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(54) MARKING OF ARTICLES

(57) A method of marking an article (1) comprising a marking step wherein the article (1) including a first (100) and a second (200) colour-forming layer provided on at least part of a support (500), each colour-forming layer capable of forming respectively a first and a second col-

our upon marking, is marked thereby forming an image (350, 350'), characterized in that first and the second colour are formed simultaneously in at least part of the marking step.

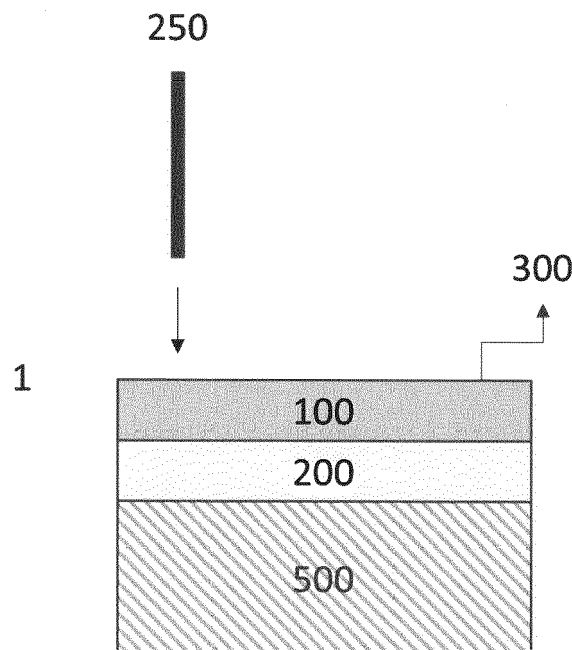


Figure 1

Description**Technical field of the Invention**

[0001] The present invention relates to a method of marking articles, in particular heat-sensitive articles such as packaging and security articles.

Background art for the invention

[0002] A principal objective of security cards and also of other "security documents", such as banknotes, is that they cannot be easily modified or reproduced in such a way that the modification or reproduction is difficult to distinguish from the original.

[0003] Rainbow, also referred to as iris printing, is a special printing technique used for security documents, such as banknotes, passports, ID-cards and other security articles, preventing accurate colour separation or illegal reproduction of the documents by subtly merging colours into each other, resulting in a gradual colour change.

[0004] Conventional rainbow printing is one-dimensional. In such one-dimensional rainbow printing two or more inks of different colours are mixed along a single axial direction, transversely to the path of the substrate being printed. Printing equipment suitable for one-dimensional rainbow printing is for example disclosed in WO2010/056711 (KBA-NOTASYS). Such one-dimensional rainbow printing results in prints of which the colour varies smoothly in one-direction.

[0005] Two-dimensional rainbow printing resulting in prints wherein the colour varies in two directions is also known. For example, WO2008/099330 and WO2019/101683 (both from KBA-NOTASYS) disclose such systems. However, the methods disclosed are rather complex and may suffer from registration problems due to the use of two different printing plates.

[0006] Rainbow printing is typically carried out with offset printing technology. However, with offset rainbow printing a consistent reproduction of the rainbow colours is extremely difficult and a lot of technical skills are required from the operator. Moreover, offset printing is typically used for printing non-variable information on a document or packaging.

[0007] Laser marking is a well known technique to provide information on security documents and/or packaging.

[0008] EP-A 2648920 (Agfa Gevaert NV) discloses a laser markable security document comprising a so-called colour-forming layer including a leuco dye, a developing agent and an optothermal converting agent. A colour may be formed when the colour-forming layer is exposed with an IR laser.

[0009] EP-A 2722367 (Agfa Gevaert NV) discloses security documents capable of forming a full colour image upon laser marking. The security documents comprise three different colour-forming layers, the colour-forming layers each comprising a different leuco dye and a different infrared dye. Exposing the security document with three different IR lasers results in full colour laser marked images.

Summary of the invention

[0010] It is an object of the present invention to provide a method to produce rainbow patterns on a security article or packaging characterized by a reduced complexity, less registration problems and that may be used for providing variable data.

[0011] That object has been realised by the method as defined in claim 1.

[0012] Further objects of the invention will become apparent from the description hereinafter.

Brief description of drawings

[0013]

Figure 1: A schematic representation of a preferred embodiment of a method according to the present invention.

Figure 2: A schematic representation of a rainbow pattern (a one-dimensional pattern in Figure 2A, a two-dimensional pattern in Figure 2B) obtained with a preferred embodiment of a method according to the present invention.

Figure 3: A schematic representation of a preferred embodiment of an article used in a method according to the present invention.

Figure 4: A schematic representation of a preferred embodiment of a security card used in a method according to the present invention.

Definitions

[0014] Unless otherwise specified the term "alkyl" means all variants possible for each number of carbon atoms in the

alkyl group i.e. methyl, ethyl, for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethyl-propyl and 2-methyl-butyl, etc.

[0015] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C₁ to C₆-alkyl group.

[0016] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C₂ to C₆-alkenyl group.

[0017] Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C₂ to C₆-alkynyl group.

[0018] Unless otherwise specified a substituted or unsubstituted aralkyl group is preferably a phenyl or naphthyl group including one, two, three or more C₁ to C₆-alkyl groups.

[0019] Unless otherwise specified a substituted or unsubstituted alkaryl group is preferably a C₇ to C₂₀-alkyl group including a phenyl group or naphthyl group.

[0020] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group

[0021] 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.

[0022] 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

[0023] 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 -NO₂.

Method of marking an article

[0024] The method of marking an article according to the present invention comprises a marking step wherein the article (1) including a first (100) and a second (200) colour-forming layer, each layer capable of forming respectively a first and a second colour upon marking, provided on at least part of a support (500) is marked thereby forming an image (350, 350'),

characterized in that the first and second colours are formed simultaneously in at least part of the marking step.

[0025] Marking is preferably carried out with heat, radiation or pressure, more preferably by heat.

[0026] A colour image is typically marked by selectively addressing colour-forming layers, for example using three different lasers as disclosed in EP-A 2722367 (Agfa Gevaert). In the method according to the present invention, both layers are simultaneously addressed by for example a single laser or a printhead or a pressure. This means that the second colour is always formed in combination with the first colour. The marked image does not include the "pure" second colour but a colour that is a mix of the first and the second colour.

[0027] The article may further comprises a third colour-forming layer capable of forming a third colour upon marking. The image formed in the marking step, also referred to as image formation step, is preferably composed with the first, second and third colour. In the marking step at least two of the first, second and third colours are formed simultaneously in at least part of the marking step.

[0028] In a preferred embodiment marking is carried out with heat. The method of marking then includes a marking step wherein a heat-sensitive article (1) including a first (100) and a second (200) colour-forming layer, capable of forming respectively a first and a second colour upon exposure to heat, provided on at least part of a support (500) is exposed to heat thereby forming an image (350, 350'),

characterized in that the first and second colours are formed simultaneously in at least part of the marking step.

[0029] A heat treatment is used in the marking step to form the colours. The heat treatment may be a direct heat treatment, for example using a thermal print head. Alternatively, the heat treatment is an indirect heat treatment, wherein radiation such as UV or IR radiation is applied and converted by an opthothermal converting agent into heat.

[0030] In a preferred embodiment, heat is provided by means of a laser, preferably an infrared (IR) laser, more preferably a Near Infrared (NIR) laser.

[0031] A particularly preferred method of preparing a marked article according to the present invention comprises an image formation step wherein a laser markable article (1) including a first (100) and a second (200) colour-forming layer, capable of forming respectively a first and a second colour upon exposure with a laser (250), provided on at least part of a support (500) is exposed with the laser (250) at varying energy densities measured on a surface (300) of the article thereby forming an image (350, 350'), characterized in that the first and the second colours are formed simultaneously in at least part of the image formation step.

[0032] The colour-forming layers preferably comprise a leuco dye and a developing agent.

[0033] The colour-forming layers may comprise one, two, three or more leuco dyes. When the colour-forming layers

each comprise one leuco dye, the leuco dyes are different from each other and are capable of forming a different colour. When the colour-forming layers comprise more than one leuco dye, i.e. a mixture of leuco dyes, then each mixture of leuco dyes is capable of forming a different colour.

[0034] Each colour-forming layer may comprise a different developing agent. However, it is preferred that all colour-forming layers comprise the same developing agent.

[0035] When heat is provided by means of a laser, at least one of the colour-forming layers preferably includes an optothermal converting agent. However, when a CO₂ laser is used, the colour-forming composition preferably do not contain an optothermal converting agent. The colour-forming layers may comprise different optothermal converting agents, however it is preferred that the optothermal converting agent is the same for all colour-forming layers.

[0036] In a preferred embodiment, a UV blocking layer (400) may be provided on top of the colour-forming layers to improve the daylight stability of the marked image (See Figure 3).

[0037] Also, an overlay (600) may be provided on top of the colour-forming layers (100 and 200) or the optional UV blocking layer (400) to protect the marked image for example from physical damage or moisture (See Figure 3).

[0038] Also, an interlayer (300) may be provided between the colour-forming layers or between a colour-forming layer and a UV blocking layer (See Figure 3). The interlayer may also contain optothermal converting agents or developing agents.

[0039] The colour-forming layers and the optional UV blocking layer and interlayer may be provided on the complete surface or on a part of the surface.

[0040] The manufacturing method of the article is described below. The colour-forming layers are prepared by applying a colour-forming composition on a support or on another colour-forming layer or interlayer.

Method of preparing a markable article

[0041] The method of preparing a markable article according to the present invention comprises the steps of applying at least two colour-forming compositions as described below on at least part of a support thereby forming at least two colour-forming layers on the support.

[0042] The compositions may be provided onto a support by co-extrusion or any conventional coating technique, such as dip coating, knife coating, extrusion coating, spin coating, spray coating, slide hopper coating and curtain coating.

[0043] The compositions may also be provided onto a support by any printing method such as intaglio printing, screen printing, flexographic printing, offset printing, inkjet printing, valve jet printing, rotogravure printing, etc. Using a printing method is preferred when only a part or several parts of a support has to be provided with the colour-forming layers.

[0044] Each coated or printed layer is preferably dried before a subsequent layer is applied.

[0045] Drying is preferably carried out at a temperature between 15 and 130°C, preferably between 25°C and 100°C, most preferably between 40 and 80 °C.

[0046] Upon drying/heating, covalent bonds can optionally be formed, resulting in better adhesion or mechanical properties. This may be realized by adding cross-linking agents or cross-linkable binders to the colour-forming or other layers, as disclosed in EP-A 19216842.5 and EP-A19216821.9, both from Agfa NV and filed on 17-12-2019.

[0047] When radiation curable colour-forming compositions as described below are used, a curing step is carried out after applying the colour-forming layers. Preferably, a curing step is carried out between application of a first colour-forming layer and a second colour-forming layer.

[0048] The curing step is preferably carried out with UV radiation, preferably LED UV radiation.

[0049] Interlayers maybe provided between the colour-forming layers and top-layers on top of the second or third colour-forming layer. These interlayers and/or top layers may also be prepared from radiation curable compositions.

Colour-forming composition

[0050] The colour-forming compositions used to manufacture the colour-forming layers of the laser markable article preferably include a leuco dye, a developing agent and an optional optothermal converting agent.

[0051] The colour-forming composition may be an aqueous or non-aqueous composition.

[0052] A preferred aqueous based composition includes encapsulated leuco dyes. Such aqueous compositions where-in the leuco dyes are encapsulated are disclosed in for example EP-A 3297837, EP-A 3470134 and EP-A 3470135, all from Agfa Gevaert NV.

[0053] The aqueous based composition may be radiation curable, preferably UV curable. Such radiation curable aqueous composition are disclosed in EP-A 3626471 and EP-A 3626472 (both from Agfa Gevaert NV).

[0054] Non-aqueous colour-forming compositions are disclosed in for example EP-A 3083261 (Agfa Gevaert NV).

[0055] The non-aqueous colour-forming compositions are preferably radiation curable, more preferably UV curable. Such radiation curable compositions preferably comprise a polymerizable compound and a photoinitiator. Such radiation curable composition may further comprise a polymerization inhibitor.

Leuco dye

[0056] The colour-forming composition preferably comprises a leuco dye.

[0057] A leuco dye is a substantially colourless compound, which may form a coloured dye upon an inter- or intra-molecular reaction. The inter- or intra-molecular reaction may be triggered by heat, preferably heat formed during exposure with an IR laser.

[0058] Examples of leuco dyes are disclosed in WO2015/165854 (Agfa Gevaert), paragraph [069] to [093]. Preferred leuco dyes are fluoran and phthalide leuco dyes.

[0059] The colour-forming layer may comprise more than one leuco dye. Using two, three or more leuco dyes may be necessary to realize a particular colour or to achieve a better solubility of the leuco dyes.

[0060] The total amount of leuco dye in the colour-forming layer is preferably in the range from 0.05 to 2 g/m², more preferably in the range from 0.1 to 1 g/m².

Developing agent

[0061] The colour-forming composition preferably comprises a developing agent.

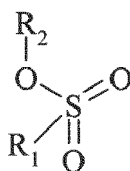
[0062] A developing agent is capable of reacting with a colourless leuco dye resulting in the formation of a coloured dye upon laser marking. Typically, upon laser marking a compound is released that may react with a leuco dye thereby forming a coloured dye.

[0063] All publicly-known photo- or thermal acid generators can be used as developing agent. Thermal acid generators are for example widely used in conventional photoresist material. For more information, see for example "Encyclopaedia of polymer science", 4th edition, Wiley or "Industrial Photoinitiators, A Technical Guide", CRC Press 2010.

[0064] Preferred classes of photo- and thermal acid generators are iodonium salts, sulfonium salts, ferrocenium salts, sulfonyl oximes, halomethyl triazines, halomethylarylsulfone, α -haloacetophenones, sulfonate esters, t-butyl esters, allyl substituted phenols, t-butyl carbonates, sulfate esters, phosphate esters and phosphonate esters.

[0065] Preferred developing agents for aqueous laser markable compositions are disclosed in EP-A 3470134 (Agfa Gevaert NV), paragraph [0142] to [0149]. A particular preferred developing agent is a metal salt of salicylic acid, for example zinc salicylate. A particularly preferred colour developing agent is zinc 3,5-bis(α -methylbenzyl) salicylate.

[0066] For non-aqueous laser markable compositions, and in particular for radiation curable non-aqueous laser markable compositions, a preferred developing agents has a structure according to Formula (I)



Formula I

wherein

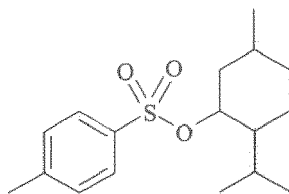
R1 represent an optionally substituted alkyl group, an optionally substituted (hetero)cyclic alkyl group, an optionally substituted alkanyl group, an optionally substituted alkenyl group, an optionally substituted alkynyl group, an optionally substituted (hetero)aryl group, an optionally substituted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

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

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

[0067] Such developing agents according to Formula I and their preparation is disclosed in WO2015/091688, paragraph [052] to [070] (Agfa Gevaert NV).

[0068] A particular preferred developing agent according to Formula I is menthyl p-toluene sulfonate and has the following chemical structure.



[0069] The amount of developing agent in the colour-forming layer is preferably in the range from 0.05 to 5 g/m², more preferably in the range from 0.1 to 3 g/m².

Optothermal converting agent

[0070] The colour-forming composition may comprise an optothermal converting agent.

[0071] The optothermal converting agent may also be present in a layer adjacent to the colour-forming layer, for example an interlayer or an UV blocking layer.

[0072] An optothermal converting agent generates heat upon absorption of radiation.

[0073] The optothermal converting agent preferably generates heat upon absorption of infrared (IR) radiation, more preferably near infrared (NIR) radiation.

[0074] Near infrared radiation has a wavelength between 750 and 2500 nm.

[0075] The optothermal converting agents may be an infrared radiation absorbing pigment, an infrared radiation absorbing dye or a combination thereof.

[0076] The optothermal converting agent may be different for each colour-forming layer but preferably each colour-forming layer includes the same optothermal converting layer.

[0077] The amount of the optothermal converting agents in the colour-forming layers is preferably optimized to obtain optimal rainbow effects. The amount may be identical for each colour-forming layer or may be different. It is preferred that, when the same optothermal converting agent is used, it is present in the layers in different amounts. The reason is that it is possible to selectively activate one layer with low laser densities, and increasingly activate the second and optionally third layer with increasing energy densities. It is therefore preferred that only one layer contains the optothermal converting agent. If there are three layers, it is preferred that the top or bottom layer contains the optothermal converting agent.

[0078] It is also possible that the optothermal converting agent is present in an intermediate layer, a primer, or a top coating.

[0079] The amount of optothermal converting agent in the colour-forming layer is preferably at least 10⁻¹⁰ g/m², more preferably between 0.0001 and 0.5 g/m², most preferably between 0.0005 and 0.1 g/m².

Infrared radiation absorbing inorganic pigments

[0080] Any Near Infrared absorbing pigment may be used in the present invention.

[0081] A preferred inorganic infrared absorber is a copper salt as disclosed in WO2005/068207 (DATALASE).

[0082] Another preferred inorganic infrared absorber are non-stoichiometric metal salts, such as disclosed in WO2007/141522 (DATALASE).

[0083] 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. A particular preferred tungsten oxide is cesium tungsten oxide (CTO).

Carbon black

[0084] Another preferred infrared radiation absorbing pigment (IR pigment) is carbon black, such as acetylene black, channel black, furnace black, lamp black, and thermal black.

[0085] Due to its light absorption in the visible region, i.e. between 400 nm and 700 nm, a too high amount of carbon black may result in an increase of the background colour of the layer comprising the carbon black.

[0086] For that reason, the amount of carbon black in the laser markable layer is preferably less than 0.1 g/m², more preferably less than 0.01 g/m², most preferably less than 0.005 g/m². Infrared radiation absorbing dyes

[0087] 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.

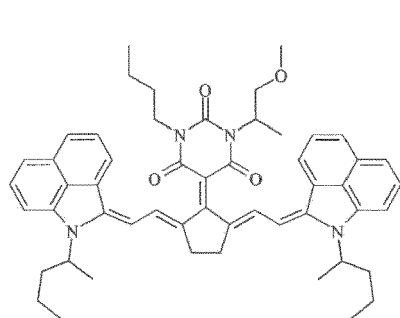
[0088] Any IR dye may be used, for example the IR dyes disclosed in "Near-Infrared Dyes for High Technology

Applications" (ISBN 978-0-7923-5101-6).

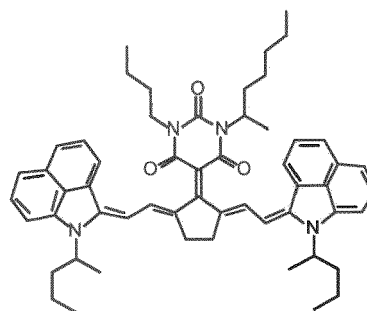
[0089] Preferred IR dyes are polymethine dyes due to their low absorption in the visible region and their selectivity, i.e. narrow absorption peak in the infrared region. Particular preferred polymethine IR dyes are cyanine IR dyes.

[0090] 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], both from Agfa Gevaert NV.

[0091] IR dyes having an absorption maximum between 1000 nm and 1100 nm are preferably selected from the group consisting of quinoline dyes, indolenine dyes, especially a benzo[cd]indoline dye. A particularly preferred IR dye is 5-[2,5-bis[2-[1-(1-methylbutyl)-benz[cd]indol-2(1H)-ylidene]ethylidene]-cyclopentylidene]-1-butyl-3-(2-methoxy-1-methyl-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

[0092] 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.

[0093] Other preferred NIR absorbing compounds are those disclosed in WO2019/007833, paragraph [0034] to [0046]. It has been observed that these NIR absorbing compounds have a better daylight stability compared to the IR dyes described above and are therefore more suitable to be used in UV curable compositions.

Acid Scavenger

[0094] The colour-forming layer or an interlayer of the laser markable article may contain one or more acid scavengers.

[0095] Acid scavengers include organic or inorganic bases. Examples of the inorganic bases include hydroxides of alkali metals or alkaline earth metals; secondary or tertiary phosphates, borates, carbonates; quinolines and metalborates of alkali metals or alkaline earth metals; a combination of zinc hydroxide or zinc oxide and a chelating agent (e.g., sodium picolinate); hydrotalcite such as Hycite 713 from Clariant; ammonium hydroxide; hydroxides of quaternary alkylammoniums; and hydroxides of other metals. Examples of the organic bases include aliphatic amines (e.g., trialkylamines, hydroxylamines and aliphatic polyamines); aromatic amines (e.g., N-alkyl-substituted aromatic amines, N-hydroxylalkyl-substituted aromatic amines and bis[p-(dialkylamino)phenyl]-methanes), heterocyclic amines, amidines, cyclic amidines, guanidines and cyclic guanidines.

[0096] Other preferred acid scavengers are HALS compounds. Example of suitable HALS include Tinuvin™ 292, Tinuvin™ 123, Tinuvin™ 1198, Tinuvin™ 1198 L, Tinuvin™ 144, Tinuvin™ 152, Tinuvin™ 292, Tinuvin™ 292 HP, Tinuvin™ 5100, Tinuvin™ 622 SF, Tinuvin™ 770 DF, Chimassorb™ 2020 FDL, Chimassorb™ 944 LD from BASF; Hostavin 3051, Hostavin 3050, Hostavin N 30, Hostavin N321, Hostavin N 845 PP, Hostavin PR 31 from Clariant.

[0097] Further examples of acid scavengers are salts of weak organic acids such as carboxylates (e.g. calcium stearate).

[0098] A preferred acid scavenger is an organic base, more preferably an amine.

[0099] A particular preferred acid scavenger is an organic base having a pK_b of less than 7.

[0100] It has been observed that acid scavengers may improve the storage stability of the laser markable article.

UV absorbers

[0101] The markable article may also comprise an UV-absorber. The UV-absorber may be present in a colour-forming layer or may also be present in another layer. An UV-absorber is preferably present in an UV blocking layer.

[0102] Examples of suitable UV-absorbers include 2-hydroxyphenyl-benzophenones (BP) such as Chimassorb™ 81 and Chimassorb™ 90 from BASF; 2-(2-hydroxyphenyl)-benzotriazoles (BTZ) such as Tinuvin™ 109, Tinuvin™ 1130, Tinuvin™ 171, Tinuvin™ 326, Tinuvin™ 328, Tinuvin™ 384-2, Tinuvin™ 99-2, Tinuvin™ 900, Tinuvin™ 928, Tinuvin™

Carboprotect™ Tinuvin™ 360, Tinuvin™ 1130, Tinuvin™ 327, Tinuvin™ 350, Tinuvin™ 234 from BASF, Mixxim™ BB/100 from FAIRMOUNT, Chiguard 5530 from Chitec; 2-hydroxy-phenyl-s-triazines (HPT) such as Tinuvin™ 460, Tinuvin™ 400, Tinuvin™ 405, Tinuvin™ 477, Tinuvin™ 479, Tinuvin™ 1577 ED, Tinuvin™ 1600 from BASF, 2-(2,4-dihydroxyphenyl)-4,6-bis-(2,4-dimethylphenyl)-s-triazine (CASRN1668-53-7) from Capot Chemical Ltd and 4-[4,6-bis(2-methyl-phenoxy)-1,3,5-triazin-2-yl]-1,3-benzenediol (CASRN13413-61-1); titanium dioxide such as Solasorb 100F from Croda Chemicals; zinc oxide such as Solasorb 200F from Croda Chemicals; benzoxazines such as Cyasorb UV-3638 F, CYASORB™ UV-1164 from CYTEC; and oxamides such as Sanduvor VSU from Clariant.

[0103] Preferred UV absorbers have in the wavelength region between 300 and 400 nm a maximum absorption above 330 nm, more preferably above 350 nm.

[0104] Particular preferred UV absorbers are hydroxyphenyl benzotriazoles and 2-hydroxyphenyl-s-triazines having a maximum absorption above 350 nm in the wavelength region 300-400 nm.

[0105] It has been observed that the presence of UV absorbers may improve the daylight stability of the laser marked image.

Polymerizable compound

[0106] A radiation curable markable composition preferably comprises at least one polymerizable compound. The composition may comprise one, two, three or more different polymerizable compounds.

[0107] The polymerizable compounds may be monomers, oligomers or prepolymers.

[0108] The polymerizable compounds may be diluted or dispersed, for example in water.

[0109] The polymerizable compounds may be free radical polymerizable compounds or cationic polymerizable compounds.

[0110] Preferred monomers and oligomers are those listed in paragraphs [0103] to [0126] of EP-A 1911814 (Agfa NV).

[0111] Cationic polymerization is superior in effectiveness due to lack of inhibition of the polymerization by oxygen. However it is expensive and slow, especially under conditions of high relative humidity. If cationic polymerization is used, it is preferred to use an epoxy compound together with an oxetane compound to increase the rate of polymerization.

[0112] Radical polymerization is the preferred polymerization process. Preferred free radical polymerizable compounds include at least one acrylate or methacrylate group or at least one acrylamide or methacrylamide group as polymerizable group, referred to herein as (meth)acrylate or (meth)acrylamide monomers, oligomers or prepolymers. Due to their higher reactivity, particularly preferred polymerizable compounds are acrylate monomers, oligomers or prepolymers.

[0113] Other preferred monomers, oligomers or prepolymers are N-vinylamides, such as N-vinylcaprolactam and acryloylmorpholine.

[0114] Particularly preferred (meth)acrylate monomers, oligomers or prepolymers are selected from the group consisting of tricyclodecanedimethanol diacrylate (TCDDMDA); isobornyl acrylate (IBOA); ethoxylated [4] bisphenol A diacrylate; 1,10 decanediol diacrylate; dipropylene glycol diacrylate (DPGDA); ethoxylated [4] bisphenol diacrylate and urethane acrylate oligomer.

[0115] The total amount of polymerizable compounds is preferably at least 50 wt%, more preferably at least 70 wt%, most preferably at least 80 wt%, relative to the total weight of the composition.

Photoinitiator

[0116] A radiation curable markable composition preferably contains a photoinitiator. The initiator typically initiates the polymerization reaction. The photo-initiator may be a Norrish type I initiator, a Norrish type II initiator or a photo-acid generator, but is preferably a Norrish type I initiator, a Norrish type II initiator or a combination thereof.

[0117] A preferred Norrish type I-initiator is selected from the group consisting of benzoinethers, benzil ketals, α,α -dialkoxyacetophenones, α -hydroxyalkylphenones, α -aminoalkylphenones, acylphosphine oxides, acylphosphine sulfides, α -haloketones, α -halosulfones and α -halophenylglyoxalates.

[0118] A preferred Norrish type II-initiator is selected from the group consisting of benzophenones, thioxanthenes, 1,2-diketones and anthraquinones.

[0119] Suitable photo-initiators are disclosed in CRIVELLO, J.V., et al. VOLUME III:

Photoinitiators for Free Radical Cationic & Anionic Photopolymerization. 2nd edition.

Edited by BRADLEY, G.. London,UK: John Wiley and Sons Ltd, 1998. p.287-294 .

[0120] In order to increase the photosensitivity further, the radiation curable composition may additionally contain co-initiators.

[0121] A preferred co-initiator is selected from the group consisting of an aliphatic amine, an aromatic amine and a thiol. Tertiary amines, heterocyclic thiols and 4-dialkylamino-benzoic acid are particularly preferred as co-initiator.

[0122] The most preferred co-initiators are aminobenzoates for reason of shelf-life stability of the radiation curable composition.

[0123] A preferred amount of photoinitiator is 0.3 - 20 wt% of the total weight of the radiation curable composition, more preferably 1 - 15 wt% of the total weight of the radiation curable composition.

[0124] The amount of co-initiator or co-initiators is preferably from 0.1 to 20.0 wt%, more preferably from 1.0 to 10.0 wt%, based in each case on the total weight of the radiation curable composition.

Polymerization Inhibitors

[0125] For improving the shelf-life, a radiation curable markable composition may contain a polymerization inhibitor. Suitable polymerization inhibitors include phenol type antioxidants, hindered amine light stabilizers, phosphor type antioxidants, hydroquinone monomethyl ether commonly used in (meth)acrylate monomers, and hydroquinone, t-butylcatechol, pyrogallol may also be used.

[0126] Suitable commercial inhibitors are, for example, Sumilizer™ GA-80, Sumilizer™ GM and Sumilizer™ GS produced by Sumitomo Chemical Co. Ltd.; Genorad™ 16, Genorad™ 18 and Genorad™ 20 from Rahn AG; Irgastab™ UV10 and Irgastab™ UV22, Tinuvin™ 460 and CGS20 from Ciba Specialty Chemicals; Floorstab™ UV range (UV-1, UV-2, UV-5 and UV-8) from Kromachem Ltd, Additol™ S range (S100, S110, S120 and S130) from Cytec Surface Specialties.

[0127] Since excessive addition of these polymerization inhibitors will lower the sensitivity to curing, it is preferred that the amount capable of preventing polymerization is determined prior to blending. The amount of a polymerization inhibitor is preferably lower than 2 wt% of the total radiation curable laser markable composition.

Interlayer

[0128] An interlayer maybe provided between the colour-forming layers.

[0129] An interlayer maybe prepared from an aqueous or a non-aqueous coating solution. The interlayer may comprise a polymeric binder.

[0130] The interlayer preferably contains an acid scavenger as described above to prevent diffusion of an acid from one laser markable layer to another.

[0131] The interlayer preferably also contains a UV absorber as described above to improve the daylight stability of the laser marked articles.

[0132] The presence of an interlayer and the thickness of such an interlayer may have an influence on the rainbow effect. Also, an IR absorbing compound may be added to an interlayer to further optimize the rainbow effect.

UV blocking layer

[0133] A UV blocking layer (400) may be provided on the colour-forming layers, for example on the colour-forming layer (200) in Figure 3.

[0134] The UV blocking layer includes one or more UV absorbers as described above.

[0135] When the colour-forming layers are provided on only a part of the surface, it is preferred that the UV blocking layer is only applied on the colour-forming layers and not on the part of the surface not provided with the colour-forming layers.

Support

[0136] The compositions may be applied on any type of support, for example a metallic support, a glass support, a polymeric support, or a paper support. The compositions may also be applied on a textile surface.

[0137] The support may be provided with a primer to improve the adhesion between the support and the applied layers.

[0138] The support maybe transparent or opaque.

[0139] To improve the contrast of the marked image, the support may be a white support. The support then typically comprises a white dye or pigment, for example a titanium oxide pigment. Such a white support may be obtained by providing a white primer on a support.

[0140] When the markable article is used as laminate wherein the support becomes after lamination a top layer, for example to prepare a security document as described below, the support is preferably transparent.

[0141] The support may be a paper support, such as plain paper or resin coated paper, e.g. polyethylene or polypropylene coated paper.

[0142] 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.

[0143] 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.

[0144] 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.

[0145] Preferred polymeric supports are polyvinylchloride (PVC), polycarbonate (PC) and polyethylene terephthalate (PET) supports.

[0146] A preferred PET support is a biaxially stretched polyethylene terephthalate (BOPET) foil due to its very high durability and resistance to scratches and chemical substances.

[0147] The manufacturing of such BOPET foils and supports is well-known in the art of preparing suitable supports for silver halide photographic films. For example, GB 811066 (ICI) teaches a process to produce biaxially oriented polyethylene terephthalate foils and supports.

[0148] There is no restriction on the shape of the support. It can be a flat sheet, such as a paper sheet or a polymeric film or it can be a three dimensional object like e.g. packaging box or a coffee cup.

[0149] 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.

[0150] The 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.

[0151] The most commonly used shrink foils are polyolefin foils, i.e. polyethylene or polypropylene foils. However, other shrink foils include PCV foils.

Packaging

[0152] Laser marking or thermal printing is typically used to add variable data, for example batch numbers, expiry dates, addressees, barcodes, etc. on the packaging. However, laser marking or thermal printing may also be used to add a combination of fixed and variable data on a packaging. Variable and/or fixed data may also include images.

[0153] The article described above makes it possible to mark coloured data and/or images in a rainbow pattern. The rainbow effect may be used for aesthetic reasons or to make it more difficult to imitate the data and/or images.

[0154] Marking is preferably carried out in-line in the packaging process. An advantage of laser or thermal printing marking is the possibility to add data at a very late stage of the packaging process.

[0155] Another advantage of using laser marking or thermal printing instead of another printing technique, such as inkjet printing, is the absence of any chemicals in the marking process. Especially for pharmaceutical and food packaging, the absence of chemicals in the packaging line is an advantage.

[0156] Still another advantage of laser marking is the ability to provide the "image" with a laser on a 3D object or the mark through a transparent foil or layer.

[0157] A preferred packaging is folded cardboard or corrugated cardboard laminated with paper. Such packaging is preferably used for cosmetics, pharmaceuticals, food or electronics.

[0158] The heat-sensitive article according to the present invention may also be used for brand protection as it is difficult to counterfeit. For example, the heat-sensitive article may be a cap of a bottle of champagne, the sealing of the cap of a container, the label of a bottle of wine, etc.

Security Documents

[0159] The marking method, in particular using a laser in the image formation step, may also be used to prepare security documents, such as for example ID cards.

[0160] Preferably, the security document is prepared by laminating a laser markable article according to the present invention, optionally together with other foils or laminates, onto one or both sides of a core support.

[0161] A schematic representation of such a security document (2) is illustrated in Figure 4. The article (1), also referred to as a laser markable laminate, is provided on a core support. Laser marking is carried out through the support (500). For that reason, the support is preferably transparent.

[0162] The transparent support may include UV absorbers to act as a UV blocking layer. However, a UV blocking layer may also be provided on either side of the support.

[0163] Core supports typically used to prepare security documents are disclosed in EP-A 3431304 (Agfa Gevaert NV), paragraphs [0128] to [0138]. Preferred polymeric cores are based on polycarbonate (PC), polyvinylchloride (PVC), and polyethylene terephthalate (PET).

[0164] The laser markable laminate is typically laminated on one or both sides of a core support using elevated temperatures and pressures.

[0165] The lamination temperature depends on the type of core support used. For a polyester core, lamination tem-

peratures are preferably between 120 and 140°C, while they are preferably above 150°C - 160°C for a polycarbonate core.

Rainbow marking

[0166] Rainbow printing is a widely used security feature used in for example ID cards and banknotes. By subtly merging different colours a gradual colour change is realized. Rainbow printing protects the security documents from colour separation and copying.

[0167] Such rainbow printing with offset is very cumbersome and needs a lot of technical skills of the operator. Also, the rainbow effect obtained with offset printing is typically in one direction. Offset may be used to obtain the rainbow effect in two directions, as disclosed in WO2008/099330 and WO2019/10163 (both from KBA) but in such methods a rather complicated workflow is necessary.

[0168] With the method according to the present invention, a rainbow effect can be generated in any direction. The direction of the rainbow effect is determined by the direction in which the laser or thermal print head move on the article. Figure 2 illustrates the formation of a one-dimensional (Fig2a) and a two-dimensional (Fig2b) rainbow pattern.

[0169] An additional advantage of the method according to the present invention is the possibility to generate variable data having a rainbow pattern. With Offset printing, which is now used to print rainbow patterns, it is not possible to print variable data.

Laser marking

[0170] In principle any laser may be used.

[0171] The laser can be a solid state laser, such as a disk laser, a Nd:Yag laser or a Fiber laser. The laser can be a gas laser, such as a He-Ne laser, a CO₂-laser, or an Excimer laser.

[0172] The laser can be a semiconductor laser, such as a diode laser or a VCSEL laser. The laser can also be a liquid laser such as a 580 nm Ring Dye laser.

[0173] The laser is preferably an infrared (IR) laser.

[0174] The IR laser may be a continuous wave or a pulsed laser.

[0175] 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.

[0176] A particularly preferred NIR laser is an optically pumped semiconductor laser. Optically pumped semiconductor lasers have the advantage of unique wavelength flexibility, different from any other solid-state based laser. The output wavelength can be set anywhere between about 900 nm and about 1250 nm. This allows a perfect match between the laser emission wavelength and the absorption maximum of an optothermal converting agent present in the laser markable layer.

[0177] 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.

[0178] Laser marking may also be carried out using a so-called Spatial Light Modulator (SLM) as disclosed in WO2012/044400 (Vardex Laser Solutions).

[0179] The energy density per unit of length (E_d) is dependent on the average laser power of the laser beam (P_{avg}) and the velocity of the laser beam (v) as described in the following Formula:

$$E_d \text{ [J/m]} = \frac{P_{avg} \text{ [W]}}{v \text{ [m/s]}}$$

[0180] The average laser power P_{avg} relates to the laser power according to the following Formula:

$$P_{avg} \text{ [W]} = P * f * W$$

wherein

P is the laser power [W];

f is the frequency [Hz] and
W is the pulse width [s]

[0181] Referring to Figure 1, lower energy densities will result in a first colour formed in the first colour-forming layer. As the energy density of the laser increases, a second colour will be formed in the second colour-forming layer, in addition to the first colour. By varying the energy density of the laser, a gradual colour change is generated, resulting in a rainbow pattern.

[0182] The image maybe laser marked using a vector mode or a raster mode.

[0183] Raster and vector are different graphic file types which require different modes of laser processing. The main difference between vector and raster graphics is that raster graphics are composed of pixels, while vector graphics are composed of paths or lines.

[0184] In raster mode, laser marking uses the same type of process used by inkjet printers, where a file, the raster file, representing the image is printed line by line. The raster file is a bitmap, which means it is made up of pixels. The image is marked with a laser line by line, point by point, similar to the way in which an inkjet printer applies ink, but instead of ink being applied, the laser marks the material. This is a "bi-directional" process in which marking is done in alternating fashion in both directions.

[0185] During the line-by-line raster marking process, the speeds of the two axes are very different. The speed is high on the x axle (the axle to which the laser head is attached) and lower by comparison on the y axle.

[0186] In raster mode, the ppi parameter (pulses per inch) is important because it controls the density of the laser points.

[0187] In vector mode, the file representing the image to be marked is a graphic file consisting of vectors (lines and curves of a geometry). In vector mode laser marking, the axes move simultaneously, and more slowly than in raster mode.

Thermal printing

[0188] Heat may be applied to the heat-sensitive article by means of a so-called thermal print heads.

[0189] In principle any type of thermal print head may be used. A thermal print head comprises heating elements. The heating elements convert electrical energy into heat through the process of Joule heating. Electric current through the element encounters resistance, resulting in heating of the element. The amount of electrical energy supplied to the heating elements can be varied by varying the amount of electric current within a particular time interval and/or varying the time interval during which electric current is supplied.

[0190] The number of heating elements of a print head determines the print resolution. Typical values are 200 to 300 heating elements (dots) per inch (dpi). However, thermal printers with a resolution of 400 and 600 dpi are also available.

[0191] Thermal printers and thermal printing methods are disclosed in for example US850287 (Zinc Imaging), Datalase (WO2020/020901) and US2020/016904 (Canon).

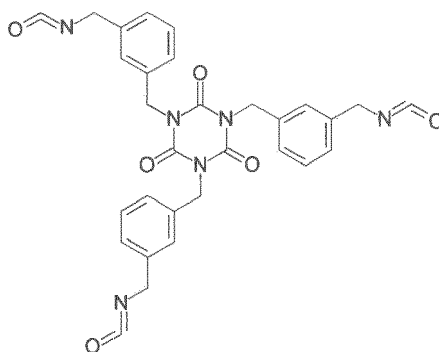
[0192] Referring to Figure 1, lower temperatures will result in a first colour formed in the first colour-forming layer. As the temperature increases, a second colour will be formed in the second colour-forming layer, in addition to the first colour. By varying the temperature, a gradual colour change is generated, resulting in a rainbow pattern.

EXAMPLES

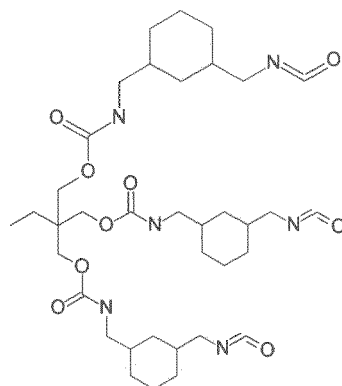
MATERIALS

[0193] All materials used in the following examples were readily available from standard sources such as ALDRICH CHEMICAL Co. (Belgium) and ACROS (Belgium) unless otherwise specified. The water used was deionized water.

[0194] **Takenate D131N** is an XDI Isocyanurate commercially available from Mitsui. The structures are shown below.



[0195] **Takenate D120N** are aliphatic triisocyanates (H6XDI-TMP adduct) commercially available from Mitsui, with the following structure:



[0196] **Olfine E1010** is a wetting agent commercially available from Shin-Etsu Chemical Company.

[0197] **Mowiol 4 88** is a polyvinyl alcohol commercially available from Kuraray.

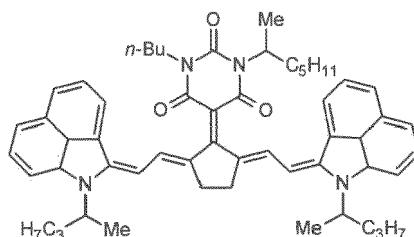
[0198] **Red 40** is a red leuco dye commercially available from Mitsui.

[0199] **Orange DCF** is an orange leuco dye commercially available from Connect Chemicals.

[0200] **Blue-63** is a blue leuco dye commercially available from Mitsui.

[0201] **GN-2** is a blue leuco dye commercially available from Mitsui.

[0202] **IR1064** is an infrared absorbing dye with the following structure,



IR1064 can be prepared according to the synthetic methods reported in EP-A 2463109 (Agfa), paragraphs [0150] to [0159].

[0203] **Arlo** is a 15 wt% aqueous solution of Marlon A365, commercially available from Brenntag

[0204] **Proxel K** is a 5 wt% solution of the biocide CAS 127553-58-6 prepared by diluting Promex Clear, supplied by Prom Chem UK.

[0205] **MOW** is an aqueous solution of 15 wt% Mowiol 4 88 and 0.2 wt% Proxel Ultra 5.

[0206] **DISFLAMOLL TKP** is a low volatility halogen free phosphate plasticizer from Lanxess.

[0207] **Zinc 3,5-bis(alpha methylbenzyl) salicylate** (CASRN53770-52-8) is a developing agent, commercially available from Sanko Europe.

[0208] **Ethyl Maleate** is commercially available from TCI Europe.

[0209] **Genocure DMHA** is the photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone available from COVESTRO.

[0210] **Genocure CPK** is the photoinitiator 1-hydroxycyclohexyl phenyl ketone commercially available from RAHN.

[0211] **Genocure TPO** is the photoinitiator (2,4,6-trimethylbenzoyl)phosphine oxide commercially available from RAHN.

[0212] **Inimix** is a 1/1/1 mixture of Genocure DMHA, Genocure CPK and Genocure TPO.

[0213] **Desmolux XP 2587** is an aliphatic urethane acrylate commercially available from Allnex.

[0214] **PEG200DA** is a polyethylene (200) diacrylate commercially available from IGM resins.

[0215] **Mixture** is obtained by mixing 50 g Desmolux XP 2587, 40 g PEG200DA and 10 g of Inimix.

Preparation of encapsulated leuco dyes

Magenta Leuco Dye Capsules (M-LD)

[0216] 7.01 g Red 40 (Mitsui) and 4.73 g Orange DCF (CAS 21934-68-9) were added to 60.24 g ethyl acetate.

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[0217] 13.38 g TAKENATE D131 N was added to the mixture. The mixture was heated to the boiling point and stirred until all components were dissolved.

[0218] The mixture was then cooled to 30 °C.

[0219] In a separate flask, 0.15 g of OLFINE E1010 was added to 84.5 g of a 6.3 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 16000 rpm during 5 minutes.

[0220] Ethyl acetate was removed under reduced pressure. During the process, also 5 mL of water was evaporated and therefore, the same amount of water was added to the mixture after evaporation. 1.71 g of tetraethylenepentamine (CAS 112-57-2) was added and the mixture was stirred for 16 hours at 95 °C and afterwards cooled to 25 °C.

[0221] Large particles were removed by filtering the mixture using a cloth filter with 60 µm pores.

Cyan Leuco Dye Capsules (C-LD)

[0222] 6.67 g Blue-63 (MITSUI) and 5.03 g GN-2 (MITSUI) were added to a mixture of 15 g ethyl acetate and 15 g DCM. 11.27 g TAKENATE D131N (MITSUI) was added to the mixture. The mixture was heated to the boiling point and stirred until all components were dissolved.

[0223] The mixture was then cooled to 35 °C.

[0224] The ethyl acetate-based solution was added to 79 g of a 4 wt% MOWIOL 4 88 solution. The mixture was emulsified using a T25 digital Ultra-Turrax® with an 18N rotor commercially available from IKA at 15000 rpm during 5 minutes.

[0225] Ethyl acetate and DCM were removed under reduced pressure. During the process, also 15 mL of water was evaporated and therefore, the same amount of water was added to the mixture after evaporation. 1.05g of tetraethylenepentamine (CAS 112-57-2) was added and the mixture was stirred for 16 hours at 95 °C.

[0226] After cooling to room temperature, large particles were removed by filtering the mixture using a cloth filter with 60 µm pores.

Preparation encapsulated IR compounds

IR1064

[0227] 6.72 g of Takenate D120N was dissolved in 33.45 g of MEK and 0.167 g of IR1064 was added. This mixture was added to 103 g of a 10.4 wt% MOW 488 solution.

[0228] The mixture was emulsified using a T25 digital Ultra-Turrax® with an 18N rotor commercially available from IKA at 15000 rpm during 5 minutes.

[0229] Ethyl acetate and DCM were 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 overnight at room temperature.

[0230] Large particles were removed by filtering the mixture using a cloth filter with 60 µm pores.

Preparation of developing agent dispersion

Developer

[0231] 55 g Arlo, 4.4 g Proxel Ultra 5 (commercially available from Avecia) and 366.674 MOW were added to 524.601 g water in Pot A. The mixture was stirred for 5 minutes at 50°C in order to dissolve all components.

[0232] 10.725 g 4,4'-Thiobis(6-tert-butyl-m-cresol) (commercially available from TCI Europe), 10.725 g Ralox 46 (commercially available from Raschig), 33 g Tinuvin 928 (commercially available from BASF), 8.25 g DISFLAMOLL TKP (commercially available from Lanxess), 4.125 g Ethyl Maleate (commercially available from TCI Europe) and 181.5 g Zinc 3,5-bis(alpha methylbenzyl) salicylate (CASRN53770-52-8, commercially available from Sanko Europe) were added to 495 g ethyl acetate in Pot. The mixture was stirred for 30 minutes at 50°C in order to dissolve all components.

[0233] While Pot A was stirred with a HOMO-REX high speed homogenizing mixer, the solution in Pot B was added to Pot A. The mixture was further stirred during 5 minutes with the HOMO-REX mixer. Ethyl acetate was removed from the mixture under reduced pressure.

Preparation of laser markable compositions**Magenta forming composition 1 (M-01)**

- 5 **[0234]** 0.3 g magenta leuco dye (M LD), 1.07 g Developer and 1.73 g Mixcure are mixed together and stirred for 5 minutes with a magnetic stirrer.

Cyan forming composition 1 (C-01)

- 10 **[0235]** 0.3 g cyan leuco dye (C LD), 1.07 g Developer, 0.36 g IR dye (IR1064) and 1.73 g of Mixcure are mixed together and stirred for 5 minutes with a magnetic stirrer.

Preparation of PET-C

- 15 **[0236]** A coating composition SUB-1 was prepared by mixing the components according to Table 1 using a dissolver.

Table 1

wt% of components	SUB-1
deionized water	76.66
CCE	18.45
Resorcinol	0.98
PAR-sol	0.57
PEA-sol	0.68
DOW-sol	1.33
Surfynsol	1.33

20 **[0237]** A 1100 μm thick polyethylene terephthalate sheet was first longitudinally stretched and then coated on both sides with the coating composition SUB-1 at a wet coating thickness of 10 μm . After drying, the longitudinally stretched and coated polyethylene terephthalate sheet was transversally stretched to produce a double side subbed 63 μm thick sheet PET-C, which was transparent and glossy.

Preparation of laser markable article

35 **[0238]** On a PET-C support, a magenta forming composition is coated using an Elcometer Bird Film Applicator (from Elcometer instruments) with a wet thickness of 10 μm . The coated substrate was UV cured using 1 pass through a UVIO curing station (20 m/min; D-bulb at 80% power; 880.5 mJ/cm² in one pass).

40 **[0239]** On this coating, a cyan forming composition is coated using a bar coater with a wet thickness of 10 μm . The coated substrate was UV cured using 1 pass trough a UVIO curing station (20 m/min; D-bulb at 80% power; 880.5 mJ/cm² in one pass).

Lasering of the laser markable article

45 **[0240]** The laser markable article was then laser marked with an optically pumped semiconductor laser emitting at 1064 nm (Genesis MX 1064-10000 MTM from COHERENT). A series of 10 squares, each 6 x 6 mm in size, was laser marked as follows:

50 **[0241]** Each square consists of a horizontal line of 6 mm length, laser marked "as a vector graphics line-object" with a speed v of 200 mm/s and a pulse repetition rate f of 10 kHz. Each square has its own setting of the pulse length PW (= time during which the laser is actually ON, which is a certain fraction of the pulse period $T = 1 / f$). So PW / T is the duty cycle. The 6 mm long line is repeated in the vertical direction 240 times with a displacement of 25 μm . Thus a square of 6 x 6 mm is created.

Evaluation of the laser markable article

55 **[0242]** The CIE Lab color coordinates (illuminant D50, 2° observer) of each square was measured with a GretagMacbeth

spectrophotometer of type SPM50.

[0243] The gradual change of a^* and b^* represents the gradual change of the color along the set of 10 squares. As laser power P , speed v and pulse rate f are kept constant across all 10 squares, and only pulse width PW decreases gradually, the energy density, impinging on the material, decreases accordingly for every square. And the resulting colour on the material changes as a function of the energy density.

Table 2

	L^*	a^*	b^*
1	67,00	16,42	-16,03
2	66,89	16,75	-16,08
3	68,28	12,59	-16,59
4	69,26	8,96	-16,74
5	70,49	4,96	-16,47
6	70,94	3,53	-16,52
7	72,83	0,37	-15,78
8	76,26	-3,14	-13,59
9	79,01	-5,63	-11,84
10	83,25	-6,41	-8,34

[0244] It is clear from the results of Table 2 that a rainbow pattern wherein a gradual shift of the colour is obtained by exposing the laser markable article with a single laser at varying energy densities on the surface of the article.

Claims

1. A method of marking an article (1) comprising a marking step wherein the article (1) including a first (100) and a second (200) colour-forming layer provided on at least part of a support (500), each colour-forming layer capable of forming respectively a first and a second colour upon marking, is marked thereby forming an image (350, 350'), **characterized in that** the first and the second colour are formed simultaneously in at least part of the marking step.
2. The method according to claim 1 wherein the article further comprises a third colour-forming layer capable of forming a third colour upon marking.
3. The method according to claim 1 or 2 wherein marking is carried out by exposing the article to heat, radiation or pressure.
4. The method according to any of the preceding claims wherein the image is a rainbow pattern.
5. The method according to claim 4 wherein the rainbow pattern is selected from a one dimensional or two dimensional rainbow pattern.
6. The method according to claim 4 or 5 wherein the image includes variable information.
7. The method according to any of the preceding claims wherein marking is carried out with a laser (250).
8. The method according to claim 7 wherein the laser is a nearinfrared (NIR) laser.
9. The method according to any of the preceding claims wherein marking is carried out with a thermal print head.
10. The method according to any of the preceding claims wherein the colour-forming layers include a leuco dye and a developing agent.

11. The method according to any of the preceding claims wherein at least one of the colour-forming layers include an optothermal converting agent.

12. The method according to claim 10 or 11 wherein the leuco dye and/or optothermal agent are encapsulated.

13. The method according to any of the preceding claims wherein the article further includes a UV-blocking layer (400), an overlay (600), an interlayer (300) or a combination thereof.

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

15. A method of preparing an article as defined in any of the preceding claims including the step of applying a first and second colour-forming composition on at least part of a support (500) thereby forming the first (100) and second (200) colour-forming layers on the support, each colour forming layer capable of forming respectively a first and a second colour upon exposure to radiation, heat or pressure.

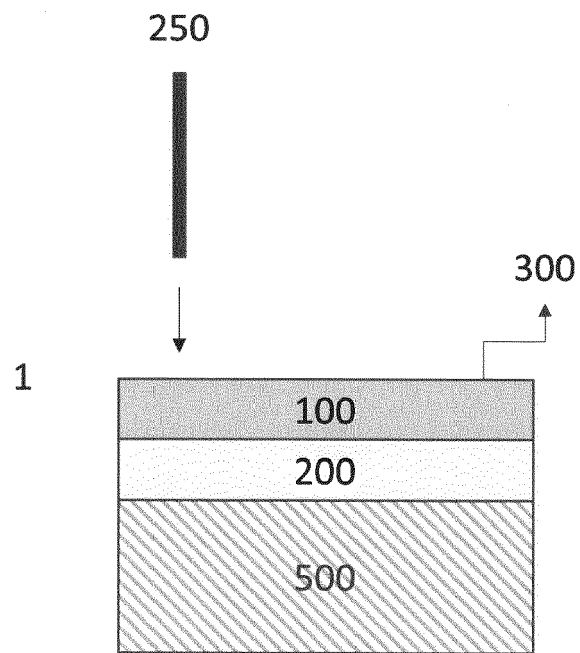


Figure 1

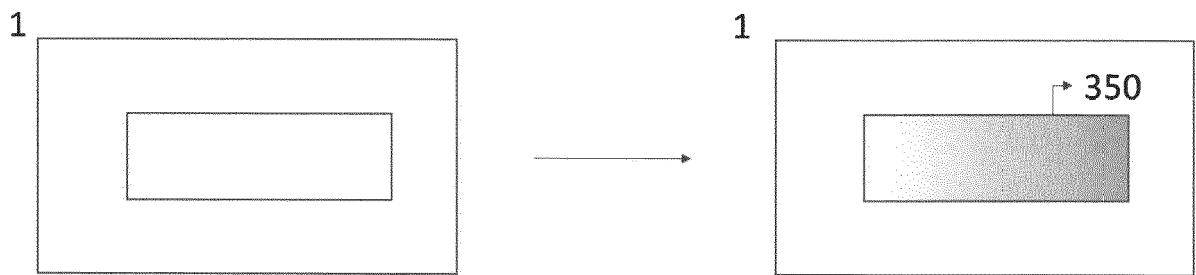


Figure 2A

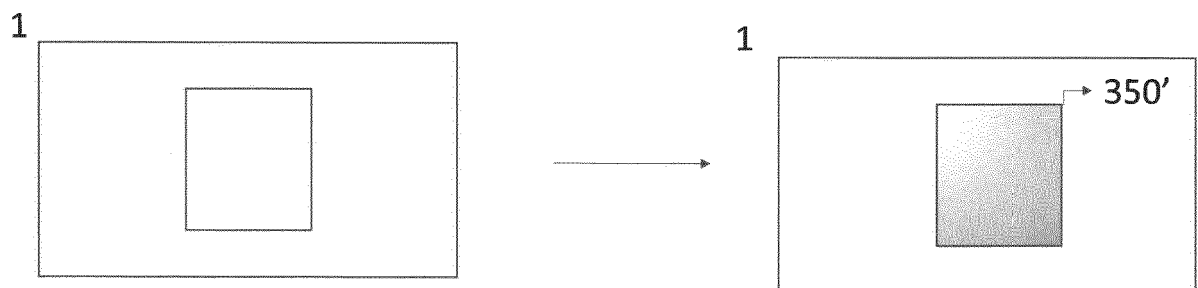


Figure 2B

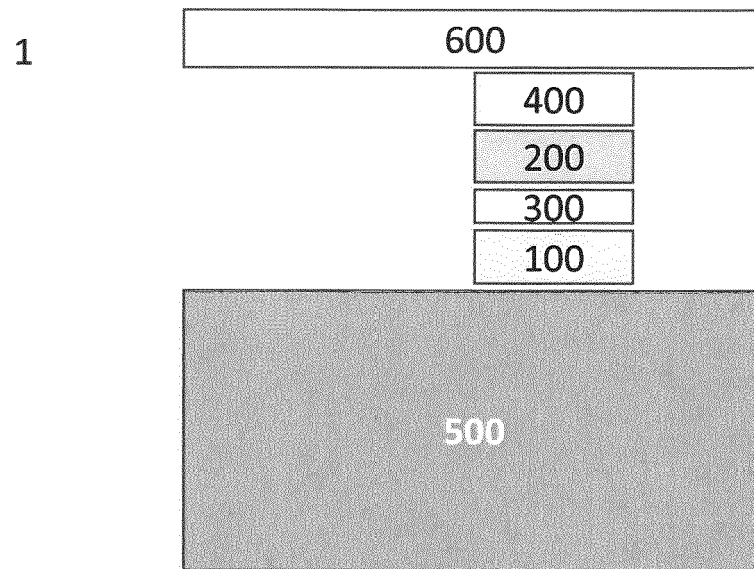


Figure 3

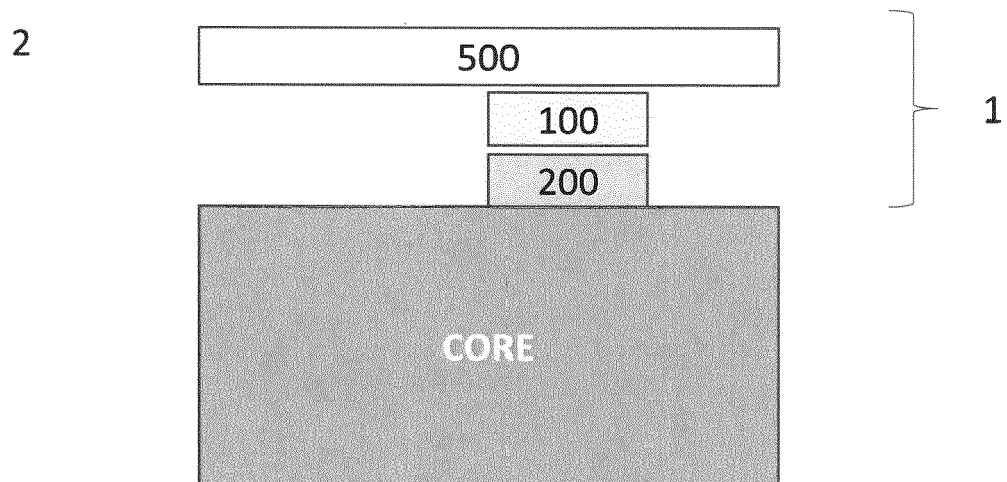


Figure 4



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 Application Number
 EP 20 18 1353

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Place of search Munich		Date of completion of the search 15 December 2020	Examiner Pulver, Michael
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