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

(11) EP 3 626 472 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.03.2020 Bulletin 2020/13

(51) Int Cl.:
B41M 5/323 *(2006.01)* ***B41M 5/337*** *(2006.01)*

(21) Application number: **18196211.9**

(22) Date of filing: **24.09.2018**

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

(71) Applicants:
- **AGFA NV**
  2640 Mortsel (BE)
- **AGFA-GEVAERT NV**
  2640 Mortsel (BE)

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

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

(54) LASER MARKABLE COMPOSITIONS

(57) An aqueous radiation curable laser markable composition comprising a polymerizable compound, a photoinitiator, a colourforming agent and an optional optothermal converting agent, characterized in that the photoinitiator has a Molecular Weight of at least 250.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical field of the Invention

[0001] The present invention relates to laser markable compositions and to methods of laser marking using those compositions.

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, 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 the 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 spraying or coating technique.

[0007] WO2006/067073(DATALASE) disclose a solvent-based laser markable composition comprising a metal salt of a carboxylic acid, a binder and a solvent.

[0008] WO2013/192307(SUN CHEMICAL CORP) discloses a master batch for laser markable solvent-based inks.

[0009] EP-A 2349734 (DATALASE) discloses an aqueous composition comprising a colourformer, a developer and a binder wherein the binder is an acrylate binder and the colourformer and/or developer are in an un-encapsulated form.

[0010] WO2016/039960 (SUN CHEMICAL CORP) discloses a master batch for laser markable aqueous inks.

[0011] EP-A 3095825 (AGFA GEVAERT) discloses an aqueous laser markable inkjet ink comprising an immobilized leuco dye. The leuco dyes are encapsulated or covalently bonded to polymeric particles.

[0012] EP-A 3173249 (AGFA GEVAERT) discloses a method of manufacturing a packaging wherein a laser markable composition is applied, for example by flexographic or inkjet printing, on at least part of the packaging. The laser markable compostion is an aqueous or UV curable composition.

[0013] A disadvantage of solvent-based laser markable inks, especially while printing, are their health and safety risks.

[0014] A disadvantage of aqueous based laser markable inks are often their inferior mechanical properties, such as water-resistance and poor adhesion towards various substrates.

[0015] It has been observed that a disadvantage of UV curable laser markable inks may be the stability of the opto-thermal converting agents during UV curing.

Summary of the invention

[0016] It is an object of the present invention to provide a laser markable composition having minimal health and safety risks wherewith coatings/images having improved physical properties such as stability, water-resistance and adhesion towards various substrates may be obtained.

[0017] This object has been realised by the laser markable composition as defined in claim 1.

[0018] Further objects of the invention will become apparent from the description hereinafter.

Detailed description of the invention

Definitions

[0019] 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.

[0020] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C_1 to C_6-alkyl group.

[0021] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C_2 to C_6-alkenyl group.

[0022] Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C_2 to C_6-alkynyl group.

[0023] 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.

[0024] 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.

[0025] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group

[0026] 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.

[0027] 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

[0028] 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 aqueous radiation curable laser markable composition

[0029] The aqueous radiation curable laser markable composition according to the present invention comprises a polymerizable compound, a photoinitiator, a colour forming agent and an optional optothermal converting agent, characterized in that the photoinitiator has a Molecular Weight of at least 250, preferably at least 500, more preferably at least 750.

[0030] A preferred aqueous radiation curable laser markable composition comprises a leuco dye as colour forming agent and further a developing agent.

[0031] A particular preferred composition also comprises an optothermal converting agent.

[0032] An aqueous composition as used herein means a composition wherein the amount of water is at least 50 wt%, preferably at least 65 wt%, more preferably at least 75 wt%, relative to the total weight of all solvents of the composition.

[0033] The water content of the aqueous radiation curable laser markable composition is preferably less than 60 wt%, more preferably less than 30 wt%, most preferably less than 10 wt%, relative to the total weight of the composition. A too high amount of water may result in lower laser marked densities on the printed compositions.

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

[0035] The aqueous 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, adhesion promoting compounds, biocides or antioxidants may be added to the aqueous radiation curable laser markable composition.

Colour forming agent

[0037] The aqueous radiation curable laser markable composition comprises a colour forming agent, which is capable of forming a colour upon laser marking.

[0038] All known colour forming agents may be used.

[0039] A transition metal oxide, such as molybdenum trioxide, has been disclosed in WO2008/075101 (SILTECH).

[0040] An oxyanion of a multivalent metal, such as ammonium octyl molybdate, has been disclosed in WO2002/074548 (DATALASE) and WO2007/012578 (DATALASE).

[0041] These colour forming agents are capable of forming a black colour upon laser marking.

[0042] Diacetylene compounds, such as disclosed in WO2013/014436 (DATALASE) are capable of forming multiple colours.

[0043] Preferred colour formers are leuco dyes, as described below. A leuco dye is preferably used in combination with a developing agent.

[0044] 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

[0045] A leuco dye is a substantially colourless compound, which may form a coloured dye upon an inter- or intramolecular reaction. The inter- or intra-molecular reaction may be triggered by heat, preferably heat formed during exposure with an IR laser.

[0046] Examples of leuco dyes are disclosed in WO2015/165854 (AGFA GEVAERT), paragraph [069] to [093].

[0047] 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.

[0048] The leuco dyes are preferably encapsulated, such as disclosed in for example EP-A 3297837.

Optothermal converting agent

[0049] An optothermal converting agent generates heat upon absorption of radiation.

[0050] The optothermal converting agent preferably generates heat upon absorption of infrared (IR) radiation, more preferably near infrared (NIR) radiation.

[0051] Near infrared radiation has a wavelength between 750 and 2500 nm.

[0052] Optothermal converting agents may be an infrared radiation absorbing dye, an infrared radiation absorbing pigment, or a combination thereof.

Infrared radiation absorbing inorganic pigments

[0053] A preferred infrared radiation absorbing pigment (IR pigment) is carbon black, such as acetylene black, channel black, furnace black, lamp black, and thermal black.

[0054] Aqueous dispersions of carbon black are preferably used in the present invention. Examples of such aqueous carbon black dispersions are CAB-O-JET® 200 and 300 from CABOT or the DERUSSOL® carbon black pigment dispersions from Orion Engineered Carbons. Stabilisation of such carbon black dispersions are typically anionic or non-ionic.

[0055] 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 colourof the printed laser markable ink.

[0056] A preferred inorganic infrared absorber is a copper salt as disclosed in WO2005/068207 (DATALASE).

[0057] Another preferred inorganic infrared absorber is a non-stoichiometric metal salt, such as reduced indium tin oxide as disclosed in WO2007/141522 (DATALASE).

[0058] 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.

Infrared radiation absorbing dyes

[0059] 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.

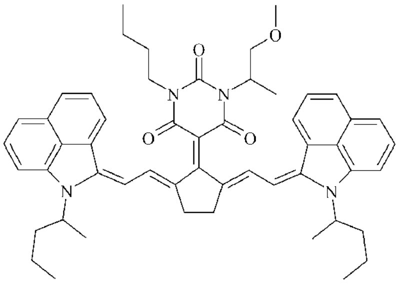
[0060] A narrow absorption band is also mandatory for multicolour laser marking using multiple laser each having a different emission wavelength, as disclosed in for example EP-A 3297838.

[0061] 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).

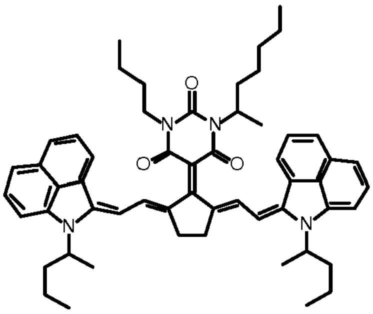
[0062] Preferred IR dyes are polymethine dyes due to their low absorption in the visible region and their selectivity, i.e. narrow absorption peak in the infrared region. Particular preferred polymethine IR dyes are cyanine IR dyes.

[0063] 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].

[0064] 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

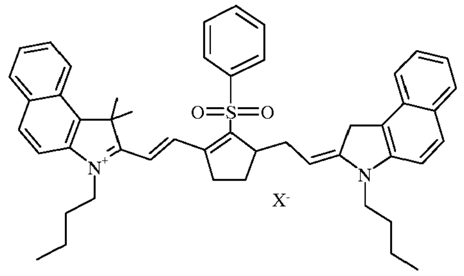
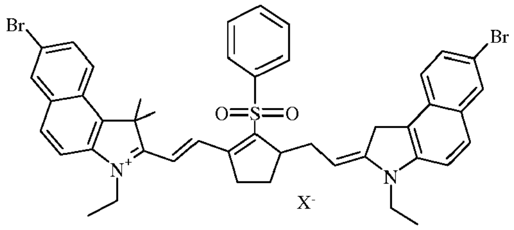
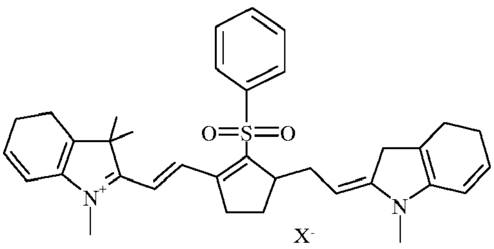
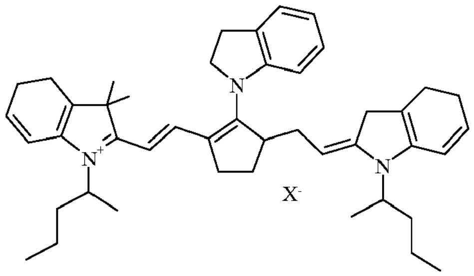


IR-2

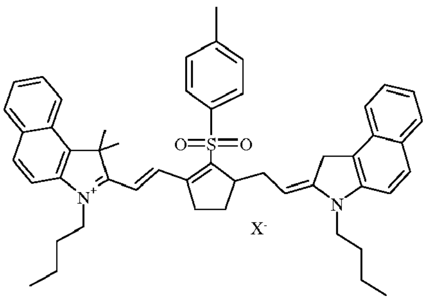
[0065] Both IR dyes IR-1 and IR-2 have an absorption maximum λ_{max} around 1052 nm making them very suitable for a Nd-YAG laser having an emission wavelength of 1064 nm.

[0066] Preferred IR dyes having an absorption maximum between 850 nm and 1000 nm are listed in Table 1.

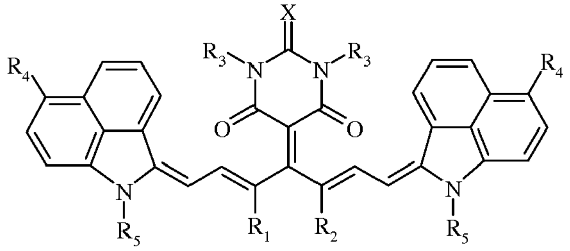
Table 1

STRUCTURES	IR Absorbers
	IR-1
	IR-2
	IR-3
	IR-4

(continued)

STRUCTURES	IR Absorbers
	IR-5

[0067] Other preferred NIR absorbing compounds have a chemical structure according to Formula I,



Formula I

wherein

X is O or S,

R_1 and R_2 represent the necessary atoms to form a substituted or unsubstituted 5 or 6 membered ring,

R_3 and R_5 are independently selected from the group consisting of an unsubstituted alkyl group, an unsubstituted alkenyl group, an unsubstituted alkynyl group, an unsubstituted aralkyl group, an unsubstituted alkaryl group and a substituted or unsubstituted (hetero)aryl group,

R_4 is selected from the group consisting of a hydrogen, an unsubstituted alkyl group, an unsubstituted alkenyl group, an unsubstituted alkynyl group, an unsubstituted aralkyl group, an unsubstituted alkaryl group, a substituted or an unsubstituted (hetero)aryl group, a halogen, an unsubstituted alkoxy group, a substituted or an unsubstituted aryloxy group, a substituted or an unsubstituted heteroaryloxy group, an ester, an amine, an amide, a nitro, a thioalkyl group, a substituted or an unsubstituted thioaryl group, a substituted or an unsubstituted thioheteroaryl group, a carbarmate, an ureum, a sulfonamide, a sulfoxide and a sulfone, with the proviso that all hydrocarbon groups in Formula I are straight chain hydrocarbon groups.

[0068] A straight chain hydrocarbon group as used herein means a linear hydrocarbon group, which is not further functionalized with hydrocarbon substituents.

[0069] A hydrocarbon group as used herein means a functional group only consisting of carbon atoms in the main chain or ring.

[0070] The hydrocarbon group is preferably selected from the group consisting of an alkyl group, an alkenyl group, an alkynyl group and an aralkyl group.

[0071] In a preferred embodiment, R_3 and R_5 are independently selected from the group consisting of an unsubstituted alkyl group, an unsubstituted alkaryl group and an unsubstituted (hetero)aryl group.

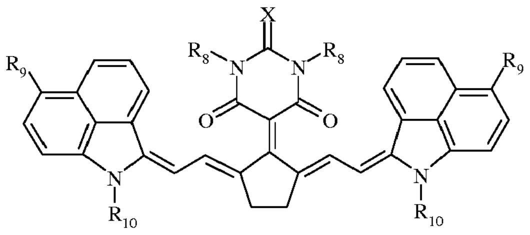
[0072] In a more preferred embodiment, R_3 and R_5 are independently selected from the group consisting of an unsubstituted lower alkyl group containing no more than six carbon atoms and an unsubstituted alkaryl group.

[0073] In a particularly preferred embodiment, R_3 and R_5 are independently selected from the group consisting of a methyl group, an ethyl group, a n-propyl group, a n-butyl group, a benzyl group and an aryl group.

[0074] In all embodiments described above, R_4 is preferably selected from the group consisting of a hydrogen, a halogen, a straight chain unsubstituted alkyl group and a straight chain unsubstituted alkoxy group.

[0075] In all these embodiments, R_4 is more preferably selected from the group consisting of a hydrogen, a chlorine, a bromine, a methyl group, an ethyl group, a methoxy group, an ethoxy group, an n-propoxy group and an n-butoxy group.

[0076] The NIR absorbing compound has preferably a chemical structure according to Formula II,



Formula II

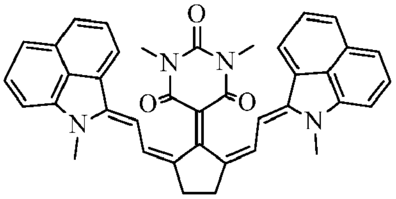
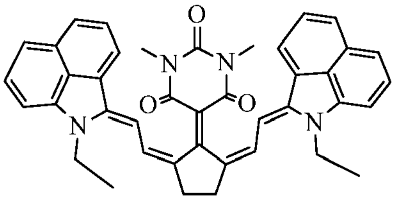
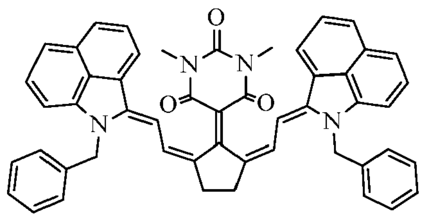
wherein

X is O or S,
R_8 and R_{10} are independently selected from the group consisting of an unsubstituted alkyl group, an unsubstituted alkenyl group, an unsubstituted alkynyl group, an unsubstituted aralkyl group, an unsubstituted alkaryl group and a substituted or unsubstituted (hetero)aryl group,
Rg is selected from the group consisting of a hydrogen, an unsubstituted alkyl group, an unsubstituted alkenyl group, an unsubstituted alkynyl group, an unsubstituted aralkyl group, an unsubstituted alkaryl group, a substituted or an unsubstituted (hetero)aryl group, a halogen, an unsubstituted alkoxy group, a substituted or an unsubstituted aryloxy group, a substituted or an unsubstituted heteroaryloxy group, an ester, an amine, an amide, a nitro, a thioalkyl group, a substituted or an unsubstituted thioaryl group, a substituted or an unsubstituted thioheteroaryl group, a carbarmate, a ureum, a sulfonamide, a sulfoxide and a sulfone.

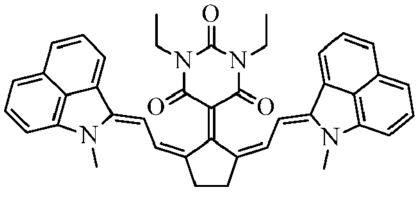
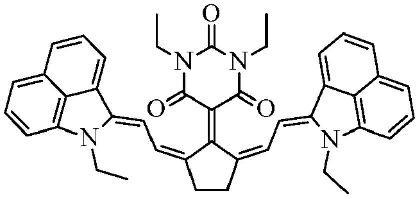
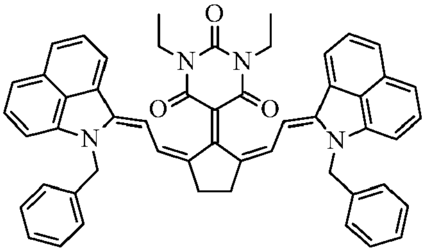
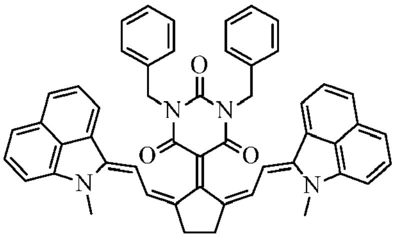
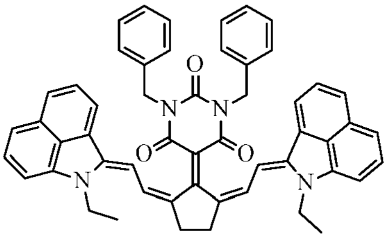
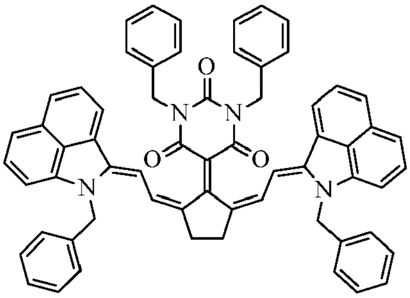
[0077] In a particularly preferred embodiment, Rg is selected from the group consisting of a hydrogen, a chlorine, a bromine, a methyl group, an ethyl group, a methoxy group, an ethoxy group, an n-propoxy group and an n-butoxy group.

[0078] Specific examples of NIR absorbing compounds according to Formula I or II are given in Table 2 without being limited thereto.

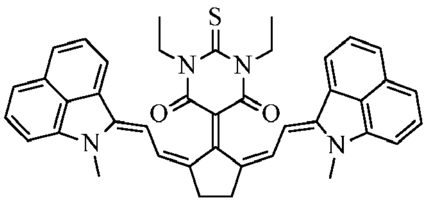
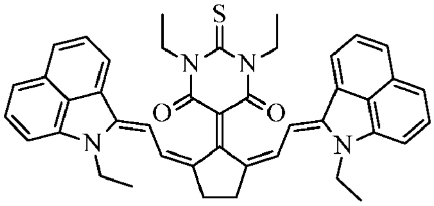
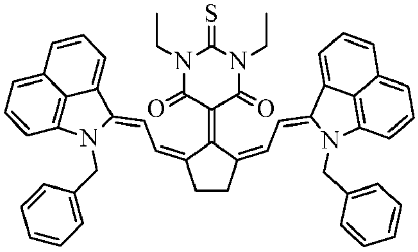
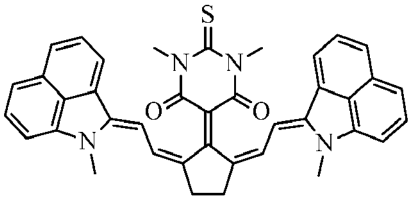
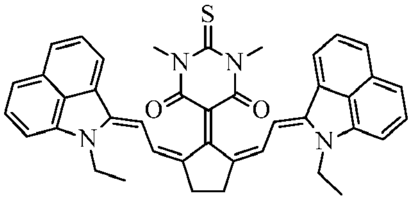
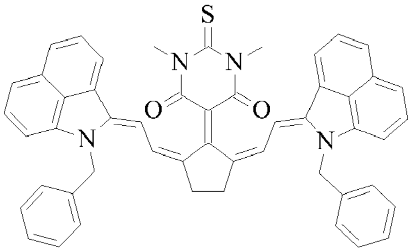
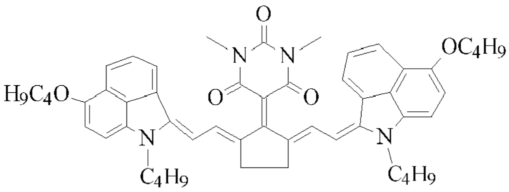
Table 2

STRUCTURES	IR Absorbers
	IR-6
	IR-7
	IR-8

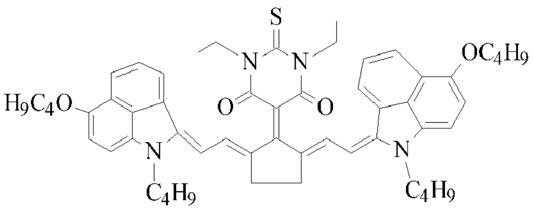
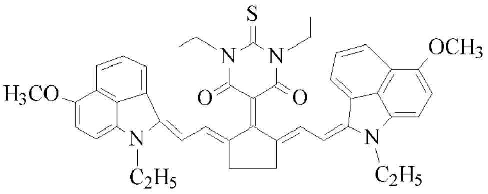
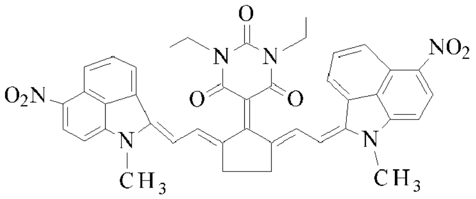
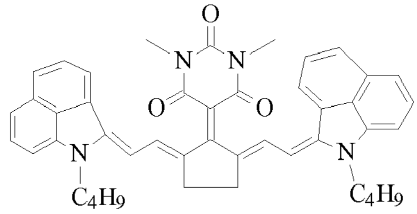
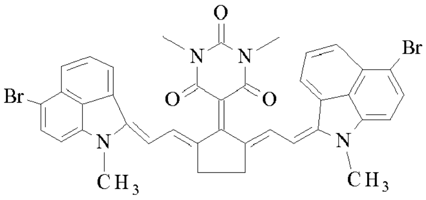
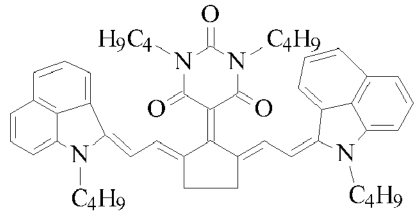
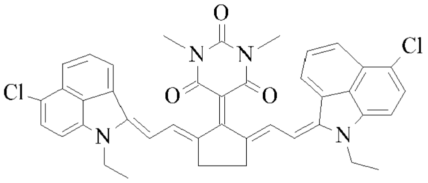
(continued)

STRUCTURES	IR Absorbers
	IR-9
	IR-10
	IR-11
	IR-12
	IR-13
	IR-14

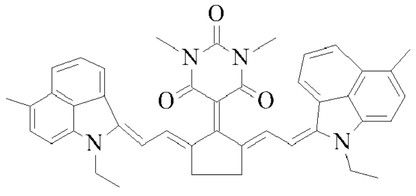
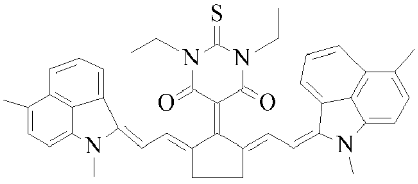
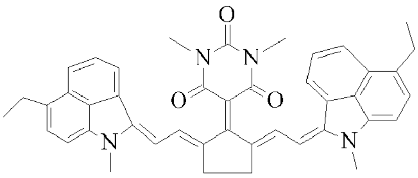
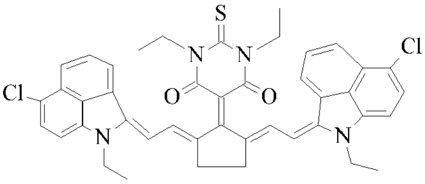
(continued)

STRUCTURES	IR Absorbers
	IR-15
	IR-16
	IR-17
	IR-18
	IR-19
	IR-20
	IR-21

(continued)

STRUCTURES	IR Absorbers
	IR-22
	IR-23
	IR-24
	IR-25
	IR-26
	IR-27
	IR-28

(continued)

STRUCTURES	IR Absorbers
	IR-29
	IR-30
	IR-31
	IR-32

[0079] The IR dyes are preferably encapsulated. It has been observed that encapsulated IR dyes are more stable against the radiation used to cure the composition, for example UV radiation. When the IR dyes decompose upon UV curing of the composition, laser marking by exposing the composition to IR radiation becomes more difficult or even impossible. Also, decomposition of the IR dyes may result in an increase of the background colour.

[0080] A combination of different optothermal converting agents may also be used.

[0081] 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.

Developing agent

[0082] A developing agent is capable of reacting with a colourless leuco dye resulting in the formation of a coloured dye.

[0083] The developing agent is preferably a water-soluble or water dispersible developing agent.

[0084] Various electron-accepting substances may be used as developing agent in the present invention. Examples thereof include phenolic compounds, organic or inorganic acidic compounds and esters or salts thereof.

[0085] Examples of developing agents that may be used are disclosed in WO2014/124052 (FUJIFILM HUNT CHEMICALS), paragraph [0069] to [0073].

[0086] Preferred developing agents are metal salts of a carboxylic acid, as dislosed in WO2006/067073 (DATALASE), page 3, line 4 to page 5, line 31.

[0087] A preferred developing agent is a metal salt of salicylic acid, for example zinc salicylate. A particularly preferred developing agent is zinc 3,5-bis(α-methylbenzyl) salicylate.

[0088] A developing agent precursor, i.e. a compound, which is capable of releasing a developing agent upon exposure to heat or IR radiation, may also be used. An advantage of such a developing agent precursor may be a better stability towards the environment.

[0089] Preferred developing agent precursors are disclosed in WO2016/184881 (AGFA GEVAERT), paragraph [086] to [0123].

Polymerizable compound

[0090] The polymerizable compound may be selected from the group consisting of a water-soluble monomer or oligomer, a water-soluble or water-dispersible polymerizable polymer or co-polymers, an emulsion of water-insoluble monomers or oligomers, capsules comprising water-insoluble monomers or oligomers and water-insoluble monomers or oligomers loaded on a polymer or co-polymer.

[0091] The polymerizable compound is preferably selected from the group consisting of a polymerizable polymer or co-polymer, an emulsion of water-insoluble monomers or oligomers and water-insoluble monomers or oligomers loaded on a polymer or a co-polymer.

[0092] The polymer or copolymer may also be referred to as polymer or co-polymer particle or latex.

[0093] A monomer as used herein is a polymerizable compound that undergoes polymerization upon exposure to radiation or thermal treatment (i.e. curing) thereby contributing constitutional units (monomer unit) to the essential structure of the obtained polymer.

[0094] An oligomer as used herein is a polymerizable compound that consists of a few monomer units, for example two, three or four monomer units.

[0095] The polymerizable compound preferably include a polymerizable group selected from the group consisting of an acrylate group, a methacrylate group, an acrylamide group, a methacrylamide group, a vinyl group, a vinyl ether group, a vinyl ester group, an olefenic group (such as butadiene, isoprene, undecane) and a styryl group.

[0096] The polymerizable compound may include more than one polymerizable group.

[0097] A preferred water-soluble monomer is a monomer containing at least one functional group selected from the group consisting of a hydroxyl group, an ethylene oxide or oligo-ethylene oxide group, a tertiary amine and an acidic function.

[0098] In a preferred embodiment, the water-soluble monomer contains at least one functional group selected from the group consisting of a hydroxyl group, an ethylene oxide or oligo-ethylene oxide group, a carboxylic acid group, a glycerol or oligoglycerine group, and a phenolic group.

[0099] The water-soluble monomer may also comprise a cationic, anionic or amphoteric group.

[0100] In a more preferred embodiment, the water-soluble monomer contains at least one functional group selected from the group consisting of an ethylene oxide or oligo-ethylene oxide group and a hydroxyl group.

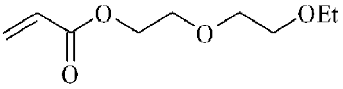
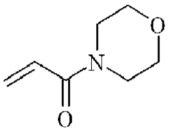
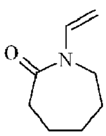
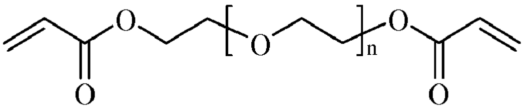
[0101] The water-soluble polymerizable monomer preferably include a polymerizable group selected from the group consisting of an acrylate group, a methacrylate group, a acrylamide group, a methacrylamide group, a vinyl group, and a styryl group.

[0102] The water-soluble polymerizable compound preferably include a polymerizable group selected from the group consisting of an acrylate group and an acrylamide group.

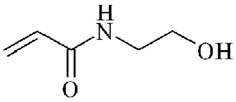
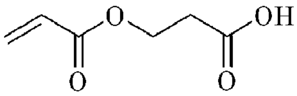
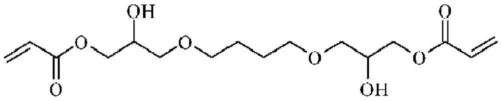
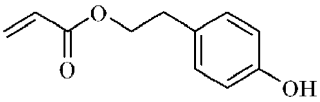
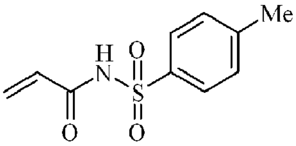
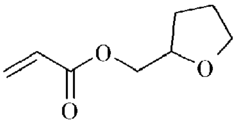
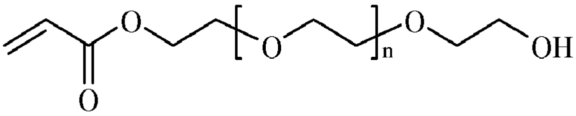
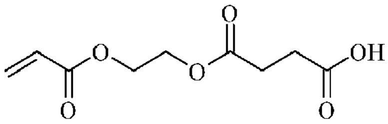
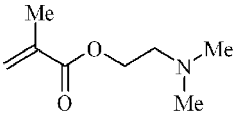
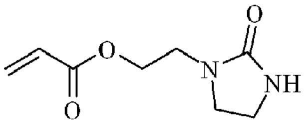
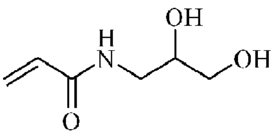
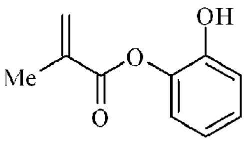
[0103] The monomer may contain one, two, three or more polymerizable groups.

[0104] Suitable water-soluble polymerizable compounds are given in Table 3 without being limited thereto.

Table 3

	Mono-1
	Mono-2
	Mono-3
	Mono-4

(continued)

	Mono-5
	Mono-6
	Mono-7
	Mono-8
	Mono-9
	Mono-10
	Mono-11
	Mono-12
	Mono-13
	Mono-14
	Mono-15
	Mono-16

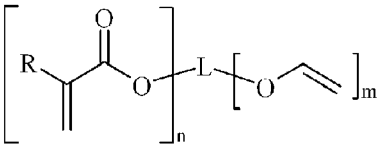
[0105] Other preferred polymerizable compounds are urethane (meth)acrylates, more preferably aliphatic urethane (meth)acrylates. Such urethane acrylates provide water resistance, high gloss, hardness or flexibility and chemical resistance for a wide variety of applications.

[0106] Particular preferred urethane (meth)acrylates are water-soluble or emulsifiable urethane acrylates such as Desmolux® XP2587 (available from Allnex); CN9210, CN963B80, CN965, CN970A60, and CN981 (available from Arkema), Ebecryl® 8402 (available from Allnex).

[0107] Other preferred acrylates are polyester acrylates, such as Ebecryl® 81 and 82 (available from Allnex).

[0108] Another preferred polymerizable compound is a monomer or oligomer having one vinylether group and one (meth)acrylate group, more preferably monomers and oligomers having one vinylether group and one acrylate group.

[0109] The vinylether (meth)acrylate monomer is preferably a monomer represented by Formula (III).



Formula (III)

wherein,

R represents hydrogen or a methyl group;
L represents a linking group comprising at least one carbon atom; and
n and m independently represent a value of 1.

[0110] According to preferred embodiment, water-insoluble monomers or oligomers are used. These may be added to the aqueous composition as an emulsion, encapsulated or loaded onto a polymer particle.

[0111] It has been observed that by using water-insoluble monomers or oligomers the stability of the aqueous UV curable and laser markable composition may be improved.

[0112] Water-insoluble monomers or oligomers referred to preferably have a solubility in water of less than 10 g/l, more preferably less than 1 g/l.

[0113] An emulsion of water-insoluble monomers or oligomers may be prepared by adding the monomers or oligomers to an organic solvent in which they are soluble. The solubilized monomers or oligomers are then added to the aqueous composition, preferably together with a dispersant, and stirred to form an emulsion of the monomers or oligomers in the aqueous composition.

[0114] Water-insoluble monomers or oligomers, or substantially water-insoluble monomers or oligomers, may also be encapsulated to bring them in the aqueous composition.

[0115] Preferrred polymerizable compounds that may be encapsulated are those disclosed in WO2015/158649 (AGFA), paragraphs [0071] to [0091]).

[0116] In another embodiment, water-insoluble monomers or oligomers, or substantially water-insoluble monomers or oligomers, may be loaded onto a polymer or co-polymer, also referred to as polymer particle or a latex, as disclosed in for example EP-A 2960306 (AGFA).

[0117] According to a particular preferred embodiment, the polymerizable compound is a polymerizable polymer or co-polymer, also referred to as a polymerizable polymer particle or as a polymerizable latex.

[0118] The polymer or co-polymer contains at least one polymerizable group.

[0119] A preferred polymerizable polymer includes at least one ethylenically unsaturated polymerizable group selected from the group consisting of an acrylate group, a methacrylate group, a vinylether group, a styrene group, an acrylamide group, a methacrylamide group, an allyl ester group, an allyl ether group, a vinyl ester group, a fumarate group, a maleate group, a maleimide group and a vinyl nitrile group.

[0120] There is no real limitation on the chemical nature of the polymerizable polymer. Suitable examples include a vinyl polymer, a condensed polymer (e.g., an epoxy resin, polyester, polyurethane, polyamide, cellulose, polyether, polyurea, polyimide, and polycarbonate), an addition polymer (e.g. using vinyl monomers) or condensation polymer (e.g.) or natural polymer (such as polysaccharides or celullose derivatives).

[0121] However for good physical properties, such as adhesion and solvent resistance, of the printed image, a polyurethane polymer or copolymer is particularly preferred.

[0122] The polymerizable polymers are preferably self-dispersible polymerizable polymers. In preparing a self-dispersing polymer latex, preferably a monomer is used selected from the group consisting of a carboxylic acid monomer, a sulfonic acid monomer, an alkylene-oxide containing monomer and a phosphoric acid monomer.

[0123] The polymerizable polymers are preferably based on a polyurethane having an acrylate or methacrylate group.

[0124] Manufacturing methods for polyurethane polymer or copolymer nanoparticles are well-known and are disclosed in for example WO2015/197472 (AGFA GEVAERT), paragraphs [0042] to [0044]).

[0125] Nanoparticles referred to have a particle diameter of less than 1000 nm, preferably less than 800 nm, more preferably less than 500 nm, most preferably less than 250 nm.

[0126] Polyurethane nanoparticles having ethylenically unsaturated groups are commercially available as aqueous dispersions from a number of sources for use in wood and floor finishes.

[0127] For example, Cytec sell such polyurethane dispersions under the Ucecoat trade mark. Examples of commercially available dispersions comprising a polyurethane having ethylenically unsaturated groups include Alberding™ Lux 399 and Lux 515 from Alberdingk Boley, Bayhydrol™ UV grades from BAYER, Laromer™ 8949 from BASF and Ucecoat™7571, 7655, 7689, 7699 and 7890 from Cytec, with Ucecoat™7655 and Bayhydrol™ UV XP 2689 being preferred.

[0128] A particular preferred radiation curable polyurethane latex is characterised by the fact that the resin has an ionic group, a polyalkylene oxide in a side chain of the polyester urethane backbone and a (meth)acrylate or (meth)acrylamide having at least one hydroxyl functional group.

[0129] Both the ionic group and the polyalkylene oxide increase the dispersibility of the resin in water. The (meth)acrylate or (meth)acrylamide components render the polyurethane resin curable via ultraviolet light or some other suitable electromagnetic radiation. The polyester urethane backbone is obtained by reacting a polyester polyol with a polyisocyanate. The polyurethane resin is thus obtained by reacting a polyester polyol, a polyether diol, a polyol containing an ionic group, a (meth)acrylate or (meth)acrylamide and a polyisocyanate.

[0130] The preparation of such a radiation curable polyurethane latex is disclosed in the unpublished EP-A 17204844.9 (filed on 01-12-2017).

Photoinitiator

[0131] The photoinitiator has a Molecular Weight (MW) of at least 250, more preferably at least 500, most preferably at least 750.

[0132] When more than one photoinitiator is used, preferably all photoinitiators have a MW of at least 250, more preferably at least 500, most preferably at least 750.

[0133] The photoinitiator is preferably a free radical photoinitiator, more specifically a Norrish type I initiator or a Norrish type II initiator. A free radical photoinitiator is a chemical compound that initiates polymerization of monomers when exposed to actinic radiation by the formation of a free radical. A Norrish Type I initiator is an initiator which cleaves after excitation, yielding the initiating radical immediately. A Norrish type II-initiator is a photoinitiator which is activated by actinic radiation and forms free radicals by hydrogen abstraction from a second compound that becomes the actual initiating free radical. This second compound is called a polymerization synergist or a co-initiator.

[0134] The photoinitiator is preferably a polymeric photoinitiator.

[0135] The photoinitiator is preferably added to the aqueous composition loaded on a polymer particle, as described above for water-insoluble polymerizable compounds. The polymer particle may be a polymerizable polymer particle described above.

[0136] Suitable polymeric initiators have been reviewed by Hrdlovic P. (Polymer News, 30(6), 179-182 (2005) and Polymer News, 30(8), 248-250 (2005)) and Corrales T. (Journal of Photochemistry and Photobiology A: Chemistry 159 (2003), 103-114).

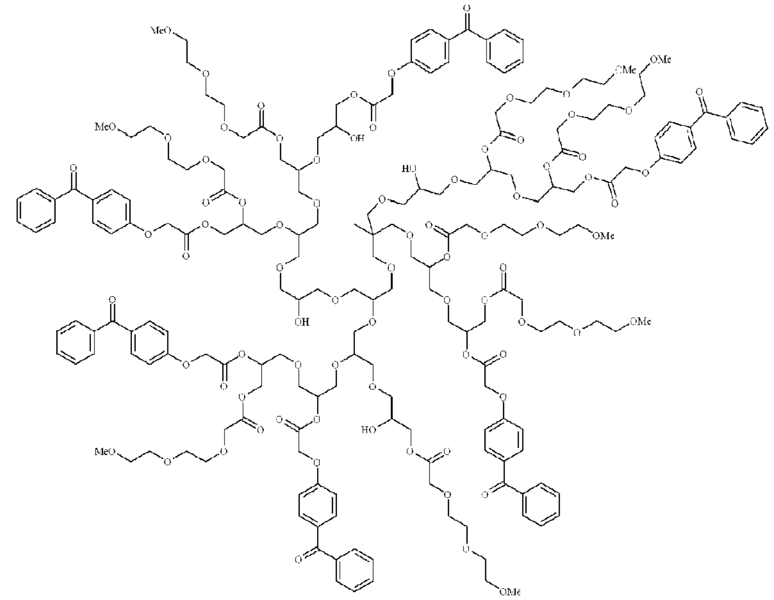
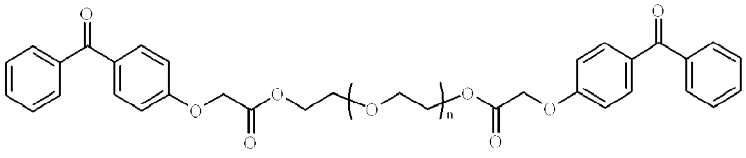
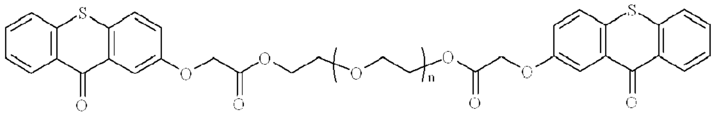
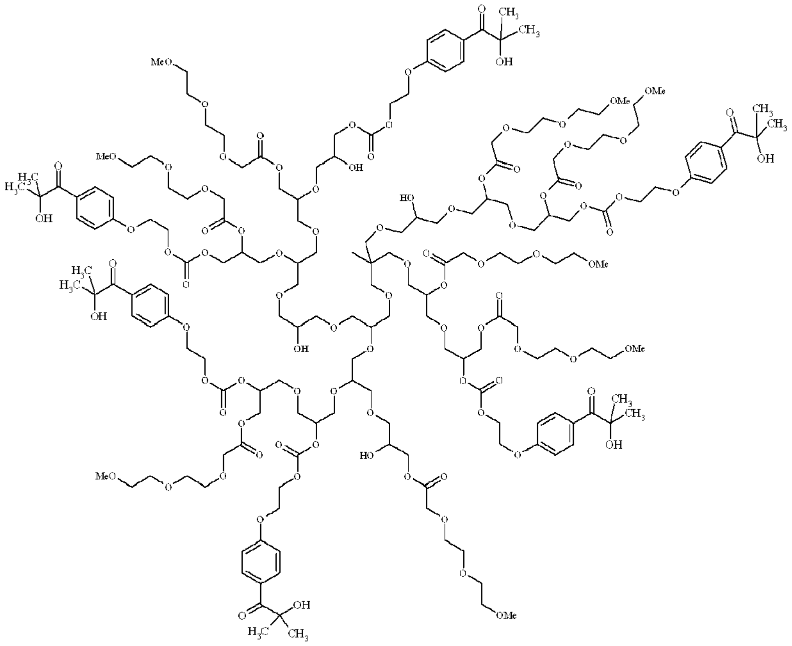
[0137] Further interesting polymeric photoinitiators can be found in CRIVELLO, J.V. et al.; Chemistry & technology of UV & EB Formulation for Coatings, Inks & Paints, Volume III: Photoinitiators for Free Radical, Cationic & Anionic Photopolymerisation, 2nd edition, John Wiley & Sons Ltd in association with SITA Technology Ltd, London, UK, 1998 edited by Dr. G. Bradley; ISBN 0471 978922, page 208-224.

[0138] Particularly suitable polymeric and oligomeric photoinitiators have been disclosed by Bertens et al. (RadTech Europe 05, Conference Proceedings (2005) 1, 473-478), in WO 2003/033452 (COATES BROTHERS) and in WO 2003/033492 (COATES BROTHERS).

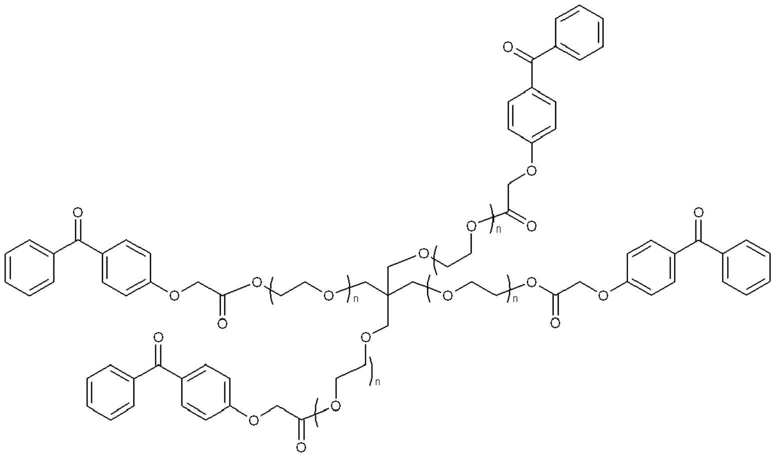
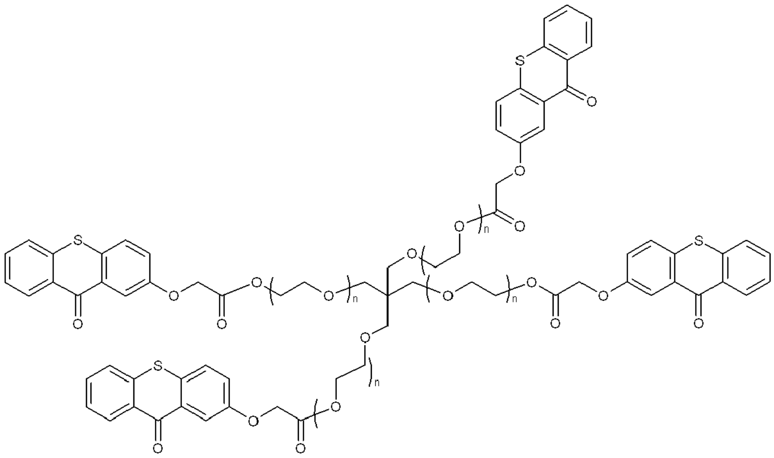
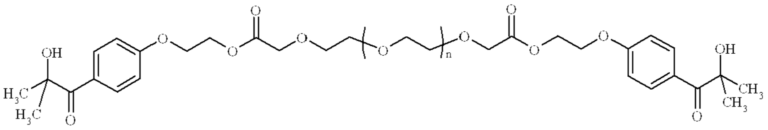
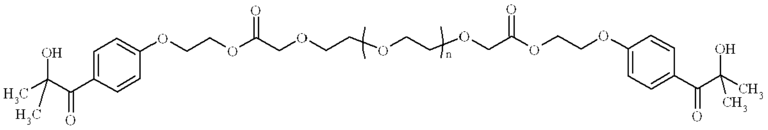
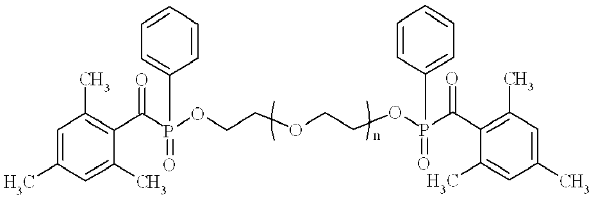
[0139] For reasons of obtaining low viscosity, a preferred polymeric architecture used in jettable radiation curable compositions and inkjet inks is a dendritic polymeric architecture, more preferably a hyperbranched polymeric architecture. Preferred hyperbranched polymeric photoinitiators are those disclosed in US 2006014851 (AGFA) and US 2006014853 (AGFA).

[0140] Suitable polymeric and oligomeric initiators are given below in Table 3 without being limited thereto. The hyperbranched structures (INI-P1, INI-P4 and INI-P11) are illustrated with one specific molecular weight and degree of substitution out of the mixture for the sake of clarity.

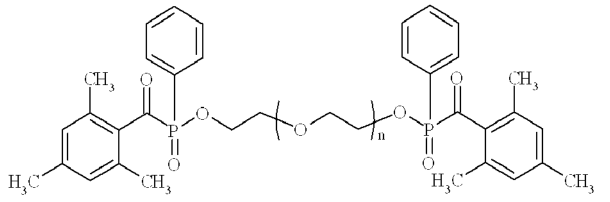
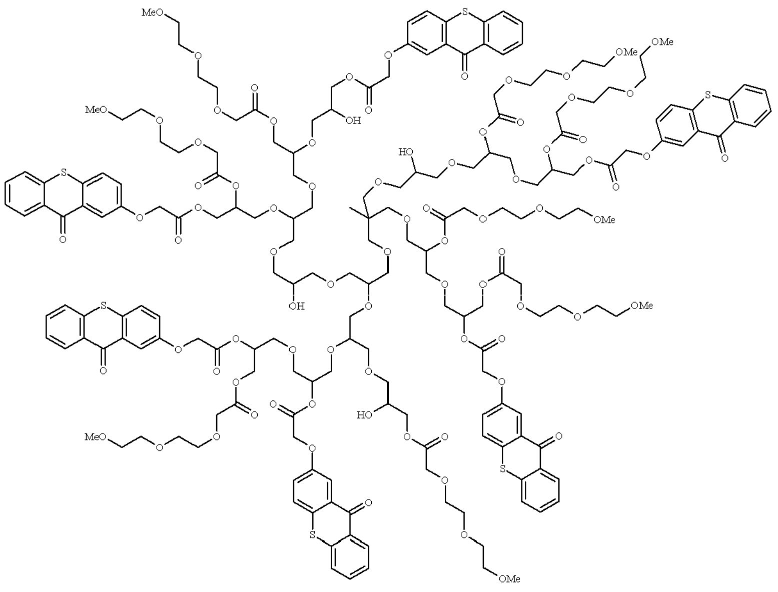
Table 4

INI-P1	
INI-P2	 n = 5 on average
INI-P3	 n = 15 on average
INI-P4	

(continued)

INI-P5	 derived from pentaerythritol ethoxylate (15/4 EO/OH)
INI-P6	 derived from pentaerythritol ethoxylate (15/4 EO/OH)
INI-P7	 derived from poly(ethylene glycol) bis(carboxymethyl) ether with MW of 250
INI-P8	 derived from poly(ethylene glycol) bis(carboxymethyl) ether with MW of 600
INI-P9	 derived from poly(ethylene glycol) with MW of 200

(continued)

INI-P10	 derived from poly(ethylene glycol) with MW of 600
INI-P11	

[0141] Commercially available polymeric photoinitiators are for example Omnipol BP, Omnipol TX, Ominpol BL 728, Omnipol 2702, Omnipol 910, Omnipol 9210 or Omnipol ASA, all available from IGM RESINS.

[0142] The aqueous UV curable laser markable composition may also comprise a so-called co-initiator, also referred as synergist. The co-initiator preferably has also a MW of at least 250, more preferably of at least 500, most preferably of at least 750.

[0143] The co-initiator or synergist is preferably a polymeric co-initiator or synergist.

[0144] Suitable polymeric co-initiators or synergists are the polymeric amine synergists disclosed in WO2017/007505 (Hewlett-Packard Development Company) and WO2017/007493 (AGFA).

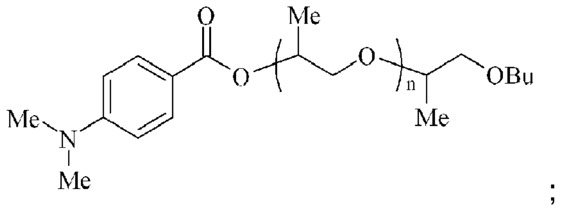
[0145] Preferred polymeric co-initiators contain a tertiary amine, more preferably one or more 4-dialkylaminobenzoate groups, most preferably one or more 4-dimethyl-aminobenzoate groups.

[0146] Other preferred tertiary amine groups for the at least one polymeric co-initiator containing a tertiary amine include aliphatic tertiary amine groups and piperazine groups.

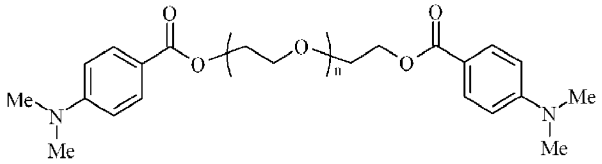
[0147] In a preferred embodiment, the at least one polymeric co-initiator containing a tertiary amine is a polyether based polymer. Particularly preferred polymeric co-initiators are derivatives from ethoxylated trimethylolpropane, propoxylated trimethylolpropane, polyethylene oxide, polypropylene oxide, ethoxylated neopentyl glycol, propoxylated neopentylglycol, ethyleneoxide propylene oxide copolymers, ethoxylated glycerol, propoxylated glycerol, ethoxylated pentaerithritol, propoxylated pentaerythritol and polytetrahydrofurane.

[0148] In a further preferred embodiment, the at least one polymeric co-initiator containing a tertiary amine has a numeric average molecular weight of no more than 1500, more preferably of no more than 1000 and most preferably of no more than 750.

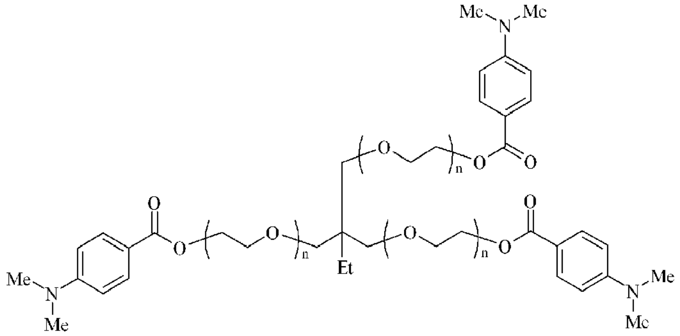
[0149] In a particularly preferred embodiment, the polymeric co-initiator containing a tertiary amine is selected from the group consisting of:



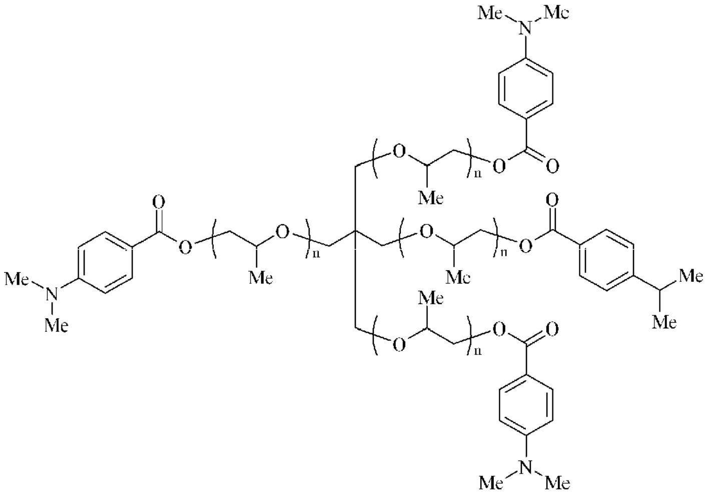
;



;



and



wherein the compound has a numeric average molecular weight of no more than 1500 or wherein n is an integer of 1 to 4.

[0150] Suitable corresponding polymeric co-initiator containing a tertiary amine are commercially available as Omnipol™ ASA (CASRN71512-90-8) from IGM Resins, Genopol™ AB-1 and AB-2 (CASRN1215019-68-3) from RAHN, and Speedcure™ 7040 (CASRN1182751-31-0) from LAMBSON.

[0151] Preferred polymeric co-initiators containing a tertiary amine are polymeric co-initiators having a dendritic polymeric architecture, more preferably a hyperbranched polymeric architecture. Preferred hyperbranched polymeric co-initiators are those disclosed in US 2006014848 (AGFA).

Surfactant

[0152] In the ink or treatment liquid of the present invention, a surfactant may be added in order to ensure wettability onto the substrate. The amount of the surfactant added is preferably 0.1 wt % to 5 wt % as an active component in the ink.

[0153] Any of an amphoteric surfactant, a non-ionic surfactant, an anionic or cationic surfactant can be used.

[0154] Non-ionic surfactants such as polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl ester, polyoxyethylene alkylamine, polyoxyethylene alkyl amide, a polyoxyethylene propylene block polymer, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester and an ethylene oxide adduct of acetylene alcohol are preferably used in terms of a relationship between dispersing stability of the colourmaterial and image quality.

[0155] In addition, a fluorine-based surfactant and a silicon-based surfactant can be used in combination (or singly) depending on formulation.

Capsules

[0156] As described above, the leuco dyes, the optothermal converting agents, the polymerizable compounds may all be encapsulated.

[0157] The capsules preferably have an average particle size of not more than 5 μm, more preferably of not more than 2 μm, most preferably of not more than 1 μm as determined by dynamic laser diffraction. Capsules having an average particle size smaller than 1 μm are typically called nanocapsules while capsules having an average particle size above 1 μm are typically called microcapsules.

[0158] Upon exposure, a rupture of the capsule, for example by heat produced by an optothermal converting agent upon absorption of IR radiation, results in a reaction between the leuco dye and a colour developing agent which then triggers colour formation.

[0159] The morphology of capsules and their preparation methods have been reviewed, for example, by Jyothi Sri.S in the International Journal of Pharma and Bio Sciences (Vol.3, Issue 1, Jan-Mar 2012).

[0160] The capsules may have different morphologies, dependent on the preparation method of the capsules. For example mononuclear capsules have a shell around a core while polynuclear capsules have multiple cores enclosed within the shell. Matrix encapsulation refers to a core material which is homogeneously distributed into the shell.

[0161] Hydrophilic polymers, surfactants and/or polymeric dispersants may be used to obtain stable dispersions of the capsules in an aqueous medium and to control the particle size and the particle size distribution of the capsules.

[0162] In a preferred embodiment, the capsules are dispersed in the aqueous medium using a dispersing group covalently bonded to the polymeric shell. The dispersing group is preferably selected from a group consisting of a carboxylic acid or salt thereof, a sulfonic acid or salt thereof, a phosphoric acid ester or salt thereof, a phosphonic acid or salt thereof, an ammonium group, a sulfonium group, a phosphonium group and a polyethylene oxide group.

[0163] The dispersing groups stabilize the aqueous dispersion by electrostatic stabilization. For example, a slightly alkaline aqueous medium will turn the carboxylic acid groups covalently bonded to the polymeric shell into ionic groups, whereafter the negatively charged capsules have no tendency to agglomerate. If sufficient dispersing groups are covalently bonded to the polymeric shell, the capsule becomes a so-called self-dispersing capsule. Other dispersing groups such as sulfonic acid groups tend to be dissociated even in acid aqueous medium and thus do not require the addition of an alkali.

[0164] The dispersing group can be used in combination with a polymeric dispersant in order to accomplish steric stabilization. For example, the polymeric shell may have covalently bonded carboxylic acid groups that interact with amine groups of a polymeric dispersant. However, in a more preferred embodiment, no polymeric dispersant is used and dispersion stability is accomplished solely by electrostatic stabilization.

[0165] The capsules may also be stabilized by solid particles which adsorb onto the shell. Preferred solid particles are colloidal silica.

[0166] There is no real limitation on the type of polymer used for the polymeric shell of the capsule. Preferably, the polymer used in the polymeric shell is crosslinked. By crosslinking, more rigidity is built into the capsules allowing a broader range of temperatures and pressures for handling the colour laser markable article.

[0167] Preferred examples of the polymeric shell material include polyureas, polyacrylates, polymethacrylates, polyurethanes, polyesters, polycarbonates, polyamides, melamine based polymers and mixtures thereof, with polyureas and polyurethanes being especially preferred.

[0168] Capsules can be prepared using both chemical and physical methods. Suitable encapsulation methodologies include complex coacervation, liposome formation, spray drying and polymerization methods.

[0169] In the present invention, preferably a polymerization method is used as it allows the highest control in designing the capsules. More preferably interfacial polymerization is used to prepare the capsules used in the invention. This technique is well-known and has been reviewed by Zhang Y. and Rochefort D. (Journal of Microencapsulation, 29(7), 636-649 (2012) and by Salitin (in Encapsulation Nanotechnologies, Vikas Mittal (ed.), chapter 5, 137-173 (Scrivener Publishing LLC (2013)).

[0170] Interfacial polymerization is a particularly preferred technology for the preparation of capsules according to the present invention. In interfacial polymerization, such as interfacial polycondensation, two reactants meet at the interface of the emulsion droplets and react rapidly.

[0171] In general, interfacial polymerization requires the dispersion of an oleophilic phase in an aqueous continuous phase or vice versa. Each of the phases contains at least one dissolved monomer (a first shell component) that is capable of reacting with another monomer (a second shell component) dissolved in the other phase. Upon polymerisation, a polymer is formed that is insoluble in both the aqueous and the oleophilic phase. As a result, the formed polymer has a tendency to precipitate at the interface of the oleophilic and aqueous phase, hereby forming a shell around the dispersed phase, which grows upon further polymerization. The capsules according to the present invention are preferably prepared from an oleophilic dispersion in an aqueous continuous phase.

[0172] Typical polymeric shells, formed by interfacial polymerization are selected from the group consisting of polyamides, typically prepared from di- or oligoamines as first shell component and di- or poly-acid chlorides as second shell component; polyurea, typically prepared from di- or oligoamines as first shell component and di- or oligoisocyanates as second shell component; polyurethanes, typically prepared from di- or oligoalcohols as first shell component and di- or oligoisocyanates as second shell component; polysulfonamides, typically prepared from di- or oligoamines as first shell component and di- or oligosulfochlorides as second shell component; polyesters, typically prepared from di- or oligoalcohols as first shell component and di- or oligo-acid chlorides as second shell component; and polycarbonates, typically prepared from di- or oligoalcohols as first shell component and di- or oligo-chloroformates as second shell component. The shell can be composed of combinations of these polymers.

[0173] In a further embodiment, polymers, such as gelatine, chitosan, albumin and polyethylene imine can be used as first shell components in combination with a di- or oligo-isocyanate, a di- or oligo acid chloride, a di- or oligo-chloroformate and an epoxy resin as second shell component.

[0174] In a particularly preferred embodiment, the shell is composed of a polyurethane, a polyurea or a combination thereof.

[0175] In a further preferred embodiment, a water immiscible solvent is used in the dispersion step, which is removed by solvent stripping before or after the shell formation. In a particularly preferred embodiment, the water immiscible solvent has a boiling point below 100°C at normal pressure. Esters are particularly preferred as water immiscible solvent. A preferred organic solvent is ethyl acetate, because it also has a low flammability hazard compared to other organic solvents.

[0176] A water immiscible solvent is an organic solvent having low miscibility in water. Low miscibility is defined as any water solvent combination forming a two phase system at 20°C when mixed in a one over one volume ratio.

[0177] The method for preparing a dispersion of capsules preferably includes the following steps:

a) preparing a non-aqueous solution of a first shell component for forming a polymeric shell, an encapsulant, and optionally a water immiscible organic solvent having a lower boiling point than water;
b) preparing an aqueous solution of a second shell component for forming the polymeric shell;
c) dispersing the non-aqueous solution under high shear in the aqueous solution;
d) optionally stripping the water immiscible organic solvent from the mixture of the aqueous solution and the non-aqueous solution; and
e) preparing the polymeric shell around the encapsulant by interfacial polymerization of the first and second shell components for forming the polymeric shell.

[0178] Different encapsulants, for example a leuco dye and an optothermal converting agent, may be added together in step (a) to the non-aqueous solution resulting in capsules wherein both encapsulants are located in the core of the capsule.

Method of preparing a laser markable article

[0179] The method of preparing a laser markable article comprises the steps of:

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

[0180] 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.

[0181] 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.

[0182] The laser markable composition is preferably applied by flexographic printing or inkjet printing.

[0183] The thickness of the applied aqueous radiation curable and laser markable composition is preferably 50 μm or less, more preferably 20 μm or less, most preferably 10 μm or less.

[0184] It has been observed that by optimizing the leuco dye and the developing agent dispersions, high density marking could be obtained, even when the thickness of the applied composition is 10 μm or less.

[0185] In flexographic printing, the thickness of the applied ink is typically 10 μm or less. It is advantageous that high marking densities maybe obtained with one layer of ink. When this is not the case, multiple layers have to be applied on top of each other, resulting in a lower throughput.

Support

[0186] 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.

[0187] The support may be provided with a primer to improve the adhesion between the support and the laser markable composition.

[0188] 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.

[0189] The support may be a paper support, such as plain paper or resin coated paper, e.g. polyethylene or polypropylene coated paper.

[0190] 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.

[0191] 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.

[0192] 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.

[0193] 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.

[0194] 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.

[0195] Another preferred polymeric support includes (co)polyesters based on cyclohexyldimethanol (CHDM).

[0196] 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.

[0197] 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.

[0198] Other polymeric supports include copolyesters based on isosorbide, e.g. copolymers of terephtalic acid and ethylene glycol and isosorbide.

[0199] The polymeric support may be a single component extrudate or co-extrudate. Examples of suitable co-extrudates are PET/PETG and PET/PC.

[0200] 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.

[0201] 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.

[0202] 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.

[0203] The most commonly used shrink foils are polyolefin foils, i.e. polyethylene or polypropylene foils. However, other shrink foils include PCV.

Laser marked article

[0204] The laser markable article is prepared by laser marking the laser markable article described above.

[0205] 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

[0206] The laser marking method according to the present invention is preferably used to laser mark a packaging.

[0207] Laser marking is typically used to add variable data, for example batch numbers, expiry dates, addressees, etc. on the packaging.

[0208] Preferably laser marking is carried out in-line in the packaging process.

[0209] The laser marked "image" on a packaging may comprises data, images, barcodes, QR codes, or a combination thereof.

[0210] 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.

[0211] 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.

[0212] 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.

[0213] By selecting a proper leuco dye, or a mixture of leuco dyes, the package may be provided with data or images in any colour.

[0214] A preferred packaging is folded cardboard or corrugated cardboard laminated with paper. Such packaging is preferably used for cosmetics, pharmaceuticals, food or electronics.

[0215] 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

[0216] The laser marking method may also be used to prepare security documents, such as for example ID cards.

[0217] 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.

[0218] Such laser markable security documents and their preparation have been disclosed in for example WO2015/091782 (Agfa Gevaert).

[0219] 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.

[0220] 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.

[0221] The laser markable laminate is typically laminated on one or both sides of a core support using elevated temperatures and pressures.

[0222] Preferred core supports are disclosed in WO2014/057018 (Agfa Gevaert), paragraphs [0112] to [0015].

[0223] 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.

[0224] The capsules of the laser markable layer have to withstand the elevated temperatures and pressures to avoid colourformation as a result of the lamination step, resulting in a too high background colour.

Laser marking

[0225] Laser marking is carried out with an infrared laser.

[0226] The infrared laser may be a continuous wave or a pulsed laser.

[0227] 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.

[0228] 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.

[0229] 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.

[0230] 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 920 nm and about 1150 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.

[0231] 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.

[0232] Laser marking may also be carried out using a so-called Spatial Light Modulator (SLM) as disclosed in WO2012/044400 (Vardex Laser Solutions).

Curing

[0233] The aqueous radiation curable laser markable composition can be cured by exposing them to actinic radiation, such as electron beam or ultraviolet radiation.

[0234] Preferably aqueous radiation curable laser markable composition is cured by exposing it to ultraviolet radiation, more preferably using UV LED curing.

EXAMPLES

Materials

[0235] **Tinuvin 928** is an UV absorber commercially available from BASF.

[0236] **WINCON 205** is a black leuco dye commercially available from Connect Chemicals.

[0237] **Pergascript black IR** is a black leuco dye commercially available from BASF.

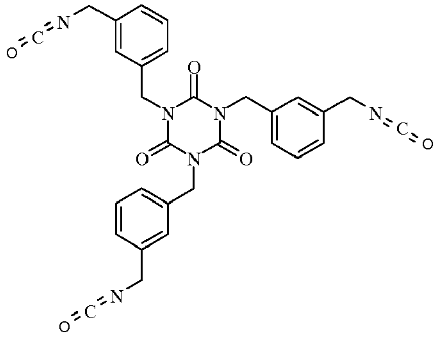
[0238] **Pergascript Black 2C** is a black leuco dye commercially available from BASF.

[0239] **Orange DCF** is an orange leuco dye commercially available from Connect Chemicals.

[0240] **MITSUI GN-169** is a cyan leuco dye commercially available from Mitsui.

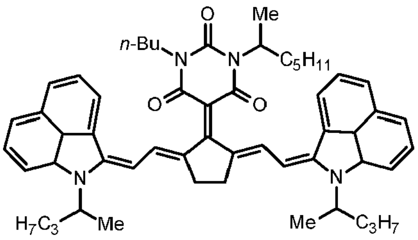
[0241] **MITSUI GN-2** is a cyan leuco dye commercially available from Mitsui.

[0242] **Polyiso-01** is a xylylene diisocyanate (XDI) isocyanurate with a structure as shown below and synthesized as described in EP-A 3115386 and EP-A3115430.



[0243] **OLFINE E1010** is a wetting agent commercially available from Shin-Etsu Chemical Company.

[0244] **1064IR** is an infrared dye with the following structure:



1064IR can be prepared according to the synthetic methods reported in EP-A 2463109 (Agfa), paragraphs [0150] to [0159].

[0245] **MOWIOL 4 88** is a polyvinyl alcohol commercially available from KURURAY.

[0246] **Proxel Ultra 5** is a biocide commercially available from Avecia.

[0247] **MOW** is an aqueous solution of 15 wt% Mowiol 4 88 and 2 wt% Proxel Ultra 5.

[0248] **Ralox 46** is a sterically hindered phenolix antioxidant from Raschig.

[0249] **DISFLAMOLL TKP** is a low volatility halogen free phosphate plasticizer from Lanxess.

[0250] **4,4'-Thiobis(6-tert-butyl-m-cresol)** is a stabilizer/anti-oxidant commercially available from TCI Europe.

[0251] **Zinc 3,5-bis(alpha methylbenzyl) salicylate** (CASRN53770-52-8) is a developing agent, commercially available from Sanko Europe).

[0252] **Ethyl Maleate** is commercially available from TCI Europe.

[0253] **Desmolux XP 2587** is an aliphatic urethane acrylate from SpecialChem.

[0254] **PEG200DA** is a polyethylene glycol (MW200) diacrylate available as Sartomer SR259 from ARKEMA.

[0255] **Genocure DMHA** is the photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone available from COVESTRO.

[0256] **Genocure CPK** is the photoinitiator 1-hydroxycyclohexyl phenyl ketone available from RAHN.

[0257] **Genocure TPO** is the photoinitiator (2,4,6-trimethylbenzoyl)phosphine oxide available from RAHN.

[0258] **Inimix** is an 1/1/1/ mixture of Genocure DMHA, Genocure CPK and Genocure TPO.

[0259] **Mixcure** is obtained by mixing 50 g Desmolux XP 2587, 40 g PEG200DA and 10 g of Inimix.

[0260] **Monomix** is a 5/4 mixture of Desmolux XP 2587 and PEG200DA

[0261] **Omnipol 910** a polymeric Type I photoiniator from IGM.

[0262] **Omnipol Asa** is a liquid polymeric amine synergist available from IGM.

[0263] **Omnipol TX** is a difunctional thioxanthene photoinitiator available from IGM.

[0264] **Inimix 2** is a 1/1/1 mixture of Omnipol 910, Omnipol Asa and Omnipol TX.

[0265] **Ebecryl 220** is a hexafunctional aromatic urethane acrylate, commercially available from Allnex.

[0266] **Genapol T800P** is a non-ionic surfactant, commercially available from Clariant.

Example 1

Leuco dye dispersion LD-01

[0267] 2.1 g Tinuvin 928, 5.47 g WINCON 205, 1.22 g Pergascript black IR, 3.04 g Pergascript Black 2C, 4.87 g Orange DCF, 4.87 g MITSUI GN-169 and 2.43 g MITSUI GN-2 were added to 32 g ethyl acetate.

[0268] 23.1 g Polyiso-01 was added to the mixture. The mixture was heated to the boiling point and stirred until all components were dissolved.

[0269] After bringing the mixture to 25 °C, 0.25 g 1064IR dissolved in 2 mL methylene chloride was added.

[0270] In a separate flask, 0.04 g of OLFINE E1010 was added to 127 g of a 7.3 wt% MOWIOL 488 solution. The ethyl acetate-based solution was added to the aqueous solution. The mixture was cooled in an ice bath and emulsified using a T25 digital Ultra-Turrax® with an 18N rotor commercially available from IKA at 15000 rpm during 5 minutes.

[0271] Ethyl acetate was removed under reduced pressure. During the process, also 10 mL of water was evaporated and therefore, the same amount of water was added to the mixture after evaporation. The mixture was stirred for 16 hours at 65 °C and afterwards cooled to 25 °C.

[0272] Large particles were removed by filtering the mixture using a cloth filter with 60 μm pores.

Preparation of DEV-01

[0273] 8.775 g of Arlo, 1.2 g Proxel K, 70.200 g MOW, 4,785 g DISFLAMOLL TKP, 2.34 g Ethyl Maleate and 105 g of Zinc 3,5-bis(alpha methylbenzyl) salicylate were added to 107.7 g water using a DISPERLUX™ dispenser.

[0274] The mixture was further mixed during 30 minutes.

[0275] The vessel was then connected to a DynoMill-RL filled with 200g of 0.4 mm yttrium stabilized zirconia beads ("high resistant zirconia grinding media" from TOSOH Co.). The mixture was circulated over the mill for 194 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.

[0276] The resulting dispersion exhibited an average particle size of 247 nm as measured with a Malvern™ Nano-S and a viscosity of 239 mPa.s at 25°C and at a shear rate of 10 s^{-1}.

Preparation of curable polyurethane latex LX-01

Preparation of Vylon 220 solution

[0277] In a double jacketed reactor of 2 liter the following compounds were weighed: 554.13 g of acetone (pro analysis) and 261.44 g of Vylon 220 (supplied by Toyobo). The polymer mixture is stirred and heated upto 45°C. When all polymer granules are dissolved the polymer solution is cooled to room temperature.

Preparation of Ymer N120 solution

[0278] The nonionic diol Ymer N120 (CAS 121483-27-7; a 1,3 diol polyether supplied by Perstorp) was preheated in an oven at 80°C, in order to obtain a liquid which can be easily handled. 125 g of Acetone and 84.19 g of Ymer N120 was weighed in an Erlenmeyer of 250 ml and stirred using a magnetic stirrer and heated to 45°C. A clear solution was obtained.

Preparation of Laromer LR8765 solution

[0279] 97.49 g of laromer LR8765 (CASR 52408-42-1, 1,4-butanediol diglycidyl ether diacrylate supplied by BASF) was dissolved in 125 g of acetone in an Erlenmeyer flask of 250 grams.

Preparation of curable polyurethane latex LX-01

[0280] The Ymer N120 and Laromer LR8765 solutions were added to the Vylon 220 solution present in the double jacketed reactor. Subsequently 9.45 g of DMPA was added to reactor. 4.34 g of dibutyl tin laurate was dissolved in 39.10 g of acetone and added to the reactor.

[0281] Then the reactor was heated to 55°C during approximately 35 minutes, allowing the DMPA to dissolve and mix homogenously.

[0282] Subsequently 187.33 Vestanat IPDI (isophorondiisocyanate from Evonik) was added dropwise via an addition funnel with a pressure equalization arm during 20 minutes. The amount isocyanate was an excess amount towards the hydroxyl amount, i.e. NCO/OH = 1.53).

[0283] The reaction was allowed to take place during 2 hours at 55°C. The isocyanato terminated prepolymer and free IPDI which was available in excess were then further reacted using a diol as chain extender. As diol 26.31 grams of 1,4 butane diol (supplied by Acros) was used.

[0284] The reaction mixture was cooled to 43°C, in order to avoid evaporation of acetone. The reaction mixture is then allowed to react overnight during 20 hours at 43°C. After reacting overnight, the reaction mixture was kept for 30 minutes at 55°C in order to reach full conversion, after which the reaction mixture was cooled to room temperature.

[0285] The obtained PU solution in acetone had a concentration of 43.93 wt%

Preparation of curable emulsion UV-01

[0286] In pot A, 10 g of Ebecryl 220 was dissolved in 40 g MEK.

[0287] In pot B, 1 g of Genapol T800P (CAS68439-49-6, commercially available from Clariant) was added to 89 g water.

[0288] Pot A was added to Pot B and stirred for 5 minutes at 14000 rpm using a T25 digital Ultra-Turrax® with an S25N rotor commercially available from IKA. MEK was then evaporated under reduced pressure.

Preparation of the loaded latex LLX-01 and LLX-02

[0289] LLX-01 was prepared by adding 50 g of LX-01 to 14.3 g Inimix 1.

[0290] The mixture was stirred until everything was dissolved.

[0291] 0.23 g of Triethylamine was added under magnetic stirring.

[0292] Afterwards, the mixture was stirred using a DISPERLUX IP series at 1000 rotations per minute and in a timeframe of 10 minutes.

[0293] Then, 40.8 g of water was added and Aceton was removed under vacuo to obtain a white-coloured loaded latex.

[0294] LLX-02 was prepared as described above for LLX-01 but using Inimix 2 instead of Inimix 1.

Preparation of the aqueous UV curable laser markable compositions LMUV-01 to LMUV-05

[0295] The UV curable laser markable compositions LMUV-01 to LMUV-05 were prepared by mixing the ingredients of Table 5.

Table 5

	LMUV-01	LMUV-02	LMUV-03	LMUV-04	LMUV-05
LD-01	1.4	=	1.23	1.3	0.2
DEV-01	2.8	=	3.2	2.45	-
Monomix	3.42	=	-	-	-
Inimix	0.38	-	-	-	-
LLX-01	-	-	2.33	-	-
LLX-02	-	-	-	2.16	-
UV-01	-	-	-	-	3

Storage stability of the compositions LMUV-01 to LMUV-05

[0296] The aqueous UV curable laser markable compositions were stored at 60 °C overnight to assess their storage stability. Those compositons having a sufficient storage stability did not show substantial colourformation under these storage conditions.

[0297] The results are shown in Table 6.

Laser marking of the compositions LMUV-01, LMUV-03 and LMUV-04

[0298] An optically pumped semiconductor laser emitting at 1064 nm (Genesis MX 1064-10000 MTM from COHERENT) was used for producing a black wedge of 0.6 cm x 0.6 cm square boxes of increasing optical density in the laser markable layer. The laser was used at a power level of 4 W measured at the sample, a dither of 0.025, a scan speed of 200 mm/s and at a pulse repetition rate of 10 kHz.

[0299] The optical density of the laser marked areas were measured in reflection using a spectrodensitometer type GretagMacbeth SPM50 using a visual filter

[0300] The laser markable compositions LMUV-01, LMUV-03 and LMUV-04 were marked after coating them a wet thickness of 10 μm, using an Elcometer Bird Film Applicator (from ELCOMETER INSTRUMENTS), on an unsubbed biaxially stretched polyethylene terephthalate sheet (thickness 175 μm) and UV curing (1 pass through a UVIO curing station (20 m/min; D-bulb at 80% power; 880.5 mJ/cm^2 in one pass).

[0301] The results are shown in Table 6.

Table 6

	LMUV-01	LMUV-02	LMUV-03	LMUV-04	LMUV-05
Storage stability	NOK	+/- OK	NOK	OK*	OK
Marking	Black	-	Black	Black	-
* no colour formation after 6 days at 60°C					

[0302] It is clear from the results of Table 6 that the aqueous UV curable laser markable composition comprising a photoinitiator having a MW of at least 250 (LMUV-04) has a much better storage stability compared with those comprising low MW photoinitiator (LMUV-01, LMUV-03).

[0303] It is also clear that the storage stability of compositions comprising water-insoluble polymerizable compounds, which are added as an emulsion (LMUV-04) or as a polymerizable polymer particle (LMUV-04) have a better storage stability compared to those comprising water-soluble polymerizable compounds (LMUV-01 and LMUV-02).

Claims

1. An aqueous radiation curable laser markable composition comprising a polymerizable compound, a photoinitiator, a colour forming agent and an optional optothermal converting agent, **characterized in that** the photoinitiator has a Molecular Weight of at least 250.

2. The aqueous radiation curable laser markable composition according to claim 1 wherein the photoinitiator is a polymeric photoinitiator.

3. The aqueous radiation curable laser markable composition according to claim 1 or 2 wherein the polymerizable compound is insoluble in water.

4. The aqueous radiation curable laser markable composition according to claim 3 wherein the polymerizable compound is emulsified, encapsulated or loaded onto a polymer or co-polymer.

5. The aqueous radiation curable laser markable composition according to any of the preceding claims wherein the polymerizable compound is a polymerizable polymer or co-polymer.

6. The aqueous radiation curable laser markable composition according to claim 4 or 5 wherein the polymer or co-polymer is a polyurethane.

7. The aqueous radiation curable laser markable composition according to any of the preceding claims wherein the colour forming agent is an encapsulated leuco dye and wherein the composition further comprises a developing agent.

8. The aqueous radiation curable laser markable composition according to any of the preceding claims wherein the optothermal converting agent is an infrared dye.

9. The aqueous radiation curable laser markable composition according to claim 8 wherein the infrared dye is encapsulated.

10. A method of preparing a laser markable article comprising the steps of:

    - providing an aqueous radiation curable laser markable composition as defined in any of the claims 1 to 9 on a support; and
    - curing the applied composition by exposing it to UV radiation.

11. The method of preparing a laser markable article according to claim 10 wherein the laser markable composition is provided on a support by intaglio printing, screen printing, flexographic printing, offset printing, inkjet printing, or rotogravure printing.

12. The method of preparing a laser markable article according to claim 10 or 11 wherein the thickness of the applied aqueous radiation curable laser markable is 10 μm or less.

13. A laser markable article obtained by a method as defined in any of the claims 10 to 12.

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

15. A method of preparing a laser marked article comprising the step of exposing a laser markable article as defined in claims 13 or 14 with an infrared laser thereby forming a laser marked image.

Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 19 6211

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 Y	US 2008/090925 A1 (HLADIK MOLLY L [US] ET AL) 17 April 2008 (2008-04-17) * paragraphs [0017], [0023], [0025], [0026], [0028] - [0032], [0036], [0037], [0039], [0040], [0046], [0058], [0062], [0063], [0065], [0066]; claims 1-3 *	1,3-15 1,2,10, 13,15	INV. B41M5/323 B41M5/337
Y,D	EP 2 349 734 B1 (DATALASE LTD [GB]) 28 March 2018 (2018-03-28) * paragraphs [0085] - [0089], [0107], [0108], [0128], [0130], [0135] - [0137], [0142], [0145]; claims 1,8,9,10 *	1,2,5,6, 8,10-13, 15	
Y	EP 3 024 858 B1 (ALLNEX BELGIUM SA [BE]) 18 October 2017 (2017-10-18) * paragraphs [0001], [0006], [0064] *	1,2,5,6, 8,10-13, 15	

TECHNICAL FIELDS SEARCHED (IPC)
B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	3 April 2019	Pulver, Michael

1

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

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

EP 18 19 6211

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

03-04-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008090925 A1	17-04-2008	CN 101522432 A	02-09-2009
		DE 112007002401 T5	30-07-2009
		US 2008090925 A1	17-04-2008
		WO 2008048860 A1	24-04-2008
EP 2349734 B1	28-03-2018	EP 2349734 A1	03-08-2011
		JP 5645832 B2	24-12-2014
		JP 2012506786 A	22-03-2012
		US 2012045624 A1	23-02-2012
		US 2015361289 A1	17-12-2015
		WO 2010049281 A1	06-05-2010
EP 3024858 B1	18-10-2017	CN 105392809 A	09-03-2016
		EP 3024858 A1	01-06-2016
		TW 201504262 A	01-02-2015
		US 2016130380 A1	12-05-2016
		WO 2015010729 A1	29-01-2015

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- WO 2006067073 A **[0007] [0086]**
- WO 2013192307 A **[0008]**
- EP 2349734 A **[0009]**
- WO 2016039960 A **[0010]**
- EP 3095825 A **[0011]**
- EP 3173249 A **[0012]**
- WO 2008075101 A **[0039]**
- WO 2002074548 A **[0040]**
- WO 2007012578 A **[0040]**
- WO 2013014436 A **[0042]**
- WO 2013068729 A **[0044]**
- WO 2015165854 A **[0046] [0063]**
- EP 3297837 A **[0048]**
- WO 2005068207 A **[0056]**
- WO 2007141522 A **[0057]**
- WO 2009059900 A **[0058]**
- WO 2015015200 A **[0058]**
- EP 3297838 A **[0060]**
- EP 2722367 A **[0063]**
- WO 2014124052 A **[0085]**
- WO 2016184881 A **[0089]**
- WO 2015158649 A **[0115]**
- EP 2960306 A **[0116]**
- WO 2015197472 A **[0124]**
- EP 17204844 A **[0130]**
- WO 2003033452 A **[0138]**
- WO 2003033492 A **[0138]**
- US 2006014851 A **[0139]**
- US 2006014853 A **[0139]**
- WO 2017007505 A **[0144]**
- WO 2017007493 A **[0144]**
- US 2006014848 A **[0151]**
- EP 2719540 A **[0215]**
- EP 2719541 A **[0215]**
- WO 2015091782 A **[0218]**
- WO 2014057018 A **[0222]**
- WO 2012044400 A **[0232]**
- EP 3115386 A **[0242]**
- EP 3115430 A **[0242]**
- EP 2463109 A **[0244]**

Non-patent literature cited in the description

- *Near-Infrared Dyes for High Technology Applications,* ISBN 978-0-7923-5101-6 **[0061]**
- *CHEMICAL ABSTRACTS,* 223717-84-8 **[0064]**
- **HRDLOVIC P.** *Polymer News,* 2005, vol. 30 (6), 179-182 **[0136]**
- *Polymer News,* 2005, vol. 30 (8), 248-250 **[0136]**
- **CORRALES T.** *Journal of Photochemistry and Photobiology A: Chemistry,* 2003, vol. 159, 103-114 **[0136]**
- Chemistry & technology of UV & EB Formulation for Coatings, Inks & Paints. **CRIVELLO, J.V. et al.** Volume III: Photoinitiators for Free Radical, Cationic & Anionic Photopolymerisation. John Wiley & Sons Ltd in association with SITA Technology Ltd, 1998, vol. III, 208-224 **[0137]**
- **BERTENS et al.** *RadTech Europe 05, Conference Proceedings,* 2005, vol. 1, 473-478 **[0138]**
- *CHEMICAL ABSTRACTS,* 71512-90-8 **[0150]**
- *CHEMICAL ABSTRACTS,* 1215019-68-3 **[0150]**
- *CHEMICAL ABSTRACTS,* 1182751-31-0 **[0150]**
- **JYOTHI SRI.S.** *International Journal of Pharma and Bio Sciences,* January 2012, vol. 3 (1 **[0159]**
- **ZHANG Y. ; ROCHEFORT D.** *Journal of Microencapsulation,* 2012, vol. 29 (7), 636-649 **[0169]**
- **SALITIN.** Encapsulation Nanotechnologies. Scrivener Publishing LLC, 2013, vol. 5, 137-173 **[0169]**
- *CHEMICAL ABSTRACTS,* 53770-52-8 **[0251]**
- *CHEMICAL ABSTRACTS,* 121483-27-7 **[0278]**
- *CHEMICAL ABSTRACTS,* 52408-42-1 **[0279]**
- *CHEMICAL ABSTRACTS,* 68439-49-6 **[0287]**