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(54) **LASER MARKABLE ARTICLES**

(57) A laser markable article (1) comprising a laser markable layer including a colour forming agent (20) and a layer adjacent to the laser markable layer including an optothermal converting agent (30).

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Description**Technical field of the Invention**

5 **[0001]** The present invention relates to laser markable articles and to methods of preparing such laser markable articles.

Background art for the invention

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

15 **[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.

20 **[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] Typically, a laser markable composition includes a so-called optothermal converting agent that converts radiation energy into heat and a colour forming agent.

[0008] In most cases infrared radiation is used for laser marking.

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

30 **[0012]** A laser markable composition includes a colour forming agent that forms a colour upon laser marking. Several colour forming agents are proposed.

[0013] A transition metal oxide, such as molybdenum trioxide, has been disclosed in WO2008/075101 (Siltech).

[0014] An oxyanion of a multivalent metal, such as ammonium octyl molybdate, has been disclosed in WO2002/074548 and WO2007/012578 (both from Datalase).

35 **[0015]** These colour forming agents are capable of forming a black colour upon laser marking.

[0016] Diacetylene compounds, such as disclosed in WO2013/014436 (Datalase) are capable of forming multiple colours.

[0017] Leuco dyes are disclosed in for example WO2015/165854 (Agfa Gevaert).

[0018] Advantages of leuco dyes are a superior colour gamut that may be achieved by selecting the proper dyes.

40 **[0019]** A disadvantage of leuco dyes may be a limited stability of the dyes formed upon laser marking. It has been observed that different colours may be obtained due to alteration, for example decomposition, of the formed dyes due to the heat generated during laser marking. This may result in a limited operational window of the laser marking parameters, for example laser power, that can be used in the laser marking process.

45 **[0020]** There is thus a need for laser markable article comprising leuco dyes as colour forming agents that has an improved colour stability.

Summary of the invention

50 **[0021]** It is an object of the present invention to provide a laser markable article that combines superior colour gamut with sufficient temperature stability.

[0022] This object has been realised by the laser markable article as defined in claim 1.

[0023] Further objects of the invention will become apparent from the description hereinafter.

Brief description of drawings

55 **[0024]** Figure 1 illustrates an embodiment of a laser markable article according to the present invention. In Figure 1a, a laser markable layer covers the whole surface of a support (10) while in Figure 1b the laser markable layer (20) covers part of the surface of the support (10).

Detailed description of the invention**Definitions**

- 5 **[0025]** 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.
- [0026]** Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C₁ to C₆-alkyl group.
- [0027]** Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C₂ to C₆-alkenyl group.
- 10 **[0028]** Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C₂ to C₆-alkynyl group.
- [0029]** Unless otherwise specified a substituted or unsubstituted aralkyl group is preferably a phenyl or naphthyl group including one, two, three or more C₁ to C₆-alkyl groups.
- [0030]** Unless otherwise specified a substituted or unsubstituted alkaryl group is preferably a C₇ to C₂₀-alkyl group including a phenyl group or naphthyl group.
- 15 **[0031]** Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group
- [0032]** 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.
- 20 **[0033]** 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
- [0034]** 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
- 25 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 -NO₂.

The laser markable article

- 30 **[0035]** The laser markable article according to the present invention comprises a laser markable layer (20) including a colour forming agent and a layer adjacent to the laser markable layer including an optothermal converting agent (30).
- [0036]** Both layers referred to above are preferably contiguous to each other.
- [0037]** In a preferred laser markable article, both layers are applied on a support (10).
- 35 **[0038]** In a preferred laser markable article, the layer including the optothermal converting agent (30) is provided on top of the laser markable layer including the colour forming agent (20), as depicted in Figure 1.
- [0039]** A layer referred to herein may cover the whole surface of the support, as depicted in Figure 1. However, the layer may also cover a part of the surface of the support as depicted in Figure 2.
- [0040]** The layers referred to are prepared by applying a laser markable composition including a colour forming agent and a composition including an optothermal converting agent on a support, as described below.
- 40 **[0041]** Both compositions may be aqueous compositions or solvent based compositions.
- [0042]** The compositions may be radiation curable, preferably UV curable.
- [0043]** A preferred laser markable composition comprises a developing agent.
- [0044]** The laser markable composition including a colour forming agent and/or the composition including the optothermal converting agent are preferably radiation curable compositions, more preferably UV curable compositions.
- 45 **[0045]** To optimize the coating or printing properties, and also depending on the application for which it is used, various additives may be added to both compositions, such as surfactants, wetting/levelling agents, colorants, rheology modifiers, adhesion promoting compounds, biocides or antioxidants.

Laser markable composition

- [0046]** The laser markable composition includes a colour forming agent.
- [0047]** A preferred laser markable composition includes a leuco dye and a developing agent.
- [0048]** The laser markable composition may be aqueous or non-aqueous, the latter also referred to herein as solvent
- 55 based.
- [0049]** A preferred aqueous based composition includes encapsulated leuco dyes. Such aqueous compositions wherein the leuco dyes are encapsulated are disclosed in for example EP-A 3297837, EP-A 3470134 and EP-A 3470135, all from Agfa Gevaert.

[0050] The aqueous based composition may be radiation curable, preferably UV curable. Such radiation curable aqueous composition are disclosed in EP-A 18196206.9 and EP-A 18196211.9 (both from Agfa Gevaert and filed on 24-09-2018).

[0051] Non-aqueous laser markable compositions are disclosed in for example EP-A 3083261 (Agfa Gevaert).

[0052] The non-aqueous laser markable composition are preferably radiation curable, more preferably UV curable. Such radiation curable compositions preferably comprise a polymerizable compound and optionally a photoinitiator and a polymerization inhibitor.

Composition including an optothermal converting agent

[0053] The composition including an optothermal converting agent may be aqueous or non-aqueous, the latter also referred to herein as solvent based.

[0054] A preferred aqueous based composition includes an encapsulated optothermal converting agent. Especially the infrared radiation absorbing dyes described below are preferably encapsulated in an aqueous composition.

[0055] Such aqueous compositions wherein the optothermal converting agents are encapsulated are disclosed in for example EP-A 3297837 and EP-A 3470134.

[0056] The non-aqueous compositions including an optothermal converting agent are preferably radiation curable, more preferably UV curable. Such radiation curable compositions preferably comprise a polymerizable compound and optionally a photoinitiator and a polymerization inhibitor.

[0057] Preferably, both composition, i.e. the laser markable composition and the composition including the optothermal converting agent are radiation curable, more preferably UV curable. In this case, it is preferred that both solutions comprise the same polymerizable compounds and photoinitiators.

Colour forming agent

[0058] The laser markable composition comprises a colour forming agent, which is capable of forming a colour upon laser marking.

[0059] All known colour forming agents may be used.

[0060] A transition metal oxide, such as molybdenum trioxide, has been disclosed in WO2008/075101 (Siltech).

[0061] An oxyanion of a multivalent metal, such as ammonium octyl molybdate, has been disclosed in WO2002/074548 (Datalase) and WO2007/012578 (Datalase).

[0062] These colour forming agents are capable of forming a black colour upon laser marking.

[0063] Diacetylene compounds, such as disclosed in WO2013/014436 (Datalase) are capable of forming multiple colours.

[0064] Preferred colour formers are leuco dyes, as described below. A leuco dye is preferably used in combination with a developing agent.

[0065] 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

[0066] 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.

[0067] Examples of leuco dyes are disclosed in WO2015/165854 (AGFA GEVAERT), paragraph [069] to [093].

[0068] 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.

[0069] The amount of leuco dye in the laser markable layer is preferably in the range from 0.05 to 2 g/m², more preferably in the range from 0.1 to 1 g/m².

Developing agent

[0070] The laser markable composition preferably comprises a developing agent.

[0071] 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.

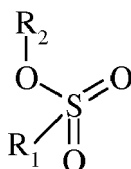
[0072] All publicly-known photo- or thermal acid generators can be used as developing agent. Thermal acid generators

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.

[0073] 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.

[0074] Preferred developing agents for aqueous laser markable compositions are disclosed in EP-A 3470134, paragraph [0142] to [0149]. A particular preferred developing agent is a metal salt of salicylic acid, for example zinc salicylate. A particularly preferred colour developing agent is zinc 3,5-bis(α -methylbenzyl) salicylate.

[0075] For non-aqueous laser markable compositions, and in particular for radiation curable non-aqueous laser markable compositions, a preferred developing agents has 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.

[0076] Such developing agents according to Formula I and their preparation is disclosed in WO2015/091688.

[0077] The amount of developing agent in the laser markable layer is preferably in the range from 0.05 to 5 g/m², more preferably in the range from 0.1 to 3 g/m².

Optothermal converting agent

[0078] An optothermal converting agent generates heat upon absorption of radiation.

[0079] The optothermal converting agent preferably generates heat upon absorption of infrared (IR) radiation, more preferably near infrared (NIR) radiation.

[0080] Near infrared radiation has a wavelength between 750 and 2500 nm.

[0081] 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

[0082] A preferred inorganic infrared absorber is a copper salt as disclosed in WO2005/068207 (Datalase).

[0083] Another preferred inorganic infrared absorber is a non-stoichiometric metal salt, such as reduced indium tin oxide as disclosed in WO2007/141522 (Datalase).

[0084] 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

[0085] Another preferred infrared radiation absorbing pigment (IR pigment) is carbon black, such as acetylene black, channel black, furnace black, lamp black, and thermal black.

[0086] 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 layer comprising the carbon black.

[0087] For that reason, the amount of carbon black in the laser markable layer is preferably less than 0.1 g/m², more preferably less than 0.01 g/m², most preferably less than 0.005 g/m².

Infrared radiation absorbing dyes

[0088] 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.

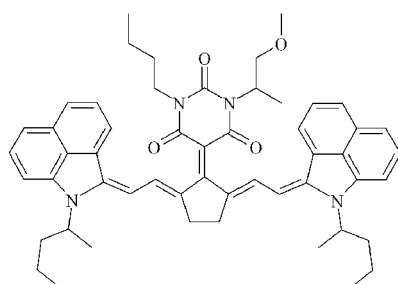
[0089] A narrow absorption band is also mandatory for multicolour laser marking using multiple laser each having a different emission wavelength, as disclosed in for example EP-A 3297838.

[0090] 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).

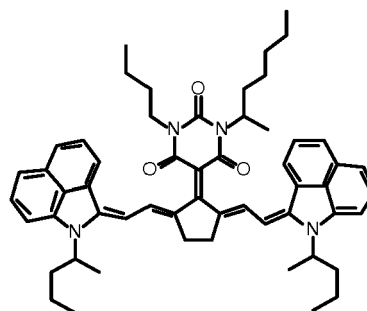
[0091] Preferred IR dyes are polymethine dyes due to their low absorption in the visible region and their selectivity, i.e. narrow absorption peak in the infrared region. Particular preferred polymethine IR dyes are cyanine IR dyes.

[0092] 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].

[0093] 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-methyl-ethyl)-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

[0094] Both IR dyes IR-1 and IR-2 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.

[0095] 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.

[0096] A combination of different optothermal converting agents may also be used.

[0097] The amount of optothermal converting agent is preferably at least 10⁻¹⁰ g/m², more preferably between 0.0001 and 0.5 g/m², most preferably between 0.0005 and 0.1 g/m².

Polymerizable compound

[0098] The laser markable composition including the color forming agent and/or the composition including the optothermal converting agent may be radiation curable compositions, preferably UV curable compositions.

[0099] Such radiation curable compositions comprise a polymerizable compound.

[0100] The polymerizable compounds may be monomers, oligomers or prepolymers.

[0101] The polymerizable compounds may be free radical polymerizable compounds or cationic polymerizable compounds.

[0102] 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.

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

[0104] 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 mon-

omers, oligomers or prepolymers. Due to their higher reactivity, particularly preferred polymerizable compounds are acrylate monomers, oligomers or prepolymers.

[0105] Other preferred (meth)acrylate monomers, oligomers or prepolymers are N-vinylamides, such as N-vinylcaprolactam and acryloylmorpholine.

[0106] Particular 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.

Photoinitiator

[0107] 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.

[0108] 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.

[0109] A preferred Norrish type II-initiator is selected from the group consisting of benzophenones, thioxanthenes, 1,2-diketones and anthraquinones.

[0110] 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 .

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

[0113] 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.

[0114] The most preferred co-initiators are aminobenzoates for reason of shelf-life stability of the radiation curable composition.

[0115] 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.

[0116] 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

[0117] For improving the shelf-life, the radiation curable compositions 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.

[0118] 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.

[0119] 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

[0120] The radiation curable laser markable compositions 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.

[0121] Preferred surfactants are selected from fluoro surfactants (such as fluorinated hydrocarbons) and/or silicone surfactants.

[0122] 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.

[0123] Silicone surfactants are often preferred in 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.

[0124] 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 polysiloxane hexaacrylate from CYTEC INDUSTRIES BV and Efka™-3000 series (including Efka™-3232 and Efka™-3883) from EFKA CHEMICALS B.V..

Inorganic filler

[0125] The laser markable composition preferably comprises at least 1 wt% of an inorganic filler, relative to the total weight of the composition.

[0126] Examples of inorganic fillers that may be used are selected from the group consisting of calciumcarbonate, clays, alumina trihydrate, talc, mica, and calcium sulphate.

[0127] Preferably, an inorganic nanofiller is used to obtain optimal transparency of the laser markable composition. A preferred nanofiller is nanosilica.

[0128] Nanosilica as referred to herein consist of amorphous silicon dioxide particles having a nano-particle size.

[0129] 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.

[0130] Preferably dispersions of nanosilica in acrylate monomers are used. Such commercially available dispersions are for example the Nanocryl® nanosilica dispersions available from Evonik.

[0131] 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.

[0132] After printing the composition on a support, the amount of the inorganic filler is preferably in the range from 0.1 to 1.5 g/m², more preferably in the range from 0.2 to 1 g/m², most preferably in the range from 0.25 to 0.75 g/m².

Method of preparing a laser markable article

[0133] The method of preparing a laser markable article comprises the steps of applying the laser markable composition including a colour forming agent and the composition including an optothermal converting agent both as described above, on a support (10).

[0134] Both compositions may be applied in any order on the substrate. However, according to a preferred embodiment, the method comprises the steps of, in order:

- applying a laser markable composition including a colour forming agent on a support (10) thereby forming a laser markable layer (20);
- applying a composition including the optothermal converting agent on the laser markable layer thereby forming an adjacent layer including the optothermal converting agent (30).

[0135] Both 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.

[0136] 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, 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.

[0137] The compositions are preferably applied by flexographic printing or inkjet printing.

[0138] The thickness of the applied compositions is preferably 50 μm or less, more preferably 20 μm or less, most preferably 10 μm or less.

[0139] When radiation curable composition are used, the method further comprises a curing step, preferably a UV curing step.

[0140] A curing step may be carried out after the application of each composition or may be carried out after the application of both compositions.

Support

[0141] The compositions may be applied on any type of surface, 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.

[0142] The support may be provided with a primer to improve the adhesion between the support and the applied layers.

[0143] 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.

[0144] The support may be a paper support, such as plain paper or resin coated paper, e.g. polyethylene or polypropylene coated paper.

[0145] 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.

[0146] 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.

[0147] 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.

[0148] 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.

[0149] 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.

[0150] Another preferred polymeric support includes (co)polyesters based on cyclohexyldimethanol (CHDM).

[0151] 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.

[0152] 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.

[0153] Other polymeric supports include copolyesters based on isosorbide, e.g. copolymers of terephthalic acid and ethylene glycol and isosorbide.

[0154] The polymeric support may be a single component extrudate or co-extrudate. Examples of suitable co-extrudates are PET/PETG and PET/PC.

[0155] 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.

[0156] 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.

[0157] 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.

[0158] The most commonly used shrink foils are polyolefin foils, i.e. polyethylene or polypropylene foils. However, other shrink foils include PCV.

Laser marked article

[0159] The laser markable article is prepared by the method described above.

[0160] 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

[0161] The laser marking method according to the present invention is preferably used to laser mark a packaging.

[0162] Laser marking is typically used to add variable data, for example batch numbers, expiry dates, addressees, etc. on the packaging.

[0163] Preferably laser marking is carried out in-line in the packaging process.

[0164] The laser marked "image" on a packaging may comprises data, images, barcodes, QR codes, or a combination thereof.

[0165] 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.

[0166] 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.

[0167] 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.

[0168] By selecting a proper leuco dye, or a mixture of leuco dyes, the package may be provided with data or images in any colour.

[0169] A preferred packaging is folded cardboard or corrugated cardboard laminated with paper. Such packaging is preferably used for cosmetics, pharmaceuticals, food or electronics.

[0170] 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

[0171] The laser marking method may also be used to prepare security documents, such as for example ID cards.

[0172] 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.

[0173] Such laser markable security documents and their preparation have been disclosed in for example WO2015/091782 (Agfa Gevaert).

[0174] 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.

[0175] 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.

[0176] The laser markable laminate is typically laminated on one or both sides of a core support using elevated temperatures and pressures.

[0177] Preferred core supports are disclosed in WO2014/057018 (Agfa Gevaert), paragraphs [0112] to [0015].

[0178] 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

[0179] 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.

[0180] The infrared laser may be a continuous wave or a pulsed laser.

[0181] 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.

[0182] 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.

[0183] 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.

[0184] Laser marking may also be carried out using a so-called Spatial Light Modulator (SLM) as disclosed in WO2012/044400 (Vardex Laser Solutions).

Curing

[0185] The radiation curable laser markable composition can be cured by exposing them to actinic radiation, such as electron beam or ultraviolet radiation.

[0186] Preferably, the radiation curable laser markable composition is cured by exposing it to ultraviolet radiation,

more preferably using UV LED curing.

EXAMPLES

MATERIALS

[0187] 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.

[0188] **WR** is an abbreviation used for WinCon-Red, a magenta leuco dye from Connect Chemicals GmbH.

[0189] **CpTs** is an abbreviation for cyclohexyl p-toluenesulfonate with the CAS number 953-91-3 from Chemgo.

[0190] **Genocure DMHA** is a photoinitiator from RAHN AG.

[0191] **Omnirad 481** is a photoinitiator from IGM Resins b.v.

[0192] **Speedcure TPO** is a photoinitiator from Lambson Limited.

[0193] **Photomer 4012** is isobornyl acrylate (IBOA), a monofunctional acrylic monomer from IGM.

[0194] **Sartomer 508** is dipropylene glycol diacrylate, a difunctional acrylic monomer from Arkema.

[0195] **Sartomer 601E** is ethoxylated [4] bisphenol diacrylate, a difunctional acrylic monomer from Arkema.

[0196] **BYK-UV 3510** is a surface additive from BYK-Chemie GmbH.

[0197] **CTO** is an inorganic pigment of cesium tungsten oxide from Keeling & Walker Limited.

[0198] **Cupferron AL** is aluminum N-nitrosophenylhydroxylamine from WAKO CHEMICALS LTD.

[0199] **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

[0200] **EFKA PX4733** is a high-molecular-weight dispersant from BASF SE.

[0201] **DISP1** 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] **OPV** is a concentrated solution prepared as follow: 1.00g of DISP1 and 9.00g of Sartomer 601E were added into a 30mL brown glass container with a plastic screw cap and stirred at 250rpm with a magnetic stirring bar at room temperature for 3 hours.

Example 1

[0203] The solutions S1 to S3 were prepared by mixing the ingredients according to Table 2 expressed in grams. The solutions were mixed in 30mL brown glass flasks with a plastic screw cap and stirred at 350 rpm with a magnetic stirring bar at room temperature overnight.

Table 2

Ingredients (g)	S1	S2	S3
WR	0.25	-	0.25
CpTs	0.44	-	0.44
Genocure DMHA	0.26	0.29	0.26
Omnirad 481	0.26	0.29	0.26

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(continued)

Ingredients (g)	S1	S2	S3
Speedcure TPO	0.26	0.29	0.26
Sartomer 601E	6.92	7.53	8.42
BYK-UV 3510	0.10	0.10	0.10
OPV	1.50	1.50	-

[0204] 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 255 g/m² 510 * 720 mm SG 450 µm) with a wet coating thickness of 10 µm. Each layer was cured right after being applied with 1 pass using a curing station (Aktiprint Mini 18 - 2.75 cm belt, 230 V, 50 Hz from Technigraf GmbH) at a speed of 22 m/min and with the lamp being at the second lowest position (second closest to the substrate).

[0205] The layer build-up can be seen in Table 3.

Table 3

	C1	I1	I2
First layer applied	S1	S2	S3
Second layer applied	-	S3	S2

[0206] Sample C1 was prepared by applying a single layer on the substrate, whereas samples I1 and I2 were prepared by applying two layers. The first layer was cured before applying the second one. The first layer is touching the substrate, whereas the second layer is above the first one and therefore in contact with air.

[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 4.0 W, a spot size in X of 78.9 µm at 1/e² and a spot size in Y of 90.6 µm at 1/e². The used laser settings are depicted 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:

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

Table 4

Type	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]	2.54
Energy density [mJ/cm ²]	1129

[0208] 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 CIE L*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 D_c, D_m, D_y and D_b correspond respectively to the densities in cyan, magenta, yellow and black according to the density filters of ANSI A. The density D_m was of more interest because here the laser marks are magenta. Measurements were done for both

[0209] The colour of the laser marks was measured for samples for which the optothermal converting agent is at different places. Their a* and b* values were measured. The higher the a*, the more magenta the colour. The lower the a*, the greener the colour. The higher the b*, the more yellow the colour. The lower the b*, the bluer the colour.

[0210] 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*.

[0211] Looking at the colour measurements in Table 5, it becomes evident that when the optothermal converting agent is in an adjacent layer no "burning" appears (b* values are lower).

Table 5

Sample	C1	I1	I2
a*	34.69	55.62	57,98
b*	-9.32	-27,12	-27,53

[0212] During laser marking, smoke was sometimes detected, probably the result of decomposition of ingredients from the laser markable layer. The presence or absence and the colour of the smoke are shown in Table 6.

[0213] In addition, the sensitivity of the samples towards laser marking was assessed by measuring the D_m (see above). These values are also shown in Table 6.

Table 6

Sample	C1	I1	I2
Smoke	A lot	A bit	A bit
Color of the smoke	Magenta	Magenta	White
D _m	0.57	0.85	0.91

[0214] The results of Table 6 clearly indicate that when optothermal converting agent is in an adjacent layer, less smoke is produced, possibly increasing the colour density of the laser mark (D_m).

[0215] Also, when the optothermal converting agent is in the top layer, the colour does not seem to sublime (white smoke), possibly further increasing the colour density (D_m).

Claims

1. A laser markable article (1) comprising a laser markable layer including a colour forming agent (20) and a layer adjacent to the laser markable layer including an optothermal converting agent (30).
2. The laser markable article according to claim 1 wherein the laser markable layer including the colour forming agent (20) and the layer including the optothermal converting agent (30) are provided on a support (10).
3. The laser markable article according to claim 2 wherein the adjacent layer (30) is provided on top of the laser markable layer (20).
4. The laser markable article according to any of the preceding claims wherein the colour forming agent is a leuco dye.
5. The laser markable article according to claim 4 wherein the laser markable layer further includes a developing agent.
6. The laser markable article according to any of the preceding claims wherein the optothermal converting agent is an infrared absorbing compound.

7. The laser markable article according to claim 6 wherein the infrared absorbing compound is a pigment.
8. The laser markable article according to claim 7 wherein the pigment is selected from carbon black, a copper salt, reduced indium tin oxide or cesium tungsten oxide.
9. A method of preparing the laser markable article (1) as defined in any of the preceding claims comprising the step of applying a laser markable composition including a colour forming agent and a composition including an optothermal converting agent on a support (10).
10. The method according to claim 9 wherein the laser markable composition including a colour forming agent and the composition including an optothermal converting agent are provided on the support by flexographic printing.
11. The method according to claim 9 or 10 comprising the steps of, in order:
- applying a laser markable composition including a colour forming agent on a support (10) thereby forming a laser markable layer (20);
 - applying a composition including an optothermal converting agent on the laser markable layer thereby forming a layer including an optothermal converting agent (30).
12. The method according to any of the claims 9 to 11 wherein at least one of the laser markable composition including the colour forming agent and the composition including the optothermal converting agent are radiation curable.
13. The method according to claim 12 further comprising a curing step.
14. The method according to claim 13 wherein a curing step is carried out after the application of each composition.
15. A method of laser marking comprising the step of exposing a laser markable article as defined in any of the claims 1 to 8 with an infrared laser.

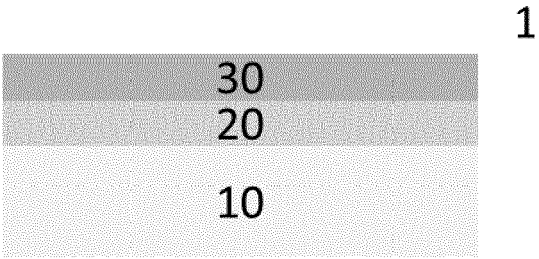


Figure 1a

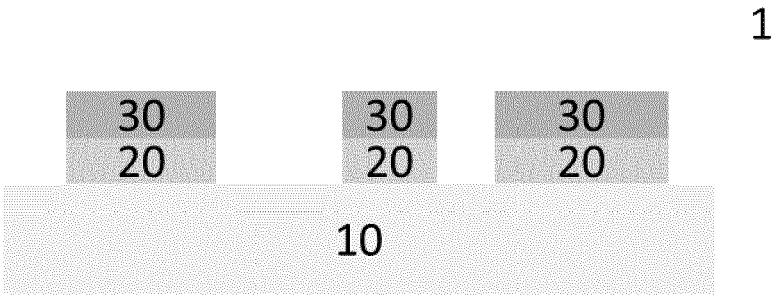


Figure 1b



EUROPEAN SEARCH REPORT

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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 3 118 007 A1 (RICOH CO LTD [JP]) 18 January 2017 (2017-01-18) * paragraph [0123] - paragraphs [0178], [0181]; figures 4A, 4B, 5 *	1-15	INV. B41M5/323 B41M5/46
X	EP 1 923 226 A2 (LINTEC CORP [JP]) 21 May 2008 (2008-05-21) * paragraph [0005] - paragraph [0106]; figure 1 *	1-15	ADD. B41M5/333
			TECHNICAL FIELDS SEARCHED (IPC)
			B41M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 9 April 2020	Examiner Patosuo, Susanna
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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ON EUROPEAN PATENT APPLICATION NO.**

EP 19 20 2694

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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09-04-2020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3118007 A1	18-01-2017	CN 106232369 A	14-12-2016
		EP 3118007 A1	18-01-2017
		JP 6264446 B2	24-01-2018
		JP WO2015137310 A1	06-04-2017
		US 2018009234 A1	11-01-2018
		WO 2015137310 A1	17-09-2015

EP 1923226 A2	21-05-2008	CN 101239545 A	13-08-2008
		EP 1923226 A2	21-05-2008
		JP 2008146030 A	26-06-2008
		US 2008113863 A1	15-05-2008

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2005068207 A [0010] [0082]
- WO 2007141522 A [0010] [0083]
- WO 2015015200 A [0010] [0084]
- WO 2014057018 A [0011] [0177]
- WO 2008075101 A [0013] [0060]
- WO 2002074548 A [0014] [0061]
- WO 2007012578 A [0014] [0061]
- WO 2013014436 A [0016] [0063]
- WO 2015165854 A [0017] [0067] [0092]
- EP 3297837 A [0049] [0055]
- EP 3470134 A [0049] [0055] [0074]
- EP 3470135 A [0049]
- EP 18196206 A [0050]
- EP 18196211 A [0050]
- EP 3083261 A [0051]
- WO 2013068729 A [0065]
- WO 2015091688 A [0076]
- WO 2009059900 A [0084]
- EP 3297838 A [0089]
- EP 2722367 A [0092]
- WO 2019007833 A [0095]
- EP 1911814 A [0103]
- GB 811066 A [0149]
- EP 2719540 A [0170]
- EP 2719541 A [0170]
- WO 2015091782 A [0173]
- WO 2012044400 A [0184]

Non-patent literature cited in the description

- Encyclopaedia of polymer science. Wiley [0072]
- Industrial Photoinitiators, A Technical Guide. CRC Press, 2010 [0072]
- *Near-Infrared Dyes for High Technology Applications*, ISBN 978-0-7923-5101-6 [0090]
- *CHEMICAL ABSTRACTS*, 223717-84-8 [0093]
- **CRIVELLO, J.V. et al.** Photoinitiators for Free Radical Cationic & Anionic Photopolymerization. John Wiley and Sons Ltd, 1998, vol. III, 287-294 [0110]