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(54) Title: INK COATINGS FOR SECURITY DOCUMENTS TO PREVENT FORGERY BY MEANS OF HEAT SENSITIVE ERASABLE INK

(57) Abstract: Disclosed is a solvent-borne or UV-curable fugitive ink composition for application to a substrate that is to be provided with indicia. The ink composition comprises at least one halochromic compound and at least one filler compound and is capable of preventing indicia formed with a heat sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment from becoming invisible to an unaided eye.

INK COATINGS FOR SECURITY DOCUMENTS TO PREVENT FORGERY BY MEANS OF HEAT SENSITIVE ERASABLE INK

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to the field of the protection of value documents against forgery. Particularly the invention relates to the protection of value documents against forgery involving heat sensitive erasable ink compositions and the use of pens comprising a refill containing such heat sensitive erasable inks.

2. Discussion of Background Information

The commercialization of a new type of ball point pens comprising an ink refill containing heat sensitive erasable ink, also called in the patent literature Thermochromic Coloring Color-Memory Composition, represents a potential threat in the field of security documents.

Heat sensitive erasable ink compositions, in particular heat sensitive erasable aqueous ink compositions, are disclosed, for example, in EP 2 138 550, U.S. Patent Nos. 4,720,301 and 7,494,537, US 2009/0050013 A1, US 2010/0120614 A1, US 2011/0008095 A1, EP 1 820 662, EP 2 072 277, JP 2010-241867 and JP 2010-229333, the entire disclosures of which are incorporated by reference herein.

Ball point pens containing a refill containing heat sensitive erasable aqueous inks are now widely commercially available (e.g. FriXion™ Ball pens from Pilot or uni-ball fanthom™ pens from Mitsubishi). The writing implement comprising the heat sen-

sitive erasable ink formulation have been disclosed for instance in US 2011/0008095 A1, the entire disclosure of which is incorporated by reference herein.

The specific properties of a heat sensitive erasable ink are disclosed e.g. in U.S. Patent No. 4,720,301. The heat sensitive erasable ink composition comprises, as the main components, an electron-donating organic dye, a phenolic compound and an ester compound. The electron-donating organic dye acts as base; its protonated form is coloured while its unprotonated form is colourless. The phenolic compound acts as acid. The ester compound acts as a matrix for the acid-base pair. The ester compound is characterized by its melting and cloud points which are comprised in a range between 5°C and 50°C. The specific properties of the heat sensitive erasable ink are imputed to the large thermal maximum hysteresis between the different coloured states of the ink.

Indicia or texts written with a heat sensitive erasable aqueous ink may become discoloured by thermal treatment of the indicia: the ink forming the indicia is not physically removed from the substrate; however, through a thermal treatment, the written indicia become invisible to the naked eye of an observer. The thermal treatment may be produced by a heat source, e.g. an open flame or a hair-drier; or alternatively the thermal treatment of the indicia may simply consist in a mechanical rubbing of the ink layer, for instance with a conventional eraser or with a piece of synthetic rubber. The commercialized ball point pens comprising heat sensitive erasable ink refills are equipped with a rubber tip useful to render invisible ("to delete") written indicia or text.

The ink refills of the commercial pens comprising heat reversible thermal discoloration ink (i.e. heat sensitive erasable ink) are removable and refills are commercially available separately. Thus, a forger may insert an ink refill containing a heat sensitive erasable ink composition, for instance a heat sensitive erasable aqueous ink composition, into an ordinary or a luxury pen and urge a person to use this pen to fill in a value document, for instance a bank cheque; the forger could then easily alter the hand-written information.

In view of the foregoing facts such ball point pens containing a heat sensitive erasable ink formulation and the corresponding refills present a threat in the field of security documents. Forgers may use them for the falsification of value documents, for instance of identity documents, bank cheques, vouchers, fiduciary acts, deeds or certificates.

It is known in the art that value documents, such as for instance cheques, are protected against forgery or tampering attempts through the use of special inks for the background printing. In particular, specific inks have been developed to coat with a printed layer the background of the value document or cheques, in particular in the document areas that must be completed with hand-written information: thus the indicia or the text hand-written in these areas cannot be fraudulently altered or deleted. Usually tampering attempts are performed by using solvents or acids to dissolve the ink of hand-written indicia; or alternatively forgers attempt to delete the information with a conventional eraser. By using specific inks to print the documents background, any tampering attempts leave a clearly visible mark on the document. Specific inks used for this purpose are for instance solvent reactive inks, water fugitive inks or mechanically erasable inks. The protection of the security docu-

ments relies upon a colour fading, a colour change or disappearance, or a bleeding off when the document is subject to a falsification attempt by any means such as e.g. an eraser, an organic solvent or an aqueous solution. Fugitive inks are known in the art (see e.g. The Printing Ink Manual, Ed by R.H. Leach and R.J.Pierce, 5th edition, page 341. EP 0 835 292, the entire disclosure of which is incorporated by reference herein, discloses for instance such a solvent bleeding ink composition used to print value documents.

However, neither solvent reactive inks nor water fugitive inks would prevent indicia written with a heat sensitive erasable ink to be deleted or rendered invisible through a thermal treatment.

Thus there is a need for a new ink composition, in particular among printers manufacturing value documents, for instance identity documents, bank cheques, vouchers, fiduciary acts, deeds or certificates or other value documents. The new ink composition should combine the forgery prevention properties of the known fugitive ink compositions with new properties aimed at preventing forgery by means of heat sensitive erasable inks.

SUMMARY OF THE INVENTION

The present invention provides a solvent-borne or UV-curable fugitive ink composition for application (e.g. coating) onto a substrate which is to be provided with indicia (e.g. a signature). The ink composition comprises at least one halochromic compound (e.g. one, two, three or more halochromic compounds), at least one filler compound, and the ink composition is capable of preventing indicia that have been formed with a (preferably aqueous) heat sensitive erasable ink (i.e. heat reversible thermal discoloration ink) on an area of the substrate to which the fugitive ink composition has been applied and which indicia have

thereafter been subjected to a thermal treatment from becoming invisible to an unaided eye. In other words, the fugitive ink composition of the present application forms a heat-un-erasable *(or a heat un-sensitive)* mark when an indicia is formed with a heat sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment.

In one aspect of the ink composition, the at least one halochromic compound may be or comprise a compound that changes its color when subjected to a pH change at a pH of equal to or lower than 7.0. For example, the at least one halochromic compound may change its color from a colorless or pale colored state at a lower pH to a (more) colored state at a higher pH.

In another aspect of the composition, the composition may comprise from 0.1 % to 5 % by weight, e.g., from 0.5 % to 2 % by weight of the at least one halochromic compound, based on the total weight of the composition.

The at least one filler compound (one or more filler compound) is preferably an ionic filler compound and may be selected from the group consisting of carbon fibers, talc, mica (e.g. muscovite), wollastonite, calcinated clay, kaolin, carbonates (e.g. calcium carbonate, sodium aluminum carbonate), silicates (e.g. magnesium silicate, aluminium silicate), sulfates (e.g. magnesium sulfate, barium sulphate), titanates (e.g. potassium titanate), titanium dioxide, montmorillonite, graphite, vermiculite, wood flour, quartz flour, natural fibers, synthetic fibres and combinations thereof. Preferably, the one or more fillers are selected from the group consisting of talc, mica (preferably muscovite), wollastonite, calcinated clay, kaolin, silicates (preferably magnesium silicate and/or aluminium silicate), car-

bonates (preferably calcium carbonate), montmorillonite and combinations thereof. The one or more fillers are preferably present in an amount from at or about 0.1 to at or about 40 wt-%, more preferably from at or about 1 to at or about 30 wt-%, the weight percentages being based on the total weight of the fugitive ink composition.

In yet another aspect, the ink composition may further comprise at least one organic dye that becomes luminescent (e.g., fluorescent) upon irradiation with UV light. For example, the composition may comprise from 1 % to 15 % by weight, e.g., from 1 % to 10 % by weight, or from 1 % to 5 % by weight of the at least one organic dye, based on the total weight of the ink composition.

In yet another aspect, the ink composition of the present invention may further comprise one or more additives selected from the group consisting of a wax, a solvent, an antioxidant, a drying agent, a dyestuff, an anti-foaming additive, a UV stabilizer, and a photoinitiator.

In a still further aspect, the ink composition of the present invention may be selected from the group consisting of solvent reactive inks, water fugitive inks, mechanically erasable inks, solvent reactive and water fugitive inks, solvent reactive and mechanically erasable inks, water fugitive and mechanically erasable inks, and water fugitive and solvent reactive and mechanically erasable inks.

In yet another aspect, the ink composition of the present invention, upon treatment of heat-treated indicia with an acidic liquid, may be capable of leaving visible marks on the area of the substrate carrying the ink composition.

The present invention also provides a substrate which comprises the fugitive ink composition of the present invention as set forth above (including the various aspects thereof) in at least one surface area thereof. For example, the substrate may be at least one selected from the group consisting of a commercial good, a value document, an identity document, an identity card, a passport, a driver's license, a bank cheque, a money transfer order, a voucher, a fiduciary act, a deed, and a certificate.

The present invention also provides a method of making a fugitive ink composition of the present invention as set forth above. The method comprises combining a (conventional) fugitive ink composition (e.g., a known fugitive ink composition) with at least one halochromic compound.

The present invention also provides a method of protecting a commercial good or security document from forgery. The method comprises applying the fugitive ink composition of the present invention as set forth above onto at least one area of the good or document that is to be provided with indicia.

In one aspect of the method, the ink composition may be applied by a printing method. For example, the printing method may be selected from the group consisting of offset, flexographic, gravure, inkjet, letterpress and screen printing.

In another aspect of the method, the fugitive ink composition may be selected from the group consisting of evaporation-drying inks, absorption-drying inks, oxidative-drying inks, and radiation-curable inks.

The present invention also provides the use of a fugitive ink composition of the present invention as described above for pre-

venting an indicia formed with a heat sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment from becoming invisible to an unaided eye.

According to a further aspect of said use, said fugitive ink composition is capable of leaving a mark that is visible with an unaided eye on the area of the substrate that carries the ink composition when indicia applied to said area with a heat sensitive erasable ink are first heat treated and subsequently treated with an acidic liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings,

- Figures 1a - 1d show photographs of samples prepared and treated according to the procedures described in Example 1 below;
- Figures 2a and 2b show photographs of samples prepared and treated according to the procedures described in Example 2 below;
- Figures 3a - 3c show photographs of samples prepared and treated according to the procedures described in Example 3 below; and
- Figures 4a and 4b show photographs of samples prepared and treated according to the procedures described in Comparative Example 1 below.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The particulars shown herein are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the pre-

sent invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description in combination with the drawings making apparent to those skilled in the art how the several forms of the present invention may be embodied in practice.

The fugitive ink composition of the present invention preferably dries to form a solid matrix remaining sensitive to solvents, water, acids, bleaches or other chemical reagents, and reacts with heat sensitive erasable ink compositions (i.e. heat reversible thermal discoloration ink compositions), in particular with heat sensitive erasable aqueous ink compositions (i.e. heat reversible thermal discoloration aqueous ink compositions). Thus, forgery attempts perpetrated on documents coated with an ink composition of the present invention, including forgery attempts using heat sensitive erasable inks, can easily be detected.

This effect is for instance exemplified in Figures 1 and 4 of the present invention. In particular, **Fig. 1a** shows a picture of a substrate completely printed with a coating layer made of an ink composition according to the present invention; the ink composition is a solvent reactive ink containing a halochromic compound as described in example 1 below. Visible indicia (hand-written text) have been written on the substrate with a pen containing a heat sensitive erasable ink formulation (FriXion™ Ball pen from Pilot). **Fig. 1b** shows a picture of the same substrate as in **Fig. 1a** after the hand-written text has been rubbed with the rubber tip of the pen or with a conventional eraser: the text remains visible to an unaided eye.

By contrast, **Figs. 4a** and **4b** show pictures of a sample prepared with a known fugitive ink. **Fig. 4a** shows a picture of a substrate completely printed with a coating layer made with a known solvent reactive ink (not part of the present invention) as described in comparative example 1. Visible indicia (hand-written text) have been written on the substrate with a pen containing a heat sensitive erasable ink formulation. **Fig. 4b** shows a picture of the same substrate as in **Fig. 4a**, after the hand-written text, which was visible in **Fig. 4a**, has been rubbed with the pen rubber tip or with a conventional eraser: the text is no longer visible.

Thus, indicia hand-written with heat sensitive erasable ink on document background printed with the ink composition of the present invention remain visible to an unaided eye, even after thermal treatment or forgery attempts by chemical means.

The present invention provides a new ink composition for printing (coating), e.g., a background layer on, for example, a value document. The new ink composition is useful to coat completely or partially (e.g., in one or more areas that are to be provided with indicia) the value document in order to provide a background layer withstanding forgery attempts based on heat sensitive erasable ink. The forgery resistance of the background layer may, for example, be due to a chemical reaction of the ink composition of the present invention with the heat sensitive erasable ink formulation used to hand-write on the value document: in this case even upon thermal treatment or forgery attempts by chemical means the indicia remain visible.

The ink composition of the present invention combines the security features of the known inks used for printing the background layer of value documents such as for instance bank cheques with

additional functionalities designed specifically to prevent forgery with heat sensitive erasable inks. In particular, the ink composition of the present invention combines the security features provided by fugitive inks as known in the art with additional new security features designed specifically for preventing alteration of heat sensitive erasable inks. Thus the ink composition of the present invention is a fugitive ink that may be used to print the background layer of value documents and is characterized in that it forms permanently visible indicia or marks when printed, marked or put into contact with a heat sensitive erasable ink (i.e. a heat reversible thermal discoloration ink), in particular with a heat sensitive erasable aqueous ink (i.e. a heat reversible thermal discoloration aqueous ink).

The fugitive ink composition of the present invention comprises a (at least one) halochromic compound in addition to the usual components of a conventional fugitive ink composition. The fugitive ink containing the halochromic compound may, for example, be a solvent reactive ink, a water fugitive ink or a mechanically erasable ink.

As used herein, the term "*halochromic compound*" describes a material which changes optical state, in particular color, upon a change in pH. Thus a change in the acidity or basicity of the ink composition containing the halochromic compound results in a change of the optical absorbance of the halochromic material.

The halochromic component may be (and preferably is) a pH indicator having a transition pH range (color change) at a pH value equal or lower than 7.0. Preferably the halochromic component switches from a colourless or very pale coloured state at lower pH to a coloured state at higher pH.

Non-limiting examples of halochromic compounds which are suitable for use in the present invention include malachite green, brilliant green, eosine yellowish, erythhrosin B, methyl green, methyl violet, picric acid, cresol red, crystal violet, metanil yellow, m-cresol purple, thymol blue, p-xylenol blue, eosin bluish, naphtol yellow 2B, quinaldine red, 2,4-dinitrophenol, bromochlorophenol, bromophenol blue, bromocresol green, bromocresol green sodium salt, 2,5-dinitrophenol, alizarinsulfonic acid sodium salt, phloxine B, methyl red, methyl orange, chrysoidin, cochineal, chlorophenol red, bromocresol purple, bromophenol red, brilliant yellow, rosolic acid, 4-nitrophenol, o-cresolphthalein, bromoxylenol blue, alizarin, nitrazine yellow, bromothymol blue sodium salt, bromothymol blue, phenol red, phenol red sodium salt, 3-nitrophenol, phenolphthalein, mordant orange, thiazol yellow G, thymolphthalein, alizarin yellow GG, indigo carmine, and titan yellow, to name just a few.

The ink composition of the present invention may optionally contain further additives such as for instance dyes or pigments. In particular, the ink composition of the present invention may further contain from 1 to 15 %, preferably from 1 o 5% (weight %) of one or more organic dyes selected from dyes that are luminescent under UV-light illumination. Non-limiting examples of suitable organic dyes include xanthene (e.g. C.I. acid red 52, C.I. No. 45100), pyrene (e.g. C.I. solvent green 7, C.I. No 59040), methane (e.g. C.I. basic violet 21, C.I. No 48030), stilbene (e.g. direct yellow 106, C.I. No 40300), coumarin (e.g. C.I. No 551100), cyanine (e.g. C.I. No 48016), oxazine (e.g. C.I. No 51180), uranine (e.g. C.I. acid yellow 73, C.I. 45350) and/or C.I. acid yellow 245. Such dyes are known in the art and have been used for instance for colouring oxidised metal surfaces as disclosed in WO 2011/038829, the entire disclosure of which is incorporated by reference herein.

As used herein, the term "*permanent visible indicia*" denotes indicia that is visible to an unaided human eye and remains visible even after the indicia have been subjected to a physical or a chemical treatment, such as, for instance, exposure to a heat source, mechanical rubbing, or application of a solvent or an aqueous solution.

As used herein, the term "*fugitive inks*" refers to inks that irreversibly fade, disappear or change colour once water, aqueous solutions, bleaches or organic solvents are applied to surfaces printed with the fugitive inks under common conditions of forgery (i.e. conditions which do not adversely affect the substrate carrying on its surface the printed fugitive inks, e.g. the surface and/or the material of the value document carrying the fugitive inks); alternatively, the term "*fugitive inks*" refers to inks that irreversibly fade, disappear or change colour once surfaces printed with the fugitive inks are rubbed with, for instance, a conventional eraser. Such fugitive inks are known in the art and are used for instance to print backgrounds of value documents: any alteration of the background aspect represents an undisputable hint of a forgery attempt.

Fugitive inks known in the art may be classified as follows:
i) *solvent reactive ink*: an ink that irreversibly fades, disappears or changes colour when an organic solvent, e.g. alcohol, petrol, aromatic solvents e.g. toluene, is applied to a surface printed with this solvent-reactive ink under common conditions of forgery (i.e. conditions which do not adversely affect the substrate carrying on its surface the printed fugitive inks, e.g. the surface and/or the material of the value document carrying the fugitive inks);
ii) *water-fugitive ink*: an ink that irreversibly fades, disappears or changes colour when water, an aqueous solution or a

bleaching solution is applied to a surface coated with this water-fugitive ink under common conditions of forgery (i.e. conditions which do not adversely affect the substrate carrying on its surface the printed fugitive inks, e.g. the surface and/or the material of the value document carrying the fugitive inks);
iii) *mechanically erasable ink:* an ink that irreversibly fades, disappears or changes colour when the surface printed with this mechanically erasable ink is rubbed with a friction body, such as e.g. an eraser.

Thus, according to the present invention *fugitive inks* preferably comprise an ink selected from the group consisting of a solvent reactive ink, a water fugitive ink or a mechanically erasable ink; alternatively, as used herein, the term "*fugitive ink*" also comprises an ink combining the properties of at least two inks selected from the group of solvent reactive, water fugitive and mechanically erasable inks, for instance, an ink that is both solvent reactive and mechanically erasable.

As used herein, the term "*heat sensitive erasable ink*" refers to an ink formulation that *reversibly* fades or changes colour once subjected to a heat source. The reversible discoloration behaviour of the ink formulation results from the broad maximum hysteresis width of the colour density versus temperature curve. Thus, the ink formulation becomes discoloured upon application of a heat treatment of the printed ink layer; the ink layer maintains the colourless invisible state until the temperature is decreased below a threshold temperature; at this threshold temperature and below it, the ink layer reverts to its coloured visible state.
The heat sensitive erasable ink formulations suitable in the context of the present invention are reversible thermal discoloration compositions comprising

a) an electron-donating chromatic organic compound A (i.e. a Lewis base)
b) an electron-accepting compound (a Lewis acid) or a compound having an acidic proton (a Brönsted acid), as compound B
c) a compound C acting as the reaction medium controlling the reaction of compounds A and B, compound C being characterized by the temperature difference between its melting point and its clouding point, the temperature difference ranging between 5°C and 50°C.

Typical heat sensitive erasable ink formulations suitable for the present invention have been described in e.g. EP 2 138 550, U.S. Patent Nos. 4,720,301 and 7,494,537, US 2009/0050013 A1, US 2010/0120614 A1, US 2011/0008095 A1, EP 1 820 662, EP 2 072 277, JP 2010-241867 and JP 2010-229333.

As used herein, the term "*heat* sensitive *erasable ink*" does not refer to thermochomic inks based on liquid crystals material or on metallic compounds.

The ink composition of the present invention is a solvent-borne ink composition or a UV-curable ink composition. On the other hand, the ink composition of the present invention may not be a waterborne ink composition. The ink composition of the present invention may be dried by, for example, solvent evaporation, by absorption drying, by oxypolymerization or by radiation energy such as UV-light or e-beam (electronic beam).

According to one embodiment, the ink composition of the present invention is a solvent-borne ink composition. As used herein, the term "*solvent-borne ink composition*" refers to an ink composition whose liquid medium or carrier substantially consists of one or more organic solvents. The liquid medium of a solvent-

borne ink composition in accordance with the present invention comprises at most 5 wt.-% water, preferably at most 1 wt.-% water, and most preferred less than 0.1% water. The solvent-borne ink composition comprises the liquid medium usually in an amount of from 1 to 70% by weight, especially from 1 to 50% by weight, and more especially from 2 to 45% by weight, based on the total weigth of the ink.

Examples of such solvents include alcohols (such as e.g. methanol, ethanol, isopropanol, n-propanol, ethoxy propanol, n-butanol, sec-butanol, tert-butanol, iso-butanol, 2-ethylhexyl-alcohol); polyol (such as e.g. glycerol, 1,5-pentanediol or 1,2,6-hexanetriol); esters (such as e.g. ethyl acetate, propyl acetate, n-butyl acetate); carbonates (such as e.g. dimethyl carbonate, diethylcarbonate, di-n-butylcarbonate, 1,2-ethylencarbonate, 1,2-propylenecarbonate or 1,3-propylencarbonate); aromatic solvents (such as e.g. toluene, xylene); ketones (such as e.g. acetone, methyl ethyl ketone, methyl isobutyl ketone, diacetone alcohol, cyclohexanone); amides (such as e.g. dimethylformamide or dimethyl-acetamide); aliphatic or cycloaliphatic hydrocarbons; chlorinated hydrocarbons (such as e.g. dichloromethane); nitrogen-containing heterocyclic compound (such as e.g. N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone); ethers (such as e.g. diethyl ether, tetrahydrofuran, dioxane); alkyl ethers of a polyhydric alcohol (such as e.g. 2-methoxyethanol or 1-methoxypropan-2-ol); alkylene glycols, alkylene thioglykols, polyalkylene glycols or polyalkylene thioglykols (such e.g. ethylene glycol, polyethylene glycol (such as e.g. diethylene glycol, triethylene glycol, tetraethylene glycol), propylene glycol, polypropylene glycol (such as e.g. dipropylene glycol, tripropylene glycol,), butylene glycol, thiodiglycol, hexylene glycol or mixtures thereof); nitriles (such as e.g. acetonitrile, propionitrile), sulfur-

containing compounds (such as e.g. dimethylsulfoxide or sulfolan) and mixtures thereof.

Most preferably the liquid medium comprises a solvent selected from the group comprising aliphatic or cycloaliphatic hydrocarbons, nitrogen-containing heterocyclic compounds, polyalkylene glycol, esters and mixtures thereof.

According to another embodiment, the ink composition of the present invention is a UV-curable ink composition, preferably a radically UV-curable ink, i.e. inks curable through a radical curing mechanism.

As used herein, the term *"UV-curable ink composition"* refers to an ink composition which may be cured by UV-Visible light radiation (hereafter referred as UV-curable) and/or by E-beam radiation (hereafter referred as EB). When a UV-curable ink composition is used, it is preferred that the ink compositions is cured by UV-visible light radiation. Radiation curable compositions are known in the art and can be found in standard textbooks such as the series "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints", published in 7 volumes in 1997-1998 by John Wiley & Sons in association with SITA Technology Limited. Preferably the UV-curable ink compositions described herein comprise a) a binder compound which comprises oligomers (also referred in the art as prepolymers), preferably selected from the group consisting of radically curable compounds.

Radically curable compounds are cured by free radical mechanisms consisting of the activation by energy of one or more photoinitiators which liberate free radicals which in turn initiate the polymerization of the binder compound(s). Preferably, the binder consists of oligomers selected from the group consisting

of oligomeric (meth)acrylates, vinyl and propenyl ethers, and mixtures thereof, and more preferably the binder compound is selected from the group consisting of epoxy (meth)acrylates, (meth)acrylated oils, polyester (meth)acrylates, aliphatic or aromatic urethane (meth)acrylates, silicone (meth)acrylates, amino (meth)acrylates, acrylic (meth)acrylates, and mixtures thereof. A second binder may be added to the UV-Vis-curable optically variable compositions described herein, such a binder may be selected from the group consisting of monomeric acrylates such as for example trimethylolpropane triacrylate (TMPTA), pentaerytritol triacrylate (PTA), tripropyleneglycoldiacrylate (TPGDA), dipropyleneglycoldiacrylate (DPGDA), hexanediol diacrylate (HDDA) and their polyethoxylated equivalents such as for example polyethoxylated trimethylolpropane triacrylate, polyethoxylated pentaerythritol triacrylate, polyethoxylated tripropyleneglycol diacrylate, polyethoxylated dipropyleneglycol diacrylate and polyethoxylated hexanediol diacrylate. UV-Vis curing of a monomer, oligomer or prepolymer may require the presence of one or more photoinitiators and may be effected in a number of ways. As known by those skilled in the art, the one or more photoinitiators are selected according to their absorption spectra and are selected to fit with the emission spectra of the radiation source. Depending of the binder compound(s) comprised in the UV-curable ink compositions described herein, different photoinitiators might be used.

Suitable examples of free radical photoinitiators are known to those skilled in the art and include without limitation acetophenones, benzophenones, alpha-aminoketones, alpha-hydroxyketones, phosphine oxides and phosphine oxide derivatives and benzyldimethyl ketals. Other examples of useful photoinitiators can be found in standard textbooks such as "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints", Volume

III, "Photoinitiators for Free Radical Cationic and Anionic Polymerization", 2nd edition, by J. V. Crivello & K. Dietliker, edited by G. Bradley and published in 1998 by John Wiley & Sons in association with SITA Technology Limited. It may also be advantageous to include a sensitizer in conjunction with the one or more photoinitiators in order to achieve efficient curing. Typical examples of suitable photosensitizers include without limitation isopropyl-thioxanthone (ITX), 1-chloro-2-propoxy-thioxanthone (CPTX), 2-chloro-thioxanthone (CTX) and 2,4-diethyl-thioxanthone (DETX) and mixtures thereof. The one or more photoinitiators comprised in the UV-curable ink compositions are preferably present in an amount from about 0.1 to about 20 weight percent, more preferably about 1 to about 15 weight percent, the weight percents being based on the total weight of the UV- curable ink compositions.

Among chemicals used for forgery attempts, it is known in the art that acid is often used to attempt dissolving or discolouring the ink of the written indicia. As the forgery resistance of the new ink composition relies mainly on the presence of the halochromic component, the resistance against acid treatment preferably represents a key characteristic thereof. This resistance is exemplified, for instance, in the examples and figures below.

The ink composition of the present invention may be prepared by adding a (at least one) halochromic compound to a conventional fugitive ink composition. For instance, an ink composition according to the present invention may be prepared by the addition of from 0.1 % to 5 %, preferably 0.5 % to 2 % (weight percent) of a halochromic compound to a conventional fugitive ink formulation, e.g., to a solvent reactive ink formulation or to a water fugitive ink formulation.

Examples of typical conventional fugitive ink compositions for offset printing for instance may consist of or comprise the following components, depending on the drying mechanism and on the type of fugitive ink:

- oxidative-drying solvent reactive ink composition for offset printing

Component	**weight-%**
Varnish	40-80
Wax compound	0-5
Filler	2-30
Solvent	1-10
Antioxidant	0.5-2
Drier	0.5-2
Dyestuff	0-20

- oxidative-drying water fugitive ink composition for offset printing:

Component	**weight-%**
Varnish	40-80
NMP	5-20
Filler	2-30
Dyestuff	0-20

- UV-curable solvent-fugitive ink for offset printing:

Component	weight-%
Prepolymers e.g. polyurethane acrylate and/or polyester acrylate	20-70
Monomer oligomers e.g. oligomer acrylate	5-30
UV stabilizer	0.5-5
Mineral Filler	1-25
Dyestuff	0-20
Photoinitiator	1-15

The ink composition of the present invention may be applied on a substrate such as a value document by any printing method. Suitable methods include offset, flexographic, gravure, inkjet, letterpress and screen printing. The ink composition of the present invention may be used to print (coat) the whole surface or only one or more particular areas of the substrate.

Examples

Example 1

Example 1a:

An offset-printing solvent-fugitive ink was prepared by mixing the following components:

Component	**weight-%**
Varnish (alcohol soluble phenolic resin (40%) in propylene glycol)	60
Filler ($CaCO_3$)	29
Dyestuff (CI Solvent red 89	3
Solvent (Propylene glycol)	5
Antioxidant(Hydroquinone)	0.5
Cobalt Drier	0.5
Halochromic component	2

A paper substrate (Type Drewsen) was printed by offset printing with the ink composition. Indicia (text consisting of the check value, date and signature) were applied with a blue ball point pen FriXion™ from the firm Pilot (Sample picture shown in **Fig. 1a**).

Figs. 1a-1d represent pictures of the sample prepared according to the **Example 1**. This example serves to show the interaction of a solvent reactive ink of the present invention with indicia written with a commercial pen comprising a refill of a heat sensitive erasable ink.

Fig. 1a shows a picture of the substrate (in this example a check) completely printed with a coating layer made of an ink composition according to example 1. Visible indicia (hand-written text) have been written on the substrate with a pen containing a heat sensitive erasable ink formulation (FriXion™ Ball pen from Pilot).

Example 1b:

The written text of **Example 1a** was rubbed with the rubber tip of the pen: even after prolonged rubbing with the rubber tip, the

text remained visible to an unaided eye (Sample picture shown in **Fig. 1b**). Or alternatively, the written text was subjected to the open flame of a cigarette lighter: also in this case, the text remained visible. Similar results were obtained if the written text was subjected to another heat source such as e.g. a hair-dryer.

Example 1c:

The text of the sample of **Example 1b** was covered with a 10% aqueous solution of oxalic acid: the aqueous solution was applied with a cotton pad following the text trace. Capillarity absorption resulted in the spreading of the aqueous acidic solution on the paper substrate (Sample picture shown in **Fig. 1c**): the attempted forgery was evidenced by the mark left by the aqueous acidic solution on the background. **Fig. 1c** is a picture of the **Example 1c. Fig. 1c** (**Example 1c**) illustrates the above described forgery attempt perpetrated on the document of **Example 1b** carrying the indicia that has been treated with a thermal treatment. In **Fig. 1c**, the indicia is hardly visible to an unaided eye; however, the acid treatment of the substrate leaves visible traces on the fugitive background ink layer.

Example 1d:

The text of the sample of **Example 1b** was covered with a 20% aqueous solution of sulphuric acid in the same manner as in **Example 1c** (Sample shown in **Fig. 1d** below). **Fig. 1d** illustrates the result of **Example 1d. Example 1d** is identical to **Example 1c** except that a 20% sulphuric acid solution was used instead of the oxalic solution. In this case, the hand-written indicia were clearly visible along with the traces left by the acid solution on the fugitive background ink layer.

Example 2

Example 2a

An offset-printing water-fugitive ink was prepared by mixing the following components:

Component	weight-%
Varnish (alcohol soluble maleic resin (50%) and amine solubilizer (9%) in diethylene glycol)	60
Filler (Aluminium silicate)	28
Dyestuff (Duasyn Blue 2R Clariant)	2
Solvent (N-Methyl Pyrrolidone)	8
Halochromic component	2

A paper substrate was printed with the water fugitive ink composition and treated as described in **Example 1a** (**Fig. 2a**).

Figs. 2a-2b represent pictures of the sample prepared according to the **Example 2**. This example serves to show the interaction of a water fugitive ink of the present invention with indicia written with a commercial pen comprising a refill of heat erasable ink.

Fig. 2a shows a picture of the substrate (in this example a check) printed on its entire surface with a coating layer made with an ink composition according to example 2a. Visible indicia (hand-written text) have been written on the substrate with a pen containing a heat sensitive erasable ink formulation (FriXion™ Ball pen from Pilot).

For **Example 2b** the sample prepared in **Example 2a** was treated in the same manner as described in **Example 1b.** The result is shown in **Fig. 2b:** the indicia were rubbed with the rubber tip of the pen; the hand-written text remained clearly visible. Thus forgery attempts are easily detectable under daylight (unaided eye).

Example 3

Example 3a was prepared in the same way as **Example 1a** except that a black uni-ball fanthom™ pen from Mitsubishi was used to hand-write the indicia (**Fig. 3a**).

Figs. 3a-3c represent pictures of the sample prepared according to the **Example 3** as a further example of the present invention. **Example 3** serves to show that the permanence of the indicia obtained with the ink composition of the present invention is independent of the heat sensitive erasable ink.

Fig. 3a shows a picture of the substrate (in this example a check) printed on its entire surface with a coating layer made with an ink composition according to example 1a. Visible indicia (hand-written text) have been written on the substrate with a pen containing a heat sensitive erasable ink formulation (uni-ball fanthom™ pen from Mitsubishi); the pen and the heat sensitive erasable ink formulation are thus different from those employed in **Example 1.**

Example 3b (**Figure 3b**) and **Example 3c** (**Figure 3c**) were prepared as **Example 1b - 1c** respectively, using the sample prepared in **Example 3a. Fig. 3c** is a picture of the **Example 3c. Fig. 3c** (**Example 3c**) illustrates a forgery attempt perpetrated on the document of **Example 3b** carrying the indicia that has been treated

with a thermal treatment. In **Example 3c**, the document of **Fig. 3b** was treated with an aqueous acidic solution (10% oxalic acid) to attempt deleting or altering (by discolouration) the hand-written text: in this case, the indicia remained clearly visible to an unaided eye. When sulphuric acid was used instead of oxalic acid (**Example 3b**), the indicia remained even more clearly visible. (Figure 3b).

Comparative Example 1: (not part of the present invention)

Comparative Example 1a

An offset-printing solvent reactive ink was prepared by mixing the following components:

Component	**weight-%**
Varnish (alcohol soluble phenolic resin (40%) in propylene glycol)	61
Filler ($CaCO_3$)	29
Dyestuff (CI Solvent red 89)	4
Solvent (Propylene glycol)	5
Antioxidant (Hydroquinone)	0.5
Cobalt Drier	0.5

(same solvent reactive ink composition as in **Example 1** except that in this case the ink composition does not contain a halochromic compound; the weight % of varnish and dyestuff were accordingly adapted (no influence on the ink fugitive properties).

A paper substrate was printed in a similar way as in **Example 1a.** A text was written as in **Example 1a** with a blue ball point pen

FriXion™ from the company Pilot (Sample picture shown in **Figure 4a**).

Comparative Example 1b (**Fig. 4b**) was prepared in the same manner as **Example 1b**, using the sample prepared in **Comparative Example 1a**.

Figs. 4a-4b represent pictures of the samples prepared in the **Comparative Examples 1a-1b**. In **Comparative Example 1**, a substrate (for instance a check) was coated with the printed coating layer made of a prior art fugitive ink composition according to comparative example 1a (**Figure 4a**). In this case, the fugitive ink composition was a prior art solvent reactive ink; it does not contain a halochromic compound.

When the indicia were subjected to a thermal treatment as described in **Comparative Example 1b**, they became invisible under daylight (unaided eye) (**Fig. 4b**). Thus the perpetrated forgery became undetectable.

In contrast to **Comparative Example 1 (Figure 4)**, **Example 1** (**Figure 1**), **Example 2** (**Figure 2**) and **Example 3** (**Figure 3**) clearly demonstrate the effect of the halochromic compound added to the fugitive inks. The indicia remain visible under daylight to an unaided eye only when the fugitive inks comprise the halochromic compound.

It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to an exemplary embodiment, it is understood that the words which have been used herein are words of description and illustration, rather than

words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A solvent-borne or UV-curable fugitive ink composition for application to a substrate that is to be provided with indicia, wherein the ink composition comprises at least one halochromic compound and at least one filler compound and is capable of preventing indicia formed with a heat sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment from becoming invisible to an unaided eye.

2. The ink composition according to claim 1, wherein the at least one filler compound is selected from the group consisting of carbon fibers, talc, mica, wollastonite, calcinated clay, kaolin, carbonates, silicates (e.g. magnesium silicate, aluminium silicate), sulfates, titanates, titanium dioxide, montmorillonite, graphite, vermiculite, wood flour, quartz flour, natural fibers, synthetic fibres and combinations thereof.

3. The ink composition according to claim 1, wherein the at least one filler compound is selected from the group consisting of talc, mica, wollastonite, calcinated clay, kaolin, silicates, carbonates, montmorillonite and combinations thereof.

4. The ink composition according to any one of claims 1 to 3, wherein the heat sensitive erasable ink is an aqueous ink.

5. The ink composition according to any one of claims 1 to 4, wherein the at least one halochromic compound changes its

color when subjected to a pH change at a pH of equal to or lower than 7.0.

6. The ink composition according to any one of claims 1 to 5, wherein the at least one halochromic compound changes its color from a colourless or pale coloured state at a lower pH to a(more) colored state at a higher pH.

7. The ink composition according to any one of claims 1 to 6, wherein the composition comprises from 0.1 % to 5 %, preferably from 0.5 % to 2 % by weight, of the at least one halochromic compound, based on the total weight of the composition.

8. The ink composition according to any one of claims 1 to 7, wherein the composition further comprises at least one organic dye that becomes luminescent upon irradiation with UV light.

9. The ink composition according to claim 8, wherein the composition comprises from 1 % to 15 %, preferably from 1 % to 10 %, more preferably from 1 % to 5 % by weight of the at least one organic dye, based on the total weight of the ink composition.

10. The ink composition according to any one of claims 1 to 9, wherein the composition further comprises one or more additives selected from the group consisting of a wax, a solvent, and antioxidant, a drying agent, a dyestuff, an antifoaming additive, a UV stabilizer, and a photoinitiator.

11. The ink composition according to any one of claims 1 to 10, wherein the ink composition is selected from the group con-

sisting of solvent reactive inks, water fugitive inks, mechanically erasable inks, solvent reactive and water fugitive inks, solvent reactive and mechanically erasable inks, water fugitive and mechanically erasable inks, and water fugitive and solvent reactive and mechanically erasable inks.

12. The ink composition according to any one of claims 1 to 11, wherein the ink composition is selected from the group consisting of evaporation-drying inks, absorption-drying inks, oxidative-drying inks, and radiation-curable inks.

13. The ink composition according to any one of claims 1 to 12, wherein said composition is capable of leaving a mark that is visible with an unaided eye on the area of the substrate that carries the ink composition when indicia applied to said area with a heat sensitive erasable ink are first heat treated and subsequently treated with an acidic liquid.

14. A substrate comprising the fugitive ink composition according to any one of claims 1 to 13 in at least one area of the surface thereof.

15. The substrate according to claim 14, wherein the substrate is at least one selected from the group consisting of a commercial good, a value document, an identity document, an identity card, a passport, a driver's license, a bank cheque, a money transfer order, a voucher, a fiduciary act, a deed, and a certificate.

16. A method of making a fugitive ink composition according to any one of claims 1 to 13, wherein the method comprises

combining a conventional fugitive ink composition with at least one halochromic compound.

17. The method according to claim 16, wherein the fugitive ink composition is selected from the group consisting of solvent reactive inks, water fugitive inks, mechanically erasable inks, solvent reactive and water fugitive inks, solvent reactive and mechanically erasable inks, water fugitive and mechanically erasable inks, and water fugitive and solvent reactive and mechanically erasable inks and/or is selected from the group consisting of evaporation-drying inks, absorption-drying inks, oxidative-drying inks, and radiation-curable inks.

18. A method of protecting a commercial good or security document from forgery, wherein the method comprises applying the fugitive ink composition according to any one of claims 1 to 13 onto at least one area of the good or document that is to be provided with indicia.

19. The method of claim 18, wherein the ink composition is applied by a printing method, preferably by one or more selected from the group consisting of offset, flexographic, gravure, inkjet, letterpress and screen printing.

20. The method according to any one of claims 18 and 19, wherein the fugitive ink composition is selected from the group consisting of evaporation-drying inks, absorption-drying inks, oxidative-drying inks, and radiation-curable inks.

21. Use of a fugitive ink composition according to any one of claims 1 to 13 for preventing an indicia formed with a heat

sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment from becoming invisible to an unaided eye.

22. Use according to claim 21, wherein said fugitive ink composition is capable of leaving a mark that is visible with an unaided eye on the area of the substrate that carries the ink composition when indicia applied to said area with a heat sensitive erasable ink are first heat treated and subsequently treated with an acidic liquid.

Fig. 1a

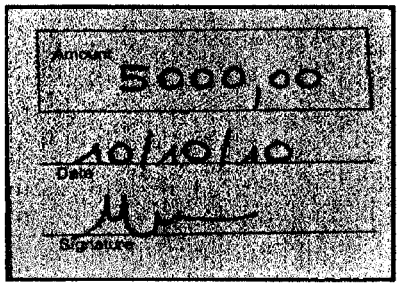


Fig. 1b

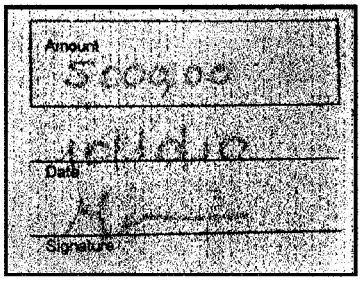


Fig. 1c

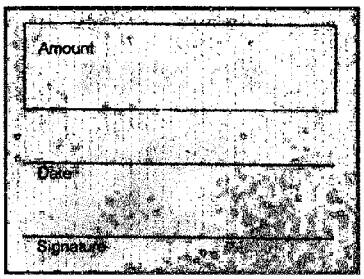


Fig. 1d

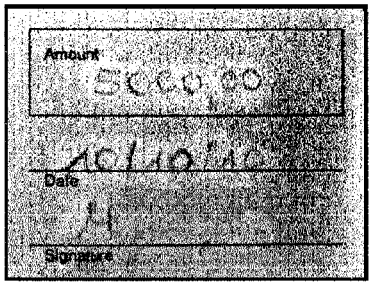


Fig. 2a

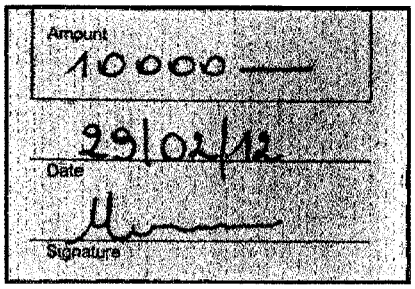


Fig. 2b

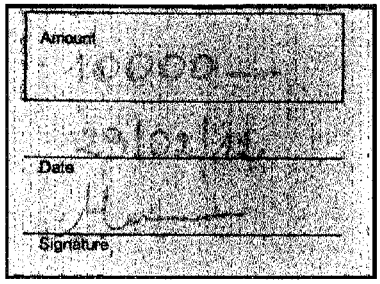


Fig. 3a

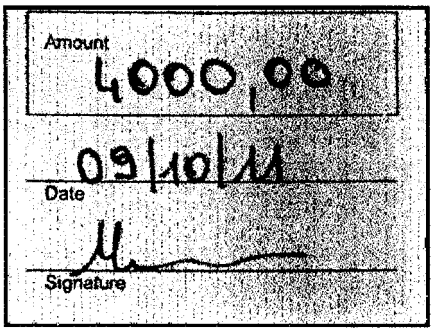


Fig. 3b

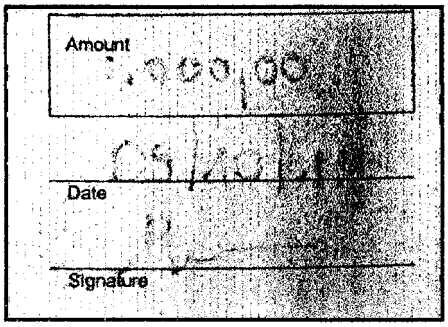


Fig. 3c

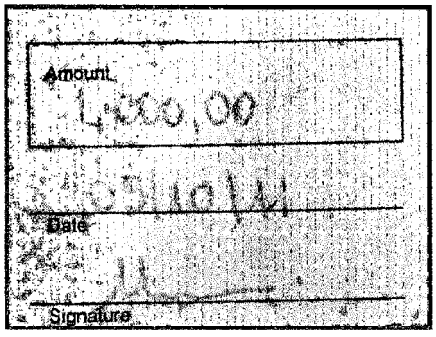


Fig. 4a

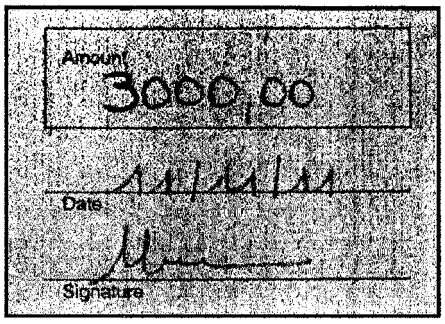
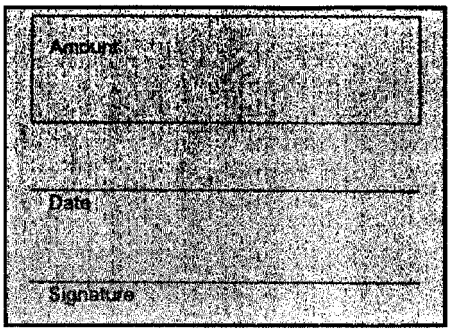


Fig. 4b



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/067682

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/00 C09D11/02 B41M3/14
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D B41M

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/017876 A1 (GEN ELECTRIC [US]; MISNER MATTHEW JEREMIAH [US]; PATEL BEN PURUSHOTAM) 5 February 2009 (2009-02-05) claims; examples	1-22
X	EP 0 704 505 A2 (BINNEY & SMITH INC [US]) 3 April 1996 (1996-04-03) paragraph [0074]; claims; examples	1-22
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X	US 5 232 494 A (MILLER RICHARD E [US]) 3 August 1993 (1993-08-03) column 11, line 24 - line 32; claims; examples	1-22

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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
12 October 2012	31/10/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schmitz, Volker

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/067682

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/215620 A1 (CELLA JAMES ANTHONY [US] ET AL) 27 August 2009 (2009-08-27) paragraph [0034] - paragraph [0037]; claims; examples	1-20
X	US 2007/017413 A1 (KWAN WING SUM V [US] ET AL KWAN WING SUM VINCENT [US] ET AL) 25 January 2007 (2007-01-25) examples 8,9; table x	1-22
A	EP 0 279 526 A2 (METAL BOX PLC [GB]) 24 August 1988 (1988-08-24) examples	1-22
A	US 5 601 683 A (MARTIN J PHILIP [US]) 11 February 1997 (1997-02-11) examples	1-22

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/067682

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(54)发明名称

借助热敏性可擦除墨防止伪造的用于安全文件的墨涂料

(57)摘要

公开了用于应用于待提供标记的基质上的溶剂性或UV固化性易褪色性墨组合物。墨组合物包含至少一种加酸显色化合物和至少一种填料化合物，且能够防止带有易褪色性墨组合物的基质面积上用热敏性可擦除墨形成且其后经受热处理的标记变得肉眼不可见。

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1. 用于应用于待提供标记的基质上的溶剂性或UV固化性易褪色性墨组合物，其中该墨组合物包含至少一种加酸显色化合物和至少一种填料化合物，且能够防止带有易褪色性墨组合物的基质面积上用热敏性可擦除墨形成且其后经受热处理的标记变得肉眼不可见。

2. 根据权利要求1的墨组合物，其中至少一种填料化合物选自碳纤维、滑石、云母、硅灰石、煅烧粘土、高岭土、碳酸盐、硅酸盐（例如硅酸镁、硅酸铝）、硫酸盐、钛酸盐、二氧化钛、蒙脱石、石墨、蛭石、木粉、石英粉、天然纤维、合成纤维及其组合。

3. 根据权利要求1的墨组合物，其中至少一种填料化合物选自滑石、云母、硅灰石、煅烧粘土、高岭土、硅酸盐、碳酸盐、蒙脱石及其组合。

4. 根据权利要求1-3中任一项的墨组合物，其中热敏性可擦除墨为水性墨。

5. 根据权利要求1-4中任一项的墨组合物，其中至少一种加酸显色化合物在经受等于或低于7.0的pH下的pH变化时改变其颜色。

6. 根据权利要求1-5中任一项的墨组合物，其中至少一种加酸显色化合物从较低pH下的无色或浅色状态至较高pH下的（更）有色状态改变其颜色。

7. 根据权利要求1-6中任一项的墨组合物，其中该组合物包含基于组合物的总重量0.1-5重量%，优选0.5-2重量%的至少一种加酸显色化合物。

8. 根据权利要求1-7中任一项的墨组合物，其中组合物进一步包含至少一种在UV光照射时变得发光的有机染料。

9. 根据权利要求8的墨组合物，其中该组合物包含基于墨组合物的总重量1-15重量%，优选1-10重量%，更优选1-5重量%的至少一种有机染料。

10. 根据权利要求1-9中任一项的墨组合物，其中该组合物进一步包含一种或多种选自如下的添加剂：蜡、溶剂和抗氧化剂、干燥剂、染料、消泡添加剂、UV稳定剂和光引发剂。

11. 根据权利要求1-10中任一项的墨组合物，其中墨组合物选自溶剂反应性墨、水易褪色性墨、机械可擦除墨、溶剂反应性且水易褪色性墨、溶剂反应性且机械可擦除墨、水易褪色性且机械可擦除墨，和水易褪色性且溶剂反应性且机械可擦除墨。

12. 根据权利要求1-11中任一项的墨组合物，其中墨组合物选自蒸发干燥墨、吸收干燥墨、氧化干燥墨和辐射固化性墨。

13. 根据权利要求1-12中任一项的墨组合物，其中当首先将用热敏性可擦除墨应用于带有墨组合物的基质面积上的标记热处理，随后用酸性液体处理时，所述组合物能够在所述带有墨组合物的基质面积上留下肉眼可见的标志。

14. 在至少一个其表面积中包含根据权利要求1-13中任一项的易褪色性墨组合物的基质。

15. 根据权利要求14的基质，其中基质为选自如下的至少一种：商品、有价值文件、身份证件、身份证、护照、驾驶证、银行支票、汇款单、凭证、信用证书、契据和证书。

16. 制备根据权利要求1-13中任一项的易褪色性墨组合物的方法，其中所述方法包括将常规易褪色性墨组合物与至少一种加酸显色化合物组合。

17. 根据权利要求16的方法，其中易褪色性墨组合物选自溶剂反应性墨、水易褪色性墨、机械可擦除墨、溶剂反应性且水易褪色性墨、溶剂反应性且机械可擦除墨、水易褪色性且机械可擦除墨，和水易褪色性且溶剂反应性且机械可擦除墨，和/或选自蒸发干燥墨、吸收干燥墨、氧化干燥墨和辐射固化性墨。

18. 保护商品或安全文件以防伪造的方法，其中所述方法包括将根据权利要求 1-13 中任一项的易褪色性墨组合物应用于待提供标记的商品或文件的至少一个面积上。

19. 根据权利要求 18 的方法，其中墨组合物通过印刷方法，优选通过一种或多种选自如下的印刷方法应用：胶版印刷、柔性版印刷、凹版印刷、喷墨印刷、凸版印刷和丝网印刷。

20. 根据权利要求 18 和 19 中任一项的方法，其中易褪色性墨组合物选自蒸发干燥墨、吸收干燥墨、氧化干燥墨和辐射固化性墨。

21. 根据权利要求 1-13 中任一项的易褪色性墨组合物在防止在带有易褪色性墨组合物的基质面积上用热敏性可擦除墨形成且其后经受热处理的标记变得肉眼不可见中的用途。

22. 根据权利要求 21 的用途，其中当首先将用热敏性可擦除墨应用于带有墨组合物的基质面积上的标记热处理，随后用酸性液体处理时，所述易褪色性墨组合物能够在所述带有墨组合物的基质面积上留下肉眼可见的标志。

借助热敏性可擦除墨防止伪造的用于安全文件的墨涂料

[0001] 发明背景

[0002] 1. 发明领域

[0003] 本发明一般性地涉及保护有价值文件以防伪造的领域。特别地，本发明涉及保护有价值文件以防伪造，其涉及热敏性可擦除墨组合物，以及包含含有这类热敏性可擦除墨的笔芯的笔的用途。

[0004] 2. 背景信息讨论

[0005] 包含含有热敏性可擦除墨，在专利文献中也称为热致变色颜色记忆组合物的笔芯(ink refill)的新一类圆珠笔的商业化代表安全文件领域中的潜在威胁。

[0006] 热敏性可擦除墨组合物，特别是热敏性可擦除水性墨组合物公开于例如EP2138550、美国专利Nos.4,720,301和7,494,537、US2009/0050013A1、US2010/0120614A1、US2011/0008095A1、EP1820662、EP2072277、JP2010-241867和JP2010-22933中，通过引用将其全部公开内容并入本文中。

[0007] 包含含有热敏性可擦除水性墨的笔芯的圆珠笔是目前广泛市售的(例如来自Pilot的FriXion™圆珠笔或来自Mitsubishi的Uni-ball fanthom™笔)。包含热敏性可擦除墨配制剂的书写工具公开于例如US2011/0008095A1中，通过引用将其全部内容并入本文中。

[0008] 热敏性可擦除墨的具体性能公开于例如美国专利No.4,720,301中。热敏性可擦除墨组合物包含给电子有机染料、酚类化合物和酯化合物作为主要组分。给电子有机染料充当碱；它的质子化形式是有色的，而它的非质子化形式是无色的。酚类化合物充当酸。酯化合物充当酸-碱对的基体。酯化合物的特征是其5-50℃范围内的熔点和浊点。热敏性可擦除墨的具体性能归因于墨的不同有色状态之间大的最大热滞后。

[0009] 用热敏性可擦除水性墨书写的标记或文字可通过标记的热处理而变得脱色：形成标记的墨不能从基质上物理地除去；然而，通过热处理，书写的标记变成是观察者肉眼不能看见的。热处理可通过热源，例如明火或吹风机产生，或者作为选择，标记的热处理可简单地在于将墨层机械擦除，例如用常用擦除器或用一片合成橡胶。包含热敏性可擦除墨笔芯的商业化圆珠笔装配有用于赋予不可见(“用于删除”)书写标记或文字的橡皮尖。

[0010] 包含热可逆性热脱色墨(即热敏性可擦除墨)的商业笔的墨笔芯为可移除的且笔芯可单独购买。因此，伪造者可将含有热敏性可擦除墨组合物如热敏性可擦除水性墨组合物的笔芯插入普通或奢侈品笔中并促进人们使用该笔以填写有价值文件如银行支票；伪造者然后可容易地更改手写信息。

[0011] 鉴于前述事实，含有热敏性可擦除墨配制剂和相应笔芯的圆珠笔代表安全文件领域中的威胁。伪造者可使用它们伪造有价值文件，例如身份证件、银行支票、凭证、信用证书、契据或证书。

[0012] 本领域中已知通过使用用于背景印刷的专用墨而保护有价值文件如支票以防伪造或篡改企图。特别地，开发了专用墨以用印刷层涂覆有价值文件或支票的背景，在必须用手写信息完成的文件领域中特别如此：因此，在这些领域中手写的标记或文字不能欺骗性

地更改或删除。通常，篡改企图通过使用溶剂或酸溶解手写标记的墨而进行，或者作为选择，伪造者企图用常用擦除器删除信息。通过使用专用墨印刷文件背景，任何篡改企图在文件上留下清晰可见的标志。用于该目的的专用墨例如为溶剂反应性墨、水易褪色性墨或机械可擦除墨。安全文件的保护依赖于褪色、颜色改变或消失，或者颜色当文件遭遇通过任何方式如擦除器、有机溶剂或水溶液的伪造企图时析出。易褪色性墨是本领域中已知的（例如参见 The Printing Ink Manual，R. H. Leach 和 R. J. Pierce 编辑，第 5 版，第 341 页）。EP0835292（其公开内容通过引用并入本文）公开了例如用于印刷有价值文件的这类溶剂析出墨组合物。

[0013] 然而，溶剂反应性墨和水易褪色性墨都不会防止用热敏性可擦除墨书写的标记通过热处理删除或使其不可见。

[0014] 因此，需要新的墨组合物，特别是在生产有价值文件如身份证件、银行支票、凭证、信用证书、契据或证书或其它有价值文件的印刷机中。新墨组合物应结合已知易褪色性墨组合物的防伪性能和旨在借助热敏性可擦除墨防伪的新性能。

[0015] 发明概述

[0016] 本发明提供溶剂性或 UV 固化性易褪色性墨组合物以应用（例如涂覆）于待提供标记（例如签名）的基质上。该墨组合物包含至少一种加酸显色化合物（例如 1、2、3 或更多种加酸显色化合物）、至少一种填料化合物，且墨组合物能够防止在已应用易褪色性墨组合物的基质面积上用（优选水性）热敏性可擦除墨（即热可逆热脱色墨）形成且其后经受热处理的标记变得肉眼不可见。换言之，当标记在带有易褪色性墨组合物的基质面积上用热敏性可擦除墨形成且其后经受热处理时，本申请的易褪色性墨组合物形成不可热擦除的（或非热敏性的）标志。

[0017] 在墨组合物的一个方面中，至少一种加酸显色化合物可以为或者包含在经受等于或低于 7.0 的 pH 下的 pH 变化时改变其颜色的化合物。例如，该至少一种加酸显色化合物可从较低 pH 下的无色或浅色状态至较高 pH 下的（更）有色状态改变其颜色。

[0018] 在组合物的另一方面中，该组合物可包含基于组合物的总重量 0.1-5 重量 %，例如 0.5-2 重量 % 的至少一种加酸显色化合物。

[0019] 至少一种填料化合物（一种或多种填料化合物）优选为离子填料化合物并且可选自碳纤维、滑石、云母（例如白云母）、硅灰石、煅烧粘土、高岭土、碳酸盐（例如碳酸钙、碳酸铝钠）、硅酸盐（例如硅酸镁、硅酸铝）、硫酸盐（例如硫酸镁、硫酸钡）、钛酸盐（例如钛酸钾）、二氧化钛、蒙脱石、石墨、蛭石、木粉、石英粉、天然纤维、合成纤维及其组合。优选一种或多种填料选自滑石、云母（优选白云母）、硅灰石、煅烧粘土、高岭土、硅酸盐（优选硅酸镁和 / 或硅酸铝）、碳酸盐（优选碳酸钙）、蒙脱石及其组合。一种或多种填料优选以约 0.1 或约 0.1 至约 40 或约 40 重量 %，更优选以约 1 或约 1 至约 30 或约 30 重量 % 的量存在，重量百分数基于易褪色性墨组合物的总重量。

[0020] 在又一方面中，墨组合物可进一步包含至少一种有机染料，所述有机染料在用 UV 光照射时变得发光（例如发荧光）。例如，组合物可包含基于墨组合物的总重量 1-15 重量 %，例如 1-10 重量 % 或 1-5 重量 % 的至少一种有机染料。

[0021] 在又一方面中，本发明墨组合物可进一步包含一种或多种选自如下的添加剂：蜡、溶剂、抗氧化剂、干燥剂、染料、消泡添加剂、UV 稳定剂和光引发剂。

[0022] 在又一方面中，本发明墨组合物可选自溶剂反应性墨、水易褪色性墨、机械可擦除墨、溶剂反应性且水易褪色性墨、溶剂反应性且机械可擦除墨、水易褪色性且机械可擦除墨，和水易褪色性且溶剂反应性且机械可擦除墨。

[0023] 在又一方面中，本发明墨组合物在将热处理的标记用酸性液体处理时可在带有墨组合物的基质面积上留下可见标志。

[0024] 本发明还提供在其至少一个表面积中包含如上所述本发明易褪色性墨组合物（包括其各个方面）的基质。例如，基质可以为选自如下的至少一种：商品、有价值文件、身份证件、身份证、护照、驾驶证、银行支票、汇款单、凭证、信用证书、契据和证书。

[0025] 本发明还提供制备如上所述本发明易褪色性墨组合物的方法。该方法包括将（常规）易褪色性墨组合物（例如已知易褪色性墨组合物）与至少一种加酸显色化合物组合。

[0026] 本发明还提供保护商品或安全文件以防伪造的方法。该方法包括将如上所述本发明易褪色性墨组合物应用于待提供标记的商品或文件的至少一个面积上。

[0027] 在该方法的一个方面中，墨组合物可通过印刷方法应用。例如，印刷方法可选自胶版印刷、柔性版印刷、凹版印刷、喷墨印刷、凸版印刷和丝网印刷。

[0028] 在该方法的另一方面中，易褪色性墨组合物可选自蒸发干燥墨、吸收干燥墨、氧化干燥墨和辐射固化性墨。

[0029] 本发明还提供如上所述本发明易褪色性墨组合物在防止在带有易褪色性墨组合物的基质面积上用热敏性可擦除墨形成且其后经受热处理的标记变得肉眼不可见中的用途。

[0030] 根据所述用途的另一方面，当首先将用热敏性可擦除墨应用于带有墨组合物的基质面积上的标记热处理，随后用酸性液体处理时，所述易褪色性墨组合物能够在所述带有墨组合物的基质面积上留下肉眼可见的标志。

[0031] 附图简述

[0032] 在附图中，

[0033] 图 1a-1d 显示根据以下实施例 1 所述程序制备和处理的试样的照片；

[0034] 图 2a 和 2b 显示根据以下实施例 2 所述程序制备和处理的试样的照片；

[0035] 图 3a-3c 显示根据以下实施例 3 所述程序制备和处理的试样的照片；和

[0036] 图 4a 和 4b 显示根据以下对比例 1 所述程序制备和处理的试样的照片。

[0037] 发明详述

[0038] 本文所示细节仅作为实例和说明性地讨论本发明实施方案且为了提供被认为是对本发明原理和概念方面最有用且容易理解的描述而提出。就这点而言，没有试图比本发明的基本理解所需更详细地显示本发明的结构细节，描述与图组合使本领域技术人员了解在实践中能够如何将本发明的几种形式具体化。

[0039] 本发明易褪色性墨组合物优选干燥以形成保持对溶剂、水、酸、漂白剂或其它化学试剂敏感的固体基体，且与热敏性可擦除墨组合物（即热可逆热脱色墨组合物），特别是与热敏性可擦除水性墨组合物（即热可逆热脱色水性墨组合物）反应。因此，可容易地检测到在涂有本发明墨组合物的文件上做坏事的伪造企图，包括使用热敏性可擦除墨的伪造企图。

[0040] 该效果例如例示于本发明图 1 和 4 中。特别地，图 1a 显示完全印有由本发明墨组

合物构成的涂层的基质的图片；墨组合物为如以下实施例 1 所述含有加酸显色化合物的溶剂反应性墨。可见标记（手写文字）用含有热敏性可擦除墨配制剂的笔（来自 Pilot 的 FriXion™ 圆珠笔）书写于基质上。图 1b 显示在将手写文字用笔的橡皮尖或用常用擦除器擦除以后，与图 1a 中相同的基质的图片：文字保持肉眼可见。

[0041] 相反，图 4a 和 4b 显示用已知易褪色性墨制备的试样的照片。图 4a 显示完全印有由已知溶剂反应性墨（不是本发明的一部分）制成的涂层的基质的照片，如对比例 1 所述。可见标记（手写文字）用含有热敏性可擦除墨配制剂的笔书写在基质上。图 4b 显示在将图 4a 中可见的手写文字用笔的橡皮尖或用常用擦除器擦除以后，与图 4a 中相同的基质的图片：文字不再可见。

[0042] 因此，用热敏性可擦除墨手写在印有本发明墨组合物的文件背景上的标记保持肉眼可见，甚至在热处理或通过化学方法的伪造尝试以后。

[0043] 本发明提供用于将例如背景层印刷（涂覆）于例如有价值文件上的新墨组合物。该新墨组合物用于完全或部分（例如在待提供标记的一个或多个面积中）涂覆有价值文件以提供基于热敏性可擦除墨的经得起伪造尝试的背景层。背景层的防伪性可能例如是由于本发明墨组合物与用于书写在有价值文件上的热敏性可擦除墨配制剂的化学反应：在这种情况下，甚至在热处理或者通过化学方法的伪造尝试时，标记仍保持可见。

[0044] 本发明墨组合物结合了用于印刷有价值文件（如银行支票）的背景层的已知墨的安全特征与专门设计以防止用热敏性可擦除墨伪造的其它功能。特别地，本发明墨组合物结合了本领域中已知的易褪色性墨提供的安全特征与专门设计用于防止热敏性可擦除墨改变的其它新安全特征。因此本发明墨组合物为易褪色性墨，其可用于印刷有价值文件的背景层且特征是它在用热敏性可擦除墨（即热可逆热脱色墨），特别是用热敏性可擦除水性墨（即热可逆热脱色水性墨）印刷、做标记或与热敏性可擦除墨（即热可逆热脱色墨），特别是与热敏性可擦除水性墨（即热可逆热脱色水性墨）接触时，形成永久可见的标记或标志。

[0045] 除常规易褪色性墨组合物的常用组分外，本发明易褪色性墨组合物包含（至少一种）加酸显色化合物。包含加酸显色化合物的易褪色性墨可例如为溶剂反应性墨、水易褪色性墨或机械可擦除墨。

[0046] 如本文所用，术语“加酸显色化合物”描述当 pH 变化时改变光学状态，特别是颜色的材料。因此，包含加酸显色化合物的墨组合物的酸度或碱度变化导致加酸显色材料的吸光度变化。

[0047] 加酸显色组分可以为（优选为）具有等于或低于 7.0 的 pH 值的转变 pH 范围（颜色变化）的 pH 指示剂。优选加酸显色组分从较低 pH 下的无色或非常浅色状态转变成较高 pH 下的有色状态。

[0048] 仅举几个例子，适用于本发明的加酸显色化合物的非限定性实例包括孔雀绿、亮绿、曙红黄、赤藓红 B、甲基绿、甲基紫、苦味酸、甲酚红、结晶紫、间胺黄、间甲酚紫、百里酚蓝、对二甲苯酚蓝、曙红蓝、萘酚黄 2B、喹哪啶红、2,4- 二硝基酚、溴氯酚、溴酚蓝、溴甲酚绿、溴甲酚绿钠盐、2,5- 二硝基酚、茜素磺酸钠盐、焰红染料 B、甲基红、甲基橙、碱性菊橙、胭脂虫红、氯酚红、溴甲酚红紫、溴酚红、亮黄、玫红酸、4- 硝基酚、邻甲酚酞、溴二甲苯酚蓝、茜素、硝嗪黄、溴百里酚蓝钠盐、溴百里酚蓝、酚红、酚红钠盐、3- 硝基酚、酚酞、媒染橙、噻唑

黄 G、百里酚酞、茜素黄 GG、靛蓝胭脂红和钛黄。

[0049] 本发明墨组合物可任选包含其它添加剂如染料或颜料。特别地，本发明墨组合物可进一步包含 1-15%，优选 1-5%（重量 %）一种或多种在 UV 光照射下发光的有机染料。合适有机染料的非限定性实例包括呫吨（例如 C.I. 酸性红 52，C.I.No.45100），芘（例如 C.I. 溶剂绿 7，C.I.NO59040），甲烷（例如 C.I. 碱性紫 21，C.I.NO48030），芪（例如直接黄 106，C.I.NO40300），香豆素（例如 C.I.NO551100），花青（例如 C.I.NO48016），噁嗪（例如 C.I.NO51180），荧光素钠（例如 C.I. 酸性黄 73，C.I.45350）和 / 或 C.I. 酸性黄 245。这类染料是本领域中已知的且例如用于氧化金属表面的着色，如 WO2011/038829 所述，通过引用将其全部内容并入本文中。

[0050] 如本文所用，术语“永久可见标记”表示人肉眼可见且甚至在标记经受物理或化学处理如暴露于热源下、机械擦除或应用溶剂或水溶液以后保持可见的标记。

[0051] 如本文所用，术语“易褪色性墨”指在常用伪造条件（即不会不利地影响其表面上带有印刷的易褪色性墨的基质，例如带有易褪色性墨的有价值文件的表面和 / 或材料的条件）下将水、水溶液、漂白剂或有机溶剂应用于印有易褪色性墨的表面上时不可逆地褪色、消失或变色的墨；作为选择，术语“易褪色性墨”指在将印有易褪色性墨的表面用例如常规擦除器擦除时不可逆地褪色、消失或变色的墨。这类易褪色性墨是本领域中已知的且例如用于印刷有价值文件的背景：背景方面的任何改变代表伪造尝试的毫无疑问的暗示。

[0052] 本领域中已知的易褪色性墨可如下分类：

[0053] i）溶剂反应性墨：在常用伪造条件（即不会不利地影响其表面上带有印刷的易褪色性墨的基质，例如带有易褪色性墨的有价值文件的表面和 / 或材料的条件）下将有机溶剂如醇、汽油、芳族溶剂如甲苯应用于印有该溶剂反应性墨的表面上时不可逆地褪色、消失或变色的墨。

[0054] ii）水易褪色性墨：在常用伪造条件（即不会不利地影响其表面上带有印刷的易褪色性墨的基质，例如带有易褪色性墨的有价值文件的表面和 / 或材料的条件）下将水、水溶液或漂白溶液应用于涂有该水易褪色性墨的表面上时不可逆地褪色、消失或变色的墨；

[0055] iii）机械可擦除墨：当将印有该机械可擦除墨的表面用擦除体如擦除器擦除时不可逆地褪色、消失或变色的墨。

[0056] 因此，根据本发明，易褪色性墨优选包含选自溶剂反应性墨、水易褪色性墨或机械可擦除墨的墨；作为选择，如本文所用术语“易褪色性墨”还包括结合至少两种选自溶剂反应性、水易褪色性和机械可擦除墨的墨的性能的墨，例如溶剂反应性且机械可擦除的墨。

[0057] 如本文所用术语“热敏性可擦除墨”指当经受热源时可逆地褪色或变色的墨配制剂。墨配制剂的可逆脱色行为由色密度的宽最大滞后宽度相对于温度曲线产生。因此，墨配制剂在应用印刷墨层的热处理时变得脱色；墨层保持无色不可见状态直至温度降至阈值温度以下；在该阈值温度和它以下，墨层恢复其有色可见状态。

[0058] 适于本发明上下文中的热敏性可擦除墨配制剂是可逆热脱色组合物，其包含：

[0059] a）给电子彩色有机化合物 A（即路易斯碱），

[0060] b）受电子化合物（路易斯酸）或具有酸性质子的化合物（Brönsted 酸）作为化合物 B，

[0061] c）充当控制化合物 A 和 B 的反应的反应介质的化合物 C，化合物 C 的特征在于其

熔点与其浊点之间的温差，所述温差为 5-50℃。

[0062] 适于本发明的典型热敏性可擦除墨配制剂描述于例如 EP2138550、美国专利 Nos. 4,720,301 和 7,494,537、US2009/0050013A1、US2010/0120614A1、US2011/0008095A1、EP1820662、EP2072277、JP2010-241867 和 JP2010-229333 中。

[0063] 如本文所用，术语“热敏性可擦除墨”不指基于液晶材料或金属化合物的热致变色墨。

[0064] 本发明墨组合物为溶剂性墨组合物或 UV 固化性墨组合物。另一方面，本发明墨组合物不可以是水基墨组合物。本发明墨组合物可干燥，例如通过溶剂蒸发、吸收干燥、氧化聚合或者通过辐射能如 UV 光或 e- 束（电子束）干燥。

[0065] 根据一个实施方案，本发明墨组合物为溶剂性墨组合物。如本文所用，术语“溶剂性墨组合物”指其液体介质或载体基本由一种或多种有机溶剂组成的墨组合物。本发明溶剂性墨组合物的液体介质包含至多 5 重量 % 水，优选至多 1 重量 % 水，最优选小于 0.1 重量 % 水。溶剂性墨组合物包含基于墨的总重量通常 1-70 重量 %，尤其是 1-50 重量 %，更尤其是 2-45 重量 % 的量的液体介质。

[0066] 这类溶剂的实例包括醇（例如甲醇、乙醇、异丙醇、正丙醇、乙氧基丙醇、正丁醇、仲丁醇、叔丁醇、异丁醇、2- 乙基己醇）；多元醇（例如甘油、1,5- 戊二醇或 1,2,6- 己三醇）；酯（例如乙酸乙酯、乙酸丙酯、乙酸正丁酯）；碳酸酯（例如碳酸二甲酯、碳酸二乙酯、碳酸二 - 正丁酯、碳酸 1,2- 亚乙酯、碳酸 1,2- 亚丙酯或碳酸 1,3- 亚丙酯）；芳族溶剂（例如甲苯、二甲苯）；酮（例如丙酮、甲乙酮、甲基异丁基酮、双丙酮醇、环己酮）；酰胺（例如二甲基甲酰胺或二甲基乙酰胺）；脂族或脂环族烃；氯化烃（例如二氯甲烷）；含氮杂环化合物（例如 N- 甲基 -2- 吡咯烷酮或 1,3- 二甲基 -2- 咪唑烷酮）；醚（例如二乙醚、四氢呋喃、二噁烷）；多元醇的烷基醚（例如 2- 甲氧基乙醇或 1- 甲氧基丙 -2- 醇）；亚烷基二醇、亚烷基硫代二醇、聚亚烷基二醇或聚亚烷基硫代二醇（例如乙二醇、聚乙二醇（例如二甘醇、三甘醇、四甘醇）、丙二醇、聚丙二醇（例如二丙二醇、三丙二醇）、丁二醇、硫二甘醇、己二醇或其混合物）；腈（例如乙腈、丙腈）、含硫化合物（例如二甲亚砜或环丁砜）及其混合物。

[0067] 最优选液体介质包含选自脂族或脂环族烃、含氮杂环化合物、聚亚烷基二醇、酯及其混合物的溶剂。

[0068] 根据另一实施方案，本发明墨组合物为 UV 固化性墨组合物，优选自由基 UV 固化性墨，即可通过自由基固化机制固化的墨。

[0069] 如本文所用，术语“UV 固化性墨组合物”指可通过 UV- 可见光辐射（下文称为 UV 固化性）和 / 或通过电子束辐射（下文称为 EB）固化的墨组合物。当使用 UV 固化性墨组合物时，优选墨组合物通过 UV- 可见光辐射固化。辐射固化性组合物是本领域中已知的且可在标准教科书如 John Wiley&Sons 联合 SITA Technology Limited 于 1997-1998 在第 7 卷中公开的有关的系列“Chemistry&Technology of UV&EB Formulation for Coatings, Inks&Paints”中找到。优选本文所述 UV 固化性墨组合物包含 :a) 包含低聚物（在本领域中也称为预聚物）的粘合剂化合物，其优选选自自由基可固化化合物。

[0070] 自由基可固化化合物通过自由基机制固化，所述自由基机制由通过能量将一种或多种光引发剂活化组成，所述光引发剂释放自由基，所述自由基又引发粘合剂化合物的聚合。优选粘合剂由选自如下的低聚物组成 :低聚（甲基）丙烯酸酯、乙烯基和丙烯基醚及

其混合物，更优选粘合剂化合物选自（甲基）丙烯酸环氧基酯、（甲基）丙烯酸化油、聚酯（甲基）丙烯酸酯、脂族或芳族氨基甲酸酯（甲基）丙烯酸酯、硅氧烷（甲基）丙烯酸酯、（甲基）丙烯酸氨基酯、丙烯酸类（甲基）丙烯酸酯及其混合物。可将第二粘合剂加入本文所述 UV-Vis 固化性光学可变组合物中，这种粘合剂可选自单体丙烯酸酯，例如三羟甲基丙烷三丙烯酸酯 (TMPTA)、季戊四醇三丙烯酸酯 (PTA)、三丙二醇二丙烯酸酯 (TPGDA)、二丙二醇二丙烯酸酯 (DPGDA)、己二醇二丙烯酸酯 (HDDA) 和它们的聚乙氧基化等价物如聚乙氧基化三羟甲基丙烷三丙烯酸酯、聚乙氧基化季戊四醇三丙烯酸酯、聚乙氧基化三丙二醇二丙烯酸酯、聚乙氧基化二丙二醇二丙烯酸酯和聚乙氧基化己二醇二丙烯酸酯。单体、低聚物或预聚物的 UV-Vis 固化可能要求存在一种或多种光引发剂且可以以大量方法进行。如本领域技术人员已知，一种或多种光引发剂根据它们的吸收光谱选择且选择以匹配辐射源的发射光谱。取决于本文所述 UV 固化性墨组合物中所含的粘合剂化合物，可使用不同的光引发剂。

[0071] 自由基光引发剂的合适实例是本领域技术人员已知的且包括但不限于苯乙酮、二苯甲酮、α-氨基酮、α-羟基酮、氧化膦和氧化膦衍生物和苄基二甲基缩酮。有用光引发剂的其它实例可在标准教科书如 J. V. Crivello&K. Dietliker, G. Bradley 编辑且由 John Wiley&Sons 于 1998 年联合 SITA Technology Limited 出版的“ChemlstrV&Technology of UV&EB Formulation for Coatings, Inks&Paints”，第 III 卷，“Photoinitiators for Free Radical Cationic and Anionic Polymerization”，第 2 版中找到。还可能有利的是包含敏化剂连同一种或多种光引发剂以实现有效的固化。合适光敏剂的典型实例包括但不限于异丙基-噻吨酮 (ITX)、1-氯-2-丙氧基-噻吨酮 (CPTX)、2-氯-噻吨酮 (CTX) 和 2,4-二乙基-噻吨酮 (DETX) 及其混合物。UV 固化性墨组合物中所包含的一种或多种光引发剂优选以约 0.1 至约 20 重量%，更优选约 1 至约 15 重量% 的量存在，其中重量% 基于 UV 固化性墨组合物的总重量。

[0072] 在用于伪造尝试的化学品中，本领域中已知酸通常用于试图将书写标记的墨溶解或脱色。由于新墨组合物的防伪性主要依赖于加酸显色组分的存在，对酸处理的抗性优选代表其关键特征。该抗性例如例示于以下实施例和图中。

[0073] 本发明墨组合物可通过将（至少一种）加酸显色化合物加入常规易褪色性墨组合物中而制备。例如，本发明墨组合物可通过将 0.1-5%，优选 0.5-2%（重量%）加酸显色化合物加入常规易褪色性墨配制剂如溶剂反应性墨配制剂或水易褪色性墨配制剂中而制备。

[0074] 取决于干燥机制和易褪色性墨的类型，用于胶版印刷的典型常规易褪色性墨组合物的实例可例如由如下组分组成或者包含如下组分：

[0075] -用于胶版印刷的氧化干燥性溶剂反应性墨组合物：

[0076]

组分	重量%
清漆	40-80
蜡化合物	0-5

填料	2-30
溶剂	1-10
抗氧化剂	0.5-2
干燥剂	0.5-2
染料	0-20

[0077] - 用于胶版印刷的氧化干燥性水易褪色性墨组合物：

[0078]

组分	重量 %
清漆	40-80
NMP	5-20
填料	2-30
染料	0-20

[0079] - 用于胶版印刷的 UV 固化性溶剂易褪色性墨：

[0080]

组分	重量 %
预聚物，例如聚氨酯丙烯酸酯和 / 或聚酯丙烯酸酯	20-70
单体低聚物，例如低聚物丙烯酸酯	5-30
UV 稳定剂	0.5-5
矿物填料	1-25
染料	0-20
光引发剂	1-15

[0081] 本发明墨组合物可通过任何印刷方法应用于基质如有价值文件上。合适的方法包括胶版印刷、柔性版印刷、凹版印刷、喷墨印刷、凸版印刷和丝网印刷。本发明墨组合物可用于印刷（涂覆）基质的整个表面或仅一个或多个特定面积。

实施例

[0082] 实施例 1a：

[0083] 胶版印刷溶剂易褪色性墨通过将以下组分混合而制备：

[0084]

组分	重量 %
清漆（在丙二醇中的醇溶性酚醛树脂 (40%)）	60
填料 ($CaCO_3$)	29
染料 (CI 溶剂红 89)	3
溶剂（丙二醇）	5
抗氧化剂（氢醌）	0.5
钴催干剂	0.5
加酸显色组分	2

[0085] 通过胶版印刷将纸基质 (Drewsen 型）用墨组合物印刷。用来自 Pilot 公司的蓝色圆珠笔 FriXion™ 应用标记（由支票价值、日期和签名组成的文字）（图 1a 所示试样图片）。

[0086] 图 1a-1d 表示根据实施例 1 制备的试样的图片。该实施例用于显示本发明溶剂反应性墨与用包含热敏性可擦除墨的笔芯的商业笔书写的标记相互作用。

[0087] 图 1a 显示完全印有由根据实施例 1 的墨组合物制成的涂层的基质（在该实施例中，支票）的图片。可见标记（手写文字）用含有热敏性可擦除墨配制剂的笔（来自 Pilot 的 FriXion™ 圆珠笔）书写于基质上。

[0088] 实施例 1b：

[0089] 将实施例 1a 的书写文字用笔的橡皮尖擦除：甚至在用橡皮尖延长擦除以后，文字保持是肉眼可见的（图 1b 所示试样图片）。或者作为选择，使书写文字经受打火机的明火：在这种情况下，文字也保持是可见的。如果书写文字经受另一热源如吹风机，则得到类似的结果。

[0090] 实施例 1c：

[0091] 将实施例 1b 试样的文字用 10% 草酸水溶液覆盖：水溶液用棉垫应用于文字痕迹上。毛细管吸收导致酸性水溶液在纸基质上的铺展（图 1c 中所示试样图片）：试图的伪造由酸性水溶液在背景上留下的标志证明。图 1c 为实施例 1c 的图片。图 1c（实施例 1c）说明带有用热处理处理的标记的实施例 1b 文件上犯下的上述伪造尝试。在图 1c 中，标记几乎是肉眼不可见的；然而，基质的酸处理在易褪色性背景墨层上留下可见的痕迹。

[0092] 实施例 1d：

[0093] 以与实施例 1c 相同的方式将实施例 1b 试样的文字用 20% 硫酸水溶液覆盖（以下图 1d 所示试样）。图 1d 阐述实施例 1d 的结果。实施例 1d 与实施例 1c 相同，不同之处在于使用 20% 硫酸溶液代替草酸溶液。在这种情况下，手写标记连同通过酸性溶液保留在易褪色性背景墨层上的痕迹一起清晰可见。

[0094] 实施例 2

[0095] 实施例 2a

[0096] 胶版印刷水易褪色性墨通过将以下组分混合而制备：

[0097]

组分	重量 %
清漆（在二甘醇中的醇溶性马来酸树脂 (50%) 和胺增溶剂 (9%)）	60
填料（硅酸铝）	28
染料 (Duasyn Blue2R Clariant)	2
溶剂 (N- 甲基吡咯烷酮）	8
加酸显色组分	2

[0098] 将纸基质用水易褪色性墨组合物印刷并如实施例 1a 所述处理（图 2a）。

[0099] 图 2a-2b 表示根据实施例 2 制备的试样的图片。该实施例用于显示本发明水易褪色性墨与用包含热可擦除墨笔芯的商业笔书写的标记相互作用。

[0100] 图 2a 显示根据实施例 2a，整个表面上印有由墨组合物构成的涂层的基质的图片（在该实施例中，支票）。可见标记（手写文字）用含有热敏性可擦除墨配制剂的笔（来自 Pilot 的 FriXion™ 圆珠笔）书写在基质上。

[0101] 对于实施例 2b，将实施例 2a 中制备的试样以与实施例 1b 中相同的方式处理。结果显示于图 2b 中：将标记用笔的橡皮尖擦除；手写文字保持清晰可见。因此，伪造尝试在日光下（肉眼）容易检测到。

[0102] 实施例 3

[0103] 实施例 3a 以与实施例 1a 相同的方式制备，不同之处在于使用来自 Mitsubishi 的黑色 Uni-ball fanthom™ 笔手写标记（图 3a）。

[0104] 图 3a-3c 表示根据实施例 3 制备的试样的图片作为本发明的另一实施例。实施例 3 用于显示用本发明墨组合物得到的标记的持久性与热敏性可擦除墨无关。

[0105] 图 3a 显示整个表面上印有由根据实施例 1a 的墨组合物构成的涂层的基质（在该实施例中，支票）的图片。可见标记（手写文字）用含有热敏性可擦除墨配制剂的笔（来自 Mitsubishi 的 Uniball fanthom™ 笔）书写在基质上；因此，笔和热敏性可擦除墨配制剂与实施例 1 中所用那些不同。

[0106] 实施例 3b（图 3b）和实施例 3c（图 3c）分别使用实施例 3a 中制备的试样如实施例 1b-1c 中制备。图 3c 为实施例 3c 的图片。图 3c（实施例 3c）说明带有用热处理处理的标记的实施例 3b 文件上犯下的伪造尝试。在实施例 3c 中，将图 3b 的文件用酸性水溶液 (10% 草酸）处理以尝试删除或改变（通过脱色）手写文字：在这种情况下，标记保持是肉眼清晰可见的。当使用硫酸代替草酸时（实施例 3b），标记保持甚至更清晰可见（图 3b）。

[0107] 对比例 1（非本发明的一部分）

[0108] 对比例 1a：

[0109] 胶版印刷溶剂反应性墨通过将以下组分混合而制备：

[0110]

组分	重量 %
清漆（在丙二醇中的醇溶性酚醛树脂 (40%)）	61
填料 ($CaCO_3$)	29
染料 (CI 溶剂红 89)	4
溶剂（丙二醇）	5
抗氧化剂（氢醌）	0.5
钴催干剂	0.5

[0111]

[0112] （与实施例 1 中相同的溶剂反应性墨组合物，不同之处在于，在这种情况下，墨组合物不包含加酸显色化合物；因此调整清漆和染料的重量 %（不影响墨易褪色性性能）。

[0113] 将纸基质以与实施例 1a 中类似的方式印刷。文字如实施例 1a 中用来自 Pilot 公司的蓝色圆珠笔 FriXion™ 书写（图 4a 所示试样图片）。

[0114] 对比例 1b（图 4b）以与实施例 1b 相同的方式使用对比例 1a 制备的试样制备。

[0115] 图 4a-4b 表示对比例 1a-1b 中制备的试样的图片。在对比例 1 中，将基质（例如支票）用根据对比例 1a（图 4a）的现有技术易褪色性墨组合物构成的印刷涂层涂覆。在这种情况下，易褪色性墨组合物为现有技术溶剂反应性墨；它不包含加酸显色化合物。

[0116] 当标记经受如对比例 1b 所述的热处理时，它们变得在日光下（肉眼）不可见（图 4b）。因此，犯下的伪造变得不可检测。

[0117] 与对比例 1（图 4）相反，实施例 1（图 1）、实施例 2（图 2）和实施例 3（图 3）清楚地证明加入易褪色性墨中的加酸显色化合物的效果。标记仅在易褪色性墨包含加酸显色化合物时变得在日光下肉眼可见。

[0118] 应当指出，前述实施例仅用于解释且决不理解成对本发明的限制。尽管参考典型实施方案描述了本发明，应当理解本文所用措辞为说明和阐述性措辞，而不是限制性措辞。可在如目前陈述和修改的所附权利要求书的范围内，不偏离本发明范围和精神地作出其方面的改变。尽管此处参考特定方式、材料和实施方案描述了本发明，本发明不意欲限于本文公开的细节；而是，本发明延伸至所有功能上相同的结构、方法和用途，例如所附权利要求书范围内的。

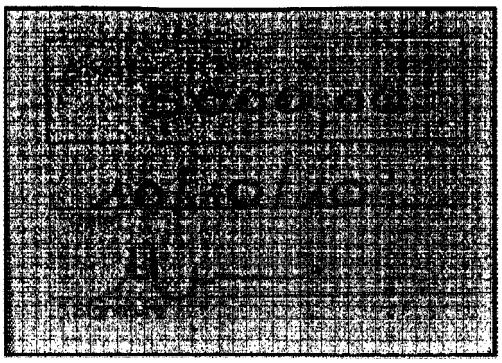

图 1a

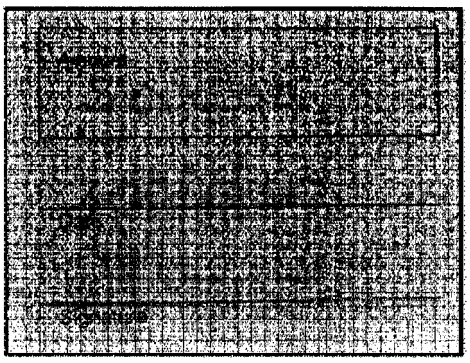

图 1b

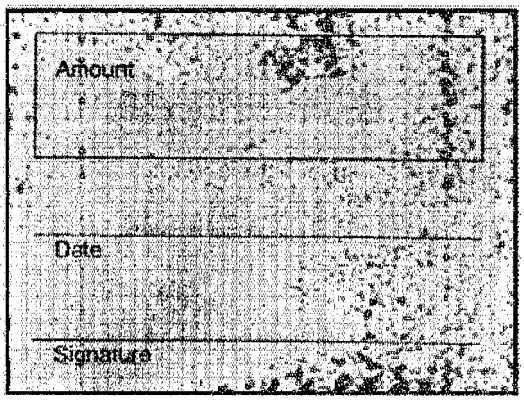

图 1c

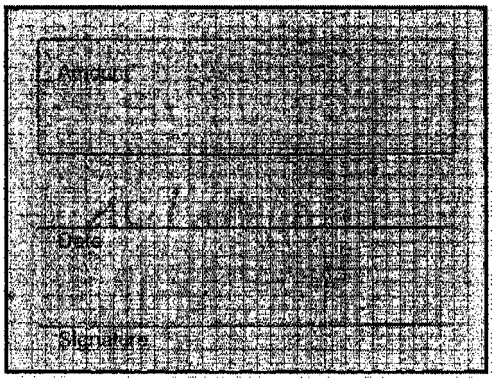

图 1d

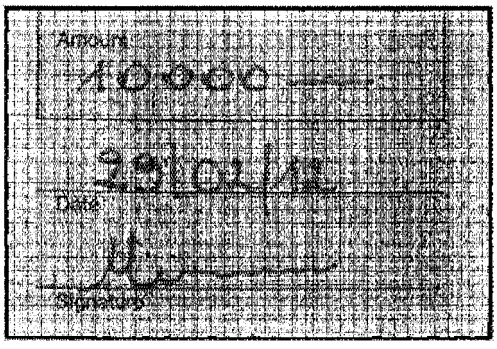

图 2a

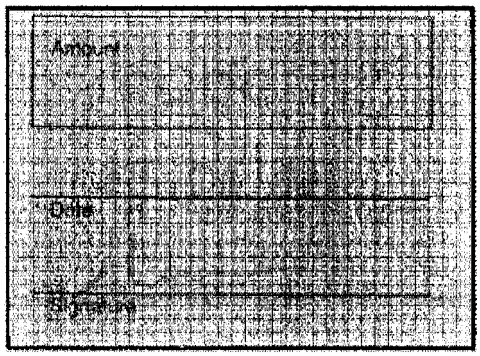

图 2b

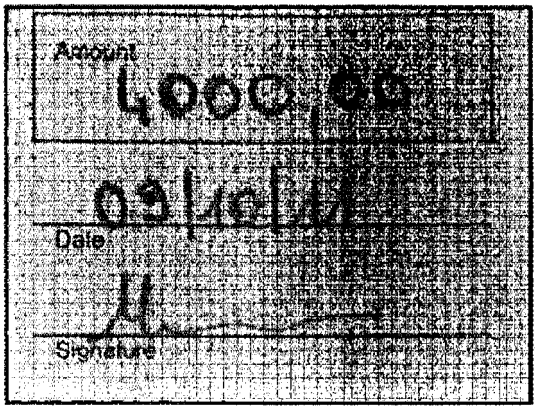

图 3a

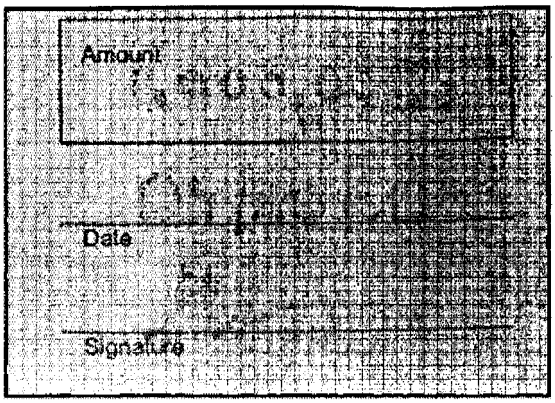

图 3b

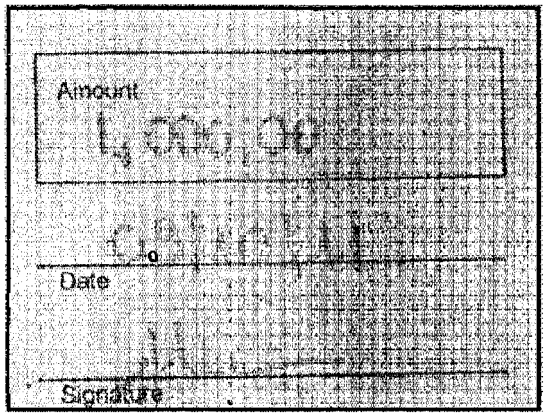

图 3c

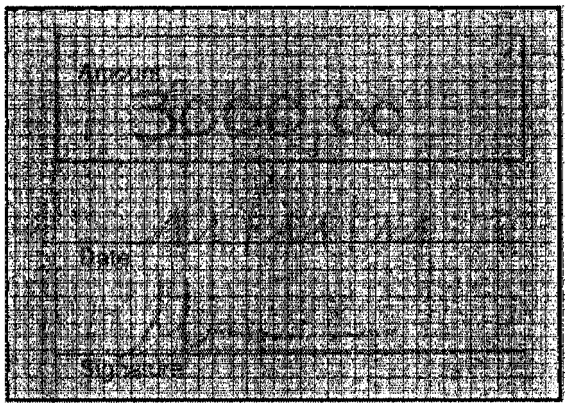

图 4a

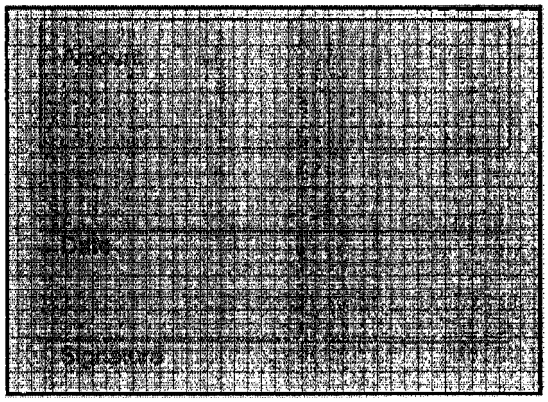

图 4b

Abstract

Disclosed is a solvent-borne or UV-curable fugitive ink composition for application to a substrate that is to be provided with indicia. The ink composition comprises at least one halochromic compound and at least one filler compound and is capable of preventing indicia formed with a heat sensitive erasable ink on an area of the substrate carrying the fugitive ink composition and thereafter subjected to a thermal treatment from becoming invisible to an unaided eye.