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

(11) **EP 3 838 609 A1**

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.06.2021 Bulletin 2021/25

(21) Application number: **19216821.9**

(22) Date of filing: **17.12.2019**

(51) Int Cl.:
B41M 5/34 *(2006.01)*
B41M 5/323 *(2006.01)*
B41M 5/333 *(2006.01)*
B41M 5/337 *(2006.01)*
B42D 25/41 *(2014.01)*

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

(71) Applicant: **AGFA NV**
2640 Mortsel (BE)

(72) Inventors:
- **VAN AERT, Hubertus**
  2640 Mortsel (BE)
- **GOETHALS, Fabienne**
  2640 Mortsel (BE)

(74) Representative: **Viaene, Kris**
AGFA NV
Intellectual Property Department
Septestraat 27
2640 Mortsel (BE)

(54) LASER MARKABLE ARTICLES

(57) A laser markable article comprising a first and a second laser markable layer, both layers comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder, characterized in that at least the first laser markable layer is crosslinked.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical field of the Invention

[0001] The present invention relates to laser markable articles and to methods of preparing such laser markable articles.

Background art for the invention

[0002] Security cards are widely used for various applications such as identification purposes (ID cards) and financial transfers (credit cards). Such cards typically consist of a laminated structure consisting of various paper or plastic laminates and layers wherein some of them may carry alphanumeric data and a picture of the card holder. So called 'smart cards' can also store digital information by including an electronic chip in the card body. A principal objective of such security cards, and also of other "security documents", such as banknotes, is that they cannot be easily modified or reproduced in such a way that the modification or reproduction is difficult to distinguish from the original.

[0003] Two techniques frequently used for preparing security documents are laser marking and laser engraving. In laser marking, a colour change is observed by local heating of material, while in laser engraving material is removed by laser ablation.

[0004] Well known in the field of laser markable security documents is the use of laser markable polymeric supports. Laser marking produces a colour change from white to black in a laser markable support through carbonization of the polymer, usually polycarbonate as disclosed in e.g. EP-A 2181858 (AGFA GEVAERT).

[0005] During the past last years, there is an increased interest of using laser markable layers. The advantage of using a laser markable layer coated on a support instead of a laser markable support, is that a support can be used which has better physical properties than the laser markable supports, such as for example a higher flexibility than a polycarbonate support as disclosed in e.g. EP-A 2567825 (AGFA GEVAERT).

[0006] There is also an increased interest in using laser marking to produce colour images, for example a picture of the card holder, in a security document.

[0007] US2005/0001419 (DIGIMARC) discloses a method of forming a full colour image wherein Cyan (C), Magenta (M), Yellow (Y) and Black (B) sub-pixels are printed on a support and covered by an opaque surface layer. Holes are then imagewise engraved in the surface layer, thereby selectively revealing the coloured sub-pixels, which may result in a colour image. The engraving process however results in a deformation of the surface, which is often considered a disadvantage.

[0008] WO2011/124774 (LAZZARI) discloses a method of forming a full colour image wherein Red (R), Green (G), Blue (B), and optionally White (W) sub-pixels, homogenously printed on a security card, are covered by a transparent protection layer. A full colour image is obtained by imagewise laser marking, i.e. carbonisation, of the transparent protection layer. Carbonisation results in dark non-reflecting areas in the protective layer, more or less covering the RGBW sub-pixels. By imagewise covering the RGBW sub-pixels a full colour image may be formed. The RGBW sub-pixels may be provided on the security card by any printing technique. As the non-reflecting areas will not 100% match the sub-pixels they have to cover, colour contamination will be very difficult to avoid.

[0009] In the method disclosed in WO2011/045180 (GEMALTO) printed RGB sub-pixels are covered by two laser sensitive layers, a transparent layer that may be transformed into different gray levels by laser exposure, and an opaque layer that may be transformed into a transparent layer by laser exposure. Imagewise exposing both layers results in some sub-pixels being revealed while others are more or less covered, thereby forming a full colour image. Again, as the non-reflecting areas will not 100% match the sub-pixels they have to cover, colour contamination will be very difficult to avoid.

[0010] US2014/0160220 (U NICA TECHNOLOGY) discloses a method wherein capsules containing a coloured dye or pigment are applied on a substrate and mapped using a spectrophotometer. The capsules are then ruptured upon imagewise exposure with a laser thereby forming a full colour image.

[0011] WO2013/068729 (DATALASE) discloses another method to produce a multicolour image by laser marking wherein both UV radiation and IR radiation are used. A blue and red colour is obtained by exposing a diacetylene containing laser markable layer to UV and IR radiation, while another colour then blue and red, for example yellow, is obtained by exposing another layer comprising a leuco dye to IR radiation. In addition, IR radiation is used to activate the diacetylene containing layer before exposing it to UV radiation.

[0012] EP-A 2648920 (AGFA GEVAERT) disclose laser markable layers that comprise colour leuco-dyes, which can change from essentially colourless or pale-coloured to coloured when exposed to heat.

[0013] The colour laser markable layers may comprise an infrared radition absorbing dye (IR dye) or an infrared radiation absorbing pigment (IR pigment), both absorbing the IR radiation and converting it into heat.

[0014] An advantage of using IR dyes is that the absorption spectrum of an IR dye tends to be narrower than that of an IR pigment. This allows the production of multicoloured articles and security documents from precursors having a plurality of laser markable layers containing different IR dyes and colour foming compounds. The IR dyes having a different maximum absorption wavelength can then be addressed by IR lasers with corresponding emision wavelengths causing colour formation only in the laser markable layer of the adressed IR dye. Such multicolour articles have been disclosed in for example US 4720449 (POLAROID), EP-A 2719540 (AGFA GEVAERT) and EP-A 2719541 (AGFA GEVAERT).

[0015] EP-A 3297838 (AGFA GEVAERT) discloses a colour laser markable article comprising three aqueous colour laser markable layers. The laser markable layers comprise leuco dyes and infrared radiation absorbing dyes (IR dyes), wherein the leuco dyes and the infrared absorbing dyes are encapsulated and wherein the absorption maxima of the IR dyes are situated in the range from 830 to more than 1125 nm. The laser markable layers may comprise a water soluble or water dispersible binder.

[0016] A problem of using multiple laser markable layers, each layer producing a different colour, is colour contamination. Such colour contamination is typically the result of diffusion of ingredients of one laser markable layer to another laser markable layer. Such colour contamination results in an inferior colour gamut that can be obtained.

[0017] There is thus a need to provide a laser markable material wherewith an improved colour gamut may be realized.

Summary of the invention

[0018] It is an object of the present invention to provide a laser markable article capable of forming multiple colours with a superior colour gamut.

[0019] This object has been realised by the laser markable article as defined in claim 1.

[0020] Further objects of the invention will become apparent from the description hereinafter.

Brief description of drawings

[0021]

Figure 1 schematically represents an embodiment of a laser markable article according to the present invention.
Figure 2 schematically represents an embodiment of a laser markable ID card according to the present invention.
Figure 3 schematically represents an embodiment of a laser markable label according to the present invention.

Detailed description of the invention

Definitions

[0022] Unless otherwise specified the term "alkyl" means all variants possible for each number of carbon atoms in the alkyl group i.e. methyl, ethyl, for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethyl-propyl and 2-methyl-butyl, etc.

[0023] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C_1 to C_6-alkyl group.

[0024] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C_2 to C_6-alkenyl group.

[0025] Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C_2 to C_6-alkynyl group.

[0026] Unless otherwise specified a substituted or unsubstituted aralkyl group is preferably a phenyl or naphthyl group including one, two, three or more C_1 to C_6-alkyl groups.

[0027] Unless otherwise specified a substituted or unsubstituted alkaryl group is preferably a C_7 to C_{20}-alkyl group including a phenyl group or naphthyl group.

[0028] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group

[0029] Unless otherwise specified a substituted or unsubstituted heteroaryl group is preferably a five- or six-membered ring substituted by one, two or three oxygen atoms, nitrogen atoms, sulphur atoms, selenium atoms or combinations thereof.

[0030] The term "substituted", in e.g. substituted alkyl group means that the alkyl group may be substituted by other atoms than the atoms normally present in such a group, i.e. carbon and hydrogen. For example, a substituted alkyl group may include a halogen atom or a thiol group. An unsubstituted alkyl group contains only carbon and hydrogen atoms

[0031] Unless otherwise specified a substituted alkyl group, a substituted alkenyl group, a substituted alkynyl group, a substituted aralkyl group, a substituted alkaryl group, a substituted aryl and a substituted heteroaryl group are preferably substituted by one or more constituents selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tertiary-butyl, ester, amide, ether, thioether, ketone, aldehyde, sulfoxide, sulfone, sulfonate ester, sulfonamide, -Cl, -Br, -I, -OH, -SH, -CN and $-NO_2$.

Laser markable article

[0032] The laser markable article according to the present invention comprises a first and a second laser markable layer, both layers comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder, characterized in that at least the first laser markable layer is crosslinked.

[0033] Preferably both laser markable laser markable layers are crosslinked.

[0034] Preferably, the laser markable article further comprises a third laser markable layer, the third laser markable layer also comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder wherein at least the first and the second laser markable layers are cross-linked. More preferably, all laser markable layers are cross-linked.

[0035] The laser markable article may comprise an interlayer comprising a polymeric binder between two laser markable layers wherein the interlayer is also crosslinked.

[0036] Preferably the first, second and third laser markable layers include a leuco dye that is capable of forming, upon laser marking, respectively a Yellow (Y), a Cyan (C), and a Magenta (M) colour.

[0037] The interlayer is preferably applied between the laser markable layer comprising a yellow colour forming leuco dye and another laser markable layer.

[0038] The laser markable layers and optional interlayer are typically provided on a support, as described below. Any order in which the laser markable layers are provided on the support may be used.

[0039] A particularly preferred laser markable article (1) is schematically represented in Figure 1 and comprises, in order,

- a support (100),
- a first laser markable layer (10) including a yellow colour forming leuco dye, a first optothermal converting agent and a developing agent,
- an optional interlayer (40),
- a second laser markable layer (20) including a cyan colour forming leuco dye, a second optothermal converting agent and a developing agent,
- a third laser markable layer (30) including a magenta colour forming leuco dye, a third optothermal converting agent and a developing agent,

wherein at least the first and second laser markable layers and the optional interlayer are crosslinked.

[0040] The manufacturing method of the laser markable article is described below.

Laser markable composition

[0041] The laser markable compositions used to manufacture the laser markable article are aqueous compositions and include a leuco dye, a developing agent, an optothemal converting agent, and a polymeric binder. Those laser markable composition that form a crosslinked layer comprise a polymeric binder capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent.

[0042] The aqueous solution referred to may in addition to water also comprise other solvents such as alcohols or other water miscible solvents.

[0043] The leuco dye and the optothermal converting agent are preferably encapsulated.

[0044] The leuco dye and the optothermal converting agent are preferably encapsulated in separate capsules. This makes it possible to optimize the encapsulation of the leuco dye and the optothermal converting agent independently from each other.

[0045] The laser markable compositions do not include photoinitiators. The crosslinking referred to above is thus not a radiation induced, for example a UV radiation induced, crosslinking.

Polymeric binder

[0046] The laser markable layers and the interlayers include a polymeric binder.

[0047] The polymeric binder is preferably a water-soluble polymer, a water-based dispersion (latex) or a re-dispersible powder.

[0048] The polymeric binder is preferably film forming at the drying temperature of the laser markable layer or the interlayer. The drying temperature is preferably between 15 and 130 °C, more preferably between 20°C and 100°C, most preferably between 40°C and 80°C. A too high drying temperature may result in a deformation of the support.

[0049] The manufacturing method of the laser markable article, described in more detail below, includes a step wherein a first aqueous laser markable composition including the polymeric binder is applied on a support thereby forming a first laser markable layer. The coating step is then followed by a drying step wherein all solvents of the first laser markable layer are substantially removed. A second aqueous laser markable composition, or an interlayer, is then applied on the dried first laser markable layer thereby forming a second laser markable layer. This means that the first laser markable layer is wetted again when the second aqueous laser markable composition is applied. However, when the first laser markable layer is crosslinked, it will not substantially solubilize or re-disperse due to the wetting. This will then result in less diffusion of the ingredients of the first laser markable layer into the other layers and may thus result in less colour contamination.

[0050] The water-soluble polymer has preferably a solubility in water of preferably 5% or more at a temperature at which the emulsification is carried out.

[0051] A water-soluble binder is preferably based on polymeric binders having a hydroxyl group such as polyvinyl alcohol, polysaccharides or cellulose. Polyvinyl alcohol co-polymers that can be used are co-polymers of vinylalcohol with the following monomer units:

> vinylacetate, versatic esters of vinylalcohol, ethylene (e.g. Exceval AQ grades available from Kuraray), vinyl trimethoxy silane (e.g. Poval R grades available from Kuraray), 3-oxo-butyric acid vinylester (e.g. Gohsenx Z grades available from Nippon Gohsei),
> acetoacetoxy ethyl methacrylate (e.g. Poval DF grades available from Shin Etsu), 3-butene-1,2-diol (Nichigo G Polymer form Nippon Gohsei), methyl methacrylate (Elvanol from Kuraray) or a polyethylene glycol based monomer (e.g. Gohsenx WO series from Nippon Gohsei). Particular preferred polymeric binders are vinylalcohol co-polymers with a low degree of hydrolysis, which may result in less layer intermixing at low levels of crosslinking, such as Gohsefime LL02 from Nippon Gohsei.

[0052] Other water-soluble hydroxyl functional binders are polyglycerol or polyglycidol. Suitable cellulose grades are hydroxyl ethyl cellulose, hydroxypropyl cellulose, hydroxyethylmethyl cellulose, hydroxypropyl methyl cellulose, hydroxybutylmethyl cellulose, methyl cellulose, carboxymethyl cellulose.

[0053] Other suitable water soluble binders are gelatin, carrageenan, dextran, gum arabic, casein, pectin, albumin, starch, collagen derivatives, collodion and agar-agar.

[0054] Besides hydroxyl functional water-soluble binders, also amino, carboxylic, vinylpyrolidone functional polymers may be used. Examples of amino functional polymers are polyvinylamine co-polymers, polyallyl amine co-polymers, polyethylene imine based polymers and polypropylene imine based polymers. Carboxylic functional polymers which can be used may contain the following monomers: acrylic acid, maleic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid. Vinyl pyrolidone based polymers may be homopolymers or co-polymers with vinyl acetate, vinylcaprolactam, hydroxyethyl methacrylate and dimethylamino ethyl methacrylate.

[0055] The water-soluble polymer or co-polymer may contain water-insoluble monomers or segments, but the content of such water-insoluble monomers or segments is less than 40 wt%, relative to the total weight of the polymer or co-polymer. For ethylene-vinyl alcohol co-polymers, the ethylene content is preferably less than 25 wt%, relative to the total weight of the co-polymer.

[0056] Among these water-soluble polymers, polyvinyl alcohol polymers or co-polymers are preferred.

[0057] Another preferred polymeric binder is a water-based polymer where the polymer is predominantly water-insoluble and present as a water-based dispersion having a particle size between 10 nm and 2000 nm (also referred to as a latex). Such polymeric binder dispersion preferably comprise a (co)-polymer including at least 40 wt%, more preferably at least 50 wt%, most preferably at least 60 wt% of water insoluble or non-dispersible monomers relative to the total weight of the (co)-polymer.

[0058] Preferred latexes or dispersions include vinylacetate (VA) latexes, polyurethane (PU) latexes and acrylic latexes. PU latexes may be non-ionic or anionic.

[0059] Preferred vinylacetate latexes are ethylene-vinylacetate (EVA) latexes.

[0060] Preferred EVA latexes are ethylene-vinylacetate co-polymers including 65 - 95 wt% ethylene units, relative to the total weight of the copolymer.

[0061] Examples of such EVA latexes are Vinavil EVA® 04, Vinavil EVA® 204 and Vinavil EVA® 2609L, all from VINAVIL.

[0062] Examples of non-ionic PU latexes are Esacote® PU 5913 from LAMBERTI, Takelac™ W6355, Takelac™XWUM3 and Takelac™XWUM2, all from MITSUI.

[0063] Examples of anionic PU latexes are Takelac™WS5100 from MITSUI and Esajet® PU 13 from LAMBERTI.

[0064] Examples of acrylic latexes are Mowinyl® 7820 and Mowinyl® RA053B8, all from Japan Coating Resin Corporation.

[0065] Other preferred water-based polymer dispersions are aqueous dispersions of polyvinylbutyral such as S Lec KW1 and S Lec KW3 available from Sekisui. Also water-based dispersion based on vinyl alcohol and vinyl acetate are in particular suitable such as Alcotex 552P and Alcotex WD30 from the company Synthomer. Nippon Gohsei (now

Mitsubishi Chemical) also provides suitable water-based dispersions based on vinyl acetate, vinylalcohol and polyethylene glycol based monomer, e.g. Gohsenx LW series having also a low degree of hydrolysis of 35-55 mol%.

[0066] Besides polymer dispersions also re-dispersible polymer powders may be used such as polymer powders based on vinylacetate and ethylene (VAE). The company Wacker is a leading supplier in this area. Polymer powders based on VAE are marketed under the trade names Vinnapas®, Vinnacel® and Etonis®. Terpolymers based on VAE and VEOVA are marketed under the trademark Vinnapas®. VEOVA and vinyl laurate monomers are marketed under the name Versa®. Co- and terpolymer powders based on vinyl chloride are marketed under the tradename Vinnapas®.

[0067] Acylic based re-dispersible powders such as for example from the Australian company Acquos with tradename dehydro™ may also be used. Re-dispersable polymer powders can also contain carboxylic monomers such as acrylic acid, crotonic acid, maleic acid, e.g. as described in the patent application EP-A 601518 by Air Products and Chemicals Inc. An example of a suitable co-polymer of vinyl acetate and crotonic acid is Synthomer MCT5 available from Synthomer in the United Kingdom.

[0068] The amount of the polymeric binder in the laser markable layers and the interlayers is preferably between 0.25 and 8 g/m^2, more preferably between 0.5 and 6 g/m^2, most preferably between 1 and 4 g/m^2.

Crosslinking agent

[0069] The laser markable composition may comprise a crosslinking agent that is capable of crosslinking the polymeric binder.

[0070] The crosslinking reaction preferably takes place at a temperature between the coating temperature and the drying temperature.

[0071] To prevent crosslinking before coating the laser markable composition, the crosslinking agent may be added to the composition just before coating.

[0072] Crosslinking of the polymeric binder results in less diffusion of ingredients from one laser markable layer to another and may result in less colour contamination.

[0073] Isocyanate based crosslinking agents are preferably used in combination with polymeric binders including hydroxyl or amine functional groups. Examples of isocyanate based crosslinking agents are Burnock® DNW-5500, Burnock® PU 8980, Burnock® PU 8985, Burnock® L-PU 8983, Burnock® L-PU 8984 all available from DIC; Bayhydur® XP 2700, Bayhydur® XP 2547, Bayhydur® XP 2858, Bayhydur® 2759, Bayhydur® 2547, Bayhydur® 2840, Bayhydur® eco 7190 and Bayhudur® 3100 all available from Covestro; Takenate™ WD-726 availabe from Mitsui; Easaqua™ X L 600 and Easaqua™ X D 401 all available from Perstorp; Duranate™ WB40-100 and Duranate™ TLA-100 all available from Asahi Kasei.

[0074] Silanes are preferably used in combination with polymeric binders including hydroxyl functional groups. Examples of silanes are Dynasylan® M, Dynasylan® A, Dynasylan® HYDROSIL 2926, Dynasilan® SIVO 160, Dynasilan® GLYMO, Dynasilan® BTSE all available from Evonik.

[0075] Epoxy resins are also preferably used in combination with polymeric binders including hydroxyl functional groups. Examples of epoxy resins that may be used are EPI-REZ™ resins available from Momentive and Aradur® resins available from Huntsman.

[0076] Oxazoline based crosslinking agents are preferably used in combination with polymeric binders including carboxylic acid groups. Examples of oxazoline based crosslinking agents are Epocros® WS-300, Epocros® WS-500, Epocros® WS-700, Epocros® K-2010E, Epocros® K-2020E and Epocros® K-2030E all available from Nippon Shokubai.

[0077] Carbodiimide based crosslinking agents are preferably used in combination with polymer binders including carboxylic acid groups. Examples of carbodiimide based crosslinking agents are Carbodilite® V-02, Carbodilite® V-02-L2, Carbodilite® SV-02, Carbodilite® E-02 and Carbodilite® E-03A all available from Nisshinbo Industries.

[0078] As an alternative, a crosslinkable polymeric binder may also be used.

[0079] Also inorganic crosslinkers can be used based on compounds comprising the elements Al, Ti, Si, B, Zn, Cr. In particular Al containing crosslinkers can be used such as Bacote 20, Zirmel 1000 and Protec ZZA available from MEL Chemicals

[0080] As an alternative, a crosslinkable polymeric binder may also be used, such as copolymers with diacetone acryl amide, acetoacetoxy ethyl methacrylate or vinyltrimethoxy silane.

Leuco dye

[0081] A leuco dye is a substantially colourless compound, which may form a coloured dye upon an inter- or intra-molecular reaction. The inter- or intra-molecular reaction may be triggered by heat, preferably heat formed during exposure with an IR laser.

[0082] Examples of leuco dyes are disclosed in WO2015/165854 (AGFA GEVAERT), paragraph [069] to [093]. Preferred leuco dyes are fluoran and phthalide leuco dyes.

[0083] The laser markable layer may comprise more than one leuco dye. Using two, three or more leuco dyes may be necessary to realize a particular colour or to achieve a better solubility of the leuco dyes.

[0084] The amount of leuco dye in the laser markable layer is preferably in the range from 0.05 to 2 g/m^2, more preferably in the range from 0.1 to 1 g/m^2.

Developing agent

[0085] A developing agent is capable of reacting with a colourless leuco dye resulting in the formation of a coloured dye.

[0086] The developing agent is preferably a water soluble or water dispersible developing agent.

[0087] Various electron accepting substances may be used as developing agent in the present invention. Examples thereof include phenolic compounds, organic or inorganic acidic compounds and esters or salts thereof.

[0088] Examples of developing agents that may be used are disclosed in WO2014/124052 (FUJIFILM HUNT CHEMICALS), paragraph [0069] to [0073].

[0089] Preferred developing agents are metal salts of a carboxylic acid, as dislosed in WO2006/067073 (DATALASE), page 3, line 4 to page 5, line 31.

[0090] A preferred colour developing agent is a metal salt of salicylic acid, for example zinc salicylate. A particularly preferred colour developing agent is zinc 3,5-bis(a-methylbenzyl) salicylate.

[0091] A developing agent precursor, i.e. a compound, which is capable of releasing a developing agent upon exposure to heat or IR radiation, may also be used. An advantage of such a developing agent precursor may be a better stability towards the environment.

[0092] Preferred developing agent precursors are disclosed in WO2016/184881 (AGFA GEVAERT), paragraph [086] to [0123].

[0093] The amount of developing agent or development agent precursor in the laser markable layer is preferably in the range from 0.05 to 5 g/m^2, more preferably in the range from 0.1 to 3 g/m^2.

Optothermal converting agent

[0094] An optothermal converting agent generates heat upon absorption of radiation.

[0095] The optothermal converting agent preferably generates heat upon absorption of infrared (IR) radiation, more preferably near infrared (NIR) radiation.

[0096] Near infrared radiation has a wavelength between 750 and 2500 nm.

[0097] The optothermal converting agents may be an infrared radiation absorbing pigment but is preferably an infrared radiation absorbing dye.

[0098] An advantage of Infrared radiation absorbing dyes (IR dyes) compared to IR pigments is their narrow absorption spectrum resulting in less absorption in the visible region and thus resulting in less background colouration.

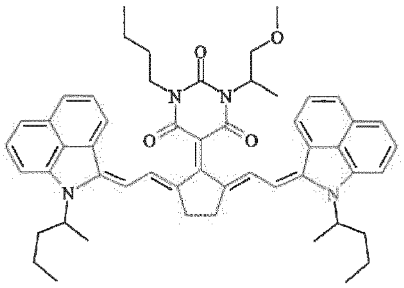
[0099] A narrow absorption spectrum is also advantageous for multicolour laser marking using multiple laser each having a different emission wavelength, as disclosed in for example EP-A 3297838 (AGFA GEVAERT). A narrow absorption spectrum of the IR dyes enables a selective addressability of the different IR dyes.

[0100] Any IR dye may be used, for example the IR dyes disclosed in "Near-Infrared Dyes for High Technology Applications" (ISBN 978-0-7923-5101-6).

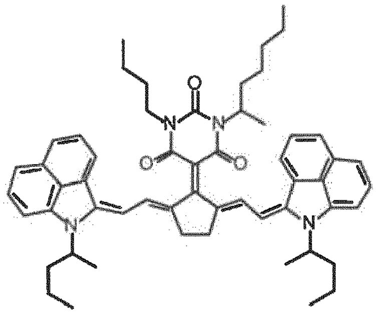
[0101] Preferred IR dyes are polymethine dyes due to their low absorption in the visible region and their selectivity, i.e. narrow absorption peak in the infrared region. Particular preferred polymethine IR dyes are cyanine IR dyes.

[0102] Preferred IR dyes having an absorption maximum of more than 1100 nm are those disclosed in EP-A 2722367 (AGFA GEVAERT), paragraphs [0044] to [0083] and WO2015/165854 (AGFA GEVAERT), paragraphs [0040] to [0051].

[0103] IR dyes having an absorption maximum between 1000 nm and 1100 nm are preferably selected from the group consisting of quinoline dyes, indolenine dyes, especially a benzo[cd]indoline dye. A particularly preferred IR dye is 5-[2,5-bis[2-[1-(1-methylbutyl)-benz[cd]indol-2(1H)-ylidene]ethylidene]-cyclopentylidene]-1-butyl-3-(2-methoxy-1-methylethyl)- 2,4,6(1H,3H,5H)-pyrimidinetrione (CASRN 223717-84-8) represented by the Formula IR-A, or the IR dye represented by Formula IR-B:



IR-A

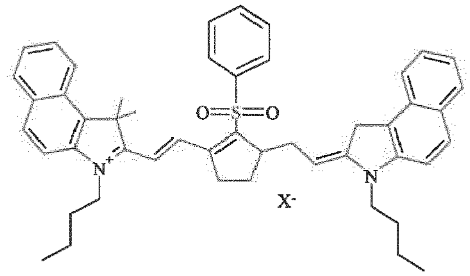
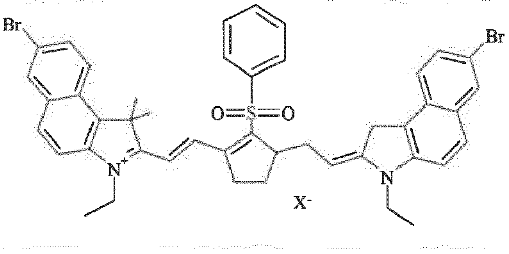
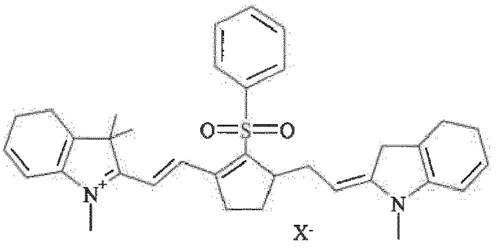
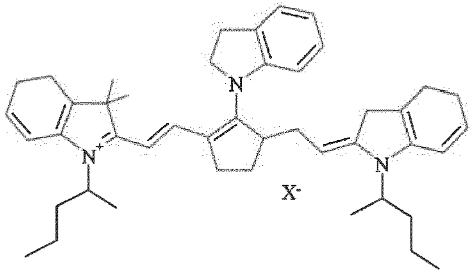


IR-B

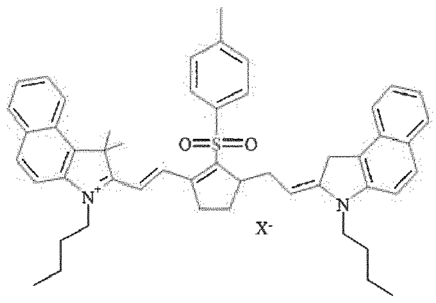
[0104] Both IR dyes have an absorption maximum λ_{max} around 1052 nm making them very suitable for a Nd-YAG laser having an emission wavelength of 1064 nm.

[0105] Preferred IR dyes having an absorption maximum between 850 nm and 1000 nm are listed in Table 1.

Table 1

STRUCTURES	IR Absorbers
	IR-C
	IR-D
	IR-E
	IR-F

(continued)

STRUCTURES	IR Absorbers
	IR-G

[0106] The laser markable layers each comprise an IR dye having an absorption maximum in the infrared region λ_{max} that differs preferably by at least 60 nm, more preferably by at least 80 nm, most preferably by at least 100 nm from each other.

[0107] When a first laser markable layer includes a first infrared dye IR-1 having an absorption maximum in the infrared region λ_{max}(IR-1), a second laser markable layer containing a second infrared dye IR-2 having an absorption maximum in the infrared region λ_{max}(IR-2), and a third laser markable layer containing a third infrared dye IR-3 having an absorption maximum in the infrared region λ_{max}(IR-3), the following conditions a) and b) are preferably fulfilled:

a)

$$\lambda_{max}(IR\text{-}1) > \lambda_{max}(IR\text{-}2) > \lambda_{max}(IR\text{-}3)\ ;$$

and

b)

$$\lambda_{max}(IR\text{-}1) > 1100\ nm\ and\ \lambda_{max}(IR\text{-}3) < 1000\ nm.$$

[0108] In a preferred colour laser markable article the condition c) is also fulfilled:
c) λ_{max}(IR-2) differs by at least 60 nm, more preferably by at least 80 nm, most preferably by at least 100 nm from λ_{max}(IR-1) and λ_{max}(IR-3).

[0109] In another preferred colour laser markable article, λ_{max}(IR-3) ≥ 830 nm and λ_{max}(IR-1) ≥ 1125 nm.

[0110] The amount of optothermal converting agent in the laser markable layer is preferably at least 10^{-10} g/m^2, more preferably between 0.0001 and 0.5 g/m^2, most preferably between 0.0005 and 0.1 g/m^2.

Acid Scavenger

[0111] The laser markable layer or the interlayer of the laser markable article may contain one or more acid scavengers.

[0112] Acid scavengers include organic or inorganic bases. Examples of the inorganic bases include hydroxides of alkali metals or alkaline earth metals; secondary or tertiary phosphates, borates, carbonates; quinolinates and metaborates of alkali metals or alkaline earth metals; a combination of zinc hydroxide or zinc oxide and a chelating agent (e.g., sodium picolinate); hydrotalcite such as Hycite 713 from Clariant; ammonium hydroxide; hydroxides of quaternary alkylammoniums; and hydroxides of other metals. Examples of the organic bases include aliphatic amines (e.g., trialkylamines, hydroxylamines and aliphatic polyamines); aromatic amines (e.g., N-alkyl-substituted aromatic amines, N-hydroxylalkyl-substituted aromatic amines and bis[p-(dialkylamino)phenyl]-methanes), heterocyclic amines, amidines, cyclic amidines, guanidines and cyclic guanidines.

[0113] Other preferred acid scavangers are HALS compounds. Example of suitable HALS include Tinuvin™ 292, Tinuvin™ 123, Tinuvin™ 1198, Tinuvin™ 1198 L, Tinuvin™ 144, Tinuvin™ 152, Tinuvin™ 292, Tinuvin™ 292 HP, Tinuvin™ 5100, Tinuvin™ 622 SF, Tinuvin™ 770 DF, Chimassorb™ 2020 FDL, Chimassorb™ 944 LD from BASF; Hostavin 3051, Hostavin 3050, Hostavin N 30, Hostavin N321, Hostavin N 845 PP, Hostavin PR 31 from Clariant.

[0114] Further examples of acid scavengers are salts of weak organic acids such as carboxylates (e.g. calcium stearate).

[0115] A preferred acid scavenger is an organic base, more preferably an amine.

[0116] A particular preferred acid scavenger is an organic base having a pKb of less than 7.

UV absorbers

[0117] The laser markable article may also comprise an UV-absorber. The UV-absorber may be present in a laser markable layer or may also be present in another layer, for example a top layer or an intermediate layer.

[0118] Examples of suitable UV-absorbers include 2-hydroxyphenyl-benzophenones (BP) such as Chimassorb™ 81 and Chimassorb™ 90 from BASF; 2-(2-hydroxyphenyl)-benzotriazoles (BTZ) such as Tinuvin™ 109, Tinuvin™ 1130, Tinuvin™ 171, Tinuvin™ 326, Tinuvin™ 328, Tinuvin™ 384-2, Tinuvin™ 99-2, Tinuvin™ 900, Tinuvin™ 928, Tinuvin™ Carboprotect™· Tinuvin™ 360, Tinuvin™ 1130, Tinuvin™ 327, Tinuvin™ 350, Tinuvin™ 234 from BASF, Mixxim™ BB/100 from FAIRMOUNT, Chiguard 5530 from Chitec; 2-hydroxy-phenyl-s-triazines (HPT) such as Tinuvin™ 460, Tinuvin™ 400, Tinuvin™ 405, Tinuvin™ 477, Tinuvin™ 479, Tinuvin™ 1577 ED, Tinuvin™ 1600 from BASF, 2-(2,4-dihydroxyphenyl)-4,6-bis-(2,4-dimethylphenyl)-s-triazine (CASRN1668-53-7) from Capot Chemical Ltd and 4-[4,6-bis(2-methyl-phenoxy)-1,3,5-triazin-2-yl]-1,3-benzenediol (CASRN13413-61-1); titanium dioxide such as Solasorb 100F from from Croda Chemicals; zink oxide such as Solasorb 200F from Croda Chemicals; benzoxazines such as Cyasorb UV-3638 F, CYASORB™ UV-1164 from CYTEC; and oxamides such as Sanduvor VSU from Clariant.

[0119] Preferred UV absorbers have in the wavelength region between 300 and 400 nm a maximum absorption above 330 nm, more preferably above 350 nm.

[0120] Particular preferred UV absorbers are hydroxyphenyl benzotriazoles and 2-hydroxyphenyl-s-triazines having a maximum absorption above 350 nm in the wavelength region 300-400 nm.

Interlayer

[0121] The interlayer is prepared from an aqueous coating solution. The coating solution includes a polymeric binder capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent that is capable of crosslinking the polymeric binder.

[0122] The interlayer preferably contains an acid scavenger as described above to prevent diffusion of an acid from one laser markable layer to another.

[0123] The interlayer preferably also contains a UV absorber as described above to improve the daylight stability of the laser markable materials.

Capsules

[0124] Leuco dyes and IR dyes are preferably encapsulated.

[0125] The particle size of the capsules is preferably between 50 and 2000 nm, more preferably between 100 and 1000 nm, most preferably between 250 and 750 nm.

[0126] The capsules may also be referred to as microcapsules or nanocapsules.

[0127] Many methods are known to prepare microcapsules, such as described in "Microspheres, microcapsules & liposomes", volume 1; preparation & chemical applications, volume 2; medical & biotechnological applications, edited by Reza Arshady (ISBN 0953218716).

[0128] Common methods for making microcapsules include spray-drying, solvent evaporation, mini-emulsion, or interfacial polymerization.

[0129] To guarantee the formation of a core-shell material, interfacial polymerization is preferably used to form capsules including the leuco dyes and/or IR dyes. With this technique, a capsule shell is formed at the oil/water interface. By growing a polymer around the encapsulant, a higher encapsulation efficiency may be obtained.

[0130] An overview of interfacial polymerization techniques is disclosed in Salaön, F. (2013) "Microencapsulation by Interfacial Polymerization", in Encapsulation Nanotechnologies (ed V. Mittal), John Wiley & Sons, Inc., Hoboken, NJ, USA.

[0131] In general, interfacial polymerization requires the dispersion of an oleophilic phase in an aqueous continuous phase or vice versa. Each of the phases contains at least one dissolved monomer (a first shell component) that is capable of reacting with another monomer (a second shell component) dissolved in the other phase. Upon polymerization, a polymer is formed that is insoluble in both the aqueous and the oleophilic phase. As a result, the formed polymer has a tendency to precipitate at the interface of the oleophilic and aqueous phase, thereby forming a shell around the dispersed phase, which grows upon further polymerization.

[0132] The capsules according to the present invention are preferably prepared from an oleophilic dispersion in an aqueous continuous phase.

[0133] A first shell component used to prepare the capsules is preferably a polyisocyanate compound as described below. The second shell component is a compound containing a reactive hydrogen.

[0134] The capsules according to the present invention are thus preferably prepared by interfacial polymerization of a polyisocyanate as described below and a compound containing a reactive hydrogen.

[0135] The polyisocyanate is preferably added to the oleophilic phase while the compound containing a reactive hydrogen is added to the aqueous phase.

[0136] The type of compound containing a reactive hydrogen determines the type of polymer formed at the interphase. Preferred compounds containing a reactive hydrogen are selected from multifunctional amines, hydrazides, alcohols, thiols, water, etc.

[0137] Preferred polymeric shells formed by interfacial polymerization are selected from the group consisting of polyurea, prepared from polyisocyanates as a first shell component and polyamines as a second shell component; polyurethanes, prepared from polyisocyanates as a first shell component and polyalcohols, also referred to as polyols, as a second shell component; and polysemicarbazides, prepared from polyisocyanates as a first shell component and polyhydrazides as a second shell component.

[0138] The shell can also be composed of combinations of these polymers.

[0139] A catalyst may be used to accelerate the interfacial polymerization. Well known catalysts are Sn based catalysts, such as dibutyl tin dilaurate or dioctyl tin laurate, Zn or Bi based catalysts, such as disclosed in EP-A 2824713 (AGFA GEVAERT).

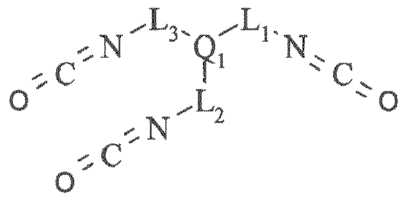
Polyisocyanates

[0140] Polyisocyanate compounds that may be used in the preparation of the capsules are disclosed in WO2013/109268 (FUJIFILM HUNT CHEMICALS), US6127314 (FUJI PHOTO FILM) and WO2014/124052 (FUJIFILM HUNT CHEMICALS).

[0141] Preferred polyisocyanate to prepare the capsules comprises at least 1 substituted or unsubstituted arylene or heteroarylene group. Preferably, the polyisocyanate comprises 1 to 3 substituted or unsubstituted arylene or heteroarylene groups.

[0142] The polyisocyanate preferably has a Molecular Weight (Mw) of 1500 or less, more preferably of 1000 or less, most preferably of 750 or less.

[0143] The polyisocyanate used to prepare the capsules is preferably a compound having a chemical structure according to Formula I, or a derivative thereof,



Formula I

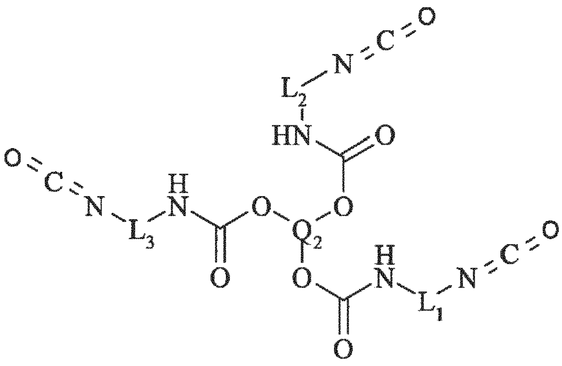
wherein

Q_1 represents an organic moiety,
L1, L2 and L3 are linking groups comprising a substituted or unsubstituted arylene or heteroarylene group.

[0144] Q_1 preferably represents an organic moiety comprising 0 to 25 atoms, more preferably comprising 1 to 15 atoms.

[0145] More preferred, Q1 represents an organic moiety comprising 0 to 8 C atoms, more preferably 1 to 5 C atoms.

[0146] In a more preferred embodiment the polyisocyanate is a compound having a chemical formula according to Formula II, or a derivative thereof,



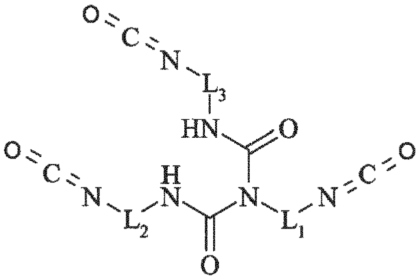
Formula II

wherein

Q2 represents an organic moiety, preferably comprising 0 to 8 C atoms, more preferably comprising 1 to 5 C atoms. L1, L2 and L3 have the same meaning as in Formula I.

[0147] Preferred compounds according to Formula II are trimethylolpropane - toluene-diisocyanate adducts (for example Desmodur IL commercially available from Bayer) or trimethylolpropane - xylylenediisocyanate adducts (for example Takenate D110N commercially available from Mitsui).

[0148] In another preferred embodiment the polyisocyanate is a compound having a chemical structure according to Formula III, or a derivative thereof,



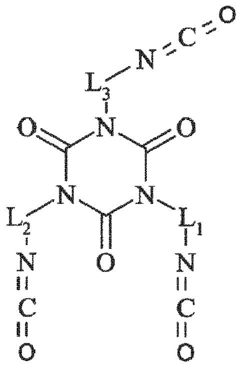
Formula III

wherein

L1, L2 and L3 have the same meaning as in Formula I.

[0149] In a particular preferred embodiment, the organic moiety Q_1 and Q_2 in Formula I and II represents a cyclic group.

[0150] In a particular preferred embodiment the polyisocyanate is a compound having a chemical structure according to Formula IV, or a derivative thereof,

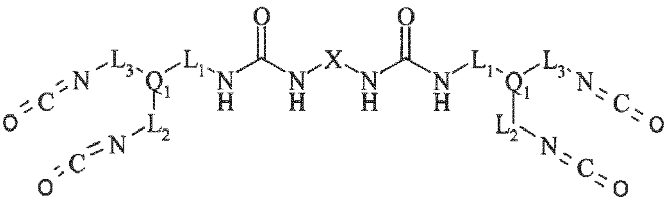


Formula IV

wherein
L1, L2 and L3 have the same meaning as in Formula I.

[0151] A derivative referred above may be an oligomer of the compound according to Formula I, II, III or IV. Such an oligomer may be formed for example by reacting an excess amount of the compound according to Formula I, II, III or IV with an amine.

[0152] For example, reacting an excess of compound according to Formula I with an amine having a formula H_2N-X-NH_2 results, amongst others, in an oligomer according to the following Formula,



[0153] An example of a polyisocyanate according to Formula IV is an isocyanurate derivative of toluene diisocyanate (commercially available from Bayer under the tradename Desmodur IL).

[0154] A particularly preferred polyisocyanate according to Formula IV is an isocyanurate derivative of xylylenediisocyanate.

[0155] The isocyanurate derivative of xylylenediisocyanate is a trimer of xylylenediisocyanate and is produced by subjecting xylylenediisocyanate to an isocyanurate-forming reaction in the presence of an isocyanurate-forming catalyst.

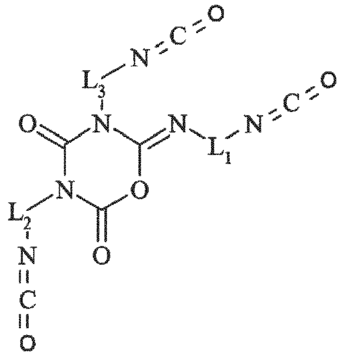
[0156] Xylylenediisocyanate includes the structural isomers 1,2-xylylenediisocyanate, 1,3-xylylenediisocyanate and 1,4-xylylenediisocyanate.

[0157] These xylylenediisocyanates may be used singly or in combination of two or more.

[0158] 1,3-xylylenediisocyanate and 1,4-xylylenediisocyanate are preferably used, more preferably 1,3-xylylenediisocyanate is used.

[0159] Isocyanurate derivatives of xylylenediisocyanates and their preparation methods are disclosed in EP-A 3115386 (MITSUI CHEMICALS), paragraphs [0015] - [0090] and EP-A 3115430 (MITSUI CHEMICALS), paragraphs [0019]-[0044]).

[0160] In another preferred embodiment of a polyisocyanate according to Formula I or II wherein the organic moiety represents a cyclic group has a chemical structure according to Formula V,



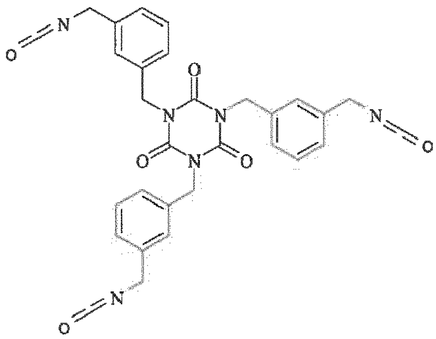
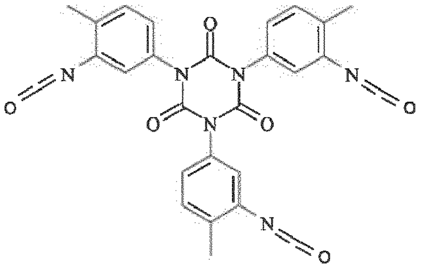
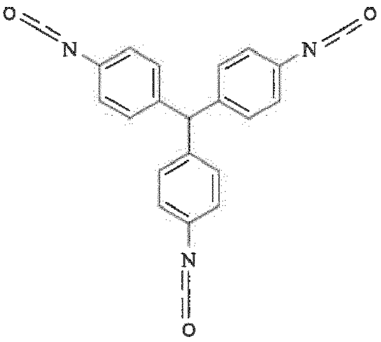
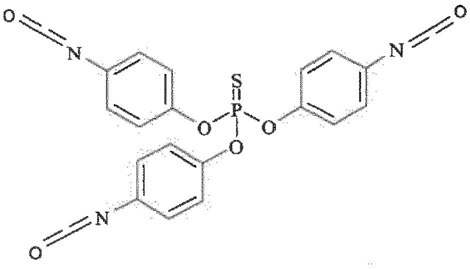
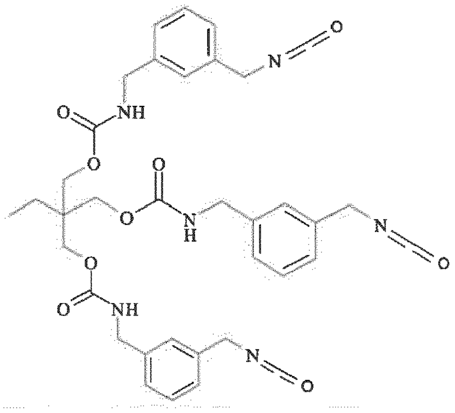
Formula V

wherein
L1, L2 and L3 have the same meaning as in Formula I.

[0161] The arylene group referred to is preferably a phenylene group.

[0162] Examples of preferred polyisocyanate compounds are shown in Table 2.

Table 2

	Polyiso-01
	Polyiso-02
	Polyiso-03
	Polyiso-04
	Polyiso-05

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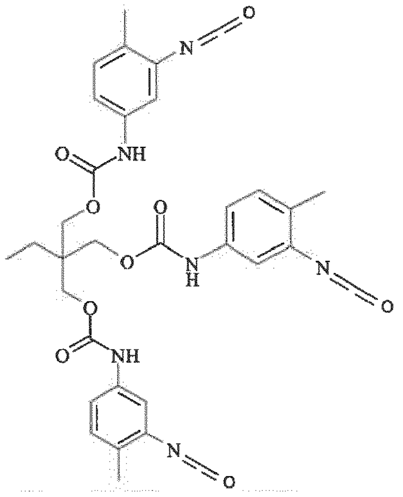
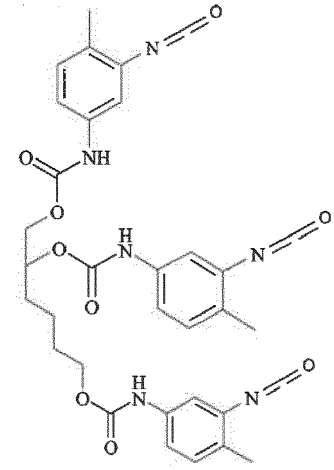
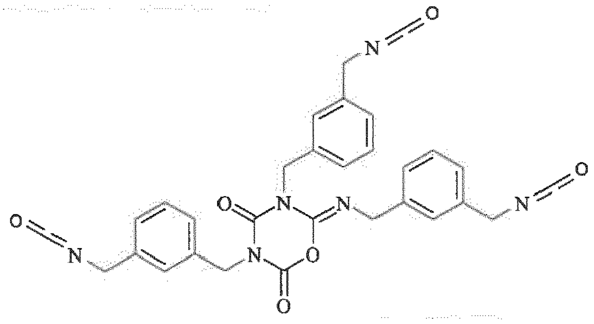
	Polyiso-05
	Polyiso-06
	Polyiso-07

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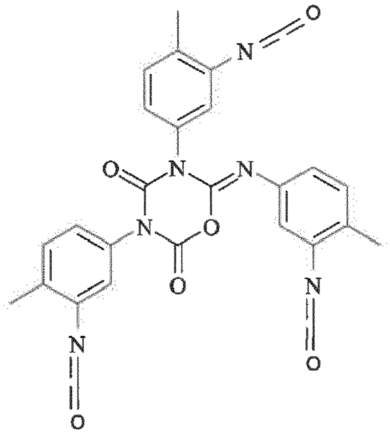
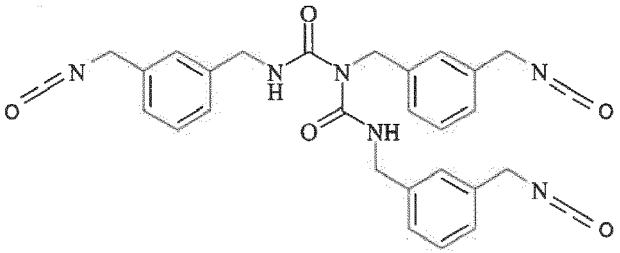
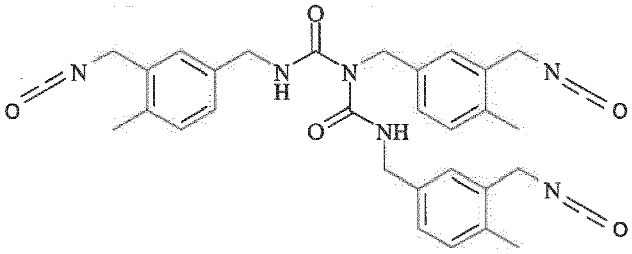
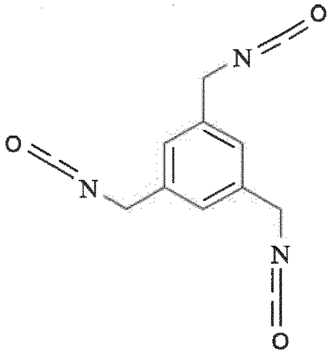
	Polyiso-08
	Polyiso-09
	Polyiso-10
	Polyiso-11

Polyamines

[0163] A polyurea shell is the result of an interfacial polymerization between a polyisocyanate compound and a polyamine.

[0164] The polyamine may be selected from a diamine, a triamine, a tetraamine, a pentamine, a hexamine or from polymeric or oligomeric polyamines such as polyallyl amine, polyvinyl amine, copolymers of vinylamine and vinylformamide or polyethylene imine.

[0165] Examples of polyamines that may be used are 1,2-diamino-propane, 1,3-diamino-propane, 1,2-diaminoethane, 1,4-diaminobutane, diphenylethylene diamine, diaminocylcohexane, diethylenetriamine, phenylenediamine, benzidine, 2,5-diamino-toluene, o-phenylene diamine, m-phenylene diamine, p-phenylene diamine, bis-(6-aminohexyl)amine, Jeffamines® D, ED and T series (polyetheramines from Huntsman), melamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexamethylenediamine, piperazine or a derivative thereof, 2,2'-(ethylene-dioxy)bis (ethylamine), guanidine salts and guanidine, tris-(2-aminoethyl)amine, N, N'-bis (3-aminopropyl)-ethylenediamine and N, N, N', N'-tetrakis(3-aminopropyl)-1, 4-butanediamine.

[0166] A particularly preferred polyamine is tetraethylenepentamine.

[0167] The amount of polyamine used is typically adjusted so that, for each mole of an isocyanate group, there are 0.1 to 3 moles, more preferably 0.5 to 2, most preferably 0.75 to 1.5 moles of amine groups.

[0168] In addition to the polyamines described above, monoamines may be used in the interfacial polymerization.

Polyols

[0169] A polyurethane shell is the result of an interfacial polymerization between a polyisocyanate compound and a polyol.

[0170] The polyols may be selected from propylene glycol, glycerol, trimethylolpropane, triethanolamine, ethyleneglycol, diethyleneglycol, triethyleneglycol, tetraethylene-glycol, dipropyleneglycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6- hexanediol, ethanolamine, pentaerythritol, sorbitol, polyvinylalcohol or (water)soluble polymeric or oligomeric polyols such as poly(glycerol), polyethylene glycol, cellulose derivatives or polysaccharides.

[0171] In addition to the polyols described above, monoalcohols may be used in the interfacial polymerization.

Preparation of the capsules

[0172] A preferred method for preparing a dispersion of capsules includes the following steps:

a) preparing a non-aqueous solution of a polyisocyanate described above and optionally a water immiscible organic solvent having a lower boiling point than water;

b) dispersing the non-aqueous solution under high shear in an aqueous solution;

c) optionally stripping the water immiscible organic solvent from the mixture of the aqueous solution and the non-aqueous solution;

d) adding a compound having an active hydrogen described above to the aqueous solution, and

e) preparing the polymeric shell by interfacial polymerization of the polyisocyanate and the compound having an active hydrogen.

[0173] The compound having an active hydrogen may already be added to the aqueous solution used in step b) or may be water itself.

[0174] In a preferred embodiment, a water immiscible solvent is used in the dispersion step, which is removed by solvent stripping before or after the shell formation. In a particularly preferred embodiment, the water immiscible solvent has a boiling point below 100°C at normal pressure. Examples of water immiscible solvents are propyl acetate, isopropyl acetate, ethyl acetate, acetone, methyl ethyl ketone, dichloroethane, methyl isobutyl ketone, isopropanol, isobutanol, toluene, xylene, and dichloromethane. Preferred solvents include propyl acetate, isopropyl acetate, ethyl acetate, methyl ethyl ketone, dichloroethane and dichloromethane.

[0175] A water immiscible solvent is an organic solvent having low miscibility in water. Low miscibility is defined as any water solvent combination forming a two phase system at 20°C when mixed in a one over one volume ratio.

[0176] Preferably, the amount of the compound having an active hydrogen and of the polyisocyanate results in a ratio of active hydrogen to isocyanate groups of 1 to 1.

[0177] The encapsulant is preferably added in step a) to the non-aqueous solution.

[0178] For preparing a laser markable composition, a leuco dye or an IR dye is added in step (a) to the non-aqueous solution resulting in capsules wherein the leuco dye or the IR dye is located in the core of the capsule.

[0179] For encapsulating the leuco dyes, the polymerization in step e) is preferably carried out at elevated temperatures, preferably at temperature above 50°C, more preferably at a temperature above 75°C, most preferably at a temperature above 85°C, particular preferred at a temperature above 90°C. It has been observed that the heat resistance increases when the polymerization is carried out higher temperatures. An improved heat resistance may result in less colour contamination upon laminating the laser markable article at high temperatures.

[0180] For encapsulating the IR dyes, it is preferred to carry out the polymerization in step e) at moderate temperatures, for example room temperature. Polymerization at higher temperatures may result in a decomposition of the IR dyes, resulting in unwanted background coloration or decreased laser marking sensitivity.

[0181] The aqueous solution preferably comprises a water-soluble polymer as a protective colloid. The water-soluble polymer may act as a dispersing medium for achieving a homogeneous dispersion easily and for stabilizing the emulsified solution.

[0182] The water-soluble polymer may be selected from known anionic polymers, nonionic polymers and amphoteric polymers.

[0183] The water-soluble polymer has a solubility in water of preferably 5% or more at a temperature at which the emulsification is carried out.

[0184] Specific examples of the water-soluble polymer include polyvinyl alcohol and modified products thereof; polyacrylic amide and derivatives thereof; ethylene-vinyl alcohol copolymer; styrene-maleic anhydride copolymer; ethylene-maleic anhydride copolymer; isobutylene-maleic anhydride copolymer; polyvinyl pyrrolidone; ethylene- acrylic acid copolymer; vinyl acetate-acrylic acid copolymer; cellulose derivatives such as carboxymethylcellulose and methylcellulose; casein; gelatin; starch derivatives; gum arabic; and sodium alginate.

[0185] The water-soluble polymer or co-polymer may contain water-insoluble monomers or segments, but the content of such water-insoluble monomers or segments is less than 40 wt%, relative to the total weight of the polymer or co-polymer. For ethylene-vinyl alcohol co-polymers, the ethylene content is preferably less than 25 wt%, relative to the total weight of the co-polymer.

[0186] Among these polymers, polyvinyl alcohol and its derivatives are preferred.

[0187] A surfactant may be added to at least one of the non-aqueous and the aqueous phase to achieve more homogenous and stable dispersions. The surfactant is preferably added to the aqueous phase.

[0188] A preferred surfactant added to the aqueous phase is a surfactant, which does not cause precipitation or aggregation caused by a reaction with the protective colloid described above and are therefore selected from anionic and nonionic surfactants.

[0189] Preferred surfactants include sodium alkylbenzenesulfonate, sodium alkylsulfate, sodium dioctyl sulfosuccinate, polyalkylene glycol (such as polyoxyethylene nonyl phenyl ether), acetylene glycol and the like.

[0190] When the non-aqueous phase is prepared, it might be advantageous to use an organic solvent having a boiling point of from 100 to 300 °C as a hydrophobic organic solvent in which the encapsulant may be dissolved.

[0191] Specific examples thereof include esters, dimethylnaphthalene, diethyl-naphthalene, diisopropylnaphthalene, dimethylbiphenyl, diisopropylbiphenyl, diisobutylbiphenyl, 1-methyl-1-dimethylphenyl-2-phenylmethane, 1-ethyl-1-dimethylphenyl-1-phenylmethane, 1-propyl-1-dimethylphenyl-1-phenylmethane, triallylmethane (such as tritoluylmethane and toluyildiphenyimethane), terphenyl compounds, alkyl compounds, alkylated diphenyl ether compounds (such as propyldiphenyl ether), hydrogenated terphenyl compounds (such as hexahydro-terphenyl), and diphenyl ether.

[0192] Among these examples, esters are particularly preferable from the viewpoints of the emulsification stability of the emulsion.

[0193] Examples of the esters include phosphate esters such as triphenyl phosphate, tricresyl phosphate, butyl phosphate, octyl phosphate and cresylphenyl phosphate; phthalic esters such as dibutyl phthalate, 2-ethylhexyl phthalate, ethyl phthalate, octyl phthalate, and butylbenzyl phthalate; dioctyl tetrahydrophthalate; benzoic esters such as ethyl benzoate, propyl benzoate, butyl benzoate, isopentyl benzoate, and benzyl benzoate; abietic esters such as ethyl abietate, and benzyl abietate; dioctyl adipate; isodecyl succinate; diocyl azelate; oxalic esters such as dibutyl oxalate and dipentyl oxalate; diethyl malonate; maleic esters such as dimethyl maleate, diethyl maleate, and dibutyl maleate; tributyl citrate; sorbic esters such as methyl sorbate, ethyl sorbate and butyl sorbate; sebacic esters such as dibutyl sebacate, and dioctyl sebacate; ethylene glycol esters such as formic monoester and diester, butyric monoester and diester, lauric monoester and diester, palmitic monoester and diester, stearic monoester and diester, and oleic monoester and diester; triacetin; diethyl carbonate; diphenyl carbonate; ethylene carbonate; propylene carbonate; boric esters such as tributyl borate and tripentyl borate.

[0194] Among them, it is preferable to use tricresyl phosphate alone or in combination with other solvent(s).

[0195] Self-dispersible capsules wherein a dispersing group is covalently bound the polymeric shell, as described WO2015/158649 (AGFA GRAPHICS), paragraphs [0037] to [0057], and wherein the shell is prepared with a polyisocyanate as described above, may also be used in the present invention.

Method of preparing a laser markable article

[0196] The method of preparing the laser markable article according to the present invention comprises the steps of applying at least two aqueous laser markable compositions, both including a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder on a support. The laser markable composition that forms a crosslinked layer comprise a polymeric binder capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent.

[0197] The compositions may be provided onto a support by co-extrusion or any conventional coating technique, such as dip coating, knife coating, extrusion coating, spin coating, spray coating, slide hopper coating and curtain coating.

[0198] The compositions may also be provided onto a support by any printing method such as intaglio printing, screen printing, flexographic printing, offset printing, inkjet printing, valve jet printing, rotogravure printing, etc. Using a printing method is preferred when only a part or several parts of a support has to be provided with a laser markable layer.

[0199] The coated layers are preferably dried before a subsequent layer is applied.

[0200] Drying is preferably carried out at a temperature between 15 and 130°C, preferably between 25°C and 100°C, most preferably beteen 40 and 80 °C.

[0201] A preferred method of preparing a laser markable article as described above comprises the steps of:

- applying a first aqueous laser markable composition comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder on a support thereby forming a first laser markable layer;
- drying the first laser markable layer;
- applying a second aqueous laser markable composition comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder on the dried first laser markable layer thereby forming a second laser markable layer;
- drying the second laser markable layer

wherein at least the first laser markable composition includes a polymeric binder that is capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent that is capable of crosslinking the binder.

[0202] In a more preferred method of preparing the laser markable article, a third aqueous laser markable composition is applied on the dried second laser markable layer followed by a drying step wherein at least the first and second laser markable compositions includes a polymeric binder that is capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent that is capable of crosslinking the binder.

[0203] When an interlayer is applied between two laser markable layers, the interlayer coating composition includes a polymeric binder that is capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent that is capable of crosslinking the binder.

[0204] In another preferred embodiment, a top layer is applied on the dried second or third laser markable layer for UV protection. The top layer preferably comprises a UV absorber as described above.

[0205] In the drying step referred above, at least part of the solvents of the laser markable composition are removed and/or that the polymeric binder of the laser markable composition at least partially starts film-forming.

Support

[0206] The compositions may be applied on any type of support, for example a metallic support, a glass support, a polymeric support, or a paper support. The compositions may also be applied on a textile surface.

[0207] The support may be provided with a primer to improve the adhesion between the support and the applied layers.

[0208] The support maybe transparent or opaque.

[0209] To improve the contrast of the laser marked image, the support maybe a white support. The support then typically comprises a white dye or pigment, for example a titanium oxide pigment. Such a white support may be obtained by providing a white primer on a support.

[0210] When the laser markable article is used as laminate wherein the support becomes after lamination a top layer, for example to prepare a security document as described below, the support is preferably transparent.

[0211] The support may be a paper support, such as plain paper or resin coated paper, e.g. polyethylene or polypropylene coated paper.

[0212] There is no real limitation on the type of paper and it includes newsprint paper, magazine paper, office paper, or wallpaper but also paper of higher grammage, usually referred to as paper boards, such as white lined chipboard, corrugated (fiber) board and packaging board.

[0213] Also, so-called synthetic papers, such as the Synaps™ synthetic papers from Agfa Gevaert, which are opaque polyethylene terephthalate sheets, may be used as support.

[0214] Suitable polymeric supports include cellulose acetate propionate or cellulose acetate butyrate, polyesters such as polyethylene terephthalate and polyethylene naphthalate, polyamides, polycarbonates, polyimides, polyolefins, polyvinylchlorides, polyvinylacetals, polyethers, polysulfonamides, polylactide (PLA) and polyimide.

[0215] Preferred polymeric supports are polyvinylchloride (PVC), polycarbonate (PC) and polyethylene terephthalate (PET) supports.

[0216] A preferred PET support is a biaxially stretched polyethylene terephthalate (BOPET) foil due to its very high durability and resistance to scratches and chemical substances.

[0217] The manufacturing of such BOPET foils and supports is well-known in the art of preparing suitable supports for silver halide photographic films. For example, GB 811066 (ICI) teaches a process to produce biaxially oriented polyethylene terephthalate foils and supports.

[0218] There is no restriction on the shape of the support. It can be a flat sheet, such as a paper sheet or a polymeric film or it can be a three dimensional object like e.g. packaging box or a coffee cup.

[0219] The three dimensional object can also be a container like a bottle or a jerry-can for including e.g. oil, shampoo, insecticides, pesticides, solvents, paint thinner or other type of liquids.

[0220] The laser markable composition may also be applied on a so-called shrink foil. Such a foil shrinks tightly over whatever it is covering when heat is applied.

[0221] The most commonly used shrink foils are polyolefin foils, i.e. polyethylene or polypropylene foils. However, other shrink foils include PCV foils.

Laser markable article

[0222] The laser markable article is prepared by the method described above.

[0223] The laser markable article is preferably selected from the group consisting of a packaging, a foil, a laminate, a security document, a label, a decorative object and an RFID tag.

Packaging

[0224] Laser marking is typically used to add variable data, for example batch numbers, expiry dates, addressees, barcodes, etc. on the packaging. However, laser marking may also be used to add a combination of fixed and variable data on a packaging.

[0225] Variable and/or fixed data may also include images.

[0226] The laser markable article described above makes it possible to laser mark coloured data and/or images. By selecting a proper leuco dye, or a mixture of leuco dyes, the package may be provided with data or images in any colour.

[0227] Preferably laser marking is carried out in-line in the packaging process.

[0228] An advantage of using laser marking in a packaging process is the ability to mark information through a wrapping foil, for example the flavour-protective foil used for cigarette packs. In such a way, variable data may be provided on the cigarette packs after the protective foil has already been provided.

[0229] Another advantage of using laser marking instead of another printing technique, such as inkjet printing, is the absence of any chemicals in the marking process. Especially for pharmaceutical and food packaging, the absence of chemicals in the packaging line is an advantage.

[0230] Still another advantage of laser marking is the ability to provide the "image" with a laser on a 3D object.

[0231] A preferred packaging is folded cardboard or corrugated cardboard laminated with paper. Such packaging is preferably used for cosmetics, pharmaceuticals, food or electronics.

[0232] Using multicolour laser markable packaging may improve the customer experience.

[0233] As more and more people make use of on-line shopping where the customer goods are delivered to the customers home, it may become more important to use the packaging material, for example the delivery box containing the customer goods, to improve the customer experience or to advertise on the delivery box.

[0234] An advantage of laser marking is the possibility to add date at a very late stage of the packaging process.

Security Documents

[0235] The laser marking method may also be used to prepare security documents, such as for example ID cards.

[0236] Typically, laser markable security documents are prepared by laminating a laser markable foil or laminate, optionally together with other foils or laminates, onto one or both sides of a core support.

[0237] Such laser markable security documents and their preparation have been disclosed in for example WO2015/091782 (AGFA GEVAERT).

[0238] Core supports typically used to prepare security documents are discloses in EP-A 3431304 (AGFA GEVAERT), paragraphs [0128] to [0138]. Preferred polymeric cores are based on polycarbonate (PC), polyvinylchloride (PVC), and polyethylene terephthalate (PET).

[0239] The laser markable laminate is typically laminated on one or both sides of a core support using elevated temperatures and pressures.

[0240] The lamination temperature depends on the type of core support used. For a polyester core, lamination temperatures are preferably between 120 and 140°C, while they are preferably above 150°C - 160°C for a polycarbonate core.

[0241] A preferred embodiment of an ID card is schematically shown in Figure 2. The ID card (2) is obtained by laminating a laser markable article according to the present invention on both sides of a core-support (500).

[0242] After lamination, with the laser markable layer in contact with the core-support, the support (100) of the laser markable article becomes a protective layer. The support (100) is preferably transparent.

[0243] When UV absorbers are added to the support, which then becomes the protective layer, the colour stability may be improved.

Label

[0244] The laser markable article may also be a label, also referred to as tape or sticker.

[0245] A first embodiment of such a laser markable layer is schematically depicted in Figure 3.

[0246] An adhesive layer (200) and optionally a release liner (220) are applied on the laser markable layer (30) or another layer of the laser markable article described above.

[0247] The support (100) is preferably a transparent support.

[0248] A release liner (220) may be provided on the adhesive layer. A release liner is a film, paper, or coated paper material that is coated with for example silicone. The coated side of a release liner preferably has the adhesive applied to it. The release liner protects the adhesive until the label is applied. The silicone coating ensures clean removal of the label and the adhesive from the release liner.

[0249] Preferably, a pressure sensitive adhesive is applied to a release liner and then affixed to the label. To stick the label onto for example a packaging, the release liner is removed and the label is affixed to the packaging. The adhesive requires pressure either by hand or by application equipment.

[0250] After affixing the label to a packaging, the support (100) becomes a protective top layer. Such a protective layer may protect the laser marked image against physical damage (for example scratches) or against UV light by incorporating a UV absorber in the support.

[0251] In a second embodiment schematically depicted in Figure 4 the laser markable article described above is provided on a (self)-adhesive support.

[0252] Such a (self)-adhesive support includes an adhesive layer (200) and optionally a release liner ((220) on a side of the support (100) opposite to the side of the support carrying the laser markable layer (30).

Laser marked article

[0253] A laser marked article is obtained by exposing the laser markable article described above with an infrared laser, i.e. the laser marking step.

Laser marking

[0254] In principle any infrared (IR) laser may be used.

[0255] The infrared laser may be a continuous wave or a pulsed laser.

[0256] To produce high resolution laser marked data, it is preferred to use a near infrared (NIR) laser having an emission wavelength between 750 and 2500, preferably between 800 and 1500 nm in the laser marking step.

[0257] A particularly preferred NIR laser is an optically pumped semiconductor laser. Optically pumped semiconductor lasers have the advantage of unique wavelength flexibility, different from any other solid-state based laser. The output wavelength can be set anywhere between about 900 nm and about 1250 nm. This allows a perfect match between the laser emission wavelength and the absorption maximum of an optothermal converting agent present in the laser markable layer.

[0258] A preferred pulsed laser is a solid state Q-switched laser. Q-switching is a technique by which a laser can be made to produce a pulsed output beam. The technique allows the production of light pulses with extremely high peak power, much higher than would be produced by the same laser if it were operating in a continuous wave (constant output) mode, Q-switching leads to much lower pulse repetition rates, much higher pulse energies, and much longer pulse durations.

[0259] Laser marking may also be carried out using a so-called Spatial Light Modulator (SLM) as disclosed in WO2012/044400 (Vardex Laser Solutions).

[0260] To produce multiple colours, multiple lasers are preferably used. For a laser markable article comprising two laser markable layers, each layer producing a different colour, two NIR lasers each having a different emission wavelength are preferably used. For a laser markable article comprising three laser markable layers, each layer producing a different colour, three NIR lasers each having a different wavelength are preferably used.

[0261] Colour contamination is minimized by using lasers in a wavelength range near the absorption maximum of the infrared dyes of the laser markable layers. Preferably the laser emission wavelengths λ(L-1), A(L-2) and A(L-3) differ by no more than 30 nm from the infrared red dye absorption maxima λ_{max}(IR-1), λ_{max}(IR-2) and respectively λ_{max}(IR-3).

Claims

1. A laser markable article comprising a first and a second laser markable layer, both layers comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder, **characterized in that** at least the first

laser markable layer is crosslinked.

2. The laser markable article according to claim 1 further comprising a third laser markable layer, the third laser markable layer also comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder wherein at least the first and second laser markable layers are cross-linked.

3. The laser markable article according to claim 1 or 2 further comprising a crosslinked interlayer between two laser markable layers.

4. The laser markable article according to any of the preceding claims wherein the polymeric binder is a water-soluble or water-dispersible binder.

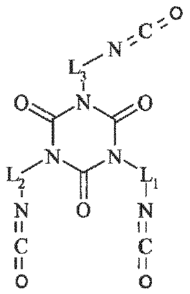
5. The laser markable article according to claim 4 wherein the binder is a polyvinylalcohol polymer or co-polymer.

6. The laser markable article according to any of the preceding claims wherein the amount of the polymeric binder in the laser markable layers is between 0.25 and 8 g/m^2.

7. The laser markable article according to any of the preceding claims wherein the leuco dyes and optothermal converting agents are encapsulated.

8. The laser markable article according to claim 7 wherein the leuco dyes are encapsulated in capsules prepared via interfacial polymerization of a polyisocyanate comprising at least 1 substituted or unsubstituted arylene or heteroarylene group and a compound including an active hydrogen.

9. The laser markable article according to claim 8 wherein the polyisocyanate is a compound having a chemical structure according to Formula IV, or a derivative thereof,



Formula IV

wherein
L1, L2 and L3 are linking groups comprising a substituted or unsubstituted arylene or heteroarylene group.

10. The laser markable article according to claim 8 or 9 wherein the interfacial polymerization is carried out at a temperature above 85°C.

11. The laser markable article according to any of the preceding claims wherein the absorption maxima in the near infrared region of the optothermal converting agents in the first and the second laser markable layer differ by at least 60 nm.

12. The laser markable article (1) according to any of the preceding claims comprising, in order,

- a support (100);
- a first laser markable layer (10) including a yellow colour forming leuco dye, a first optothermal converting agent, a developing agent and a polymeric binder;
- an optional interlayer (40);
- a second laser markable layer (20) including a cyan colour forming leuco dye, a second optothermal converting

agent, a developing agent and a polymeric binder;
- a third laser markable layer (30) including a magenta colour forming leuco dye, a third optothermal converting agent, a developing agent and a polymeric binder;

wherein at least the first and second laser markable layers and the optional interlayer are crosslinked.

13. The laser markable article according to any of the preceding claims wherein the article is selected from the group consisting of a packaging, a foil, a laminate, a security document, a label, a decorative object and an RFID tag.

14. A method of preparing a laser marked article comprising the step of exposing a laser markable article as defined in any of the preceding claims with an infrared laser thereby forming a laser marked image.

15. A method of preparing a laser markable article as defined in any of the claims 1 to 13 comprising the steps of:

- applying a first aqueous laser markable composition comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder on a support thereby forming a first laser markable layer;
- drying the first laser markable layer;
- applying a second aqueous laser markable composition comprising a leuco dye, a developing agent, an optothermal converting agent and a polymeric binder on the dried first laser markable layer thereby forming a second laser markable layer;
- drying the second laser markable layer;

wherein at least the first laser markable composition includes a polymeric binder that is capable of self-crosslinking or a polymeric binder in combination with a crosslinking agent capable of crosslinking the binder.

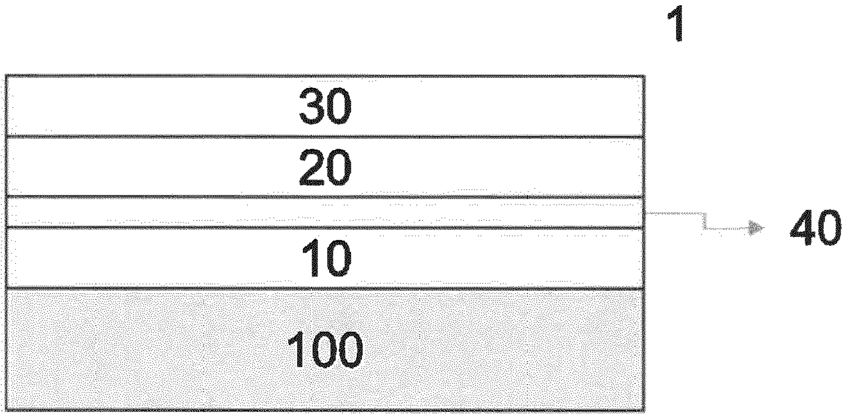


Figure 1

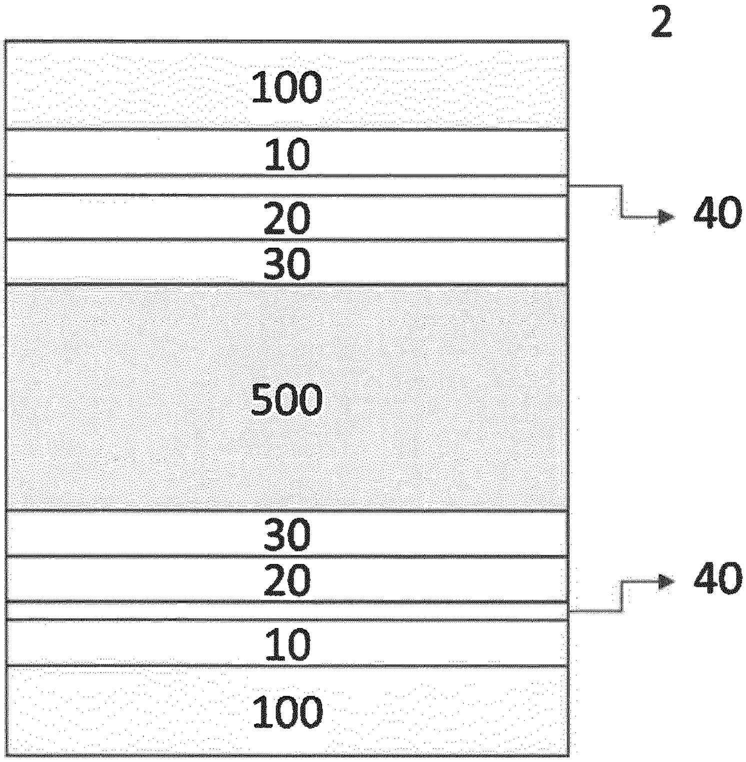


Figure 2

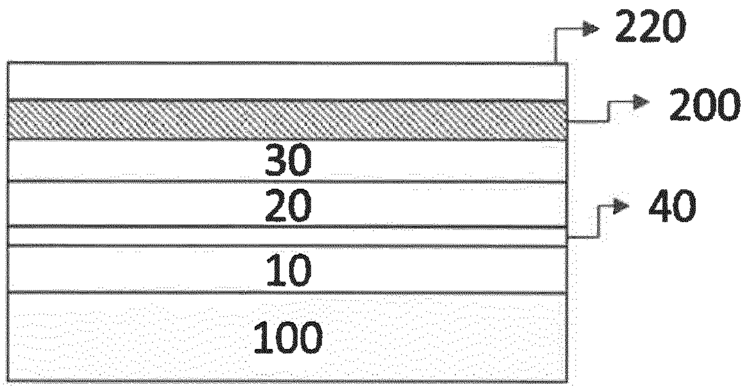


Figure 3

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EUROPEAN SEARCH REPORT

Application Number
EP 19 21 6821

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	EP 3 173 249 A1 (AGFA-GEVAERT [BE]) 31 May 2017 (2017-05-31)	1-5,7, 11-15	INV. B41M5/34 B41M5/323 B41M5/333 B41M5/337
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TECHNICAL FIELDS SEARCHED (IPC)

B41M
B42D

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
Munich	4 June 2020	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
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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)

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04-06-2020

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