaryliodonium salts, sensitizing dyes in combination with photolyzable organic halogen compounds, and light senisitive diazonium salts, and triplet sensitizers. These systems are generally free of silver halide as an active light-sensitive image forming component. The total absence of silver halides is preferred.

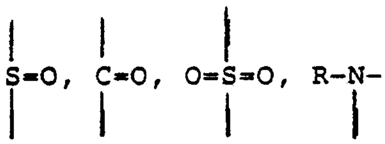
The diaryliodonium salts as referenced in U.S. Patent No. 4,386,154 may generally be described by the formulae:



wherein

R^{12} and R^{13} are individually selected from aromatic groups. Such aromatic groups may have from 2 to 20 carbon atoms (e.g. substituted or unsubstituted phenyl, napthyl, thienyl, and furanyl with substancially any subsititution,

Z is selected from a carbon-to-carbon bond, oxygen, sulfur



wherein

R is aryl (e.g. 6 to 20 carbon atoms) or acyl (e.g. 2 to 20 carbo atoms), or R^3 -C-R^5 wherein R^4 and R^5 are selected from hydrogen, alkyl groups of 1 to 4 carbon atoms, and alkenyl of 2 to 4 carbon atoms,

m is 0 or 1, and Q- is any anion.

Bis-onium salts such as those well known in the art may also be used and are included within the term onium.

Where the term group ,is used in describing substituents, substitution is anticipated on the substituent. For example, alkyl group includes ether groups (e.g. CH_3-CH_3-O-CH_2-) haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, etc. while the term alkyl includes only hydrocarbons. Substituents which react with active ingredients, such as very strong reducing or oxidizing substituents, would of course be excluded as not being sensitometrically inert or harmless.

Examples of diaryliodonium cations useful in the practice of the present invention are diphenyliodonium, 4-chlorophenyl phenyliodonium, di(4-chlorophenyl)iodonium, 4-trifluoromethylphenyl phenyliodonium, 4-ethylphenylphenyliodonium, di(4-acetylphenyl)iodonium, tolylphenyliodonium, anisylphenyl iodonium, 4-butoxyphenylphenyliodonium, di(4-phenylphenyl)iodonium, di(carbomethoxyphenyl)iodonium, 4-methoxyphenylphenyliodonium, 4-ethoxyphenylphenyliodonium, etc. Examples of these iodonium salts are disclosed in U.S. Patent Nos. 3,729,313, and 4,076,705, and as discussed in "Journal of Polymer Science; Polymer Symposium, 1976, 56, (Int. Symp. Cationic Polym, 4th) pp. 383-395.

The photolyzable organic halogen compounds are those that upon exposure to radiation dissociate at one or more carbon-halogen bonds to form free radicals. The carbon-halogen bonds form free radicals. The carbon-halogen dissociation energy should be between about 40 and 70 kilo calories per mole as taught in U.S. Patent Nos. 3,515,552 and 3,536,481. Preferred halogen compounds are non-gaseous at room temperature and have polar half-wave reduction potentials greater than about -0.9 V as described in U.S. Patent Nos. 3,640,718, 3,617,288, and 3,779,778.

Examples of photolyzable organic halogen compounds are hexabromoethane, tetrabromoxylene, carbon tertabromide, m-nitro-tribromoacetyl benzene, trichloroacetanilide, trichlorosulfonyl benzene, tribromoquinaldine, bis-(pentachloro)-cyclopentadiene, tribromomethylquinoxaline, α,α-dibromo-p-nitrotoluene, hexachloro-p-xylene, dibromotetrachloroethane,pentabromoethane, dibromodibenzoylmethane, carbon tetraiodide, halomethyl-s-triazines such as, 2,4-bis(trichloromethyl)-6-methyl-s-triazine, 2,4,6,-tris(trichloromethyl)-s-triazine, and 2,4,-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine, etc. These compounds are disclosed, as noted above, in U.S. Patent Nos. 3,515,552, 3,536,489, 3;617,288, 3,640,718, and 3,779,778.

The light sensitive compounds should be at least 0.1% by weight of the dry particle, up to 25% by weight or more. Preferably they are present at from 0.3 to 10% by weight of the particle and most preferably from 0.5 to 5%.

Light sensitive diazonium salts are well known in the art. Preferred diazonium salts of this invention are disclosed in U.S. Patent Nos. 4,370,401 and 4,394,433.

These salts comprise a light sensitive aromatic nucleus with an external diazonium group and an anion associated therewith (e.g. "Light sensitive Systems", Kosar, pp. 202-214, John Wiley and Sons, Inc., 1965, N.Y.; and "Photographic Chemistry", Vol. II, pp. 709-725, Fountain Press, London). They may be generally represented by the formula:

$ArN_2 + X-$

wherein
Ar is an aromatic nucleus, and
X- is an anion.

Any anion may be used on the diazonium salt. Anions as diverse as zinc chloride, tri-isopropyl naphthalene sulfonate, fluoroborate, (i.e. BF_4-), and bis(perfluoroalkylsulfonyl)methides may be used. The change in the anions may affect the speed of the imaging particle, but not its function. Any light sensitive aromatic diazonium nucleus, as known in the art, may also be used in the practice of the present invention. These nuclei are well known in the art, and include for example, p-anilinobenzene; N-(4-diazo-2,4-dimethoxy phenyl) pyrollidine; 1-diazo-2,4-diethoxy-4-morpholino benzene; 1-diazo-4-benzoyl amino-2,5-diethoxy benzene; 4-diazo-2,5-dibutoxy phenyl morpholine; 4-diazo-1-dimethyl aniline; 1-diazo-N,N-methyl aniline; 3-methyl-4-pyrollidone benzene; 1-diazo-4-N-methyl-N-hydroxyethyl aniline; etc. Light sentsitive oligomeric diazonium resins known in the art (e.g. U.S. Patent No. 2,714,066) are useful and are specifically included within the definition of diazonium salts as they are merely condensation products of the salts (with aldehydes such as formaldehyde) and retain their light sensitive and active properties. These salts should be present as at least about 0.1% by weight of the dried imaging particle up to 15% or more. Preferably they are present as from 0.3-10% by weight of the particle and most preferably as 0.5-5% by weight of the particle and in at least equal molar proportions to the dye or leuco dye.

A wide variety of sensitizing dyes for the diaryliodonium and photolyzable organic halogen compounds are known in the art. U.S. Patent Nos. 3,729,313 and 3,808,006 show a variety of sensitizing dyes for the iodonium salts. Most of these dyes will also sensitize the photolyzable organic halogen compounds. Preferred sensitizing dyes for the diaryliodonium and photolyzable organic halogen compounds are disclosed in U.S. Patent Nos. 4,460,677, 4,386,154 and 4,373,020.

Although the concentration ratio of the sensitizer to photosensitive compound is not critical and will depend on such factors as the desired use, the selection of sensitizer, the selection of diaryliodonium compound, etc., generally the molar concentration ratio is between 1/100 and 2/1, respectively, and preferably between 1/70 to 1/2, sensitizer to photosensitive compound.

The sensitizing dye should be present in amounts less than 0.5 times the amount of photoinitiator, preferably less than 0.3 times, and most preferably less than 0.2 times the amount of the photoinitiator. Amounts equal to or greater than 0.5 times the amount of the photoinitiators may be used, but this tends to add undesired coloration to the sheet.

The dyes that are useful in the decolorizable systems of the present invention are any bleachable dye. In some constructions it may be preferable to use those which have an oxidation potential of less than or equal to +1.0. These classes include but are not limited to methine, indamines, anthraquinones, triarylmethanes, benzylidenes, monoazos, oxazines, azines, thiazines, xanthenes indigoids, oxonols, cyanines, merocyanines, phenols, napthols, pyzazolones, and others, of which most are classified by the Colour Index. The dyes which have been specifically shown to work in the system of the present invention are disclosed in U.S. Patent No. 4,373,020.

Preferred amounts used in the present invention are disclosed in U.S. Patent No. 4.373,020.

The particle binder can be selected from any natural or synthetic water-insoluble polymeric binder for practice of the present invention. Organic polymeric resins, preferably thermoplastic resins (although thermoset resins may be used), are generally preferred. Where speed is important, water-insoluble, water impermeable, water resistant polymers should be used and an acid should be added to the system to increase the rate of colorizing (i.e. leuco dye oxidation). Such resins as phenoxy resins, polyesters, polyvinyl resins, polycarbonates, polyamides, polyvinyl butyral, polyvinylidine chloride, polyacrylates, cellulose esters, copolymers and blends of these classes of resins, and others have been used with particular success. Where the proportions and activities of leuco dyes and nitrate ion require a particular developing time and temperature, the resin should be able to withstand those conditions. Generally it is preferred that the polymer not decompose or lose its structural integrity at 260°F (167°C) for 30 seconds and most preferred that it not decompose or lose its structural integrity at 260°F (127°C) for 30 seconds. Preferred polymers are polyvinylidene chloride (e.g., Saran) and phenoxy resins (e.g. PKHH and PAHJ supplied by Union Carbide Chemical Corp.)

The particle binder serves a number of additionally important purposes in the constructions of the present invention. The imageable materials are protected from ambient conditions such as moisture. The consistency of the coating and its image quality are improved. The durability of the final image is also significantly improved. The binder should be present as at least about 25% by weight of the ingredients in the particle, more preferably as 50% to 70% by weight and most preferably about 80% by weight of dry ingredients (i.e., excluding solvents in the particle). A generally useful range is 30-98 percent by weight binder with 60 to 95 percent preferred.

The layer binder, and its solvent (if any), used to associate the various particles, is preferably not able to dissolve the active light sensitive, dry processable chemistry within the particle. If it were a very active solvent for the chemistry, it would tend to leach out the chemistry and alter the sensitometry for the system with time. This can be avoided by using different solvent systems in the layer binder and in the particles and/or using polymer systems in the respective portions which are not soluble in a common binder.

Some specific examples of the layer binders include aqueous coatable layer binders such as gelatin, polyvinyl alcohol, and hydroxyalkyl celluloses, and aliphatic or cycloaliphatic hydrocarbon solvent coatable binders such as copolymers of vinyl toluene and long chain alkyl acrylic esters, (i.e. NeoCryl S-1004, Polyvinyl Chemical Industries, and Pliolite VT-ALL), styrene/butadiene copolymers and polybutadienes.

Various other adjuvants may be added to the particle or layer of the present invention. For example, plasticizers, coating aids, antioxidants (e.g. ascorbic acid, hindered phenols, phenidone, etc., in amounts that would prevent premature oxidation of the dyes when heated), surfactants, antistatic agents, waxes, ultraviolet radiation absorbers, mild oxidizing agents in addition to the nitrate, and brighteners may be used without adversely affecting practice of the invention. These and other well-known additives may be usefully incorporated in either the particle or integral layer.

There are a wide number of advantages to the practice of the present invention that have not been available to systems of the prior art. Multicolor, single layer, light sensitive, dry processable systems can be readily made. A stable, color forming particle can be produced which can be stored and used in different systems.

These and other aspects of the present invention will be shown in the following non-limiting examples.

Methods used in the Examples

Solutions were prepared and spray dried using the appropriate safe lights. Spray drying was accomplished using Buchi Model 190 spray dryer with a 0.5mm nozzle. Typical operating conditions were:

Atomizer flow setting 800, from a 60psi air line, pump setting 12, aspirator control setting full, heat off, with an inlet temperature at ambient conditions.

Particle size was determined by visible light microscopy with an Ortholux II Polarizing Model BK microscope (Leitz) or a Zeiss Universal Model Microscope (NCI, INC.) Particle diameters generally ranged from one to 10 microns with 2 to 3 micron particle diameters common. Dispersal of the particles in the second binder layer and coating is described in the examples.

Image evaluation consisted of exposure lengthwise, of a 6"x1" strip of film construction on a diffuse incandescent light stage (3M Model 179 Contact Printer-Processor) set at full intensity to deliver about 2.4×10^6 microwatts/cm^2 (as determined with a radiometric filter) or under a 150 watt tungsten reflector spot source at a distance of 30 in., and contact of the strip, coated side up, for the indicated time to a temperature gradient heat bar (Heizbank). The temperature corresponding to the location on the strip where visual image-dye development occured is reported as the "thermal limit", and comparison versus the thermal limit of unexposed film was made. Optical densities were determined with a Macbeth TR 527 densitometer, with the appropriate filter setting corresponding to the image color.

The particular examples used demonstrate negative image forming constructions. That is, where the light of the appropriate wavelength has exposed the film in an imagewise sense, subsequent dye development requires a lower temperature than in the unexposed areas for the same thermal development time. Thus, a lower thermal limit in light exposed areas than in unexposed areas indicates an imaging light sensitive response of the film to that light.

EXAMPLE 1

Example 1

Preparation of non-sensitized, cyan image fine particles

To a solution of 22.5 g of PKHH resin and 675 g of methylene chloride, was added with agitation a solution of 4.82 g of magnesium nitrate hexahydrate, 2.97 g of 1,3,5-benzenetricarboxylic acid, and 180 g of methanol. Then, 14.52g of cyan leuco dye(Copikem II leuco, Hilton Davis), was added and the solution spray dried to afford 33.65 g of fine powder with particle diameters of 2-10 microns.

EXAMPLE 2

Preparation of cyan image film construction with green absorbing sensitizer in gelatin layer binder

To 1.0 g of the cyan powder prepared in Example 1, 1.0 g of a 2% by weight solution of polyvinyl alcohol in water was added, and the mixture ball milled for 3 days. To the obtained, dispersed cyan powder mixture, the following were added:

50.0 g warm solution of 2% by wt. solution of gelatin in distilled water
0.15 g 4-methoxyphenylphenyliodonium trifluoroacetate
.024 g green light absorbing sensitizing dye #6

The mixture was dispersed with a Polytron homogenizer (Brinkman Instruments) for about one minute. A solution of 2 g of aluminum nitrate nonahydrate, 0.6 ml of 5% sulfuric acid, and 3 ml of water was added with blending, and the mixture was dip-coated onto a 2 mil white opaque polyester film and allowed to dry at room temperature overnight to afford a dry coating thickness of 13 microns. A one minute imagewise exposure on the light stage followed by a 10 second thermal development at 82-85 °C afforded cyan images in a negative imaging sense with D_{max} of 2.45 and D_{min} of 0.38. A one minute imagewise exposure to the 150 watt spot source and 20 second contact on the heat bar afforded a thermal limit of 90 °C in unexposed areas and 79-80 °C in exposed areas with Dmax of 2.45 and Dmin of 0.13.

EXAMPLE 3

Preparation of cyan image film construction with UV absorbing diazonium salt in gelatin layer binder

A film construction was prepared as in Example 2, but in place of the iodonium salt and sensitizing dye, 0.05 g of diazonium salt #4 was used. A dry coating thickness of 20 microns was obtained. The film was imagewise exposed to the 150 watt spot source and a 20 second contact on the heat bar afforded a thermal limit of 84 °C in unexposed areas and 65 °C in exposed areas with D_{max} of 1.44 and D_{min} of 0.33. A 15 second imagewise exposure to the 150 watt spot source, followed by a 4 second thermal development at 91 °C afforded cyan images in a negative imaging sense with D_{max} of 1.9 and Dmin of 0.10.

EXAMPLE 4

Preparation of a blue sensitive, magenta image fine particles

Under red safelights, to a solution of 2.0 g of 4-ethoxyphenylphenyliodonium trifluoroacetate in 200 ml of water, a solution of 1.0 g of blue-light absorbing sensitizing dye #10 and 150 ml of water was added. The resulting diaryliodonium salt of the dye was collected by filtration, washed with water, and vacuum dried at room temperature for 3.5 hours to afford 1.42 g of sensitizing dye #11. Then 0.25 g of sensitizing dye #11 was dissolved in a solution of 15 g of PKHH resin, 450 g of methylene chloride, 5.0 g of magenta leuco #2, and 4.0 g of diphenyliodonium hexafluorophosphate. The solution was spray dried to afford 16.42 g of fine powder.

EXAMPLE 5

Preparation of blue sensitive, magenta image construction with gelatin layer binder

A film construction as in Example 2 was prepared using the powder prepared in Example 4. No sensitizing dye or initiator was added to the gelatin layer binder. Dry coating thickness was 14 microns. A one minute imagewise exposure on the light stage, followed by a 9 second thermal development at 82 °C afforded a magenta image in a negative imaging sense with D_{max} of 1.40 and D_{min} of 0.21. A one minute imagewise exposure to the light stage and a 20 second contact on the heat bar afforded a thermal limit of 73 °C in unexposed areas and 65 °C in light exposed areas with D_{max} of 1.40 and D_{min} of 0.30.

EXAMPLE 6

Preparation of green sensitive, cyan image fine particles

Under red safelights, to a solution of 3.58 g of 4-ethoxyphenylphenyliodonium trifluoroacetate and 300 ml of water, was added a mixture of 1.79 g of green-light absorbing dye #8 and 400 ml of water. The mixture was set aside in the dark for 2 days. The resulting diaryliodonium salt of the dye was collected by filtration, washed with water, and vacuum dried at room temperature for 7 hours to afford 1.88 g of sensitizing dye #9; 0.15 g of the dye was dissolved in a solution of 3.75 g of PKHH resin, 112.5 g of methlylene chloride, 2.4 g of cyan leuco #1, and 2.0 g of diphenyliodonium hexafluorophospate. The solution was spray dried to afford 4.2 g of fine powder.

EXAMPLE 7

Preparation of blue sensitive, magenta image fine particles

A solution of 15g of PKHH resin, 450 g of methylene chloride, 5.0g of magenta leuco #2, 0.24 g of blue-light absorbing sensitizing dye #11 (as prepared in Example 4), and 4.0 g of diphenyliodonium hexafluorophosphate was spray dried to afford 16 g of fine powder.

EXAMPLE 8

Preparation of green sensitive, cyan image and blue sensitive, magenta image single layer construction with gelatin layer binder

A mixture of 0.4 g of powder prepared in Example 6, 0.5g of powder prepared in Example 7, and 2.5 g of a solution of 2% by weight polyvinyl alcohol in water was ball milled for 70 hours. The composition was then blended for one minute in a Silverson Model L2R homogenizer with a warm gelatin solution containing 60 ml of 5% gelatin in water, 4 g of a 40% by weight solution of aluminum nitrate in water, and 0.4 ml of 5% sulfuric acid. The solution was dip-coated onto a 4 mil (0.1 mm) white opaque polyester film, and air dried in the dark at room temperature for 5 hours. A sample was exposed on the light stage through strips of Kodak No. 99 Wratten green filter and Kodak No. 47b Wratten blue filters for 40 seconds followed by a 10 second contact on the heat bar. Distinguishable magenta color with D_{max} of 0.80 formed in the areas exposed to the blue light, and blueish-purple colors were formed in areas exposed to white light. Color image development started (i.e. the thermal limits) respectively at 85°C, 84°C (cyan image), 80°C (magenta image), and 70°C (cyan-magenta image) in no light, green light, blue light, and white light exposed areas indicating two essentially independently acting color forming chemistries, in a single layer.

EXAMPLE 9

Preparation of red sensitive, cyan image fine particles

A solution of 3.75 g of PKHH resin, 112.5 g of methylene chloride, 1.2 g of cyan leuco #1, 0.06 g of red light absorbing sensitizing dye #12, 0.2 g of diphenyliodonium hexafluorophosphate, and 3.6 g of methanol was spray dried to afford 2.6 g of fine powder.

EXAMPLE 10

Preparation of green sensitive, magenta image fine particles

Under red safelights, to a solution of 1.0 g of 4-ethoxyphenylphenyliodonium trifluoroacetate, and 100 ml of distilled water was added a solution of 0.5 g of green-light absorbing dye #6 and 25 ml of water. The mixture was set aside in the dark overnight. The gummy solid was collected by filtration, washed with water, and dissolved in about 100 ml of methylene chloride. The solution was dried over anhydrous sodium sulfate, and evaporated "in vacuo" to afford 0.75 g of dye #7. Then 0.1 g of dye #7 was dissolved in a solution of 3.75 g of PKHH resin, 112.5 g of methylene chloride, 1.2 g of magenta leuco #2, and 0.8 g of diphenyliodonium hexafluorophosphate. The solution was spray dried to afford 2.8 g of fine powder.

EXAMPLE 11

Preparation of green sensitive, magenta image and red sensitive, cyan image single layer construction with polyvinyl alcohol layer binder

A mixture of 0.25 g of powder prepared in Example 9, 0.25 g of powder from Example 10, and 1.9 g of a 2% by weight solution of polyvinyl alcohol in water, was hand shaken with 1/8" steel balls for 3 minutes. The mixture was blended with a solution of 50 g of 5% by weight polyvinyl alcohol in water, 5.0 g of a 40% by weight solution of aluminum nitrate in water, and 0.5 ml of 5% sulfuric acid, coated onto 4 mil white opaque polyester film, and evaluated as in Example 8. Distinguishable magenta color thermally developed in areas exposed on the light stage to green light (Kodak No. 99 Wratten green filter), and cyan-magenta mixed colors were shown in areas exposed to white and red lights (Kodak #25 Wratten filter). Color image development started respectively at 78°C (cyan), 75°C (magenta), and 70°C (cyan-magenta) in red light, green light, and white light exposed areas indicating two essentially independently acting color forming imaging chemistries in a single layer.

EXAMPLE 12

Preparation of red sensitive, cyan image fine particles

To a solution of 7.5 g of PKHH resin, 225 g of methylene chloride, 0.4g of cyan leuco # 3, and 0.08 g of red-light absorbing dye #13 was added with agitation a solution of 0.13 g of magnesium nitrate hexahydrate, 0.07 g of succinic acid, and 4.5 g of methanol. Then, 0.3g of 2,4-bis(trichloromethyl)-6-methyl-1,3,5-triazine was added, and the solution spray dried to afford 5.5 g of fine powder with particle diameters of 1-8 microns.

EXAMPLE 13

Preparation of green sensitive, magenta-image fine image particles

To a solution of 7.5 g of PKHH resin, 225 g of methylene chloride, 0.6g of magenta leuco #2, and 0.02 g of green-light absorbing dye #14 was added with agitation a solution of 0.13 g of magnesium nitrate hexahydrate, 0.07 g of succinic acid, and 4.5 g of methanol. Then, 0.3g of 2,4,-bis(trichlormethyl)-6-methyl-1,3,5-triazine was added, and the solution spray dried to afford 4.6 g of fine powder with particle diameters of 1-10 microns.

EXAMPLE 14

Preparation of red sensitive, cyan image construction with organic solvent soluble layer binder

0.5 g of the powder prepared in Example 12 was dispersed by vigorous stirring with a spatula into 0.54 g of NeoCryl S-1004. The mixture was diluted with 2.04 g of cyclopentane, vigorously shaken, coated onto 4 mil white opaque polyester with a No. 30 RDS Bar coater (69 micron wet thickness, and 15 micron dry thickness) and dried for 15 minutes at room temperature, followed by 5 minutes at 50° C. A 20 second imagewise exposure on the light stage, followed by a 35 second thermal development at 93° C afforded a cyan image in a negative imaging sense with D_{max} of 1.24 and D_{min} of 0.55. The film was exposed for 20 seconds on the light stage and a 20 second contact on the heat bar afforded a thermal limit of 101° C for an unexposed sample and 91° C for an exposed sample with D_{max} of 1.46 and D_{min} of 0.67.

EXAMPLE 15

Preparation of green sensitive, magenta image construction with organic solvent soluble layer binder

A film was prepared as in Example 14, except the powder of Example 13 was used. A 13 micron dry coating was obtained. A 20 second imagewise exposure on the light stage, followed by a 35 second thermal development at 85° C, afforded a magenta image in a negative imaging sense with D_{max} of 0.93 and D_{min} of 0.50. The film was exposed for 20 seconds on the light stage, and contacted for 20 seconds on the heat bar. A thermal limit of 96° C for an unexposed sample and 80° C for an exposed sample was obtained. D_{max} was 1.05 and D_{min} was 0.46.

EXAMPLE 16

Preparation of green sensitive, magenta image and red sensitive, cyan image single layer construction with organic soluble layer binder

A film was prepared as in Example 14 or 15, except 0.5 g of the powder of Example 12 and 0.5g of the powder of Example 13 were used, and 1.08 g of NeoCryl S-1004 was used. A 15 micron dry coating was obtained. Distinguishable cyan color thermally developed in regions exposed on the light stage to red light. A magenta color thermally developed in regions exposed to green light, and mixed cyan-magenta (blue) and magenta colors thermally developed in regions exposed to white light. The film was exposed for 20 seconds on the light stage (set for a light intensity of $8.5X10^5$ microwatts/cm^2 as determined with a radiometric filter) to no light, white light,green light, and red light, and then contacted to the heat bar for 5 seconds. The results obtained are shown in Table 1.

TABLE 1

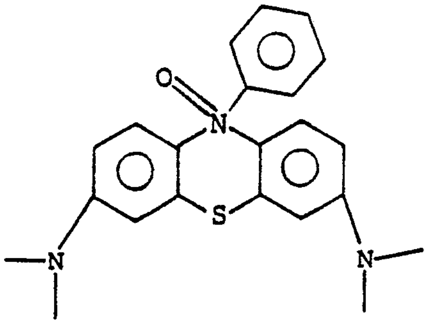
	Magenta			Cyan		
	Thermal limit	Dmax	Dmin	Thermal limit	Dmax	Dmin
no light	90 °C	---	0.60	103 °C	---	0.42
white light	70 °C	0.81-1.17	0.60	95 °C	1.21	0.42
green light	80 °C	0.81-0.92	0.60	>100 °C	0.71	0.42
red light	90 °C	0.60	0.60	99 °C	0.91	0.40

The examples demonstrate two distinct essentially independent acting color forming chemistries in a single layer. The dispersed green-light sensitized magenta image particles developed at lower temperature after exposure to green light, independently of the dispersed red-light sensitized cyan image particles. Likewise, the dispersed red-light sensitized cyan image particles developed at a lower temperature after exposure to red light, while the green-light sensitized magenta image particles did not respond to red light exposure. Both dispersed powders responded to white light exposure.

The following materials were used in the Examples:
bisphenol-A/eipichlorohydrin phenoxy resin - PKHH, Union Carbide
polyvinyl alcohol - Gelvatol 20-90
hydrocarbon soluble acrylic copolymer - Neocryl S-1004, 50% in Isopar G isodecane, Polyvinyl Chemical Industries
diphenyliodonium hexafluorophosphate
4-methoxyphenylphenyliodonium trifluoroacetate
4-ethoxyphenylphenyliodonium trifluoroacetate
Representative preparations in Journal of Polymer Research, Symposium No. 6, J.V. Crivello and J.H. W. Lam, pp. 383-395, 1976

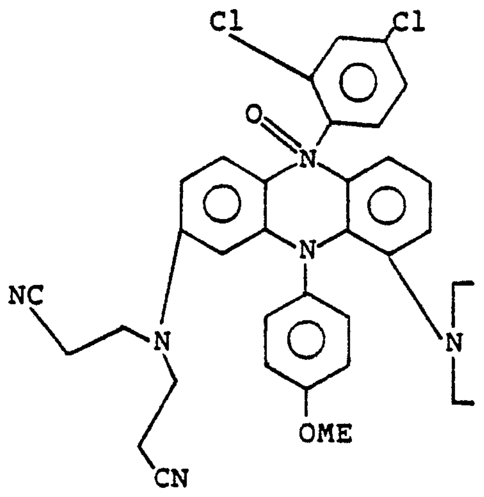
1. Copikem II leuco, Hilton-Davis

cyan leuco



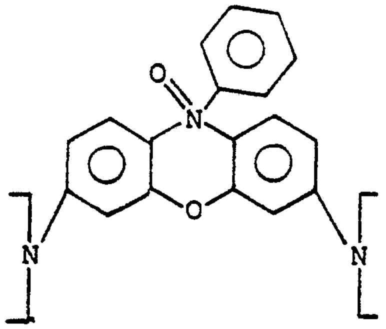
2. General preparation of oxazines, thiazines, azine leucos: A.W. Hill, British patent-GB 1271289

magenta leuco

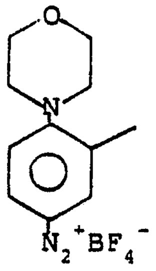


3. Pergascript Turquoise benzoyl leuco, Ciba-Geigy

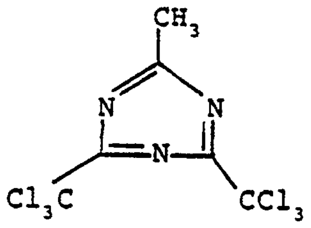
cyan leuco



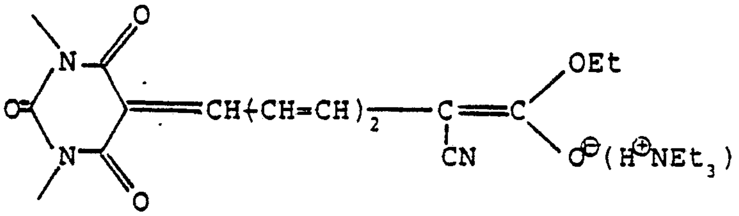
4. diazonium salt-Diazo 89



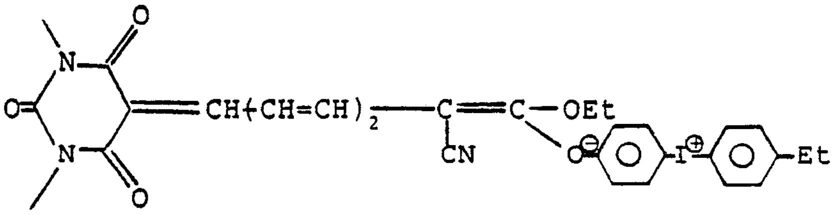
5. 2,4-bis(trichloromethyl)-6-methyl-1,3,5-triazine; preparation by K. Wakabayshi, et al, Bull. of the Chem. Soc. of Japan, Vol. 42, pp. 2924-2930,(1969).



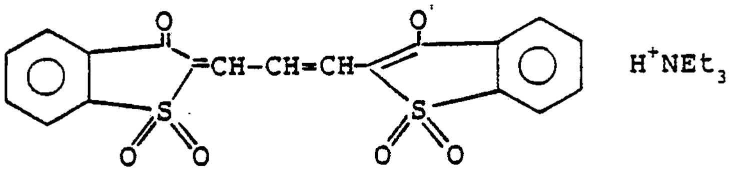
6. green sensitive sensitizer dye; U.S. Patent Number 4,632,895



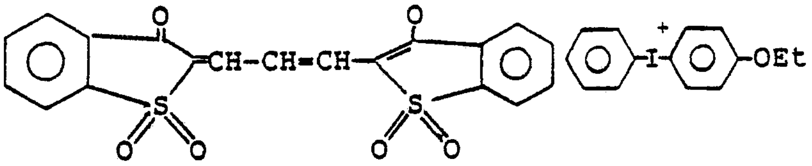
7. green senitive sensitizer dye



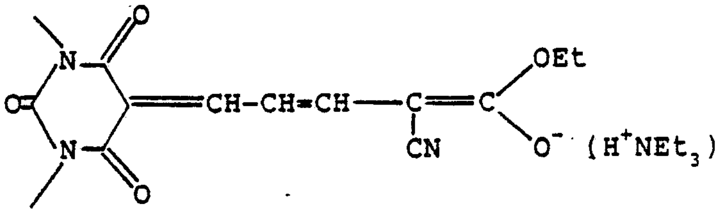
8. green sensitive sensitizer dye



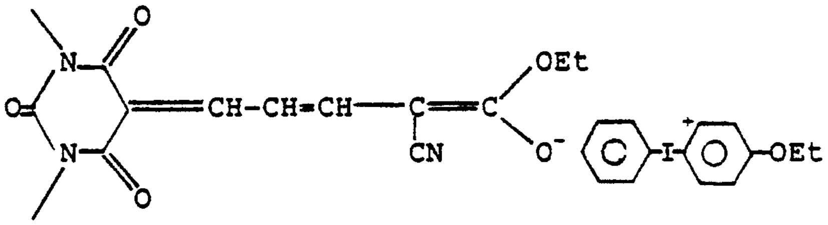
9. green sensitive sensitizer dye



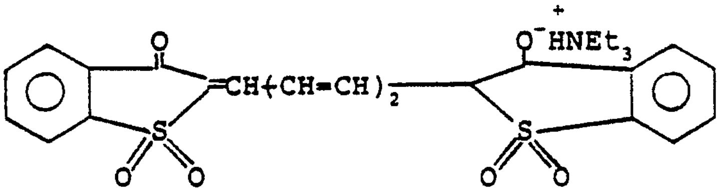
10. blue sensitive sensitizer dye



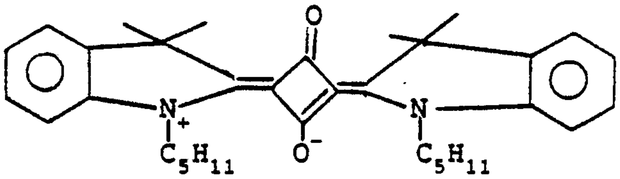
11. blue sensitive sensitizer dye



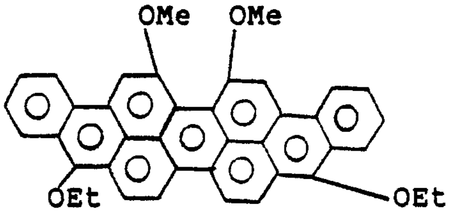
12. red sensitive sensitizer dye



13. red sensitive sensitizer dye; general preparations in Angew. Chem. Int. Ed., Vol. 7, pp. 530-535, (1968).



14. green sensitive sensitizer dye



Claims

1. An imageable particle having maximum dimensions between 0.1 and 100 microns comprising a transparent binder and a light sensitive system selected from a) bleachable dye and photosensitive compounds, b) leuco dyes and photosensitive compounds, and c) couplers and photosensitive initiators, and photosensitive compounds being selected from photosensitive onium salts and photolabile halogen compounds.

2. The particle of Claim 1 characterised in that the light sensitive system comprises a leuco dye and a photosensitive compound.

3. The particle of Claim 2 characterised in that the photosensitive compound comprises an onium salt.

4. The particle of Claim 3 characterised in that the onium salt is selected from the group consisting of iodonium sulfonium and diazonium salts.

5. The particle of Claim 4 characterised in that the onium salts are spectrally sensitized by a dye.

6. The particle of Claims 1, 2, 3 or 4 characterised in that a nitrate ion is present in the light sensitive system.

7. The particle of Claim 6 characterised in that an organic acid is present in the light sensitive systems.

8. An imageable layer comprising a multiplicity of the particles as defined in any preceding claim dispersed in a binder which is different from the transparent binder of the particle.

9. A layer as claimed in Claim 8 containing at least two different types of particles, each type of particle containing different leuco dyes and being spectrally sensitized to different portions of the electromagnetic spectrum each type of particle being capable of generating a color upon exposure which is different from the color generable by another type of particle within said layer.