(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 174 797 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
14.04.2010 Bulletin 2010/15

(21) Application number: **08017527.6**

(22) Date of filing: **07.10.2008**

(51) Int Cl.:
B42D 15/00 *(2006.01)* ***B42D 15/10*** *(2006.01)*
B41M 5/24 *(2006.01)* ***B41M 3/14*** *(2006.01)*

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

(71) Applicant: **European Central Bank**
60311 Frankfurt am Main (DE)

(72) Inventors:
- **Arrieta, Antonio Jesús**
  60311 Frankfurt am Main (DE)
- **Klein, Sylke**
  64380 Rossdorf (DE)
- **Montag, Heidemarie**
  64289 Darmstadt (DE)

(74) Representative: **Luderschmidt, Schüler & Partner Patentanwälte**
John-F.-Kennedy-Strasse 4
65189 Wiesbaden (DE)

(54) Laser-marked document showing a colour-shift effect

(57) Document comprising a coating containing at least one sort of effect pigments, wherein said document also comprises at least one laser mark having a high contrast and a strong colour shift effect

Said document is obtainable by a process, wherein, a document comprising a coating containing at least one sort of effect pigments which show different colours under different viewing angles is treated on at least a part of the coated area with a pulsed laser beam at a rate of greater than 500 mm/s and a laser mark having a colour shift effect is obtained.

The authenticity of the document can be easily checked by visual inspection from different viewing angles.

EP 2 174 797 A1

Description

BACKGROUND OF THE INVENTION

1. Field of the invention

[0001] The present invention relates to a process for the manufacture of laser-marked documents, preferably security documents, such as banknotes, passports, chequebooks, etc, which show a colour-shift effect.

2. Description of the Related Art

[0002] The use of self-authenticating security features for producing documents serves for protecting them against unauthorized reproduction by forgers. This is necessary, in particular, for securities such as banknotes, checks, traveller's checks, stocks, etc. There is also a need for security papers which do not have a direct monetary value, such as identification papers, passports etc., against unauthorized copying.

[0003] In particular, in the case of securities, which are circulated daily, for example, banknotes, a forger may succeed in copying the optically recorded document contents, for example, the optical printed image of the banknotes, in a deceptively precise way. A protection against this is the authenticity feature contained in the security paper, used for producing the documents, as a result of the structure imparted to the security paper during manufacture which authenticity feature supposedly practically cannot be copied by a forger with the means available to him. Moreover, the application of watermarks or the introduction of a security thread into the paper is known. These conventional measures, however, can no longer be considered totally satisfactory in view of the advances of the working means employed by forgers.

[0004] One possible way to overcome this problem can be seen in the use of pearlescent coatings since the angle-dependent optical effects obtained from pearlescent pigments cannot be easily copied with photocopier machines or photographic techniques making forging much more complicated and expensive.

[0005] Furthermore the interactions between coated substrates (paper, board, film, laminate) and laser irradiation are also known. It is possible to mark a coated substrate by ablating the laser-sensitive coating from the substrate or to create marks within the coating layer by a suitable laser. The penetration of the laser beam in the coated substrate becomes higher with increasing the laser energy so that the substrate get certain tactility or become thinner until the laser beam perforates finally the substrate.

[0006] For security applications like applications on banknotes or other security documents special paper types are used in that context. These papers are often made from the natural raw material cotton or they contain cotton fibres. Depending on laser wavelength, pulse frequency and laser energy the laser beam could generate in these special coated or uncoated papers the following:

Marks by ablating the coating layers

- Ablation of printing ink [*Bank of England*, DE 2836526]
- Ablation of colour layer/polymer layer [*ÖPS*, US 4,740,269]

Marks by laser effects on the coating layers

- Fine line marks in optically variable layers [*G&D*, DE 19544130]
- Laser marks in laser-markable paper or paper coatings [*Merck*, DE 19704478, DE 19732860]
- Visible marks in laser-sensitive layer creating trough a laser-transparent optically variable layer [G&D, DE 10008851]
- Dark or black marks in coated paper [G&D, DE 4243987]
- Laser marks on paper or paper coating contains oxyanions of multivalent metals [*Sherwood*, WO 02/074548]
- Marks due to laser-markable composition for paper coating contains pigment (multivalent metal compound) and conductive polymer [*Sherwood*, WO 2005/012442]

Marks by laser treatment of the substrate

- Changing of fibre structure of paper [*ÖPS*, US 4,740,269]
- Touchable marks in paper or paper coatings [G&D, DE 10232786, DE 10247591]
- Tactility due to an embossed-like surface structure without removing of the surface layer [*J.A. Ramos de Campos, ECB*, EP 1658992]
- Reduction and bleaching of paper thickness by laser etching [*Karel* Schell, US 6,395,191].

[0007] US 2006/0141391 A1 discloses a laser mark on a document of value, comprising at least one printing ink or printing-ink layer on a substrate, where the at least one printing ink or printing-ink layer comprises a laser-sensitive component, and wherein printing ink in at least one area of the at least one printing ink or printing ink layer is selectively removed by a laser, and optionally a microinscription/image is produced by the laser in a selectively removed area, and in the case where otherwise there would be complete removal of the printing ink from the mark, said microinscription/image is produced in the mark.

[0008] According to this application, the laser-sensitive component used can be any material which absorbs the laser-light energy sufficiently in the stated wavelength range and converts it into heat energy. However, particularly preferred are pigments such as mica flakes coated with one or more metal oxides. The metal oxides used here are both colourless, high-refractive-index metal oxides, such as, in particular, titanium dioxide, antimony (III) oxide, zinc oxide, tin oxide and/or zirconium dioxide, and also coloured metal oxides, such as, for example, chromium oxide, nickel oxide, copper oxide, cobalt oxide and in particular iron oxide (Fe_2O_3, Fe_3O_4). The laser-sensitive component used is particularly preferably antimony(III) oxide, alone or in combination with tin oxide.

[0009] As to the preparation of the laser marks, the document does not specify the parameters to be used in detail, but states that "the parameters of the laser used depend on the particular application and can readily be determined by the person skilled in the art in the individual case." The only example describes the use of a Nd vanadate laser (1064 nm), the power of which is varied from 30 to 80% in 10% steps at a rate of 500 mm/s and a frequency of 40 to 60 kHz in pulsed operation. However, the contrast and the colour-shift effect of the laser marks obtainable under such conditions is comparably low and difficult to identify.

SUMMARY OF THE INVENTION

[0010] The main objective of the present invention is to provide a method for the production of a more flexible and reliable security means for documents, especially security documents which have improved forgery-proof properties. Thereby it is desirable that the security means can be authenticated in an easy way. At the same time the security means shall be highly flexible regarding its design, comparable small in thickness and highly durable.

[0011] In carrying out these and other objects of the present invention, there is provided a method for laser marking a document, preferably a security document, wherein a document comprising a coating containing at least one sort of effect pigments which show different colours under different viewing angles is treated on at least a part of the coated area with a pulsed laser beam at a rate of greater than 500 mm/s and a laser mark having a high contrast and a high colour shift effect at the same time is obtained.

[0012] Thereby a highly flexible and reliable overt security means for documents is made available that has improved forgery-proof properties and that can be identified in a very simple way.

[0013] In particular, the security means of the document allows for simply checking its authenticity by visual inspection from different viewing angles. However, in some cases, some of the special features of the present security means cannot be seen by the naked eye but require special tools such as a lens due to the small line thickness of the lasered mark. For example, slightly ablated marks may be viewed by microscope to see some single colour changing particles.

[0014] In addition, the present invention overcomes the size, flexibility and durability limitations of conventional security means. The document of the present invention is extremely thin, preferably thinner than 100 μm. Furthermore, the document of the present invention exhibits a very high flexibility, and a very high durability.

[0015] Especially suitable variations of the method for laser marking a document of the present invention are described in the dependent method claims.

[0016] The product claims describes particularly suitable documents obtainable by the method of the present invention and the use claims refer to particularly favourable ways of using the document of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

FIG. 1 shows a test pattern for laser experiments in pulsed mode (Q-switch).

FIG. 2 shows a general curve of peak power of a solid state laser in pulsed mode.

FIG. 3 shows the evaluation results of laser marks for example 1 for a laser power of 90%.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The following is a detailed description of the present invention. It provides a method for laser marking a document,

preferably a security document. The term "document", as used herein, refers to a bounded physical representation of body of information designed with the capacity (and usually intent) to communicate. A document may manifest symbolic, diagrammatic or sensory-representational information and has to be understood as a paper artefact, containing information in the form of ink marks. The term "security document", as used herein, refers to all kind of documents that contain at least one feature that can be used to prevent counterfeiting by providing authentication, identification or classification of the document. In particular, they include banknotes, passports, chequebooks, identity cards, credit cards and/or debit cards.

[0019] From a technical point of view, said document may comprise various substrates, such as, for example, paper, cardboard, board, plastics, plastic films and laminates. Particularly suitable for security applications are papers containing fibres from annual plants, such as cotton (for example cotton vellum paper) or cotton fibre blends or cotton fibre mixtures with plastic fibres, which may have a single- or multilayered structure.

[0020] According to the present invention, a document comprising a coating containing at least one sort of effect pigments is treated with a laser beam under specific conditions. In that context, the term "effect pigment" comprises all kind of pigments showing different colours under different viewing angles and includes pigments with a pearl luster effect, with an iridescent interference effect and with a colour-shift effect.

[0021] Pearlescent or nacreous pigments are well known in the art and have become very popular in the creation of lustre effects in coatings. The pearlescent effect is produced by the specular reflection of light from several surfaces of the platelets with parallel orientation at various depths within the coating film. Light striking the platelets is partially reflected and partially transmitted through the platelets. A pearly lustre effect is produced by the dependence of reflection on viewing angle, and the sense of depth is created by reflection from many layers. The platelets must be extremely smooth to maximize reflected light and any surface roughness diminishes the lustrous effect. Non fine particles or pigments with rough edges can also negatively affect the lustrous appearance.

[0022] Pearlescent pigments show iridescence, i. e. an optical phenomenon characterized as the property of surfaces in which hue changes according to the angle from which the surface is viewed may be seen as may be seen of soap bubbles and butterfly wings. Iridescence is caused by multiple reflections from multi-layered, semi-transparent or transparent surfaces in which phase shift and interference of the reflections modulates the incident light by amplifying or attenuating some frequencies more than others. This process is the functional analogue of selective wavelength attenuation as seen with the Fabry-Pérot interferometer.

[0023] The special attraction of the pearlescent pigments is the soft and smooth colour shift effect, which is unique in the art. They are very useful for security applications, because the overt colour-shift feature could not be duplicated by a copy machine.

[0024] The pearlescent pigments show optical effects such as directed reflection, multiple reflection, interference, and a soft colour travel (angle-dependent optical effects), which generate their optical attractiveness because of the ability of easy parallel orientation of a multitude of platelet-like particles.

[0025] In addition, several advantages accrue from the use of pearlescent pigments. The first is the illusion of optical depth, which is created by the arrangement of a multiplicity of platelet-like particles of a pearlescent pigment. The achieved impression is the result of reflection of light at the different interfaces between pigment and binder and at the boundary layers of the effect pigment itself. Such an effect is especially strong when extended areas are profiled.

[0026] Another advantage, which can be achieved with multilayered pearlescent pigments, is the subtle to startling eye-catching effect of an angle-dependent colour. Multilayered pigments exhibiting such a startling effect are also called optically variable pigments.

[0027] Therefore, according to a preferred embodiment of the present invention, optically variable pigments (or optically variable effect pigments) are used as said effect pigments. Optically variable pigments are pigments that have at least two and at most four optically clearly distinguishable discrete colours at at least two different illumination or viewing angles, but preferably have two optically clearly distinguishable discrete colours at two different illumination or viewing angles or three optically clearly distinguishable discrete colours at three different illumination or viewing angles. In each case, only the discrete hues and not intermediate hues are preferably present, i.e. a clear change from one colour to another colour is evident on tilting the security element (or the coated substrate in this case) which comprises the optically variable pigments.

[0028] Effect pigments particularly suitable for the present invention comprise a platelet-shaped transparent or semi-transparent dielectric carrier material coated with at least one layer of a metal oxide, preferably selected from the group consisting of SiO_2, Al_2O_3, TiO_2, SnO_2, Fe_2O_3, Fe_3O_4, chromium oxides, silicon hydroxide, aluminium hydroxide or magnesium fluoride. Thereby the dielectric carrier material is preferably selected from the group consisting of platelet-shaped silicates such as natural or synthetic mica, talc, kaolin, glass plates, alumina flakes and SiO_2-platelets. Particularly preferred are effect pigments where the platelet-shaped carrier is coated with a multiple layer coating comprising layers of different metal oxides having different refractive indices. Most useful are layer sequences comprising alternating low refractive layers and high refractive layers. Thereby, the materials mentioned above are preferably used for the metal oxide layers. In especially preferred pigments, the outer layer having optical activity is a high refractive layer. Materials

with high refractive indices are materials having refractive indices which are equal or higher than 1.8 at 25°C, whereas materials with low refractive indices exhibit refractive indices which are lower than 1.8 at 25°C. The former are represented by TiO_2, SnO_2, Fe_2O_3, Fe_3O_4 and chromium oxides, the latter by SiO_2, Al_2O_3, silicon hydroxide, aluminium hydroxide and magnesium fluoride, to name only a few. With these multilayered pigments striking angle-dependent colour effects may be achieved. The refractive index increment preferably is greater than 0.1.

[0029] The coating of the document can be achieved in an usual manner. The according inks containing the effect pigments are preferably printed on suitable substrates by usual printing or coating techniques like relief printing, gravure printing, flexographic printing, direct offset printing, indirect offset printing, pad printing, intaglio printing, screen printing, paper coating, K-coating, or doctor blade application. Furthermore, application of the ink by means of partial or full-area in-line or off-line lacquering is possible.

[0030] The concentration of the effect pigments in the ink is preferably between 5 % by weight and 33 % by weight, very preferably between 10 % by weight and 20 % by weight.

[0031] Suitable binders for the inks, to be favourably used, are:

a) for aqueous systems:

acrylates, methacrylates, polyesters, polyurethanes, polyvinyl alcohols, polyvinylpyrrolidones, and copolymers of the said substances

b) for solvent-based systems:

nitrocellulose, ethylcellulose, polyamides, PVC-PVA copolymers, polyvinylbutyrals, polyisobutylene, chlorinated rubber, colophony-modified phenolic resins, maleic resins, calcium/zinc resinates, EHEC, acrylates and copolymers of the said substances

c) radiation-curing (UV, EB) systems:

epoxy acrylates, polyurethane acrylates, polyester acrylates, polyether acrylates

d) oil-based systems:

colophony-modified phenolic resins, maleic acid-modified phenolic resins, alkyd resins (for example linseed oil alkyd resin), hydrocarbon resins.

[0032] The binder content is preferably 10-50% by weight, based on the total weight of the liquid system.

[0033] Suitable solvents and cosolvents for the inks, to be favourably used, are:

a) for aqueous systems:

water, water/alcohol mixtures

b) for solvent-containing systems:

ethyl alcohol, isopropyl alcohol, n-propyl alcohol, acetone, ethyl acetate, isopropyl acetate, n-propyl acetate, methoxypropanol, ethoxypropanol, toluene, aliphatic hydrocarbons, and mixtures of the said solvents

c) for radiation-curing systems (reactive diluents):

hexanediol diacrylate, di/tripropylene glycol diacrylate, trimethylpropane triacrylate, trimethylolpropane ethoxytriarylate

d) for oil-based systems:

mineral oils, vegetable oils and mixtures of the two classes of substance.

[0034] The solvent content is preferably 30 % by weight to 70% by weight, based on the liquid system.

[0035] According to the present invention at least a part of the coating of the document containing effect pigments is treated with a laser beam. A laser is a device that emits light through a specific mechanism for which the term laser is

an acronym: light amplification by stimulated emission of radiation. The laser creates a coherent and monochromatic light with a low divergence.

[0036] A laser consists of a gain medium inside an optical cavity, with a means to supply energy to the gain medium. The gain medium is a material (gas, liquid, solid or free electrons) with appropriate optical properties. In its simplest form, a cavity consists of two mirrors arranged such that light bounces back and forth, each time passing through the gain medium. Typically, one of the two mirrors, the output coupler, is partially transparent. The output laser beam is emitted through this mirror.

[0037] Light of a specific wavelength that passes through the gain medium is amplified (increases in power); the surrounding mirrors ensure that most of the light makes many passes through the gain medium. Part of the light that is between the mirrors (i.e., is in the cavity) passes through the partially transparent mirror and appears as a beam of light. The process of supplying the energy required for the amplification is called pumping and the energy is typically supplied as an electrical current or as light at a different wavelength. In the latter case, the light source can be a flash lamp or another laser. Most practical lasers contain additional elements that affect properties such as the wavelength of the emitted light and the shape of the beam.

[0038] The laser used in the present invention preferably has a wavelength within the range of 157 nm to 10.6 μm, very preferably within the range of 355 nm to 10.6 μm. Particularly suitable lasers enclose diode lasers (808-980 nm), Nd:YAG lasers und Nd:YVO_4- lasers (355, 534 und 1064 nm) und CO_2-lasers (10.6 μm). The mean laser power is preferably within the range of 2 W to 300 W, very preferably within the range of 4 W to 30 W.

[0039] According to the present invention the laser is operated in a pulsed mode, preferably in a Q-switching mode. In the pulsed mode of operation, the output of a laser varies with respect to time, typically taking the form of alternating 'on' and 'off' periods. In a Q-switched laser, the population inversion, usually produced in the same way as in CW operation, is allowed to build up by making the cavity conditions (the 'Q') unfavourable for lasing. Then, when the pump energy stored in the laser medium is at the desired level, the 'Q' is adjusted (electro- or acousto-optically) to favourable conditions, releasing the pulse. This results in high peak powers as the average power of the laser (were it running in CW mode) is packed into a shorter time frame.

[0040] In the present invention, a rate of greater than 500 mm/s is necessary to achieve the desired results. The rate is preferably at least 1000 mm/s, more preferably at least 2000 mm/s, and most preferably within the range of 2000 to 3000 mm/s. For a laser power of 90 %, a rate of greater than 1000 mm/s, especially more than 2000 mm/s, is particularly preferred.

[0041] With decreasing the laser power, a lower laser speed is advantageous. As a general rule, the higher the laser power is, the higher the rate should be, provided that the rate is above 500 mm/s.

[0042] The laser power is preferably greater than 30%, more preferably within the range of 40% to 90%, and in particular within the range of 50 % to 90 %.

[0043] The frequency is preferably within the range of 5 kHz to 100 kHz, more preferably within the range of 10 kHz to 90 kHz, in particular within the range of 40 kHz to 90 kHz. Here too, as a general rule, a higher laser power enables a higher frequency range. Therefore, the range of 40-90 kHz applies in particular for a laser power higher than 80%, whereas a range of 10-30 kHz is in particular used for a laser power lower than 50%.

[0044] Particularly favourable results are achieved by using a rate within the range of 2000 to 3000 mm/s, a laser power within the range of 70% to 80% and a frequency of the laser within the range of 40 kHz to 60 kHz.

[0045] Under the laser irradiation the effect pigments as disclosed above interact with the laser beam. As a consequence a laser mark is formed which is characterized by a change in the optical appearance of the coating depending from the viewing angle. Thereby the laser treatment preferably results in a darkening effect, wherein the colour flop of the pigments is maintained onto the mark as well. With the help of the pulsed mode, the pigments are only removed gradually from the dark laser mark, if at all. Preferably, more than 50 % of the original amount of the effect pigments are remaining on the marking after laser treatment, more preferably more than 80%.

[0046] However, the laser mark obtainable by the process of the present invention is **characterized in that** it shows a high contrast and a high colour shift effect at the same time. Thereby, the colour shifting marking is obtained in a colour shifting surrounding, whereby the marking is of striking colour shift and the surrounding of subtile colour shift due to the dark laser mark underneath the colour shifting pigments in the marking.

[0047] The authenticity of the document of the present invention can be easily checked by visual inspection from different viewing angles.

[0048] The present invention will be further illustrated by the following examples. However, it should be noted that these examples are for illustrative purposes only and shall no limit the desired scope of protection defined by the present claims.

[0049] The laser experiments were carried out in a test matrix. The chosen parameters varied in following steps for optimizing the numbers of experiments (see FIG. 1, test pattern in QS-mode).

Laser speed:	500, 1000, 2000, 3000, 4000, 5000 mm/s
Laser frequency:	10 - 100 kHz in 10 kHz-steps
Laser power:	30, 40, 50, 60, 70, 80, 90, 100% of mean power

[0050] The evaluation was done in following graduations at the given measurement points:

1: dark mark with a strong colour-shift and optionally pearlescent effect
2: mark with colour-shift and optionally pearlescent effect
3: very dark mark without any effect

[0051] Burning effects or missed laser effects were not recorded in the following tables.

[0052] The behavior of lasered marks depended on the power curve of the laser. In Fig. 2, a general curve of peak power from a Nd:YAG laser is given for the pulsed mode (Q-switch). According to this the dark marks with a strong colour-shift and optionally pearlescent effect (evaluation "1") were found in the top area of the curve. The weaker marks with colour-shift and optionally pearlescent effect (evaluation "2") were observed left or right of the curve and the very dark mark without any effect (evaluation "3") were located under the curve at lower values of laser speed (see FIG. 3). The properties of lasered marks changed continuously within the parameter ranges.

[0053] For very low laser speed values it was found that the paper burnt. Such marks were not recorded.

[0054] The position of the peak power curve moved with decreasing the laser power to lower values of laser speed. Also the range of laser frequencies with good marks (evaluation "1" and "2" at frequencies of 40-90 kHz for laser power of 90%) was reduced to a shorter range of frequency values (about 10-30 kHz for laser power <50%) by decreasing the laser power.

1. Example

Laser marking of a layer made from ink containing effect pigments with colour-shift effect

[0055] 10 g of a plate-shaped effect pigment with a colour-shift from red to gold (multi-layered pigment based on mica) is added to 90 g screen printing binder MZ-varnish 093 (Pröll, Weißenburg). The mixture is homogenized and it is tuned in to the right viscosity. The ink is printed on banknote paper by silk-screen printing.

[0056] The laser experiments are carried out with solid state or diode lasers (wavelength range of 355 nm, 532 nm, 980 nm, 1064 nm) and a gas laser, e.g. CO_2-laser (10.6 μm), preferably with a Nd:YAG laser and Nd:YVO_4-laser.

[0057] Dark marks with a high contrast and a strong colour-shift effect are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm, mean power of 12 W) in Q-switch mode (figure 1). These parameters are exemplary, but not limited only on this laser system. Font sizes for the lasered letters or numbers are 0,2-20 mm. Area of laser marks of 5x5 mm is also possible.

Table 1: results of Example 1

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
4000 - 5000	40-70	90	1
4000 - 5000	20-30, 80-100	90	2
3000	30-70	90	1
3000	20, 80-100	90	2
2000	20, 50-100	90	1
2000	10	90	2
2000	30-40	90	2
1000	10, 50-100	90	1
1000	20-40	90	2
500	10	90	3
500	20	90	3

(continued)

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
5000	20-70	80	1
5000	80-100	80	2
4000	20-80	80	1
4000	90-100	80	2
3000	20-90	80	1
3000	100	80	2
2000	20-80	80	1
2000	10, 90-100	80	2
1000	10, 60-100	80	1
1000	20-50	80	2
500	10	80	3
5000	20-60	70	2
4000	20-30	70	1
4000	10, 50-70	70	2
3000	20-60	70	1
3000	70-80	70	2
2000	30-70	70	1
2000	80-100	70	2
2000	20	70	2
1000	40-100	70	1
1000	10-30	70	2
500	40-100	70	3
500	10-30	70	3
4000	20	60	2
3000	20-40	60	2
2000	20-30	60	1
2000	40-50	60	2
1000	10-50	60	1
1000	60	60	2
500	40-70	60	3
500	10-30	60	3
2000	20-30	50	2
1000	10-60	50	1
500	20-100	50	3
500	10	50	3
1000	10-30	40	2
500	10	40	3

2. Example

Laser marking of a layer made from ink containing effect pigments with colour-shift effect

[0058] 15 g of a plate-shaped effect pigment with a colour-shift from bronze to green (multi-layered pigment based on transparent dielectric carrier) is added to 85 g screen printing binder MZ-varnish 093 (Pröll, Weißenburg). The mixture is homogenized and it is tuned in to the right viscosity. The ink is printed on banknote paper by silk-screen printing.

[0059] The laser experiments are carried out with solid state or diode lasers (wavelength range of 355 nm, 532 nm, 980 nm, 1064 nm) and a gas laser, e.g. CO_2-laser (10.6 μm), preferably with a Nd:YAG laser and Nd:YVO_4-laser.

[0060] Dark marks with a high contrast and a strong colour-shift effect are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm, mean power of 12 W) in Q-switch mode. These parameters are exemplary, but not limited only on this laser system. Font sizes for the lasered letters or numbers are 0,2-20 mm. Area of laser marks of 5x5 mm is also possible.

Table 2: results of Example 2

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
5000	60-100	90	1
5000	30-50	90	2
4000	20, 60-100	90	1
4000	30-50	90	2
3000	70-100	90	1
3000	20-60	90	2
2000	80-100	90	1
2000	10-70	90	2
1000	10-100	90	2
500	10	90	3
5000	20-70	80	1
5000	70-100	80	2
4000	20-80	80	1
4000	90-100	80	2
3000	20-90	80	1
3000	100	80	2
2000	20-90	80	1
2000	10, 100	80	2
1000	10, 60-90	80	1
1000	20-50	80	2
500	10	80	3
5000	20-60	70	1
4000	20-70	70	1
3000	20-80	70	1
2000	20-80	70	1
2000	10, 90-100	70	2
1000	10, 40-100	70	1
1000	20-30	70	2

(continued)

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
500	10-50	70	3
4000	20-30	60	2
3000	20-30	60	1
3000	40	60	2
2000	20-40	60	1
2000	10,50	60	2
1000	10-50	60	1
1000	60-70	60	2
500	10-40	60	3
2000	10-30	50	2
1000	10-40	50	1
1000	50-60	50	2
500	10, 90-100	50	3
1000	10-30	40	2
500	50	40	3
500	10	40	3

3. Example

Laser marking of a layer made from ink containing effect pigments with pearl luster effect and slight colour-shift effect

[0061] 20 g of a plate-shaped effect pigment with a strong golden pearl luster effect and a slight golden to silver-grey colour-shift effect (multi-layered pigment based on mica) is added to 80 g screen printing binder MZ-varnish 093 (Pröll, Weißenburg). The mixture is homogenized and it is tuned in to the right viscosity. The ink is printed on banknote paper by silk-screen printing.

[0062] The laser experiments are carried out with solid state or diode lasers (wavelength range of 355 nm, 532 nm, 980 nm, 1064 nm) and a gas laser, e.g. CO_2-laser (10.6 μm), preferably with a Nd:YAG laser and Nd:YVO_4-laser.

[0063] Dark marks with a high contrast and a strong pearlescent effect exhibiting a slight colour-shift effect are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm, mean power of 12 W) in Q-switch mode. These parameters are exemplary, but not limited only on this laser system. Font sizes for the lasered letters or numbers are 0,2-20 mm. Area of laser marks of 5x5 mm is also possible.

Table 3: results of Example 3

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
5000	30-40	90	1
5000	20, 50-90	90	2
4000	30-50	90	1
4000	20, 60-100	90	2
3000	20-70	90	1
3000	80-100	90	2
2000	60-100	90	1

(continued)

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
2000	20-50	90	2
1000	10, 70-100	90	1
1000	20-60	90	2
500	10-20	90	3
5000	20-80	80	1
5000	90-100	80	2
4000	20-70	80	1
4000	80-100	80	2
3000	20-90	80	1
3000	100	80	2
2000	10, 40-80	80	1
2000	90-100	80	2
2000	20-30	80	2
1000	10, 70-90	80	1
1000	100	80	2
1000	20-60	80	2
500	10	80	3
5000	20-60	70	1
5000	70-100	70	2
4000	20-70	70	1
4000	80-100	70	2
3000	20-70	70	1
3000	10, 80-100	70	2
2000	10-80	70	1
2000	90-100	70	2
1000	40-100	70	1
1000	10-30	70	2
500	10-30	70	3
4000	20-30	60	2
3000	20	60	1
3000	30-40	60	2
2000	20-40	60	1
2000	10,50	60	2
1000	10-50	60	1
1000	60-70	60	2
500	10-40	60	3
2000	10-30	50	2
1000	10-50	50	1

(continued)

Laser speed v [mm/s]	Frequency f [kHz]	Power P [%]	Evaluation
1000	60	50	2
500	70-100	50	3
500	10	50	3
1000	10-20	40	2
500	10	40	3

4. Example

Laser marking of a layer made from ink containing effect pigments with colour-shift effect and laser-induced gradient of the colour-shift pigment concentration

[0064] 15 g of a plate-shaped effect pigment with a colour-shift effect from red to gold (multi-layered pigment based on mica) is added to 75 g screen printing binder MZ-varnish 093 (Pröll, Weißenburg). The mixture is homogenized and it is tuned in to the right viscosity. The ink is printed on banknote paper by silk-screen printing.

[0065] The laser experiments are carried out with solid state or diode lasers (wavelength range of 355 nm, 532 nm, 980 nm, 1064 nm) and a gas laser, e.g. CO_2-laser (10.6 μm), preferably with a Nd:YAG laser and Nd:YVO_4-laser. Marking letters or numbers with a high contrast, a fixed red colour and a decreasing gradient of remaining colour-shift pigments are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm, mean power of 12 W) in Q-switch mode.

Table 4: results of Example 4

Concentration of remaining colour-shift pigments [%]	Font size [mm]	Laser speed v [mm/s]	Frequency [kHz]	Power P [%]	Evaluation
> 80	14	3000	30	90	1
> 50	19	3000	50	90	1
< 5	26	500	10	90	3

Claims

1. Method for laser marking a document, **characterized in that** a document comprising a coating containing at least one sort of effect pigments which show different colours under different viewing angles is treated on at least a part of the coated area with a pulsed laser beam at a rate of greater than 500 mm/s and a laser mark having a colour shift effect is obtained.

2. Method according to claim 1, **characterized in that** the laser power is greater than 30%.

3. Method according to claim 2, **characterized in that** the laser power is within the range of 50% to 90%.

4. Method according to at least one of the preceding claims, **characterized in that** the frequency of the laser is within the range of 5 kHz to 100 kHz.

5. Method according to claim 4, **characterized in that** the frequency of the laser is within the range of 40 kHz to 90 kHz.

6. Method according to at least one of the preceding claims, **characterized in that** the rate is within the range of 2000 to 3000 mm/s.

7. Method according to claim 6, **characterized in that** the rate is within the range of 2000 to 3000 mm/s; the laser power is within the range of 70% to 80% and the frequency of the laser is within the range of 40 kHz to 60 kHz.

8. Method according to at least one of the preceding claims, **characterized in that** said effect pigments comprise

optically variable pigments.

9. Method according to at least one of the preceding claims, **characterized in that** said effect pigments comprise a transparent or semi-transparent dielectric carrier material coated with a layer of at least one oxide, wherein said dielectric carrier material is selected from the group consisting of platelet-shaped silicates such as natural or synthetic mica, talc, kaolin, glass plates, alumina flakes and SiO_2-platelets and wherein said oxide is selected from the group consisting of SiO_2, Al_2O_3, TiO_2, SnO_2, Fe_2O_3, Fe_3O_4, chromium oxides, silicon hydroxide, aluminium hydroxide or magnesium fluoride.

10. Document obtainable by a method according to at least one of the preceding claims, comprising a coating containing at least one sort of effect pigments, which show different colours under different viewing angles, wherein said coating comprises a laser mark having a colour shift effect.

11. Document according to claim 10, **characterized in that** said document is a security document.

12. Document according to claim 11, **characterized in that** said security document is a banknote, a passport, a cheque-book, an identity card, a credit card or a debit card.

13. Document according to claim 10, 11 or 12, **characterized in that** the security document is adapted for checking its authenticity by visual inspection of said security means from different viewing angles.

14. Use of a document according to at least one of the claims 10 to 13 for checking its authenticity, wherein said security means is visual inspected from different viewing angles.

FIG. 1

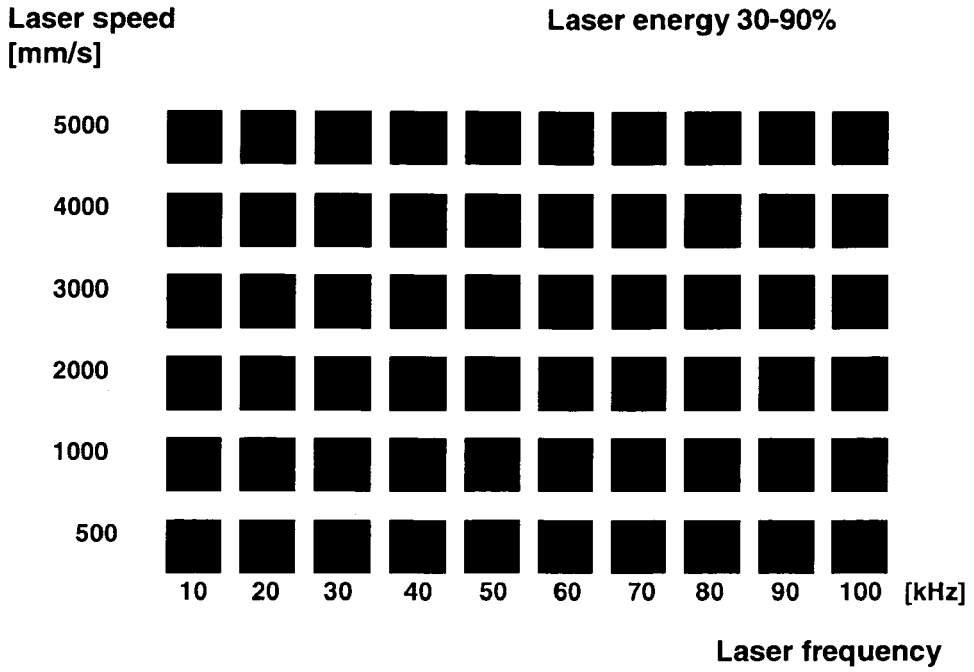

Laser speed
[mm/s]
Laser energy 30-90%
5000
4000
3000
2000
1000
500
10
20
30
40
50
60
70
80
90
100
[kHz]
Laser frequency

FIG. 2

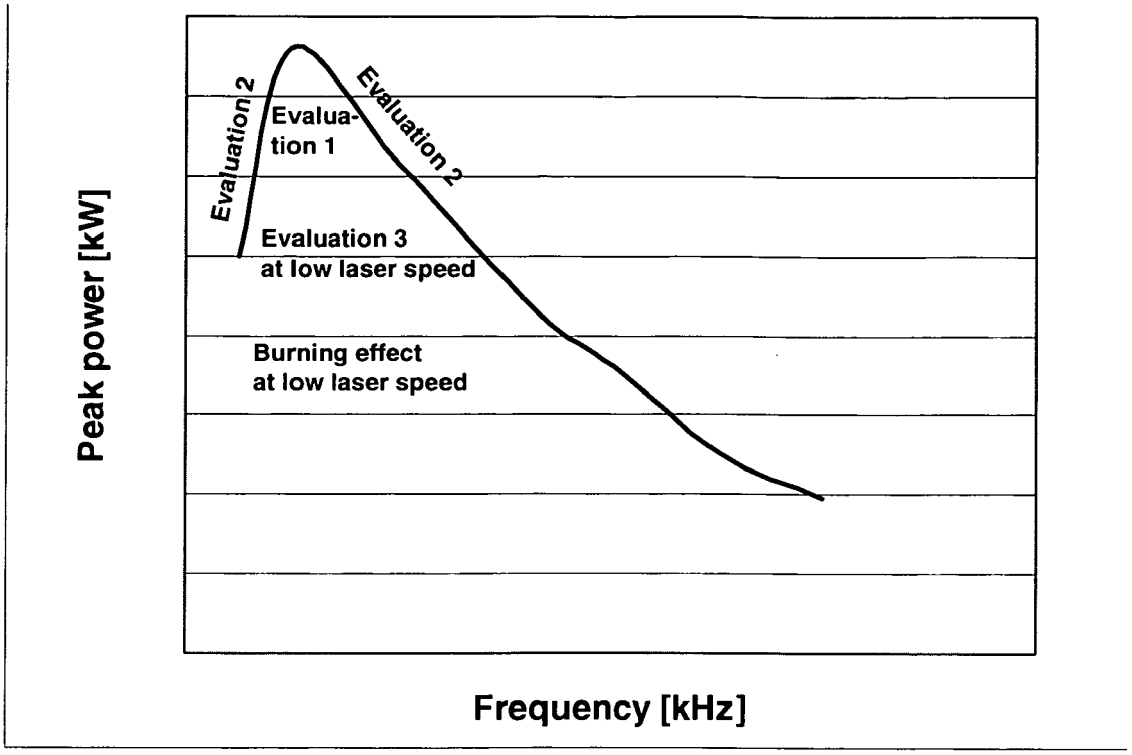
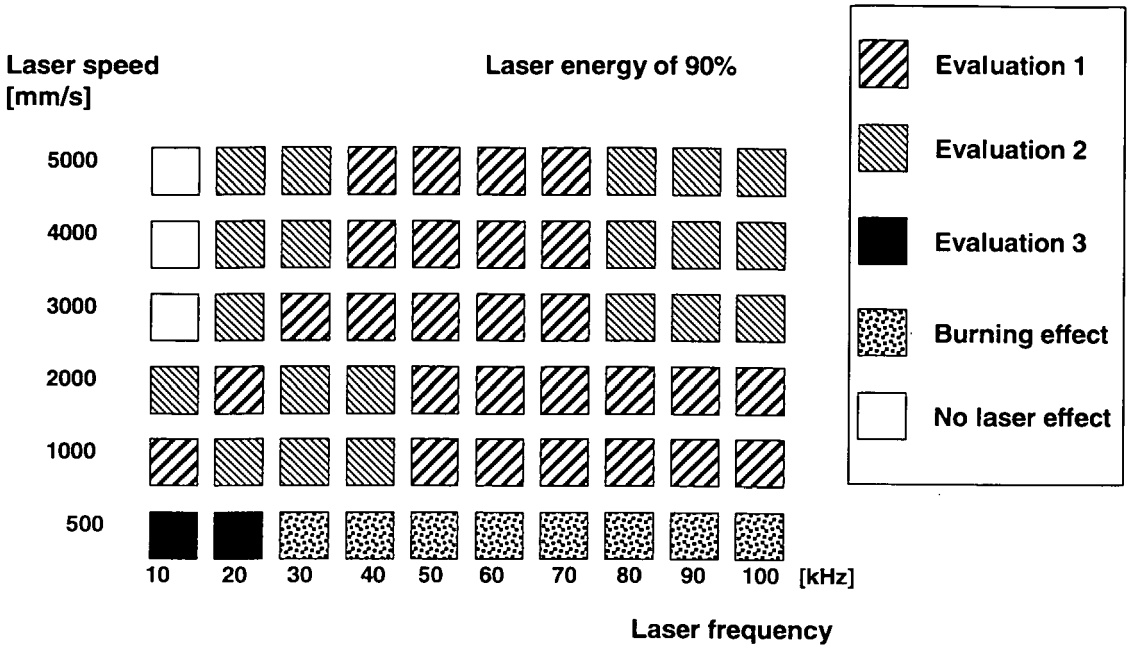

Peak power [kW]
Frequency [kHz]
Evaluation 2
Evalua-
tion 1
Evaluation 2
Evaluation 3
at low laser speed
Burning effect
at low laser speed

FIG. 3


Laser speed
[mm/s]
Laser energy of 90%
5000
4000
3000
2000
1000
500
10
20
30
40
50
60
70
80
90
100
[kHz]
Laser frequency
Evaluation 1
Evaluation 2
Evaluation 3
Burning effect
No laser effect

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 08 01 7527

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 2006/141391 A1 (KLEIN SYLKE [DE] ET AL) 29 June 2006 (2006-06-29) * paragraphs [0014] - [0019], [0023], [0025] - [0030], [0037] - [0047], [0051] - [0054], [0056] - [0079], [0113] * -----	1-5,8-14	INV. B42D15/00 B42D15/10 B41M5/24 B41M3/14
X A	DE 10 2006 057507 A1 (MERCK PATENT GMBH [DE]) 12 June 2008 (2008-06-12) * paragraphs [0015], [0018], [0020], [0021] * * paragraphs [0054] - [0061], [0067] - [0073] * * paragraphs [0111] - [0114], [0136] - [0140] * * paragraphs [0152] - [0154], [0162] - [0166] * -----	10-14 1-9	
X	WO 2007/062785 A (MERCK PATENT GMBH [DE]; KLEIN SYLKE [DE]; ULLMANN KLAUS-CHRISTIAN [DE]) 7 June 2007 (2007-06-07) * page 5, lines 11-23 * * page 6, line 3 - page 8, line 4 * * page 9, lines 6-10 * * page 10, line 1 - page 12, line 30 * * page 23; table 2 * -----	1-14	TECHNICAL FIELDS SEARCHED (IPC) B42D B41M
X	WO 2005/108110 A (GIESECKE & DEVRIENT GMBH [DE]; DEPTA GEORG [DE]; BALDUS CHRISTOF [DE];) 17 November 2005 (2005-11-17) * page 14, line 22 - page 15, line 12 * * page 20, line 19 - page 32, line 21 * -----	1-8, 10-14	
A	US 6 017 972 A (HARRIS RONALD M [US] ET AL) 25 January 2000 (2000-01-25) * column 4, lines 1-19 * * column 5, line 1 - column 10, line 27 * -----	1-14	
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 April 2009	Patosuo, Susanna

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 08 01 7527

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2004/101890 A (MERCK PATENT GMBH [DE]; KUNTZ MATTHIAS [DE]; KRIETSCH BURKHARD [DE]; W) 25 November 2004 (2004-11-25) * page 10, line 6 - page 11, line 10 * * page 11, line 28 - page 12, line 16 * * page 12, line 31 - page 18, line 21 * -----	1-14	
A	EP 1 717 059 A (VITRO LASER GMBH [DE]) 2 November 2006 (2006-11-02) * paragraphs [0025] - [0044] * -----	1-14	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 April 2009	Patosuo, Susanna

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

2

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 01 7527

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-04-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006141391 A1	29-06-2006	AU 2005239689 A1	15-06-2006
		CA 2528117 A1	30-05-2006
		CN 1807112 A	26-07-2006
		DE 102004057918 A1	01-06-2006
		EP 1661729 A2	31-05-2006
		JP 2006150972 A	15-06-2006
		KR 20060060620 A	05-06-2006
DE 102006057507 A1	12-06-2008	WO 2008067887 A2	12-06-2008
WO 2007062785 A	07-06-2007	AU 2006319474 A1	07-06-2007
		CN 101321633 A	10-12-2008
		DE 102005057474 A1	31-05-2007
		EP 1954507 A2	13-08-2008
		KR 20080080592 A	04-09-2008
		US 2008290649 A1	27-11-2008
WO 2005108110 A	17-11-2005	AU 2005240277 A1	17-11-2005
		CA 2562262 A1	17-11-2005
		CN 1946569 A	11-04-2007
		DE 102004022080 A1	24-11-2005
		EP 1744905 A1	24-01-2007
		US 2009008926 A1	08-01-2009
US 6017972 A	25-01-2000	AU 8055498 A	30-12-1998
		CA 2293571 A1	17-12-1998
		MX PA99011421 A	11-06-2002
		WO 9856594 A1	17-12-1998
		US 6627299 B1	30-09-2003
		US 6022905 A	08-02-2000
		US 5977514 A	02-11-1999
WO 2004101890 A	25-11-2004	CA 2526138 A1	25-11-2004
		CN 1791723 A	21-06-2006
		DE 10322841 A1	16-12-2004
		EP 1625255 A1	15-02-2006
		US 2007006127 A1	04-01-2007
EP 1717059 A	02-11-2006	JP 2006305633 A	09-11-2006
		US 2006249490 A1	09-11-2006

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- DE 2836526 **[0006]**
- US 4740269 A **[0006]**
- DE 19544130 **[0006]**
- DE 19704478 **[0006]**
- DE 19732860 **[0006]**
- DE 10008851 **[0006]**
- DE 4243987 **[0006]**
- WO 02074548 A **[0006]**
- WO 2005012442 A **[0006]**
- DE 10232786 **[0006]**
- DE 10247591 **[0006]**
- EP 1658992 A **[0006]**
- US 6395191 B **[0006]**
- US 20060141391 A1 **[0007]**