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(54) **Method for laser-marking a document, the document showing a fixed colour in a surrounding with a colour shift effect**

Verfahren zur Laser-Markierung eines Dokuments, das eine fixierte Farbe in einer Umgebung mit einem wechselnden Farbeffekt zeigt

Méthode de marquage par laser d'un document, le document doté d'une couleur fixe dans un environnement doté d'un effet de décalage de couleur

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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 fixed colour in a surrounding with 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.

[0010] DE 10 2006 057507 refers to a document having an optical variable security feature comprising effect pigments, which show different colours under different viewing angles and laser sensitive pigments, wherein said document also comprises a laser mark on at least part of said coating having one of the different colours of the effect pigment fixed in a surrounding with a colour shift effect.

[0011] WO 2005/108110 relates to a value document, particularly a banknote, comprising a sequence of layers into which visually and/or mechanically recognizable markings are introduced in the form of patterns, letters, numbers, or images under the effect of laser radiation. According to the application, the sequence of layers encompasses a marking layer that is composed of an ink mixture comprising a component absorbing the laser radiation and a component which is transparent to the laser radiation. The markings are visually and/or mechanically recognizable as a result of an irreversible change in the optical characteristics of the ink mixture, said irreversible change being caused by the laser radiation.

SUMMARY OF THE INVENTION

[0012] 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 and exhibits optically striking characteristics. At the same time the security means shall be highly flexible regarding its design, comparable small in thickness and highly durable.

[0013] In carrying out these and other objects of the present invention, there is provided a method for laser marking a document, wherein a document comprising a coating containing at least one sort of effect pigment which shows different colours under different viewing angles and at least one sort of laser sensitive pigment is treated on at least a part of the coated area with a laser beam operated in cw mode at a rate of 500 mm/s using a power of 90 %, calculated based on a laser having a mean power of 12 W, and a laser mark having a fixed colour is obtained, wherein said fixed colour is one of the different colours which are shown under different viewing angles by the effect pigment.

[0014] 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, exhibiting a striking optical appearance.

[0015] In particular, the security means of the document allows for simply checking its authenticity by visual inspection from different viewing angles.

[0016] 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 security document of the present invention exhibits a very high flexibility, and a very high durability.

[0017] Especially suitable variations of the method for laser marking a document of the present invention are described in the dependent method claims.

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] In addition to the effect pigments, the coating of the security document also comprises at least one sort of laser sensitive pigments. In that context, the term "laser sensitive pigments" refers to all kind of pigments, which are able to absorb the laser energy and to cause reactions within the coating layers of the substrate. Preferably, the laser sensitive pigments are able to absorb more laser energy than the effect pigments.

[0030] Examples of particularly suitable laser-sensitive pigments include

- metal compounds, especially antimony(III)oxide and/or tin oxide, zinc oxide, tin oxide and/or zircon oxide, iron oxides, copper hydroxyphosphate, copper diphosphate, molybdene disulfide, bismute oxychloride, indium tin oxide, $Sn(Sb)O_2$, TiO_2,
- anthracene,
- IR (780 nm - 1 mm)-absorbing materials, especially perylene/ rylene, pentaerythrite, carbon black, and/or graphite; and
- plate-shaped materials, especially transparent or semi-transparent pigments based on silicates, talc, kaolin, glass plates, and SiO_2-plates, wherein the plate-shaped pigments are preferably coated with at least one oxide, selected from the group consisting of SiO_2, TiO_2, $Sn(Sb)O_2$, Fe_2O_3, and Fe_3O_4.

[0031] Said laser sensitive pigments may be present together with the effect pigments in one single layer or in separate layers. Preferably, at least one kind of laser sensitive pigments and at least one kind of the effect pigments mentioned above are present in one single layer.

[0032] The weight ratio of the effect pigments to the laser-sensitive pigments is preferably between 4:1 and 1:2.

[0033] The coating of the document can be achieved in an usual manner. The according inks containing the effect pigments and the laser sensitive 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.

[0034] 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. The concentration of the laser-sensitive pigments in the ink is preferably between 5 % by weight and 33 % by weight, very preferably between 10 % by weight and 20 % by weight.

[0035] 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.

[0036] The binder content is preferably 10-50 % by weight, based on the total weight of the liquid system.

[0037] 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.

[0038] The solvent content is preferably 30 % by weight to 70 % by weight, based on the liquid system.

[0039] 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.

[0040] 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.

[0041] 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.

[0042] 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 12 W.

[0043] According to the present invention the laser is operated in cw mode. In the continuous wave (CW) mode of operation, the output of the laser is relatively consistent with respect to time. The population inversion required for lasing is continually maintained by a steady pump source.

[0044] In the present invention, a rate of 500 mm/s is used.

[0045] The laser power is 90%

[0046] Under the laser irradiation the laser effect pigments interact with the laser beam. As a consequence a laser mark is formed in which one colour of the effect pigments with colour shift effect is fixed under laser irradiation and the colour shift effect is no longer observed after the laser treatment. The fixation of one colour of the effect pigment at any place of the substrate, preferably in a surrounding with an unchanged colour shift effect, is a unique feature, which can not be realized by printing techniques.

[0047] In the present invention, the effect pigments are only removed gradually from the 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%.

[0048] The actual size of the laser mark is of minor importance in the present invention. It is possible to create both, fine lines and bigger areas, wherein the optical effect might be observed for all sizes of the marking, especially when the surrounding rests optically variable.

[0049] The authenticity of the document of the present invention can be easily checked by visual inspection from

different viewing angles.

[0050] 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 not limit the desired scope of protection defined by the present claims.

Example

Laser marking of a layer made from ink containing laser-sensitive pigments and effect pigments with effect of fixed colour

[0051] 15 g of a plate-shaped effect pigment with a colour-shift effect from red to gold (multi-layered pigment based on mica) and 15 g of a laser-sensitive pigment containing copper hydroxidyphosphate are added to 70 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.

[0052] 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 und Nd:YVO_4- laser.

[0053] Marked areas (for example a rectangle of 5x5 mm) with a high contrast and a fixed red colour are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm, mean power of 12 W) in cw-mode. These parameters are exemplary, but not limited only on this laser system. For evaluation the following ranking was applied.

1: very intensive colour with high brilliance

Table 1: Marked areas (rectangle of 5x5 mm)

Laser speed v [mm/s]	Power P [%]	Evaluation
500	90	1

[0054] Marking lines with a high contrast and a fixed red colour are obtained with the following laser parameter of a Nd:YVO_4 laser (1064 nm) in cw-mode.

Table 2: Marking lines

Laser speed v [mm/s]	Power P [%]	Evaluation
500	90	1

Claims

1. Method for laser marking a document, wherein a document comprising a coating containing at least one sort of effect pigment which shows different colours under different viewing angles and at least one sort of laser sensitive pigment is treated on at least a part of the coated area with a laser beam operated in cw mode at a rate of 500 mm/s using a power of 90 %, calculated based on a laser having a mean power of 12 W, and a laser mark having a fixed colour is obtained, wherein said fixed colour is one of the different colours which are shown under different viewing angles by the effect pigment.

2. Method according to Claim 1, **characterized in that** said effect pigments comprise optically variable pigments.

3. Method according to Claim 1 or 2, **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, 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, or aluminium hydroxide.

4. Method according to Claim 3, wherein said dielectric carrier is selected from the group consisting of natural or synthetic mica, talc, kaolin.

5. Method according to at least one of the preceding claims, **characterized in that** said laser sensitive pigments comprise antimony(III)oxide and/or tin oxide, zinc oxide, tin oxide and/or zircon oxide, iron oxides, copper hydrox-

yphosphate, copper diphosphate, molybdene disulfide, bismute oxychloride, indium tin oxide, $Sn(Sb)O_2$, and/or TiO_2.

6. Method according to at least one of the preceding claims, **characterized in that** the weight ratio of said effect pigments to said laser sensitive pigments is within the range of 4:1 to 1:2.

Patentansprüche

1. Verfahren zur Lasermarkierung eines Dokuments, bei dem ein Dokument, das eine Beschichtung umfasst, die wenigstens eine Art eines Effektpigments, das bei verschiedenen Betrachtungswinkeln verschiedene Farben zeigt, und wenigstens eine Art eines laserempfindlichen Pigments enthält, auf wenigstens einem Teil des beschichteten Bereichs mit einem Laserstrahl behandelt wird, der im CW-Betrieb bei einer Geschwindigkeit von 500 mm/s unter Verwendung einer Leistung von 90%, berechnet auf der Grundlage eines Lasers mit einer mittleren Leistung von 12 W, betrieben wird, und eine Laserkennzeichnung mit einer festen Farbe erhalten wird, wobei die feste Farbe eine der verschiedenen Farben ist, die bei verschiedenen Betrachtungswinkeln von dem Effektpigment gezeigt werden.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Effektpigmente optisch variable Pigmente umfassen.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Effektpigmente ein transparentes oder halbtransparentes, dielektrisches Trägermaterial umfassen, das mit einer Schicht aus wenigstens einem Oxid beschichtet ist, wobei das dielektrische Trägermaterial aus der aus plättchenförmigen Silicaten, Glastafeln, Aluminiumoxidflocken und SiO_2-Plättchen bestehenden Gruppe ausgewählt ist und wobei das Oxid aus der aus SiO_2, Al_2O_3, TiO_2, SnO_2, Fe_2O_3, Fe_3O_4, Chromoxiden, Siliciumhydroxid oder Aluminiumhydroxid bestehenden Gruppe ausgewählt ist.

4. Verfahren nach Anspruch 3, bei dem der dielektrische Träger aus der aus natürlichem oder synthetischem Glimmer, Talk, Kaolin bestehenden Gruppe ausgewählt ist.

5. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die laserempfindlichen Pigmente Antimon(III)-oxid und/oder Zinnoxid, Zinkoxid, Zinnoxid und/oder Zirkonoxid, Eisenoxide, Kupferhydroxyphosphat, Kupferdiphosphat, Molybdändisulfid, Bismutoxychlorid, Indiumzinnoxid, $Sn(Sb)O_2$ und/oder TiO_2 umfassen.

6. Verfahren nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Gewichtsverhältnis der Effektpigmente zu den laserempfindlichen Pigmenten im Bereich von 4:1 bis 1:2 liegt.

Revendications

1. Procédé de marquage d'un document au laser, dans lequel un document qui comporte un revêtement contenant au moins une sorte de pigment à effet qui montre différentes couleurs sous différents angles de vue et au moins une sorte de pigment sensible au laser est traité sur au moins une partie de la zone revêtue avec un faisceau laser fonctionnant en mode CW à une vitesse de 500 mm/s en utilisant une puissance de 90 %, calculée à partir d'un laser d'une puissance moyenne de 12 W, et un marquage au laser présentant une couleur fixe est obtenu, la couleur fixe étant l'une des différentes couleurs montrées par le pigment d'effet sous différents angles de vue.

2. Procédé selon la revendication 1, **caractérisé en ce que** les pigments à effet comprennent des pigments optiquement variables.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** les pigments à effet comprennent une matière support diélectrique transparente ou semi-transparente revêtue d'une couche en au moins un oxyde, la matière support diélectrique étant choisie parmi le groupe constitué de silicates en forme de plaquettes, de plaques de verre, de flocons d'oxyde d'aluminium et de plaquettes de SiO_2, et l'oxyde étant choisi parmi le groupe constitué de SiO_2, de Al_2O_3, de TiO_2, de SnO_2, de Fe_2O_3, de Fe_3O_4, d'oxydes de chrome, d'hydroxyde de silicium ou d'hydroxyde d'aluminium.

4. Procédé selon la revendication 3, dans lequel le support diélectrique est choisi parmi le groupe constitué de mica naturel ou synthétique, de talc, de kaolin.

5. Procédé selon au moins l'une des revendications précédentes, **caractérisé en ce que** les pigments sensibles au laser comprennent de l'oxyde d'antimoine (III) et/ou de l'oxyde d'étain, de l'oxyde de zinc, de l'oxyde d'étain et/ou de l'oxyde de zircon, des oxydes de fer, de l'hydroxyphosphate de cuivre, du diphosphate de cuivre, du bisulfure de molybdène, de l'oxychlorure de bismuth, de l'oxyde d'indium-étain, du $Sn(Sb)O_2$ et/ou du TiO_2.

6. Procédé selon au moins l'une des revendications précédentes, **caractérisé en ce que** le rapport de poids des pigments à effet par rapport aux pigments sensibles au laser est dans la plage entre 4:1 et 1:2.

REFERENCES CITED IN THE DESCRIPTION

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