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(54) LASER MARKABLE ARTICLES

(57) A radiation curable laser markable composition comprising a polymerizable compound, a colour forming agent and an optothermal converting agent, characterized in that the composition further includes at least 1 wt%, relative to the total weight of the composition, of an inorganic filler.

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Description

Technical field of the Invention

[0001] The present invention relates to laser markable articles and to laser markable compositions wherewith such articles may be prepared.

Background art for the invention

[0002] Various substrates, for example paper, paperboard or plastics, are very often marked with information such as logos, bar codes, expiry dates or batch numbers.

[0003] Tradionally, the marking of these substrates has been achieved by various printing techniques, such as for example inkjet or thermal transfer printing.

[0004] However, for some applications, these printing techniques are more and more replaced by laser marking as laser marking is cheaper in terms of overall economics and shows performance benefits such as high speed and contact free marking, marking of substrates with uneven surfaces, creation of marks that are so small that they are invisible or nearly invisible to the human eye, and creation of marks in the substrate rather than on the substrate.

[0005] Laser marking is typically carried out by applying a laser markable composition on a substrate followed by an image-wise laser exposure.

[0006] The laser markable composition may be applied on the substrate by inkjet printing, flexographic printing, rotogravure printing, offset printing or any other printing technique. Also, the laser markable composition may be applied on the substrate by any coating or spraying technique.

[0007] A flexographic ink may be radiation curable. With such radiation curable flexographic inks, no solvents have to be evaporated after printing. Instead, solidification of the applied ink is the result of a polymerization reaction.

[0008] Typically, a laser markable composition includes a so-called optothermal converting agent that converts radiation energy into heat. In most cases infrared radiation is used for laser marking.

[0009] Various infrared absorbing compounds that may be used as optothermal converting agents in laser markable compositions are disclosed.

[0010] For example WO2005/068207 (Datalase) discloses copper salts, WO2007/141522 (Datalase) other metal salts such as Indium Tin Oxide and WO2015/015200 (Datalase) Tungsten Bronze.

[0011] Such heavy metal containing optothermal converting agents are however to be avoided from an ecological and toxicological point of view, especially in food and pharmaceutical packaging applications.

[0012] WO2014/057018 disclose cyanine compounds that may act as optothermal converting agents.

[0013] A disadvantage of cyanine dyes maybe their daylight and temperature stability. Their poor stability also makes it difficult to use them in UV curable compositions.

[0014] An optothermal converting agent that does not contain heavy metals and that is stable is carbon black. Carbon black is disclosed as optothermal converting agent in for example WO2016/184881 (Agfa Gevaert).

[0015] A disadvantage however of using carbon black as optothermal converting agent may be low laser marking densities. The laser marking densities may often be increased by using more carbon black. However, a too high amount of carbon black may result in a too high background colour.

[0016] There is thus a need for laser marking compositions including carbon black as optothermal converting agent and wherewith sufficient laser marking densities and a low enough background colour may be obtained.

Summary of the invention

[0017] It is an object of the present invention to provide a laser markable article that combines minimal health and safety risks with sufficient laser marking and physical properties.

[0018] This object has been realised with the laser markable composition as defined in claim 1.

[0019] Further objects of the invention will become apparent from the description hereinafter.

Brief description of drawings

[0020] **Figure 1** illustrates a higher operational window for laser marking coatings containing nanosilica (Example 4, coating S8 including nanosilica versus coating S18 including no nanosilica). With S8 higher marking magenta densities are obtained (high a*) and less burning of the marked dyes is observed (burning results in a decrease of a* and increase of b*) when the laser power increases.

Detailed description of the invention

Definitions

[0021] 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-methylbutyl, etc.

[0022] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C_1 to C_6-alkyl group.

[0023] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C_2 to C_6-alkenyl group.

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

[0025] 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.

[0026] 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.

[0027] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group

[0028] 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.

[0029] 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

[0030] 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 $-NO_2$.

The radiation curable laser markable composition

[0031] The radiation curable laser markable composition according to the present invention comprises a polymerizable compound, a colour forming agent, an optothermal converting agent and at least 1 wt% of an inorganic filler.

[0032] The optothermal converting agent is preferably an infrared absorbing pigment, more preferably carbon black.

[0033] A preferred radiation curable laser markable composition comprises a leuco dye as colour forming agent.

[0034] The radiation curable laser markable composition is preferably a UV curable laser markable composition.

[0035] The radiation curable laser markable composition is preferably a flexographic or inkjet ink, more preferably a UV curable flexographic or inkjet ink.

[0036] To optimize the coating or printing properties, and also depending on the application for which it is used, various additives may be added to the composition, such as wetting/levelling agents, rheology modifiers, colorants, adhesion promoting compounds, biocides or antioxidants.

Inorganic filler

[0037] The laser markable composition comprises at least 1 wt% of an inorganic filler, relative to the total weight of the composition.

[0038] Examples of inorganic fillers that may be used are selected from the group consisting of calciumcarbonate, clays, alumina trihydrate, talc, mica, and calcium sulphate.

[0039] Preferably, an inorganic nanofiller is used to obtain optimal transparency of the laser markable composition. A preferred nanofiller is nanosilica.

[0040] Nanosilica as referred to herein consist of amorphous silicon dioxide particles having a nano-particle size.

[0041] To obtain optimal transparency of the laser markable composition the particle size of the nanosilica is preferably in the range from 5 to 250 nm, more preferably in the range from 7.5 to 100 nm, most preferably in the range from 10 to 50 nm.

[0042] Preferably dispersions of nanosilica in acrylate monomers are used. Such commercially available dispersions are for example the Nanocryl® nanosilica dispersions available from Evonik.

[0043] The amount of the inorganic filler is preferably in the range from 1 to 15 wt%, more preferably in the range from 2 to 10 wt%, most preferably in the range from 2.5 and 7.5 wt%, all relative to the total weight of the composition.

[0044] After applying the composition on a support, the amount of the inorganic filler is preferably in the range from

0.1 to 1.5 g/m^2, more preferably in the range from 0.2 to 1 g/m^2, most preferably in the range from 0.25 to 0.75 g/m^2.

Colour forming agent

[0045] The radiation curable laser markable composition comprises a colour forming agent, which is capable of forming a colour upon laser marking.

[0046] All known colour forming agents may be used.

[0047] A transition metal oxide, such as molybdenum trioxide, has been disclosed in WO2008/0751 01 (SILTECH).

[0048] An oxyanion of a multivalent metal, such as ammonium octyl molybdate, has been disclosed in WO2002/074548 (DATALASE) and WO2007/012578 (DATALASE).

[0049] These colour forming agents are capable of forming a black colour upon laser marking.

[0050] Diacetylene compounds, such as disclosed in WO2013/014436 (DATALASE) are capable of forming multiple colours.

[0051] Preferred colour formers are leuco dyes, as described below. A leuco dye is preferably used in combination with a developing agent.

[0052] Also, a combination of different colour forming agents may be used, for example to produce different colours. In WO2013/068729 (Datalase), a combination of a diacetylene compound and a leuco dye is used to produce a full colour image upon exposure to UV and IR radiation.

Leuco dye

[0053] 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.

[0054] Examples of leuco dyes are disclosed in WO2015/165854 (AGFA GEVAERT), paragraph [069] to [093].

[0055] The laser markable composition may comprise more than one leuco dye. Using two, three or more leuco dyes may be necessary to realize a particular colour.

[0056] The amount of the leuco dye in the radiation curable laser markable composition is preferably in the range from 0.5 and 20 wt%, more preferably in the range from 1 to 10 wt%, relative to the total weight of the composition.

[0057] After applying the composition on a support, the amount of leuco dye 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.

Optothermal converting agent

[0058] An optothermal converting agent generates heat upon absorption of radiation.

[0059] The optothermal converting agent preferably generates heat upon absorption of infrared (IR) radiation, more preferably near infrared (NIR) radiation.

[0060] Near infrared radiation has a wavelength between 750 and 2500 nm.

[0061] Optothermal converting agents may be an infrared radiation absorbing dye but is preferably an infrared radiation absorbing pigment, or a combination thereof.

Infrared radiation absorbing inorganic pigments

[0062] A preferred inorganic infrared absorber is a copper salt as disclosed in WO2005/068207 (DATALASE).

[0063] Another preferred inorganic infrared absorber is a non-stoichiometric metal salt, such as reduced indium tin oxide as disclosed in WO2007/141522 (DATALASE).

[0064] Particular preferred inorganic infrared absorbers are tungsten oxide or tungstate as disclosed in WO2009/059900 (DATALASE) and WO2015/015200 (DATALASE). A lower absorption in the visible region while having a sufficient absorption in the near infrared region is an advantage of these tungsten oxide or tungstate.

Carbon black

[0065] A particularly preferred infrared radiation absorbing pigment (IR pigment) is carbon black, such as acetylene black, channel black, furnace black, lamp black, and thermal black.

[0066] Due to its light absorption in the visible region, i.e. between 400 nm and 700 nm, a too high amount of carbon black may result in an increase of the background colour of the printed laser markable composition.

[0067] For that reason, the amount of carbon black is preferably less than 10.000 ppm, more preferably less than 1000 ppm, most preferably less than 500 ppm, all relative to the total weight of the composition.

[0068] After applying the composition on a support, the amount of carbon black is preferably less than 0.1 g/m^2, more preferably less than 0.01 g/m^2, most preferably less than 0.005 g/m^2.

[0069] Carbon black is preferably added to the radiation curable laser markable composition as a dispersion.

[0070] The carbon black dispersion may be prepared by all commonly known dispersion methods.

[0071] A preferred method is a mechanical dispersion method including a bead milling step.

[0072] In such a method, the carbon black is mixed with a dispersion medium to obtain a suspension. That suspension is then grinded in a bead mill to obtain a stable dispersion having a particle size below 1 μm.

[0073] The particle size of the carbon particles is preferably in the range from 10 to 500 nm, more preferably in the range from 25 to 400 nm, most preferably in the range from 50 to 300 nm.

[0074] The dispersion medium preferably includes a polymerizable compound, preferably an acrylate.

[0075] The acrylate monomers are preferably selected from the group consisting of isobornylacrylate (IBOA), dipropylene glycol diacrylate (DPGDA), pentaerythritol triacrylate and 2-(2-vinyloxyethoxy)ethyl acrylate (VEEA).

[0076] To realize stable dispersions, a dispersant is preferably added to the dispersion medium. Any commonly known dispersant may be used. A preferred dispersant is a polymeric dispersant such as Efka PX4701, available from BASF.

[0077] Examples of suitable carbon blacks are Special black 250, Special black 100, Printex G, Lamp Black 101, Printex 25, Printex A, Hiblack 40B2, XPB 545 from Orion; and Raven 410, Raven 14 from Birla Carbon.

Infrared radiation absorbing dyes

[0078] An advantage of Infrared absorbing dyes (IR dyes) compared to IR pigments is their narrow absorption spectrum resulting in less absorption in the visible region. This may be of importance for the processing of transparent resin based articles where optical appearance is of importance.

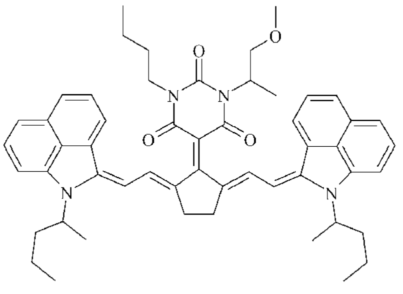
[0079] A narrow absorption band is also mandatory for multicolour laser marking using multiple laser each having a different emission wavelength, as disclosed in for example EP-A 3297838.

[0080] 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).

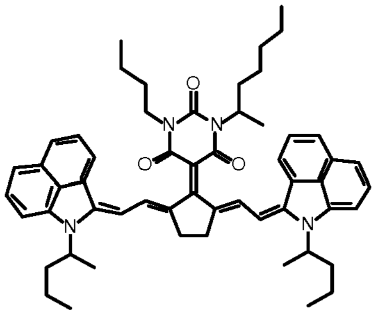
[0081] Preferred IR dyes are polymethine dyes due to their low absorption in the visible region and their selectivity, i.e. narrow absorption peak in the infrared region. Particular preferred polymethine IR dyes are cyanine IR dyes.

[0082] Preferred IR dyes having an absorption maximum of more than 1100 nm are those disclosed in EP-A 2722367, paragraphs [0044] to [0083] and WO2015/165854, paragraphs [0040] to [0051].

[0083] 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-1, or the IR dye represented by Formula IR-2:



IR-1



IR-2

[0084] Both IR dyes IR-1 and IR-2 have an absorption maximum λmax around 1052 nm making them very suitable for a Nd-YAG laser having an emission wavelength of 1064 nm.

[0085] Other preferred NIR absorbing compounds are those disclosed in WO2019/007833, paragraph [0034] to [0046]. It has been observed that these NIR absorbing compounds have a better daylight stability compared to the IR dyes described above and are therefore more suitable to be used in UV curable compositions.

[0086] A combination of different optothermal converting agents may also be used.

[0087] The amount of optothermal converting agent 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.

Polymerizable compound

[0088] The laser markable composition comprises at least one polymerizable compound.

[0089] The polymerizable compounds may be monomers, oligomers or prepolymers.

[0090] The polymerizable compounds may be free radical polymerizable compounds or cationic polymerizable compounds.

[0091] Cationic polymerization is superior in effectiveness due to lack of inhibition of the polymerization by oxygen. However it is expensive and slow, especially under conditions of high relative humidity. If cationic polymerization is used, it is preferred to use an epoxy compound together with an oxetane compound to increase the rate of polymerization.

[0092] Preferred monomers and oligomers are those listed in paragraphs [0103] to [0126] of EP-A 1911814.

[0093] Radical polymerization is the preferred polymerization process. Preferred free radical polymerizable compounds include at least one acrylate or methacrylate group as polymerizable group, referred to herein as (meth)acrylate monomers, oligomers or prepolymers. Due to their higher reactivity, particularly preferred polymerizable compounds are acrylate monomers, oligomers or prepolymers.

[0094] Other preferred (meth)acrylate monomers, oligomers or prepolymers are N-vinylamides, such as N-vinylcaprolactam and acryloylmorpholine.

[0095] Particularly preferred (meth)acrylate monomers, oligomers or prepolymers are selected from the group consisting of tricyclodecanedimethanol diacrylate (TCDDMDA), isobornyl acrylate (IBOA), dipropylene glycol diacrylate (DPGDA), ethoxylated [4] bisphenol diacrylate and urethane acrylate oligomer.

Developing agent

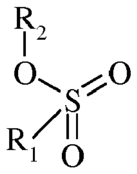
[0096] The radiation curable laser markable composition preferably comprises a developing agent.

[0097] A developing agent is capable of reacting with a colourless leuco dye resulting in the formation of a coloured dye upon laser marking. Typically, upon laser marking a compound is released that may react with a leuco dye thereby forming a coloured dye.

[0098] All publicly-known photo- or thermal acid generators can be used as developing agent. Thermal acid generators are for example widely used in conventional photoresist material. For more information see for example "Encyclopaedia of polymer science", 4th edition, Wiley or "Industrial Photoinitiators, A Technical Guide", CRC Press 2010.

[0099] Preferred classes of photo- and thermal acid generators are iodonium salts, sulfonium salts, ferrocenium salts, sulfonyl oximes, halomethyl triazines, halomethylarylsulfone, α-haloacetophenones, sulfonate esters, t-butyl esters, allyl substituted phenols, t-butyl carbonates, sulfate esters, phosphate esters and phosphonate esters.

[0100] Particularly preferred developing agents have a structure according to Formula (I)



Formula I

wherein

R1 represent an optionally substituted alkyl group, an optionally substituted (hetero)cyclic alkyl group, an optionally substituted alkanyl group, an optionally substituted alkenyl group, an optionally substituted alkynyl group, an optionally substituted (hetero)aryl group, an optionally substituted aralkyl group, an optionally substituted alkoxy group, an optionally substituted (hetero)cyclic alkoxy group, or an optionally substituted (hetero)aryl group;

R2 represent an optionally substituted alkyl, an optionally substituted aliphatic (hetero)cyclic alkyl group or an optionally substituted aralkyl group;

R1 and R2 may represent the necessary atoms to form a ring.

[0101] Such developing agents according to Formula I and their preparation are disclosed in WO2015/091688.

[0102] The amount of the developing agent in the radiation curable composition is preferably in the range from 0.5 to 25 wt%, more preferably in the range from 1 to 15 wt%, most preferably in the range from 2.5 to 10 wt%, relative to the total weight of the composition.

[0103] After applying the composition on a support, the amount of the developing agent is preferably in the range from

0.05 to 2.5 g/m^2, more preferably in the range from 0.10 to 1.50 g/m^2, most preferably in the range from 0.25 to 1.00 g/m^2.

Photoinitiator

[0104] The radiation curable laser markable composition preferably contains a photoinitiator. The initiator typically initiates the polymerization reaction. The photoinitiator may be a Norrish type I initiator, a Norrish type II initiator or a photo-acid generator, but is preferably a Norrish type I initiator, a Norrish type II initiator or a combination thereof.

[0105] A preferred Norrish type I-initiator is selected from the group consisting of benzoinethers, benzil ketals, α,α-dialkoxyacetophenones, α-hydroxyalkylphenones, α -aminoalkylphenones, acylphosphine oxides, acylphosphine sulphides, α-haloketones, α-halosulfones and α-halophenylglyoxalates.

[0106] A preferred Norrish type II-initiator is selected from the group consisting of benzophenones, thioxanthones, 1,2-diketones and anthraquinones.

[0107] Suitable photo-initiators are disclosed in CRIVELLO, J.V., et al. VOLUME III: Photoinitiators for Free Radical Cationic & Anionic Photopolymerization. 2nd edition. Edited by BRADLEY, G.. London,UK: John Wiley and Sons Ltd, 1998. p.287-294 .

[0108] In order to increase the photosensitivity further, the radiation curable composition may additionally contain co-initiators.

[0109] A preferred co-initiator is selected from the group consisting of an aliphatic amine, an aromatic amine and a thiol. Tertiary amines, heterocyclic thiols and 4-dialkylamino-benzoic acid are particularly preferred as co-initiator.

[0110] The most preferred co-initiators are aminobenzoates for reason of shelf-life stability of the radiation curable composition.

[0111] A preferred amount of photoinitiator is 0.3 - 20 wt% of the total weight of the radiation curable composition, more preferably 1 - 15 wt% of the total weight of the radiation curable composition.

[0112] The amount of co-initiator or co-initiators is preferably from 0.1 to 20.0 wt%, more preferably from 1.0 to 10.0 wt%, based in each case on the total weight of the radiation curable composition.

Polymerization Inhibitors

[0113] For improving the shelf-life, the radiation curable laser markable composition may contain a polymerization inhibitor. Suitable polymerization inhibitors include phenol type antioxidants, hindered amine light stabilizers, phosphor type antioxidants, hydroquinone monomethyl ether commonly used in (meth)acrylate monomers, and hydroquinone, t-butylcatechol, pyrogallol may also be used.

[0114] Suitable commercial inhibitors are, for example, Sumilizer™ GA-80, Sumilizer™ GM and Sumilizer™ GS produced by Sumitomo Chemical Co. Ltd.; Genorad™ 16, Genorad™ 18 and Genorad™ 20 from Rahn AG; Irgastab™ UV10 and Irgastab™ UV22, Tinuvin™ 460 and CGS20 from Ciba Specialty Chemicals; Floorstab™ UV range (UV-1, UV-2, UV-5 and UV-8) from Kromachem Ltd, Additol™ S range (S100, S110, S120 and S130) from Cytec Surface Specialties.

[0115] Since excessive addition of these polymerization inhibitors will lower the sensitivity to curing, it is preferred that the amount capable of preventing polymerization is determined prior to blending. The amount of a polymerization inhibitor is preferably lower than 2 wt% of the total radiation curable laser markable composition.

Surfactant

[0116] The radiation curable laser markable composition may contain at least one surfactant. The surfactant(s) can be anionic, cationic, non-ionic, or zwitter-ionic and are usually added in a total quantity less than 5 wt%, more preferably less than 2 wt%, based on the total weight of the composition.

[0117] Preferred surfactants are selected from fluoro surfactants (such as fluorinated hydrocarbons) and/or silicone surfactants.

[0118] The silicone surfactants are preferably siloxanes and can be alkoxylated, polyester modified, polyether modified, polyether modified hydroxy functional, amine modified, epoxy modified and other modifications or combinations thereof. Preferred siloxanes are polymeric, for example polydimethylsiloxanes. Preferred commercial silicone surfactants include BYK™ 333 and BYK™ UV3510 from BYK Chemie.

[0119] Silicone surfactants are often preferred in the radiation curable laser markable composition, especially the reactive silicone surfactants, which are able to be polymerized together with the polymerizable compounds during the curing step.

[0120] Examples of useful commercial silicone surfactants are those supplied by BYK CHEMIE GMBH (including Byk™-302, 307, 310, 331, 333, 341, 345, 346, 347, 348, UV3500, UV3510 and UV3530), those supplied by TEGO CHEMIE SERVICE (including Tego Rad™ 2100, 2200N, 2250, 2300, 2500, 2600 and 2700), Ebecryl™ 1360 a polysilixone hexaacrylate from CYTEC INDUSTRIES BV and Efka™-3000 series (including Efka™-3232 and Efka™-3883) from EFKA CHEMICALS B.V..

Method of preparing a laser markable article

[0121] The method of preparing a laser markable article comprises the steps of:

- applying the radiation curable laser markable composition as described above on a support;
- curing the applied composition.

[0122] The laser markable composition 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.

[0123] The laser markable composition may also be provided onto a support by any printing method such as intaglio printing, screen printing, flexographic printing, offset printing, inkjet 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.

[0124] The laser markable composition is preferably applied by flexographic printing or inkjet printing.

[0125] The thickness of the applied radiation curable laser markable composition is preferably 50 μm or less, more preferably 20 μm or less, most preferably 10 μm or less.

Support

[0126] The laser markable composition may be applied on any type of surface, for example a metallic support, a glass support, a polymeric support, or a paper support. The laser markable composition may also be applied on a textile surface.

[0127] The support may be provided with a primer to improve the adhesion between the support and the laser markable composition.

[0128] A primer containing a dye or a pigment, for example a white primer, may also be provided on the support, for example to improve the contrast of the laser marked image.

[0129] The support may be a paper support, such as plain paper or resin coated paper, e.g. polyethylene or polypropylene coated paper.

[0130] 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.

[0131] 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.

[0132] 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.

[0133] A preferred polymeric support is a biaxially stretched polyethylene terephthalate foil (PET-C foil) due to its very high durability and resistance to scratches and chemical substances.

[0134] The manufacturing of PET-C 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.

[0135] Another preferred polymeric support includes (co)polyesters based on cyclohexyldimethanol (CHDM).

[0136] Thermoplastic polyesters containing CHDM exhibit enhanced strength, clarity, and solvent resistance. The exact properties of the polyesters vary from the high melting crystalline poly(1,4-cyclohexylenedimethylene terephthalate), PCT, to the non-crystalline copolyesters with the combination of ethylene glycol and CHDM in the backbone. The properties of these polyesters is also dependent on the cis/trans ratio of the CHDM monomer. CHDM has low melting point and reduces the degree of crystallinity of PET homopolymer, improving its processability. With improved processability, the polymer tends to degrade less to acetaldehyde and other undesirable degradation products. The copolymer with PET is known as glycol-modified polyethylene terephthalate, PETG. PETG is used in many fields, including electronics, automobiles, barrier, and medicals etc.

[0137] Another preferred polymeric support includes (co)polyesters based on 2,5-furandicarboxylic acid (FDCA). Such PEF films have, compared to standard PET films, a 10x higher oxygen barrier, a 2~3 x higher water vapor barrier, an improved mechanical strength and are fully transparent.

[0138] Other polymeric supports include copolyesters based on isosorbide, e.g. copolymers of terephtalic acid and ethylene glycol and isosorbide.

[0139] The polymeric support may be a single component extrudate or co-extrudate. Examples of suitable co-extrudates are PET/PETG and PET/PC.

[0140] 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. a plastic coffee cup.

[0141] 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.

[0142] 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.

[0143] The most commonly used shrink foils are polyolefin foils, i.e. polyethylene or polypropylene foils. However, other shrink foils include PCV.

Laser marked article

[0144] The laser markable article is prepared by the method described above.

[0145] 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

[0146] The laser marking method according to the present invention is preferably used to laser mark a packaging.

[0147] Laser marking is typically used to add variable data, for example batch numbers, expiry dates, addressees, etc. on the packaging.

[0148] Preferably laser marking is carried out in-line in the packaging process.

[0149] The laser marked "image" on a packaging may comprises data, images, barcodes, QR codes, or a combination thereof.

[0150] 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.

[0151] Another preferred laser markable packaging is used for pharmaceutical packaging. For pharmaceutical packaging, track and trace requirements become more and more demanding to comply with the ever evolving legislation.

[0152] 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 a great advantage.

[0153] By selecting a proper leuco dye, or a mixture of leuco dyes, the package may be provided with data or images in any colour.

[0154] A preferred packaging is folded cardboard or corrugated cardboard laminated with paper. Such packaging is preferably used for cosmetics, pharmaceuticals, food or electronics.

[0155] Multiple colour, even full colour, images may be obtained when the packaging is provided with multiple laser markable compositions, each containing a different leuco dye and optothermal converting agent, as disclosed in EP-A2719540 (Agfa Gevaert) and EP-A 2719541 (Agfa Gevaert).

Security Documents

[0156] The laser marking method may also be used to prepare security documents, such as for example ID cards.

[0157] 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.

[0158] Such laser markable security documents and their preparation have been disclosed in for example WO2015/091782 (Agfa Gevaert).

[0159] The laser markable laminate may be prepared by providing a laser markable composition according to the present invention on a support. The support is described above and is preferably a transparent polymeric support.

[0160] The laser markable laminate may comprise more than one laser markable layers or may comprise additional layers such as an ink receiving layer, a UV absorbing layer, intermediate layers or adhesion promoting layers.

[0161] The laser markable laminate is typically laminated on one or both sides of a core support using elevated temperatures and pressures.

[0162] Preferred core supports are disclosed in WO2014/057018 (Agfa Gevaert), paragraphs [0112] to [0015].

[0163] 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.

Laser marking

[0164] In principle any laser may be used in the laser marking step. Preferred lasers are ultraviolet (UV) and infrared (IR) lasers, infrared laser being particularly preferred.

[0165] The infrared laser may be a continuous wave or a pulsed laser.

[0166] For example a CO_2 laser, a continuous wave, high power infrared laser having emission wavelength of typically 10600 nm (10.6 micrometer) may be used.

[0167] CO_2 lasers are widely available and cheap. A disadvantage however of such a CO_2 laser is the rather long emission wavelength, limiting the resolution of the laser marked information.

[0168] 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.

[0169] 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.

[0170] 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.

[0171] Laser marking may also be carried out using a so-called Spatial Light Modulator (SLM) as disclosed in WO2012/044400 (Vardex Laser Solutions).

Curing

[0172] The radiation curable laser markable composition can be cured by exposing them to actinic radiation, such as electron beam or ultraviolet radiation.

[0173] Preferably, the radiation curable laser markable composition is cured by exposing it to ultraviolet radiation, more preferably using UV LED curing.

EXAMPLES

Materials

[0174] All materials used in the following examples were readily available from standard sources such as ALDRICH CHEMICAL Co. (Belgium) and ACROS (Belgium) unless otherwise specified.

[0175] **WR** is an abbreviation used for WinCon-Red, a magenta leuco dye from Connect Chemicals GmbH.

[0176] CpTs is an abbreviation for cyclohexyl p-toluenesulfonate with the CAS number 953-91-3 from Chemgo.

[0177] **Genocure DMHA** is a photoinitiator from RAHN AG.

[0178] **Omnirad 481** is a photoinitiator from IGM Resins b.v.

[0179] **Speedcure TPO** is a photoinitiator from Lambson Limited.

[0180] **Sartomer 833S** is tricyclodecanedimethanol diacrylate (TCDDMDA, a difunctional acrylic monomer from Arkema.

[0181] **Photomer4012** is isobornyl acrylate (IBOA), a monofunctional acrylic monomer from IGM.

[0182] **Sartomer 508** is dipropylene glycol diacrylate, a difunctional acrylic monomer from Arkema.

[0183] **CN9245** is a urethane acrylate oligomer from Arkema.

[0184] **BYK-UV 3510** is a surface additive from BYK-Chemie GmbH.

[0185] **NANOCRYL A210** is a mixture of acrylates and 50 wt% amorphous silicon dioxide from Evonik.

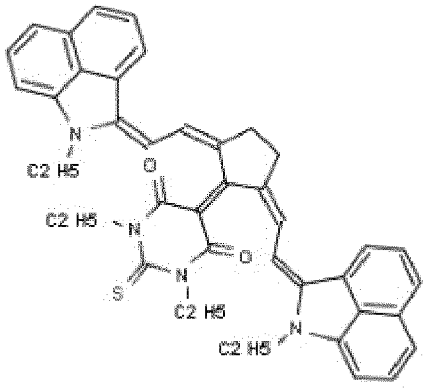
[0186] **Raven 410** is a carbon black powder from Columbian Chemicals Company.

[0187] **Lamp Black 101** is a carbon black powder from Orion Engineered Carbons GmbH.

[0188] **HiBlack 40B2** is a carbon black from Orion Engineered Carbons GmbH.

[0189] **CTO** is an inorganic pigment of cesium tungsten oxide from Keeling & Walker Limited.

[0190] **AGFAIR** is an infrared organic compound with the following formula and prepared according to patent WO2019/007833.



[0191] **Cupferron AL** is aluminum N-nitrosophenylhydroxylamine from WAKO CHEMICALS LTD.

[0192] **INHIB** is a mixture forming a polymerization inhibitor having a composition according to Table 1.

Table 1

Component	wt%
Sartomer 508	82.4
p-methoxyphenol	4.0
BHT	10.0
Cupferron AL	3.6

[0193] **EFKA PX4701** is a high-molecular-weight dispersant from BASF SE.

[0194] **OPV is** a mixture of 30w% of EFKA PX4701 and 1w% INHIB in Photomer 4012.

[0195] **DPKA** is a mixture of 40w% of EFKA PX4701 and 1w% INHIB in Sartomer 508.

[0196] **EFKA PX4703** is a high-molecular-weight dispersant from BASF SE.

[0197] **EFKA PX4733** is a high-molecular-weight dispersant from BASF SE.

[0198] **DISP1** is a concentrated pigment dispersion prepared as follows: 4.0g of Raven 410 pigment powder and 4.0g of dispersant EFKA PX4703 were mixed into 32.0g of Photomer 4012 and introduced into a 100mL plastic container. The container was filled with 160g of 3mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding material" from TOSOH Co.). The container was sealed and placed on rotating rolls for 7 days. After milling, the dispersion is separated from the beads. The resulting concentrated pigment dispersion exhibited an average particle size of 195.3nm as measured with a Malvern™ nano-S and a viscosity of 46.97mPa.s at 20°C and at a shear rate of 10 s^{-1}.

[0199] **DISP2** is a concentrated pigment dispersion prepared as follows: 35.0g of Lamp Black 101 pigment powder and 116.7g of OPV were mixed into 198.3g of Photomer 4012 using a DISPERLUX™ dispenser. Stirring was continued for 30 minutes. The vessel was connected to a DynoMill-RL mill filled with 200 g of 0.4 mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding media" from TOSOH Co.). The mixture was circulated over the mill for 188 minutes with a rotation speed of 4500 t/min. During the complete milling procedure the content in the mill was cooled to keep the temperature below 60°C. After milling, the dispersion was discharged into a vessel. The resulting concentrated pigment dispersion exhibited an average particle size of 234.9nm as measured with a Malvern™ nano-S and a viscosity of 30.7mPa.s at 20°C and at a shear rate of 10 s^{-1}.

[0200] **DISP3** is a concentrated pigment dispersion prepared as follows: 4.0g of HiBlack 40B2 pigment powder and 4.0g of dispersant EFKA PX4703 were mixed into 32.0g of Photomer 4012 and introduced into a 100mL plastic container. The container was filled with 160g or 3mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding material" from TOSOH Co.). The container was sealed and placed on rotating rolls for 7 days. After milling, the dispersion is separated from the beads. The resulting concentrated pigment dispersion exhibited an average particle size of 166.3nm as measured with a Malvern™ nano-S and a viscosity of 71.7mPa.s at 20°C and at a shear rate of 10 s^{-1}.

[0201] **DISP4** is a concentrated pigment dispersion prepared as follows: 100.0g of CTO pigment powder, 100.0g of dispersant EFKA PX4733 and 5.0g of INHIB stabilizer were mixed into 295.0g of Photomer 4012 using a DISPERLUX™ dispenser. Stirring was continued for 30 minutes. The vessel was connected to a DynoMill-RL mill filled with 200 g of 0.4 mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding media" from TOSOH Co.). The mixture was circulated over the mill for 108 minutes with a rotation speed of 4500 t/min. During the complete milling procedure the content in the mill was cooled to keep the temperature below 60°C. After milling, the dispersion was discharged into a vessel. The resulting concentrated pigment dispersion exhibited an average particle size of 131.0nm as measured with a Malvern™ nano-S and a viscosity of 134.11mPa.s at 20°C and at a shear rate of 10 s^{-1}.

[0202] **DISP5** is a concentrated pigment dispersion prepared as follows: 17.5g of AGFAIR, 43.7g of DPKA and 3.1g of INHIB stabilizer were mixed into 285.7g of Sartomer 508 using a DISPERLUX™ dispenser. Stirring was continued for 30 minutes. The vessel was connected to a DynoMill-RL mill filled with 200 g of 0.4 mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding media" from TOSOH Co.). The mixture was circulated over the mill for 188 minutes with a rotation speed of 4500 t/min. During the complete milling procedure the content in the mill was cooled to keep the temperature below 60°C. After milling, the dispersion was discharged into a vessel. The resulting concentrated pigment dispersion exhibited an average particle size of 193.0nm as measured with a Malvern™ nano-S and a viscosity of 63.0mPa.s at 20°C and at a shear rate of 10 s^{-1}.

[0203] **MB1** is a concentrated solution prepared as follow: 1.50g of WR, 2.64g of CpTs, 1.44g of Genocure DMHA, 1.44g of Omnirad 481, 1.44g of Speedcure TPO, 24.42g of Sartomer 833S, 14.52g of CN9245 and 0.60g of BYK-UV 3510 were added into a 100mL brown glass container with a plastic screw cap and stirred at 250rpm with a magnetic stirring bar at room temperature overnight.

[0204] **MB2** is a concentrated solution prepared as follow: 3.0g of WR, 5.28g of CpTs, 3.24g of Genocure DMHA, 3.24g of Omnirad 481, 3.24g of Speedcure TPO, 56.16g of Sartomer 833S, 32.64g of CN9245 and 1.20g of BYK-UV 3510 were added into a 200mL brown glass container with a plastic screw cap and stirred at 250rpm with a magnetic stirring bar at room temperature overnight.

Example 1

[0205] The coating solutions S1 to S4 were prepared by mixing the ingredients according to Table 2 expressed in grams in a 30mL brown glass flasks with a plastic screw cap and stirred at 350 rpm with a magnetic stirring bar at room temperature for 3 hours.

Table 2

Ingredients [g]	S1	S2	S3	S4
WR	0.25	=	=	=
CpTs	0.44	=	=	=
Genocure DMHA	0.25	=	=	0.24
Omnirad 481	0.25	=	=	0.24
Speedcure TPO	0.25	=	=	0.24
Sartomer 833S	5.20	4.95	4.78	4.36
CN9245	2.55	2.51	2.48	2.42
BYK-UV 3510	0.10	=	=	=
NANOCRYL A210	-	0.30	0.50	1.00
DISP1	0.70	=	=	=

[0206] The solutions were subsequently coated with a spiral bar coater (from Elcometer) using an automatic film applicator (Elcometer 4340 from Elcometer) at a speed of 20mm/s on an A4 sheet of cardboard (Incada Exel HS (GC2) NI 255g/m^2 510*720mm SG 450μm) with a wet coating thickness of 10 μm. The coatings were cured with the number of passes according to Table 3 using a curing station (Aktiprint Mini 18 - 2.75cm belt, 230 V, 50 Hz from Technigraf GmbH) at a speed of 10m/min and with the lamp being at the second lowest position (second closest to the substrate).

Table 3

	S1	S2	S3	S4
Curing passes	1	2	2	2

[0207] The coatings were subsequently exposed to an infrared laser. The infrared laser was an optically pumped semiconductor laser emitting at 1064 nm (Genesis MX 1064-10000 MTM from COHERENT) with a maximum power of 4.0W, a spot size in X of 78.9 μm at $1/e^2$ and a spot size in Y of 90.6 μm at $1/e^2$. The used laser settings are represented in Table 4. The addressability is the distance between dots centre to centre and the energy density was calculated assuming no overlap according to the following formula:

$$energy\ density\ [J.cm^{-2}] = \frac{Power\ [W] \times Period[s]}{Spot\ area\ [cm^{2}]}.$$

Table 4

	P1	P2	P3
Type	Vector Graphics	Vector Graphics	Vector Graphics
Size HxL [mmxmm]	6.00 x 6.02	=	=
Resolution [dpi]	1270	=	=
Repetition Y	300	=	=
Increment Y [mm]	0.02	=	=
Addressability [mm]	/	/	/
Speed [mm/s]	800	=	=
Frequency [kHz]	40.0	=	=
Pulse length [μs]	25	=	=
Power [W]	1.55	1.89	2.25
Energy density [mJ/cm2]	689	841	1000

[0208] Table 5 displays the laser setting at which laser exposure leads to a visible magenta mark. O represents the absence of a dense visible mark with the naked eye, while X represents its presence. The laser power increases from P1 to P3.

Table 5

	S1	S2	S3	S4
P1	○	○	○	X
P2	○	X	X	X
P3	X	X	X	X

[0209] The results of Table 5 clearly indicate that a low amount of nanosilica improves the laser sensitivity of the article.

Example 2

[0210] The coating solutions S5 to S18 were prepared by mixing the ingredients according to Table 6 expressed in grams in a 30mL brown glass flasks with a plastic screw cap and stirred at 350 rpm with a magnetic stirring bar at room temperature for 3 hours.

Table 6

Ingredients (g)	S5	S6	S7	S8	S9	S10	S11
Sartomer 833S	0.40	=	=	=	0.80	=	0.15
NANOCRYL A210	-	1.00	-	1.00	-	1.00	-
MB1	-	8.00	-	8.00	-	8.00	-
MB2	9.00	-	9.00	-	9.00	-	9.00
DISP1	0.60	=	-	-	-	-	-

(continued)

Ingredients (g)	S5	S6	S7	S8	S9	S10	S11
DISP2	-	-	0.60	=	-	-	-
DISP3	-	-	-	-	0.20	=	-
DISP4	-	-	-	-	-	-	0.85
DISP5	-	-	-	-	-	-	-
	S12	**S13**	**S14**	**S15**	**S16**	**S17**	**S18**
Sartomer 833S	0.15	-	-	0.30	0.25	0.30	0.25
NANOCRYL A210	1.00	-	1.00	-	-	-	-
MB1	8.00	-	8.00	-	-	-	-
MB2	-	9.00	-	9.00	=	=	=
DISP1	-	-	-	0.70	0.75	-	-
DISP2	-	-	-	-	-	0.70	0.75
DISP3	-	-	-	-	-	-	-
DISP4	0.85	-	-	-	-	-	-
DISP5	-	1.00	=	-	-	-	-

[0211] The solutions were subsequently coated with a spiral bar coater (from Elcometer) using an automatic film applicator (Elcometer 4340 from Elcometer) at a speed of 20 mm/s on an A4 sheet of cardboard (Incada Exel HS (GC2) NI 255 g/m^2 510*720mm SG 450 µm) with a wet coating thickness of 10 µm. The coatings were cured with 1 pass using a curing station (Aktiprint Mini 18 - 2.75cm belt, 230 V, 50 Hz from Technigraf GmbH) at a speed of 10m/min and with the lamp being at the second lowest position (second closest to the substrate).

[0212] The coatings were subsequently exposed to an infrared laser. The infrared laser was an optically pumped semiconductor laser emitting at 1064 nm (Genesis MX 1064-10000 MTM from COHERENT) with a maximum power of 4.0 W, a spot size in X of 78.9 µm at 1/e^2 and a spot size in Y of 90.6 µm at 1/e^2. The used laser settings are represented in Table 7. The addressability is the distance between dots centre to centre and the energy density was calculated assuming no overlap according to the following formula:

$$energy\ density\,[J.cm^{-2}] = \frac{Power\,[W] \times Period[s]}{Spot\ area\,[cm^2]}.$$

Table 7

	P3	P4	P5	P6	P7
Type	Vector Graphics	Vector Graphics	Vector Graphics	Vector Graphics	Vector Graphics
Size [mm x mm]	6.0 x 6.02	=	=	=	=
Resolution [dpi]	1270	=	=	=	=
Repetition Y	300	=	=	=	=
Increment Y [mm]	0.02	=	=	=	=
Adressability [mm]	/	/	/	/	/
Speed [mm/s]	800	=	=	=	=
Frequency [kHz]	40.0	=	=	=	=
Pulse Length [µm]	25	=	=	=	=

(continued)

	P3	P4	P5	P6	P7
Type	Vector Graphics	Vector Graphics	Vector Graphics	Vector Graphics	Vector Graphics
Power [W]	2.25	2.54	2.81	2.99	3.29
Energy Density [mJ/cm^2]	1000	1129	1250	1331	1466
	P8	**P9**	**P10**	**P11**	
Type	Vector Graphics	Vector Graphics	Bitmap	Bitmap	
Size [mm x mm]	6.0 x 6.02	=	9.7 x 40.2	=	
Resolution [dpi]	1270	=	508	=	
Repetition Y	300	=	/	/	
Increment Y [mm]	0.02	=	/	/	
Adressability [mm]	/	/	0.05	=	
Speed [mm/s]	800	=	200	=	
Frequency [kHz]	40.0	=	4.0	=	
Pulse Length [μm]	25	15	247	=	
Power [W]	3.51	3.24	3.48	4.01	
Energy Density [mJ/cm^2]	1563	1442	15492	17865	

[0213] The reflectance spectrum of each sample was measured two times with a X-Rite™ eXact spectrophotometer in the range from 400 up to 700 nm in steps of 10 nm. The CIEL*a*b* coordinates were determined for a 2° observer and a D50 light source. The densities were measured with the density standard ANSI A. The densities Dc, Dm, Dy and Db correspond respectively to the densities in cyan, magenta, yellow and black according to the density filters of ANSI A. The density Dm was of more interest because here the laser marks are magenta. Measurements were done for both the laser marks and the areas of the coating that were not exposed to the laser (background).

Table 8

	L* background	Laser settings	Dm
S5 (COMP)	86.91	P8	0.56
S6 (INV)	86.91	P8	0.77
S7 (COMP)	85.64	P5	0.59
S8 (INV)	85.53	P5	1.01
S9 (COMP)	89.20	P11	0.25
S10 (INV)	89.53	P11	0.36
S11 (COMP)	92.55	P9	0.72
S12 (INV)	92.84	P9	0.90
S13 (COMP)	91.15	P10	0.88
S14 (INV)	91.29	P10	0.98

[0214] From the results of Table 8 it is clear that with the inventive composition comprising a nanosilica higher laser marked densities (Dm) were obtained.

[0215] Also, it is clear that in the presence of a nanosilica it is possible to realize with carbon black as optothermal converting agent comparable laser marking densities as with CTO as optothermal converting agents while keeping a relatively light background (high L* background).

[0216] The Dm of S5 and S6 in Table 8 were measured on samples that rested 5 days at room temperature in the dark.

Example 3

[0217] After resting at room temperature in the dark for 5 days, the coatings according to Table 9 were subjected to a laser exposure using the laser settings as described above.

[0218] For each sample, the a* and b* values are given at the laser setting where a maximum a* value was obtained (Table 9)

[0219] A high a* value means a higher magenta colour while a higher b* value indicates a higher contribution of yellow in the final colour. The "yellowing" is an indication that the magenta dye is altered, probably due to the heat formed in the layers.

Table 9

		a*	b*	Laser setting
S6	INV	48.01	-20.07	P7
S5	COMP	38.45	-17.77	P8
S15	COMP	43.38	-18.86	P7
S16	COMP	41.43	-18.11	P6
S8	INV	52.56	-22.31	P5
S7	COMP	42.89	-18.94	P7
S17	COMP	44.37	-19.59	P5
S18	COMP	43.15	-19.24	P4

[0220] It is clear from the results of Table 9 that the highest a* and the lowest b* values are obtained with inventive examples S6 and S8 both comprising nanosilica and carbon black as optothermal converting agent.

Example 4

[0221] After resting at room temperature in the dark for 5 days, the coatings made with S8 and S18 were subjected to a laser exposure using the laser settings as described above.

[0222] For each sample, the a* and b* values were measured for different laser parameters.

[0223] A magenta colour is characterized by a high a*.

[0224] It has been observed that the magenta colour formed during laser marking may alter ("burn") due to the heat formed during the laser exposure. The laser marked colour then changes and becomes more "yellow". Translated into b* values this means an increase of b*.

[0225] It is clear from Figure 1 and Figure 2 that the sample comprising nanosilica has a larger operational window. It reaches denser magenta (high a*) and for longer (high a* accessible at different powers) before starting to burn (decrease of a* and increase of b*).

Claims

1. A radiation curable laser markable composition comprising a polymerizable compound, a colour forming agent and an optothermal converting agent, **characterized in that** the composition further includes at least 1 wt%, relative to the total weight of the composition, of an inorganic filler.

2. The radiation curable composition according to claim 1 wherein the amount of inorganic filler is between 1 and 15 wt%, relative to the total weight of the composition.

3. The composition according to claims 1 or 2 wherein the inorganic filler is a nanosilica.

4. The composition according to claim 3 wherein the nanosilica has a particle size in the range from 5 to 250 nm.

5. The composition according to any of the preceding claims wherein the optothermal converting agent is an infrared absorbing compound.

6. The composition according to claim 5 wherein the infrared absorbing compound is a pigment.

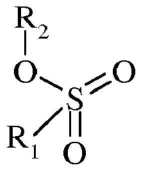
7. The composition according to claim 6 wherein the pigment is carbon black or Cesium Tungsten Oxide.

8. The composition according to any of the preceding claims wherein the polymerizable compound is selected from the group consisting of tricyclodecanedimethanol diacrylate (TCDDMDA), isobornyl acrylate (IBOA), dipropylene glycol diacrylate (DPGDA), ethoxylated [4] bisphenol diacrylate and urethane acrylate oligomer.

9. The composition according to any of the preceding claims wherein the colour forming agent is a leuco dye.

10. The composition according to claim 9 wherein the composition further comprises a developing agent.

11. The composition according to claim 10 wherein the developing agent has a chemical structure according to Formula I,



Formula I

wherein

R1 represent an optionally substituted alkyl group, an optionally substituted (hetero)cyclic alkyl group, an optionally substituted alkanyl group, an optionally substituted alkenyl group, an optionally substituted alkynyl group, an optionally substituted (hetero)aryl group, an optionally substituted aralkyl group, an optionally substituted alkoxy group, an optionally substituted (hetero)cyclic alkoxy group, or an optionally substituted (hetero)aryl group;
R2 represent an optionally substituted alkyl, an optionally substituted aliphatic (hetero)cyclic alkyl group or an optionally substituted aralkyl group;
R1 and R2 may represent the necessary atoms to form a ring.

12. A laser markable article comprising a laser markable composition as defined in any of the preceding claims provided on a support.

13. A method of preparing the laser marked article as defined in claim 12 comprising the step of providing a laser markable composition as defined in any of the claims 1 to 11 on a support.

14. The method according to claim 13 further comprising a curing step.

15. A method of laser marking comprising the step of exposing the laser markable article as defined in claim 12 with an infrared laser.

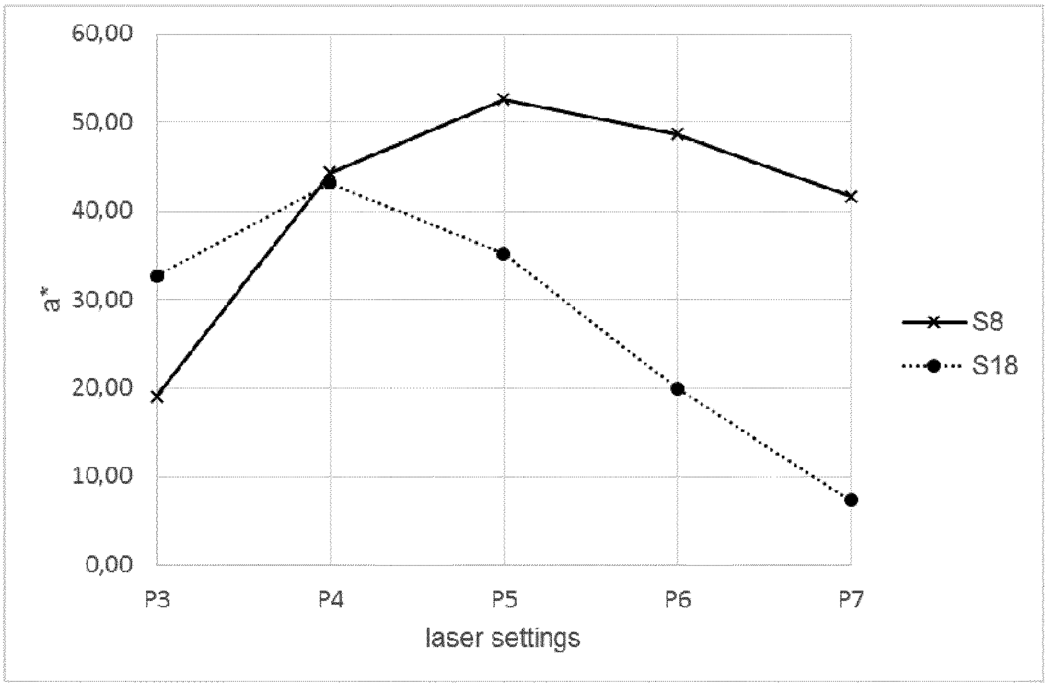


Figure 1a

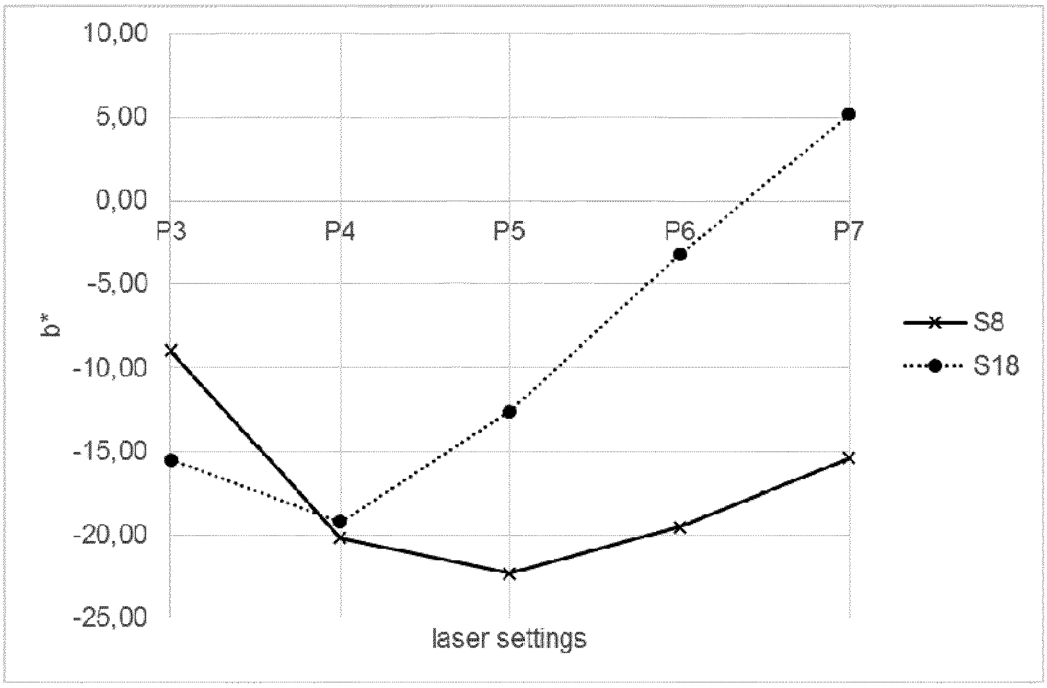


Figure 1b

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 19 20 2712

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 0 716 135 A1 (NIPPON KAYAKU KK [JP]) 12 June 1996 (1996-06-12)	1,5-15	INV. B41M5/323 B41M5/337 B41M5/46
A	* page 2, line 42 - page 9, line 31; claims 1-18 * -----	3,4	
X	WO 2016/135468 A1 (DATALASE LTD [GB]) 1 September 2016 (2016-09-01)	1,2,9, 10,12, 13,15	ADD. B41M5/333
A	* page 1, line 16 - page 17, last line * -----	3,4,8, 11,14	

TECHNICAL FIELDS SEARCHED (IPC)
B41M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	15 April 2020	Patosuo, Susanna

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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....
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 19 20 2712

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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15-04-2020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0716135 A1	12-06-1996	CN 1129458 A	21-08-1996
		DE 69420971 D1	04-11-1999
		DE 69420971 T2	06-04-2000
		EP 0716135 A1	12-06-1996
		ES 2136737 T3	01-12-1999
		JP H082106 A	09-01-1996
		KR 960703993 A	31-08-1996
		US 5824715 A	20-10-1998
		WO 9600262 A1	04-01-1996
WO 2016135468 A1	01-09-2016	CN 107429091 A	01-12-2017
		EP 3262126 A1	03-01-2018
		JP 2018511692 A	26-04-2018
		US 2018030289 A1	01-02-2018
		WO 2016135468 A1	01-09-2016

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2005068207 A **[0010] [0062]**
- WO 2007141522 A **[0010] [0063]**
- WO 2015015200 A **[0010] [0064]**
- WO 2014057018 A **[0012] [0162]**
- WO 2016184881 A **[0014]**
- WO 2008075101 A **[0047]**
- WO 2002074548 A **[0048]**
- WO 2007012578 A **[0048]**
- WO 2013014436 A **[0050]**
- WO 2013068729 A **[0052]**
- WO 2015165854 A **[0054] [0082]**
- WO 2009059900 A **[0064]**
- EP 3297838 A **[0079]**
- EP 2722367 A **[0082]**
- WO 2019007833 A **[0085] [0190]**
- EP 1911814 A **[0092]**
- WO 2015091688 A **[0101]**
- EP 2719540 A **[0155]**
- EP 2719541 A **[0155]**
- WO 2015091782 A **[0158]**
- WO 2012044400 A **[0171]**

Non-patent literature cited in the description

- *Near-Infrared Dyes for High Technology Applications,* ISBN 978-0-7923-5101-6 **[0080]**
- *CHEMICAL ABSTRACTS,* 223717-84-8 **[0083]**
- Encyclopaedia of polymer science. Wiley **[0098]**
- Industrial Photoinitiators, A Technical Guide. CRC Press, 2010 **[0098]**
- **CRIVELLO, J.V. et al.** Photoinitiators for Free Radical Cationic & Anionic Photopolymerization. John Wiley and Sons Ltd, 1998, vol. III, 287-294 **[0107]**
- *CHEMICAL ABSTRACTS,* 953-91-3 **[0176]**