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(71) Applicant: **ANHEUSER-BUSCH INBEV SA/NV**
[BE/BE]; Grand Place 1, 1000 Brussels (BE).

(72) Inventor: **STEENACKERS, Marin**; Keiberg 52, 3053
Haasrode (BE).

(74) Agent: **ROUX, Stéphane** et al.; Novagraaf International
SA, Chemin de l'Echo, 3, 1213 Onex (CH).

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(54) Title: PRINTING PROCESS FOR A BEVERAGE CONTAINER

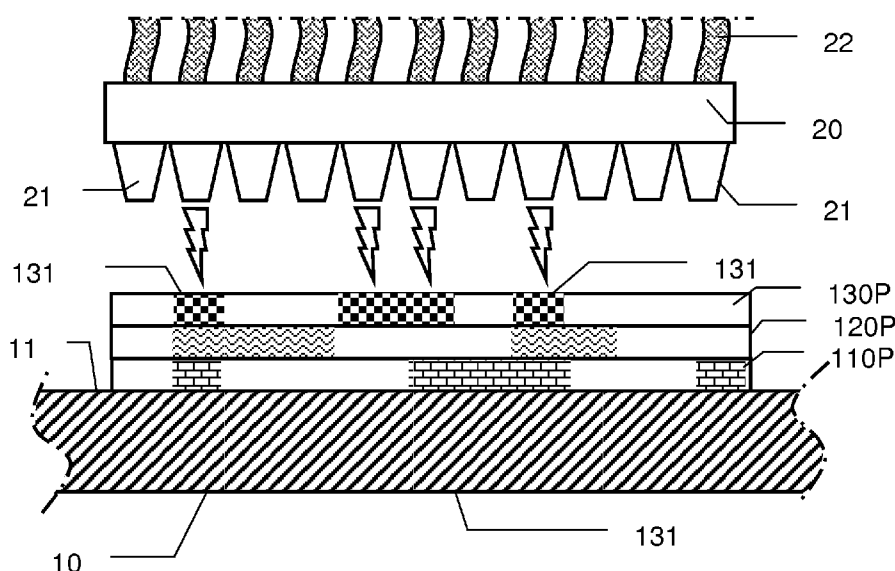


Fig. 6

(57) Abstract: A printing process for a surface (11) of an object (10), the printing process comprising the steps of: a. applying a first coating layer (110) on at least one portion of said surface (11), b. marking the first coating layer (110) with a laser device (20), c. applying at least one subsequent coating layer (120), transmitting visible light, to define at least one superposed area on said first coating layer (110), d. marking the at least one superposed area of the subsequent coating layer (120) with a laser device (20).



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PRINTING PROCESS FOR A BEVERAGE CONTAINER

FIELD OF THE INVENTION

[0001] The present invention relates to a printing process allowing a multicolor print on a surface of an object such as a beverage container or the like. The present invention further relates to a beverage container comprising
5 a surface printed by the printing process.

BACKGROUND OF THE INVENTION

[0002] A printing process allowing to print multicolor images is known from document WO2009/140083. This process involves applying a multi-layer construction comprising several thermally activatable layers and activating
10 the thermally activatable layers with a laser source to form an image. Such a multicolor image is formed by focusing the laser source on each different layer corresponding to each required color.

[0003] However, this process requires a very accurate control of the focus of the laser source, since the laser source should be focused on each
15 coating layer, usually having a thickness from 0.5 to 20 microns, to perform a selective activation. This process is thus difficult to set up, especially when used on an industrial scale. In addition, it does not allow a multicolor print on objects with important dimensional tolerances since it is then impossible to precisely set-up the laser focus.

20 [0004] Another printing process allowing to print multicolor images is known from WO2008/134548. This process involves the deposition of a laminate and the activation of the laminate material by laser lights having different wavelengths to produce a multicolor image.

[0005] However, this process requires expensive pigments or dyes
25 and only allows to use a limited number of colors, since each dye must have

an activation energy sufficiently different from the other dyes in order to prevent cross-activation.

[0006] As a result, there is a need for a printing process allowing to form a cost effective yet high-quality image on an object having important
5 dimensional tolerances.

SUMMARY OF THE INVENTION

[0007] This objective is accomplished by a printing process for a surface of an object, the printing process comprising the steps of:

- 10 a. applying a first coating layer on at least one portion of said surface,
- b. marking the first coating layer with a laser device,
- c. applying at least one subsequent coating layer, transmitting visible light, to define at least one superposed area on said first coating layer,
- 15 d. marking the at least one superposed area of the subsequent coating layer with a laser device,

wherein the first coating layer and/or any of the subsequent coating layers comprise a thermally activatable material and

characterized in that said at least one subsequent coating layer comprises a
20 greater proportion of the thermally activatable material than said first coating layer.

[0008] The printing process according to the present invention allows to print color images, patterns or texts (referred in the following text as "image") on an object having important tolerances for a limited cost. Indeed, a
25 color image comprising an extended range of colors is obtained by color subtraction between several totally or partially marked coating layers (or prints) in the superposed areas, relating for example to the CMY or the CMYK color system. By marking each coating layer independently from

another, one after the other, a color image can be obtained with standard and inexpensive dyes while limiting or even canceling the impact of dimensional tolerances. It also simplifies the printing device performing the printing process since only one sort of laser device may be required to perform marking of every coating layer, without the need of specific focus conditions. Expensive non-standard systems are thus not required by the present printing process.

[0009] In addition, laser marking allows to easily change the printed image from one object to be printed to another, for example by connecting the computer controlling the laser device to a digital images database. Laser marking may be done with UV laser light or preferably IR laser light, having a wavelength adapted to mark by activation or ablation the markable material used in the coating layers. Most preferably, laser marking is done in the near-infrared field such as 800-1200 nm, which allows a more selective marking.

[0010] Further, the thermally activatable material limits the cost of the printing operation and simplifies the printing process. Finally, the concentration gradient of thermally activatable material from a bottom coating layer to a top coating layer renders each subsequent coating layer more sensitive to laser marking than the first coating layer. This allows to limit the laser power for marking each subsequent coating layer, thus avoiding undesired marking of a coating layer during the marking operation of a subsequent coating layer. Preferably, the thermally activatable material is an infrared sensitizer or a near-infrared sensitizer.

[0011] Alternatively or in combination, the present invention consists in a printing process for a surface of an object, the printing process comprising the steps of:

- a. applying a first coating layer on at least one portion of said surface,
- b. marking the first coating layer with a laser device,

c. applying at least one subsequent coating layer, transmitting visible light, to define at least one superposed area on said first coating layer,

5 d. marking the at least one superposed area of the subsequent coating layer with a laser device,

characterized in that the printing process further comprises the step of:

applying at least one intercalary coating layer on the first coating layer and/or any of the subsequent coating layers after marking, the intercalary coating layer transmitting visible light and blocking infrared light so as to
10 prevent further marking of said first coating layer and/or any of the subsequent coating layers during marking of any further subsequent coating layer.

[0012] Such a printing process present technical advantages similar to what is described above and in particular the advantage to prevent further
15 marking of said first coating layer and/or any of the subsequent coating layers during marking of any further subsequent coating layer, thus allowing to print better quality images. For example, the first coating layer and/or any of the subsequent coating layers comprise a thermally activatable material which increase the sensitivity of the coating layer. However, the incorporation of
20 such a thermally activatable material is not mandatory as some coating layers can be sensitive enough to laser light to allow marking with the laser device without a thermally sensitive material.

[0013] In one mode of carrying out the present invention, the thermally activatable material comprises a leuco dye and marking of said first
25 coating layer and/or any of the subsequent coating layers comprises a laser activation of said leuco dye to perform a colored mark. Such leuco dyes are known to allow the production of high-quality images for a low cost. In addition, leuco dyes might allow for a quick printing process when the image to be printed does not comprise many colored areas, i.e. when the image to
30 be printed comprises some blank areas.

[0014] In another mode of carrying out the invention, the thermally activatable material comprises a bleachable material and marking of said first coating layer and/or any of the subsequent coating layers comprises a laser bleaching of said bleachable material to perform a mark. This process might
5 reduce the duration of the printing process when an image comprising wide colored areas is to be printed, since only the areas of the coating layers where no color is desired are bleached by laser marking.

[0015] In another mode of carrying out the invention, the thermally activatable material comprises an ablatable material and marking of said first
10 coating layer and/or any of the subsequent coating layers comprises a laser ablation of said ablatable material to perform a mark. This process allows the production of images with relief producing a topographic feeling (comparable to embossing) on objects having important dimensional tolerances.

[0016] The above described modes are not exclusive and a printing
15 process according to the present invention may combine at least two above-described modes. For example, a leuco dye may be chosen for a color present in limited areas of the image to be printed while a bleachable material may be chosen for a coating layer intended to be widely colored and an ablatable material may be chosen for the top coating layer to create a relief.
20 As a result, the present printing process allows an extended choice of materials for the coating layers and for laser devices.

[0017] Preferably, the thermally activatable material comprises a near-infrared sensitizer and wherein said laser device is a Fiber-Coupled Laser Diode Array (FC-LDA). This combination is valuable to print high
25 quality images at very high speed. Indeed, a near-infrared sensitizer provides for a selective marking, since materials do not usually absorb light in the near-infrared spectrum. In addition, FC-LDA allows to print quickly high resolution digital images.

[0018] In a preferable mode of carrying out the invention, at least the subsequent coating layers are transparent, in order to print an image with sharp details and extended color-space.

[0019] In a more preferable mode of carrying out the present
5 invention, all the coating layers are transparent and further comprising a preliminary step of applying a metallic coating layer on said at least one portion of said surface, before applying the first coating layer. This preferred mode allows to obtain a digital colored metallic image or artwork, i.e having metallic colors by the superposition of transparent colored coating layers with
10 the metallic coating layer.

[0020] Preferably, a curing step is performed to cure the first coating layer and/or any of the subsequent coating layers before or after marking said first coating layer and/or any of the subsequent coating layers. For example, curing may be done by UV light enabling cross-linking of the coating layers.
15 UV-light is valuable when the object to be printed is a beverage container such as a round bottle, since a UV-cured print is less sensitive to pasteurization heat. A UV curing thus allows pasteurizing printed beverage containers after filling. Alternatively, curing may be done by heating, cooling or solvent removal.

20 [0021] Preferably, the first coating layer and any of the subsequent coating layers are applied on a non-planar surface. Such a printing process thus allows an inexpensive image print on non-planar surfaces that are usually labeled.

[0022] For example, a non-planar surface may define a beverage
25 container such as a round bottle. The round bottle may be a glass bottle, a PET bottle or a steel or aluminum can, containing a liquid such as beer, water, juice, wine or oil. The round bottle may be cylindrical or may have a more complex shape. Alternatively, the non-planar surface may define a household glass, an automotive glass or glassware for home or lab use.

[0023] In a preferable mode of carrying out the invention, said non-planar surface defines a round bottle and the printing process according to the present invention further comprises the initial steps of:

- providing the round bottle on a rotator,
- 5 • applying a rotational movement on the round bottle with the rotator;

and wherein the coating layer is applied during a first portion of the rotational movement, and the laser marking is performed during a second portion of a rotational movement. Applying the printing process on a rotated round bottle allows to print images on the round bottle with a high speed and a low cost
10 and simplifies the printing device performing the printing process according to the present invention.

[0024] Preferably, the application of a coating layer and the laser marking of said coating layer are performed during a same rotation, for an optimized printing time. Preferably the curing step is also performed during
15 the same rotation.

[0025] A second aspect of the present invention is a beverage container having a surface comprising a printed image, text or pattern obtained by a printing process according to the first aspect of the present invention.

20 [0026] Preferably, the surface is a metallic surface and the coating layers of the printing process are transparent, which allows obtaining an image with metallic colors by the superposition of the transparent colored coating layer with the metallic surface of the beverage container.

[0027] Preferably, a background coating layer comprising an opaque
25 portion is located between the surface of the beverage container and the first coating layer.

[0028] A third aspect of the present invention is a printing process for a metallic surface of an object, the printing process comprising the steps of:

- a. applying a first transparent coating layer on at least one portion of said metallic surface,
- b. marking the first coating layer with a laser device,
- c. applying at least one subsequent transparent coating layer, to
5 define at least one superposed area on said first coating layer,
- d. marking the at least one superposed area of the subsequent coating layer with a laser device.

[0029] The printing process according to the present aspect is similar to the printing process according to the first aspect but allows to print images
10 comprising metallic colors by superposition of colored transparent coating layers (or transparent print) onto a metallic surface. This process is valuable for its reduced cost in comparison with a process involving expensive metallic inks of different colors.

[0030] Preferably, the metallic surface defines a metallic object such
15 as a metallic beverage container.

[0031] Alternatively, the printing process comprises a first preliminary step of applying a metallic coating layer on said object, before applying the first coating layer, to obtain said metallic surface. This preferable process is valuable to obtain metallic colors on a non metallic object, such as a glass
20 object.

[0032] Preferably, the printing process further comprises:

- a second preliminary step of applying a background coating layer onto the metallic coating layer,
- a third preliminary step of marking the background
25 coating layer with a laser to produce at least one opaque pixel.

This preferable process allows to hide at least a portion of the metallic coating layer from the view, and is valuable to obtain metallic colors on

certain portions of an image to be printed and non-metallic colors on other portions of the image to be printed.

[0033] It is understood that all preferred modes of the first aspect of the present invention are also applicable to the third aspect.

5 BRIEF DESCRIPTION OF THE DRAWINGS

[0034] Further advantages and preferred mode of carrying out the present process will become apparent from the following detailed description and drawings, in which:

10 - Figs. 1 to 6 show cross section lateral views of a printing process according to a first mode of carrying out the present invention.

- Fig. 7 shows a cross section lateral view of a printed surface resulting from the printing process of Figs. 1 to 6.

- Figs. 8 and 9 show cross section lateral views of a printing process according to a second mode of carrying out the present invention.

15 - Fig. 10 shows a cross section lateral view of the marking step of a printing process according to a third mode of carrying out the present invention.

- Fig. 11 shows a cross section lateral view of a printed surface resulting from the printing process of Fig. 10.

20 - Fig. 12 to 14 show cross section lateral view of a printing process according to a fourth mode of carrying out the present invention.

- Fig. 15 shows a schematic top view of an example of a printing device to perform the printing process of the present invention.

DETAILED DESCRIPTION

25 [0035] The present printing process is intended for printing an image, a text or a pattern (referred to as "an image" in the following) on a surface of all kind of object. In particular, the object could comprise a flat surface to be printed, such as a plastic card, for example a credit card, an ID card or

packaging such as a cardboard. Preferably, the object comprises a non-planar surface to be printed, such as a convex surface of a round glass bottle or a metallic can.

[0036] Generally speaking, the present printing process realizes an
5 image print by applying a coating layer on the surface to be printed and by laser marking the coating layer to produce a colored print. These two steps are repeated at least once and as many times as necessary to obtain each desired color of the final print in order to produce an image by color combination or subtraction between superposed areas of coating layers
10 transmitting visible light.

[0037] As a result, the present printing process can be used with any color system such as CMY (Cyan-Magenta-Yellow), CMYK (Cyan-Magenta-Yellow-black), CcMmYK (with the addition of light cyan and light magenta), RYB system (Red-Yellow-Blue) or a hexachrome system such as CMYKOG
15 (Cyan-Magenta-Yellow-black-Orange-Green). In addition, one or several additional coating layers may be used to produce specific colors (so-called spot colors) which are not easily obtained by subtraction, or special effects such as a glowing effect, an image visible under black light or an image revealing under cold temperature. For the sake of simplicity, the detailed
20 modes below are described with a CMY system.

[0038] The application of a coating layer (first step of the present printing process) is not limited and may comprise any coating process selected from the group consisting of coating techniques (such as spray coating, chemical vapor deposition, physical vapor deposition, roll-to-roll
25 coating, dip coating, etc.), printing techniques (such as flexographic printing, valve-jet printing, tampon printing, gravure printing, screen printing, offset printing, inkjet printing, etc.), foiling techniques (such as metallic foil stamping, inline foiling, etc.), labeling techniques (e.g. wet glue labelling, pressure sensitive labelling, etc.) and combination thereof. For the sake of

simplicity, the detailed modes below are described with an application by spray coating.

[0039] The coating layers typically include a liquid vehicle and one or more solids, such as dyes or pigments and polymers. Coating layers can be
5 roughly divided into:

- water-based, wherein a drying mechanism involves absorption, penetration and evaporation;
- solvent-based, wherein a drying mechanism primarily involves evaporation;
- 10 • oil-based, wherein a drying mechanism involves absorption and penetration;
- hot melt or phase change, in which the ink is liquid at the ejection temperature but solid at room temperature and wherein drying is replaced by solidification; and
- 15 • energy-curable, in which drying is replaced by polymerization induced by exposing the ink to a radiating energy source such as UV, X-ray, gamma-ray or e-beams or a thermal energy source.

[0040] The first three types of coating layer are more suitable for an absorbing surface to be printed, whereas hot melt coating layers and energy-
20 curable coating layers can also be applied on a non-absorbing surface to be printed. Due to thermal requirements i.e. posed by hot melt inks on the substrates, radiation curable coating layers are especially valuable in the field of beverage containers.

[0041] Consequently, the coating layers according to the present
25 process are preferably photopolymerizable coatings and are cured by UV light. Such coating layers may contain a single monomer or mixture of monomers which are preferably compatible with the activatable material to the extent that a clear, non-cloudy print is produced by laser marking.

Monomers that can be used in the photopolymerizable layer are well known in the art. Examples of such monomers can be found in documents US4323636; US4753865; US4726877; and US4894315. It is preferred that the monomer be present in at least an amount of 5% by weight of the photopolymerizable layer.

[0042] As previously mentioned, the coating layers according to the present invention may be cured by solvent or water removing (drying), heating, X-ray, gamma-ray or e-beams. For the sake of simplicity, the detailed modes below are described with UV curing step.

[0043] Finally, the coating layer material according to the present invention can comprise additional components such as polymeric binders, transparent polymeric supports, core supports, wetting agent, stabilizers, organic and/or inorganic nanoparticles, cross-linkers, adhesion promoters, initiator such as photoinitiator, subbing layers and coating solvents, as detailed in "Coatings Technology Handbook", CRC Press 2005 and "BASF Handbook on Basics of Coating Technology", Vincentz Network 2007.

[0044] The marking of the coating layer is performed in the present process by a laser light which activates or ablates the material of a coating layer in order to produce a print comprising marks of a certain color. As a result, the laser device and the material of the coating layer must be chosen in order to allow a thermal and/or electronic interaction, i.e. the laser light wavelength must correspond to the activation or ablation wavelength of the coating layer to realize a marking.

[0045] Preferably, the laser light is chosen in the range of infrared or near infrared and the laser device is a laser diode or a set of laser diodes, a single laser device or a set of laser device of the Nd:YAG type (Neodymium-doped Yttrium Aluminum Garnet; $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$) emitting a light having a wavelength of 1064 nm. Preferably, the laser device is a Fiber Coupled - Laser Diode Array (FC-LDA) device such as described in document US7542499.

[0046] Alternatively, the laser light may be in the field of ultraviolet or near ultraviolet, for example having a wavelength from 200 to 320 nm. The laser device could be a single or a set of Gallium Nitride laser diodes or Excimer-type lasers, for example emitting a light having a wavelength of
5 351 nm.

[0047] For example, the activation of the coating layer can lead to a change in color from colorless to colored (leuco dye activation - first mode below), from colored to colorless (bleaching - second mode below) or from the presence of a colored coating layer to the absence of a colored coating
10 layer (ablation - third mode below). In addition, the marking by activation or ablation of the coating layer may be only partial, in order to obtain a pale color or a thin colored coating layer. In other words, not all markable material of an area intended to be marked is activated or ablated by the laser light. This allows to produce a wide range of colors by combination with
15 superposed colored coating layers having a different color intensity and/or a different thickness. For the sake of simplicity, the detailed modes below are described with a complete activation/ablation of the coating layers.

[0048] As a result, the coating layers material may comprise all required compounds allowing such an interaction such as a thermally
20 activatable material, for example a pigment, a dye, an accelerator, a sensitizer and their combinations. Examples of such compounds are given for the modes described below.

Cross-activation

[0049] As already explained, the present printing process allows to
25 use the same laser device for marking every coating layers, since the coating layers are marked independently, one after the other. However, there is a risk to produce an undesired mark on an underneath coating layer during marking of a coating layer, so-called cross-activation. This problem is overcome in the present process by two different features, which could be used alone or in
30 combination.

[0050] The first feature is a gradient of increasing concentration of the markable material in the superposition of coating layers, i.e. the activatable or the ablatable material concentration is increased from the bottom coating layer to the top coating layer. This markable material is for example a dye
5 and/or a sensitizer such as a (near) infrared sensitizer. For example, the concentration of the markable material could be in the first layer from 10 mg/m² to 20 mg/m² and each subsequent layer could show an increase in concentration from 5 mg/m² to 10 mg/m². Thanks to this gradient, a top layer under marking absorbs more laser light than a below coating layer, which
10 allows a laser light of decreasing intensity from the bottom coating to the top coating. This gradient of concentration thus contributes to limit or cancel cross-activation and enhances the accuracy and sharpness of the printed image. In addition, it also contributes to obtain an extended color space.

[0051] The second feature allowing to overcome the problem of
15 cross-activation is the application of an intercalary coating layer on each marked coating layer (or print) and before the application of the subsequent coating layer. This intercalary coating layer is transparent to visible light but opaque to the laser light and comprises IR-absorber in the case of an IR laser light or UV-absorber in the case of an UV laser light. These intercalary layers
20 prevent cross-activation and contribute to enhancing the quality of the final printed image, i.e. to print images with a better accuracy and a better sharpness.

[0052] Examples of suitable IR-absorber include poly(substituted)phthalocyanine compounds; cyanine dyes; squarylium dyes;
25 chalcogenopyrrolylidene dyes; bis(chalcogenopyrrolyl)polymethine dyes; oxyindolizine dyes; bis(aminoaryl)polymethine dyes; merocyanine dyes; croconium dyes; metal thiolate dyes; and quinoid dyes. Also suitable are dark inorganic pigments such as carbon black, graphite, copper chromite, chromium oxides and cobalt chrome aluminate; metals such as aluminum,
30 copper or zinc; and alloys of bismuth, indium and copper.

[0053] 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-
5 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™
10 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-methylphenoxy)-1,3,5-triazin-2-yl]-1,3-benzenediol (CASRN13413-61-1); titanium dioxide such as Solasorb 100F from Croda Chemicals; zink oxide such as Solasorb 200F from Croda Chemicals; benzoxazines such as
15 Cyasorb UV-3638 F, CYASORB™ UV-1164 from CYTEC; and oxamides such as Sanduvor VSU from Clariant.

[0054] In addition, the same or another intercalary coating layer may have heat-insulating properties to prevent heat transmission to a bottom coating layer during the marking of a top or subsequent coating layer. For
20 example, a heat-insulating property may be obtained from an intercalary coating layer comprising nanopores or hollow nanoparticles. An opaque intercalary coating layer may also be partially applied between a coating layer and a subsequent coating layer to promote a color effect on a specific area of the printed image.

[0055] The above-described features can be used alternatively or in
25 combination with every marking method that are described in the four modes below. These modes illustrate the present printing process with coating layers comprising leuco dyes (first mode), bleachable material (second mode) or ablatable material (third mode), as well as with a metallic coating layer to
30 produce metallic colors (fourth mode).

First Mode

[0056] In a first mode of carrying out the invention according to Figs. 1 to 6, the process according to the present invention is illustrated with activatable materials comprising leuco dyes.

5 [0057] The term "leuco dye" as used herein refers to compounds which can change from essentially colorless or pale-colored to colored when irradiated with UV light, IR light and/or heated. All publicly known leuco dyes can be used and are not restricted. They are, for example, widely used in conventional pressure-sensitive, photosensitive or thermally sensitive coating
10 materials. For more information about leuco dyes, see for example "Chemistry and Applications of Leuco Dyes," Ramaiah Muthyala, Plenum Press 1997.

[0058] A number of classes of leuco dyes may be used as color-forming compounds in the present invention, such as for example: spiropyran
15 leuco dyes such as spirobenzopyrans (e.g. spiroindolinobenzopyrans, spirobenzopyranobenzopyrans, 2,2-dialkylchromenes), spironaphthooxazine and spirothiopyran; leuco quinone dyes; azines such as oxazines, diazines, thiazines and phenazine; phthalide- and phthalimidine-type leuco dyes such as triarylmethane phthalides (e.g. crystal violet lactone), diarylmethane
20 phthalides, monoarylmethane phthalides, heterocyclic substituted phthalides, alkenyl substituted phthalides, bridged phthalides (e.g. spirofluorene phthalides and spirobenzanthracene phthalides) and bisphthalides; fluoran leuco dyes such as fluoresceins, rhodamines and rhodols; triarylmethanes such as leuco crystal violet; ketazines; barbituric acid leuco dyes and
25 thiobarbituric acid leuco dyes.

[0059] Leuco dyes are preferably present in the coating material in an amount of 0.05 to 5.0 g/m², more preferably in an amount of 0.1 to 3.0 g/m², most preferably in an amount of 0.2 to 1.0 g/m².

[0060] In the present invention, leuco dyes can optionally be
30 combined with a sensitizer such as a photosensitizing dye and/or a photo or

thermally acid generator. Photo and thermally acid generator are known for example from the "Encyclopaedia of polymer science," 4th edition, Wiley and from "Industrial Photoinitiator, A Technical Guide," CRC press 2010 and comprise iodonium salts, sulfonium salts, ferrocenium salts, sulfonyl oximes, 5 halomethyl triazines, halomethylarylsulfone, α -haloacetophenones, sulfonate esters, *t*-butyl esters, allyl substituted phenols, *t*-butyl carbonates, sulfate esters, phosphate esters and phosphonate esters.

[0061] In addition, leuco dyes of the type used in direct thermal paper may also be used in the present invention. They comprise triaryl methane 10 phthalide dyes, such as Yamamoto Blue 4450, or fluoran dyes, such as Pergascript Black 2C. Furthermore, Crystal Violet lactone may also be used, as well as Yamamoto Red 40 to produce red or magenta. Yellow can be produced by the protonation of a triaryl pyridine, such as Copikem Yellow 37. These dyes have a colorless leuco form when crystalline or when in a pH 15 neutral environment, but become colored when dissolved in a melt and exposed to an acidic environment.

[0062] Leuco dyes, in general, provide little color when melted unless they are melted in conjunction with one or more organic acids. Examples of organic acids suitable for thermochromic papers are phenols such as 20 Bisphenol A (BPA) and Bisphenol S (BPS). Other suitable acidic materials are sulfonyl ureas such as BTUM and Pergafast 201. Zinc salts of substituted salicylic acids, such as zinc di-*tert*-butylsalicylate have also been commercially used as developers.

[0063] Leuco dyes of the type used in thermally sensitive paper are 25 often unstable and return to their original colorless, crystalline forms when stored in hot or humid conditions. To stabilize the metastable glass formed by the leuco dye, developer and sensitizer, a fourth type of material called a stabilizer is often added to thermal papers. Stabilizers often share similarities with developers and are often complex multifunctional phenols that inhibit

recrystallization of the dye and developer, thereby stabilizing the printed image.

[0064] The light produced by the laser device has a wavelength and an intensity allowing to perform a mark into the coating material, in other words, to activate the leuco dye in order for the coating material to become from colorless or pale-colored to colored. When a laser device of FC-LDA type is used, a sensitizer is usually required to activate the leuco-dye.

[0065] Now referring to Fig. 1, an object 10 comprising a surface 11 to be printed is coated in a first step by a first coating layer 110 comprising a leuco dye material. In the present mode, the leuco dye is capable of becoming from colorless to cyan upon activation by a laser light and the coating layer comprises a concentration of sensitizer of 10 mg/m². This first coating layer 110 is applied by a spray nozzle (not shown in Fig. 1).

[0066] In Fig. 2, this first coating layer is marked in a second step using a laser device 20 in the form of a Fiber-Coupled Laser Diode Array (FC-LDA) device comprising a plurality of laser heads 21, for example 256, each connected to an optical fiber 22 coupled to a laser light generator (not shown). In order to produce the required image, not every laser heads 21 are activated but only the laser heads in view of the areas of the first coating layer 110 where a cyan color is required. In addition, the time and/or intensity of the laser light is not similar for every laser head 21 but depends on the intensity of the color mark to be performed. Indeed, each laser head 21 can mark a single minimal area of the first coating layer 110 corresponding to a pixel 111, where a cyan color is required to produce a first print 110P or first marked coating layer. This first print 110P is intended either to appear cyan in the final printed image or to appear as a different color when combined with colors from subsequent superposed coating layers.

[0067] At the end of the first marking step shown in Fig. 2, the first print 110P is cured by an UV light (not shown) in order to be fixed and solidified.

[0068] In the third step of Fig.3, a second coating layer 120 is applied on the first print 110P by spraying. This second coating layer is transparent to allow the visibility of the first print and comprises a leuco dye material capable of becoming from colorless to magenta upon activation by a laser light. In addition, the concentration of sensitizer in the second coating layer 120 is greater than the concentration of sensitizer in the first coating layer 110. Namely, the concentration of sensitizer is 20 mg/m². Indeed, a greater concentration of sensitizer in the second coating layer 120 contributes to limit or avoid cross-activation, as previously explained.

10 [0069] In Fig. 4, the second coating layer 120 is marked in a fourth step by the laser device 20 in order to produce magenta pixels 121. The laser heads 21 activated in this fourth step may be the same or different or both than the laser heads 21 activated in the second step and may have different impulsion time and/or intensity in order to produce a second print or second
15 printed coating layer 120P comprising magenta pixels 121.

[0070] At the end of the second marking step shown in Fig. 4, the second print 120P is cured by an UV light (not shown) in order to be fixed and solidified.

[0071] In Fig. 5, a third coating layer 130 is applied in a fifth step on
20 the second print 120P by spraying. This third coating layer is transparent to allow the visibility of the first print 110P and the second print 120P and comprises a leuco dye material capable of becoming from colorless to yellow upon activation by a laser light. In addition, the concentration of sensitizer in such a third coating layer 130 is greater than the concentration of sensitizer in
25 the second coating layer 120, in order to prevent cross activation. Namely, the concentration of sensitizer in the third coating layer is 30 mg/m².

[0072] Now referring to Fig. 6, the third coating layer 130 is marked in a sixth step by the laser device 20 in order to produce yellow pixels. The activated laser heads 21 in this sixth step are the same or different or both
30 from the laser heads 21 activated in the second and fourth steps and have

different impulsion time and intensity in order to produce a third print or third printed coating layer 130P comprising yellow pixels 131.

[0073] At the end of the third marking step shown in Fig. 6, the third print 130P is cured by an UV light (not shown) in order to be fixed and solidified. The final print 100 is hence obtained by the three prints 110P, 120P, 130P corresponding to cyan, magenta and yellow, which forms by subtraction the image to be printed in the CMY system.

[0074] Optionally, a fourth coating layer comprising leuco dyes activatable by laser light to produce black pixels or "key" can be applied on the third print 130P and marked by laser light similarly to what is detailed above for the other colors, thus obtaining a CMYK image. The concentration of sensitizer in such a fourth coating layer should be greater than the concentration of leuco dye in the third coating layer, in order to prevent cross activation. For example, the concentration of leuco dye in the fourth coating layer could be 40 mg/m².

[0075] In a last step, a transparent protection coating layer 140 is applied on the third print 130P in order to protect the final print 100 against wear, moisture and/or UV light, as visible in Fig. 7, thus obtaining the final printed image.

20 Second mode

[0076] In a second mode of carrying out the invention, the process according to the present invention is illustrated with activatable materials comprising bleachable material.

[0077] The term "bleachable material" as used herein refers to compounds which can change from colored to essentially colorless or pale-colored when irradiated with visible light, UV light, IR light and/or heated. All known bleachable materials can be used and are not restricted. The bleaching process can be selected from those known in the art and includes thermal bleaching and photobleaching.

[0078] In thermal bleaching, the application of heat to the thermally activatable material causes the spectral properties of the dye to change. While many types of thermal bleaching processes are known from the skilled person and can be used in the present process, two of the most common
5 processes involve (1) the decomposition of a dye by removal of an acidic component by heat, or (2) the neutralization of the acid component of a dye by a heat generated base. Examples of documents that disclose thermally bleachable dyes are US3269839; US3769019; US4081278 and US Re29168. As already explained, the bleachable material is adapted to
10 absorb laser light at the wavelength of the laser light emitted by the laser device. Further, the thermally bleachable dye should preferably be selected to be bleachable at a temperature below, or not much higher than, the Tg of the material of the object to be printed.

[0079] Bleaching can also be accomplished by photolysis, i.e.,
15 photobleaching. In this case, various sensitizers or accelerators, such as allylthiourea, can be added to the coating layer to enhance the bleaching process. In general, during the photobleaching process, the dye is reduced or oxidized as a result of absorbing radiation, depending on the particular dye type. For example, methylene blue, which can be sensitized with reducing
20 agents such as thiosinamine, undergoes photoreduction and forms colorless leuco-forms, whereas polymethine dyes are oxidized to colorless forms. Certain types of dyes are readily photobleachable without an added accelerator. Numerous photobleachable dyes are known in the art and are useful in practicing the present invention. For example, see
25 document US3984248 and Kosar, Light-Sensitive Systems published by John Wiley & Sons, Inc. (1965) at 387–401 for a discussion of the photobleaching process and of particular dyes useful therein.

[0080] Figs. 8 and 9 show an application step and a marking step of a first coating layer 210 to produce a first print 210P similar to the first
30 print 110P according to the first mode shown in Fig. 2.

[0081] In Fig.8, a first coating layer 210 is applied on a surface 11 of an object 10 to be printed. The first coating layer comprises a cyan-colored bleachable material and is applied by a spray nozzle in a first step similarly to what is described in the first mode and in reference with Fig. 1.

5 [0082] In Fig. 9, the first coating layer 210 is marked by the light of the laser device 20 in order to bleach areas of the first coating layer 210. To obtain a first print 210P similar to the first print 110P of the first mode, the activated laser heads 21 correspond to the laser heads that were not activated during marking of the first print 110P, in the second step of the first
10 mode (Fig.2). Indeed, bleaching is a marking process “opposite” to leuco dye activation and instead of forming colored pixels, the image is printed by “removing” colored pixels from a colored coating layer.

[0083] Other aspects of the printing process according to the second mode are similar to the first mode. Namely, cross-activation can be prevented
15 by increasing the concentration of the bleachable material and/or the sensitizer from the first coating layer to the top coating layer.

[0084] Moreover, intercalary layers such as previously described, in particular intercalary layers transparent to the visible light but opaque to the laser light of the laser device may be added in addition or alternatively to the
20 above gradient of concentration.

[0085] Finally, a transparent protection coating layer may be applied, similarly to the coating layer 140 of the first mode and Fig.7.

Third mode

[0086] A third mode of carrying out the present invention of the
25 present invention is a printing process illustrated with activatable material comprising ablatable material.

[0087] The term “ablatable material” as used herein refers to compounds that can be ablated, i.e., vaporized or ablated, by exposure to light or radiation, preferably infrared light. Such an ablatable material should

have a strong absorption in the region of the infrared radiation, typically having a wavelength from 750 to 20 000 nm such as produced by excimer- or CO₂-type laser devices. Examples of suitable infrared absorbers have been provided above, with reference to the intercalary coating layer.

5 [0088] Now referring to Fig. 10, a laser marking step of a first colored coating layer 310 applied by spraying is shown to obtain a first print 310P similar to first prints 110P and 210P. The laser heads 21 are activated in a similar way than the example of Figure 9 referring to the second mode. However, in the third mode, the material of the first coating layer 310 is
10 removed or volatilized by the laser irradiation in the ultraviolet spectrum or preferably the infrared spectrum, thus letting visible the surface 11 of the object 10 to be printed.

 [0089] Colored pixels 311 results from the removal of colored portions of the first coating layer 310 and appear by contrast with the
15 surface 11. Alternatively, a bottom opaque layer may be applied below the first coating layer 310, i.e. between the surface 11 and the first coating layer 310 in order to bring contrast and to produce a more attractive image.

 [0090] Fig. 11 shows a final print 300 similar to final print 100 according to Fig. 6 but produced by ablation, thus resulting in a rugged final
20 print, i.e. a final printed image with relief. However, due to the limited thickness of the coating layers, typically from 1 micron to 20 microns, this relief is hardly visible to naked eyes and does not limit the visibility of the final print 300.

 [0091] In addition, it is possible to apply thick coating layers in order
25 to increase the relief of the final print for marketing or artistic reasons or to allow blind reading.

 [0092] Other aspects of the process according to this third mode are similar to the process according to the first and second modes, in particular the gradient of concentration, the intercalary layers and the transparent
30 protective layer.

[0093] The three modes of the present invention described above are not exclusive and any combination is possible. For example, a first coating layer may be marked by leuco dye activation, a second coating layer may be marked by bleaching and a third coating layer may be marked by ablation.

- 5 The process according to the present invention thus allows a wide choice in terms of coating materials, possible colors and aesthetics.

Fourth mode

[0094] A fourth mode of carrying out the present invention is a printing process comprising at least a first preliminary step of applying a metallic layer
10 on the at least one portion of the surface of the object to be printed. This fourth mode is similar to the first mode detailed above but allows to obtain metallic colors by application of a metallic color layer in a preliminary step.

[0095] The term "metallic coating layer" as used herein refers to any coating layer having a metallic aspect applicable to the object to be printed,
15 for example a beverage container in PET, glass or cardboard. The metal is preferably steel or aluminum and the application process can be made by any suitable process, selected from the group consisting of coating techniques (such as spray coating, chemical vapor deposition, physical vapor deposition, roll-to-roll coating, dip coating, etc.), printing techniques (such as flexographic
20 printing, valve-jet printing, tampon printing, gravure printing, screen printing, offset printing, inkjet printing, etc.), foiling techniques (such as metallic foil stamping, inline foiling, etc.), labeling techniques (e.g. wet glue labelling, pressure sensitive labelling, etc.) and combination thereof.

[0096] Preferably, the metallic coating layer is applied by spraying
25 and comprises an aluminum effect pigment such as described in document EP2017310. Alternatively or in combination, the metallic layer comprises a pearlescent pigment such as described in document WO2011000491.

[0097] Figs. 12, 13 and 14 show an application step of a metallic coating layer (Fig. 12), a background coating layer 402P (Fig. 13) obtained by
30 another application step and a marking step, and a final print 400 (Fig.14)

obtained by performing the printing process according to the first mode of the carrying out the invention on said metallic coating layer 401 and said background layer 402P.

[0098] Now referring to Fig. 12, the object 10 comprising a surface 11
5 to be printed is coated in a first preliminary step by a metallic coating layer 401 comprising aluminum pigments. In the present mode, the metallic coating layer 401 is applied on the surface 11 by spraying.

[0099] After the application step, the metallic coating layer is cured by an UV light (not shown) in order to be fixed and solidified, as previously
10 explained. The metallic coating layer appears as a aluminum-like layer.

[0100] An optional background print 402P may be obtained by the second and third preliminary steps detailed below. Such a background print 402P may be similar to an opaque intercalary layer according to the first mode and is similar to one of the prints 110P, 120P, 130P of the first mode
15 but comprises an opaque mark able to mask the metallic coating layer 401 from the view.

[0101] To obtain this background print 402P, a background coating layer is applied by spraying onto the metallic coating layer 40 in a second preliminary step (not shown) and is subsequently cured by UV light (not
20 shown) as previously detailed. The background coating layer comprises an opaque to transparent switch or a transparent to opaque switch, for example a chemical compound or a chemical system able to switch from transparent to opaque or the opposite upon laser activation, such as known from "Handbook of Laser technology and Application," CRC press 2003.

[0102] This chemical compound or chemical system may be a gas
25 producing system or compound that produces micro quantities of carbonic gas upon activation thus switching desired portions of the background layer from transparent to opaque, for example white. A similar effect may also be obtained from a polycarbonate polymer able to decompose in opaque

material. In addition, an nano crystalline opaque component can be switched to amorphous and transparent upon laser activation.

[0103] In a third preliminary step (not shown), the background coating layer 402 is marked by the light of a laser device 20 in the form of a FC-LDA
5 such as previously described with reference to Fig. 2, in order to produce white opaque pixels 412 and to obtain a background print 402P comprising a white opaque mark in the center, as represented in Fig.13. Because of the opaque pixels 412, the metallic coating layer is only visible through the transparent extremities 412E of the background print 402P. Alternatively, an
10 opaque coating may be selectively deposited by ink-jet, in order to mask portion of the metallic coating layer. In this case, no laser activation is required.

[0104] A printing process similar to the printing process according to the first mode of the present invention, detailed with reference to Figs. 1 to 7,
15 is then performed in order to obtain a final print 400 visible in Fig. 14. The final print 400 comprises the metallic coating layer 401 and the background print 402P as well as a first print 410P, a second print 420P and a third print 430P similar to the first print 110P, the second print 120P and the third print 130P detailed with reference to the first mode above. The final print 400 is
20 further provided with a transparent protection coating layer 440 similar to the transparent protection coating layer 140 according to the first mode of carrying out the present invention.

[0105] The printing process used to obtain the first print 410P, the second print 420P and the third print 430P is not limited to a printing process
25 according to the first mode of carrying out the present invention but may be according to the second mode, the third mode or their combination. In addition, the background print 402P could also be produced by bleaching or ablation (second and third mode), providing it comprises an opaque mark.

[0106] The printing process according to this fourth mode of carrying
30 out the present invention thus allows to obtain an image with metallic colors

for a limited cost, since different metallic color can be obtained by adding colored transparent coating layer on top of a single metallic coating layer. In addition, the image to be printed with metallic colors can be easily changed for each printed object, thus allowing to produce personalized objects with a metallic print at very high speed and for a limited cost.

Printing device

[0107] An example of a printing device to perform the printing process of the present invention is described in reference with Fig.15. The object to be printed is a round bottle 12 comprising a non-planar surface 13 intended to receive the image print. The round bottle 12 is placed on rotation means such as a rotator (not shown) transmitting rotation to the round bottle 12. For example, the rotation speed can be from 0.05 to 1 second per rotation, preferably from 0.2 to 0.5 second per rotation. Located around the round bottle 12 to be printed, the printing device comprises means for applying coating layers, means for curing coating layers and means for marking coating layers.

[0108] A means for applying coating layer is an applicator 30 formed by three spray nozzles 31, 32, 33 for each color of the CMY color system and an additional head 34 for the transparent protective layer. At 90 ° from the applicator 30 is located a means for curing coating layers in the form of a curing device 40 such as an UV lamp and at 180 ° from the applicator 30 is located a means for marking coating layers in the form of a laser device 20 of FC-LDA type, as already shown in the previous figures.

[0109] Performing the printing process according to the first mode of carrying out the present invention on a round bottle 12 is now described with reference to the printing device of Fig. 15.

[0110] In a first step, the first coating layer 110 comprising a cyan leuco dye is applied on the rotating round bottle 12 by the first head 31. The first coating layer 110 is cured by the curing device 40 and then marked by the laser device 20 to obtain the first print 110P visible in Fig. 2.

[0111] In a second step, the second coating layer 120 comprising a magenta leuco dye is applied on the rotating round bottle 12 by the second nozzle 32. The second coating layer 120 is cured by the curing device 40 and then marked by the laser device 20 to obtain the second print 120P visible in
5 Fig. 4.

[0112] In a third step, the third coating layer 130 comprising a yellow leuco dye is applied on the rotating round bottle 12 by the third nozzle 33. The third coating layer 120 is cured by the curing device 40 and then marked by the laser device 20 to obtain the third print 130P visible in Fig. 6.

10 [0113] In a last step, the transparent protection coating layer 140 is applied on the rotating round bottle 12 by the fourth head 34 and cured by the curing device 40. The final printed image as shown in Fig.7 is thus obtained and the round bottle 12 can be further processed such as filled up with a liquid, pasteurized, closed and packaged before shipping to customers.

15 [0114] Each of the above step can be done during a single rotation of the round bottle 12, thus allowing for a very fast printing process. However, for some images, several rotations may be required for the full application of a wide coating layer and/or full marking of a complex print.

[0115] To speed-up the printing process, several laser devices may
20 be added to the above printing device in order to print a complex image during a single rotation.

[0116] In the above process, additional spray nozzles could be provided to allow the application of additional colors or intercalary layers. The curing system 40 could also be placed after the laser device 20, in order to
25 perform marking on non-cured coating layers. Alternatively, two curing systems may be provided before and after the laser device in order to pre-cure a coating layer before laser marking and to finish curing after marking. Other tools may also be provided such as a suction pipe in order to remove particles and prevent contamination of the inside of the round bottle 12.

[0117] Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the scope of the present invention being limited only by the terms of the

5 appended claims.

CLAIMS

1. A printing process for a surface (11; 13) of an object (10), the printing process comprising the steps of:
 - 5 a. applying a first coating layer (110) on at least one portion of said surface (11; 13),
 - b. marking the first coating layer (110) with a laser device (20),
 - c. applying at least one subsequent coating layer (120), transmitting visible light, to define at least one superposed area on said first coating layer (110),
 - 10 d. marking the at least one superposed area of the subsequent coating layer (120) with a laser device (20),wherein the first coating layer (110) and/or any of the subsequent coating layers (120) comprise a thermally activatable material and characterized in that said at least one subsequent coating layer (120)
15 comprises a greater proportion of the thermally activatable material than said first coating layer (110).
2. A printing process for a surface (11; 13) of an object (10), the printing process comprising the steps of:
 - 20 a. applying a first coating layer (110) on at least one portion of said surface (11; 13),
 - b. marking the first coating layer (110) with a laser device (20),
 - c. applying at least one subsequent coating layer (120), transmitting visible light, to define at least one superposed area on said first coating layer (110),
 - 25 d. marking the at least one superposed area of the subsequent coating layer (120) with a laser device (20),

characterized in that the printing process further comprises the step of:

applying at least one intercalary coating layer on the first coating layer (110) and/or any of the subsequent coating layers (120) after marking, the intercalary coating layer transmitting visible light and blocking infrared light so
5 as to prevent further marking of said first coating layer (110) and/or any of the subsequent coating layers (120) during marking of any further subsequent coating layer.

3. A printing process according to the previous claim, wherein the first coating layer (110) and/or any of the subsequent coating layers (120)
10 comprise a thermally activatable material.

4. A printing process according to claim 1 or 3, wherein the thermally activatable material comprises a leuco dye and wherein marking of said first coating layer (110) and/or any of the subsequent coating layers (120) comprises a laser activation of said leuco dye to perform a colored
15 mark.

5. A printing process according to claim 1 or 3, wherein the thermally activatable material comprises a bleachable material and wherein marking of said first coating layer (110) and/or any of the subsequent coating layers (120) comprises a laser bleaching of said bleachable material to
20 perform a mark.

6. A printing process according to claim 1 or 3, wherein the thermally activatable material comprises an ablatable material and wherein marking of said first coating layer (110) and/or any of the subsequent coating layers (120) comprises a laser ablation of said ablatable material to perform a
25 mark.

7. A printing process according to claim 1 or 3, wherein the thermally activatable material comprises a near-infrared sensitizer and wherein said laser device (20) is a fiber-coupled laser diode array.

8. A printing process according to any of the previous claims, wherein at least the subsequent coating layers (120,130) are transparent.

9. A printing process according to any of the previous claims, wherein all the coating layers are transparent and further comprising a preliminary step of applying a metallic coating layer on said at least one portion of said surface, before applying the first coating layer.

10. A printing process according to any of the previous claims wherein a curing step, preferably by an UV light, is performed to cure the first coating layer and/or any of the subsequent coating layers.

11. A printing process according to any of the previous claims, wherein the first coating layer (110) and any of the subsequent coating layers (120,130) are applied on a non-planar surface (13), preferably defining a round bottle (12).

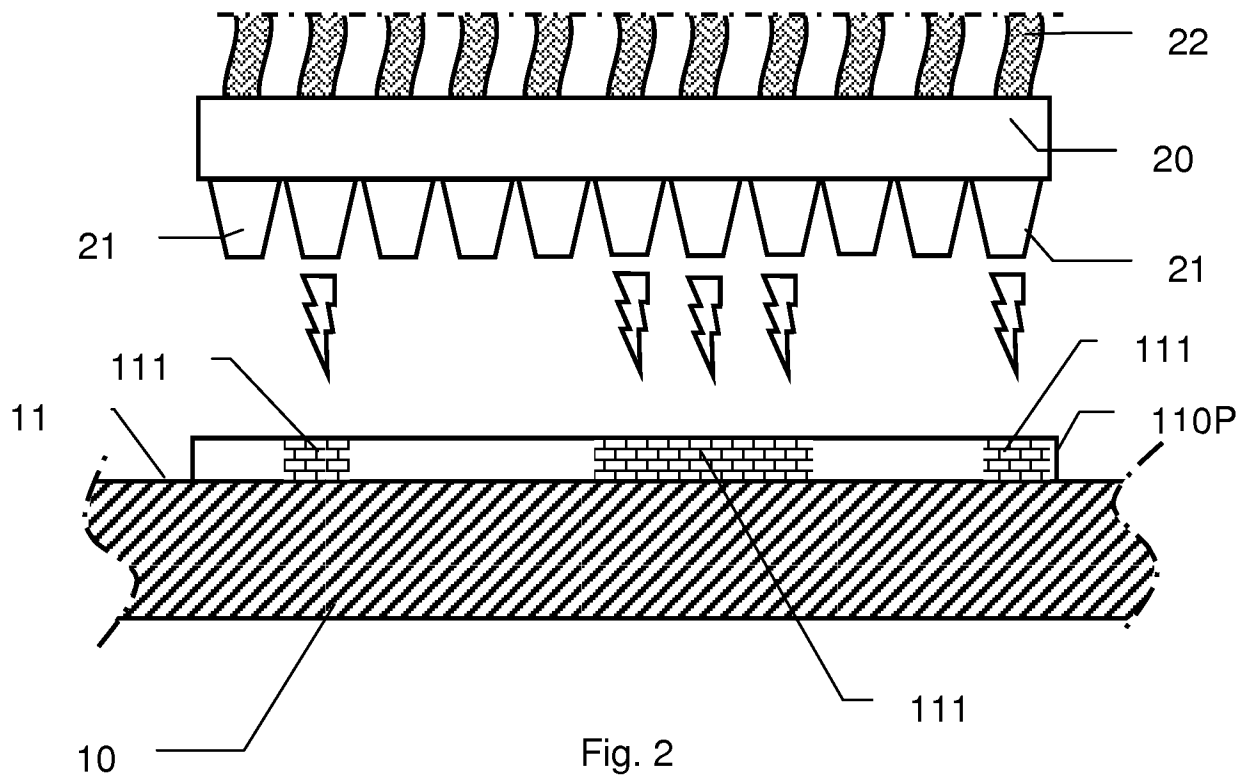
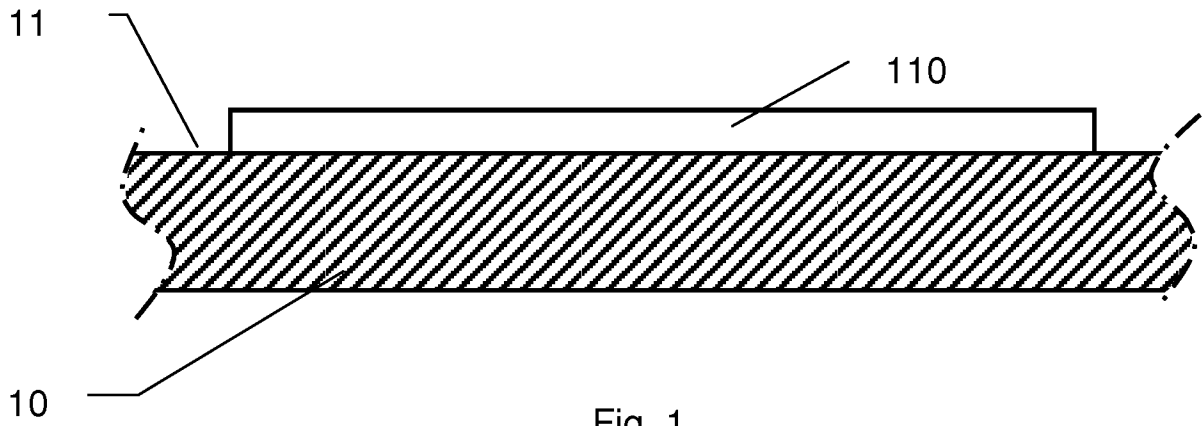
12. A printing process according to the previous claim, further comprising the initial steps of:

- providing the round bottle (12) on a rotator,
- applying a rotational movement on the round bottle (12) with the rotator;

and wherein each coating layer is applied during a first portion of the rotational movement, and the laser marking is performed during a second portion of a rotational movement.

13. A beverage container having a surface comprising a printed image, text or pattern obtained by a printing process according to any of the previous claims.

14. A beverage container according to the previous claim, wherein said surface is a metallic surface and all the coating layers of the printing process are transparent.



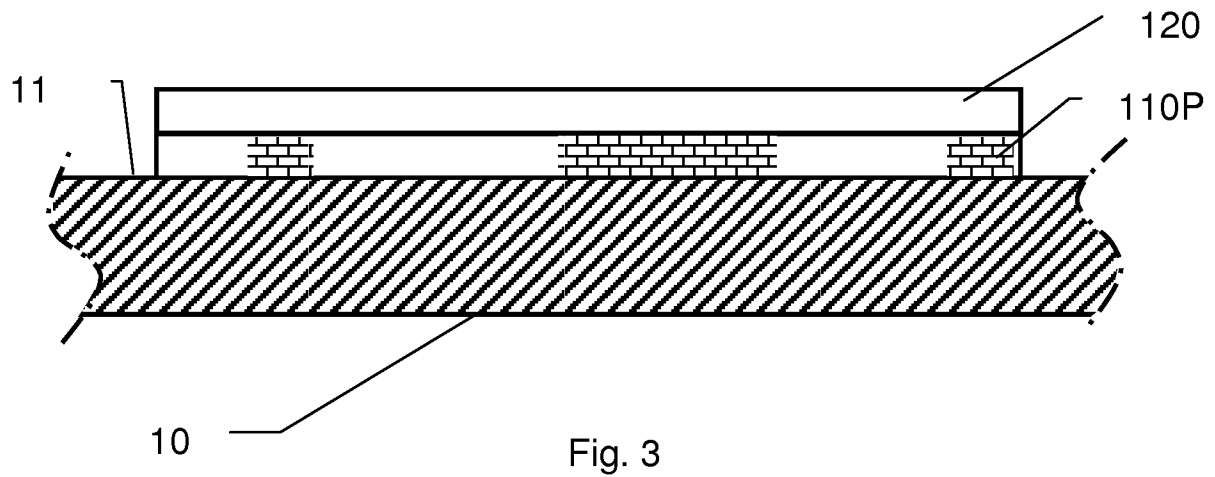


Fig. 3

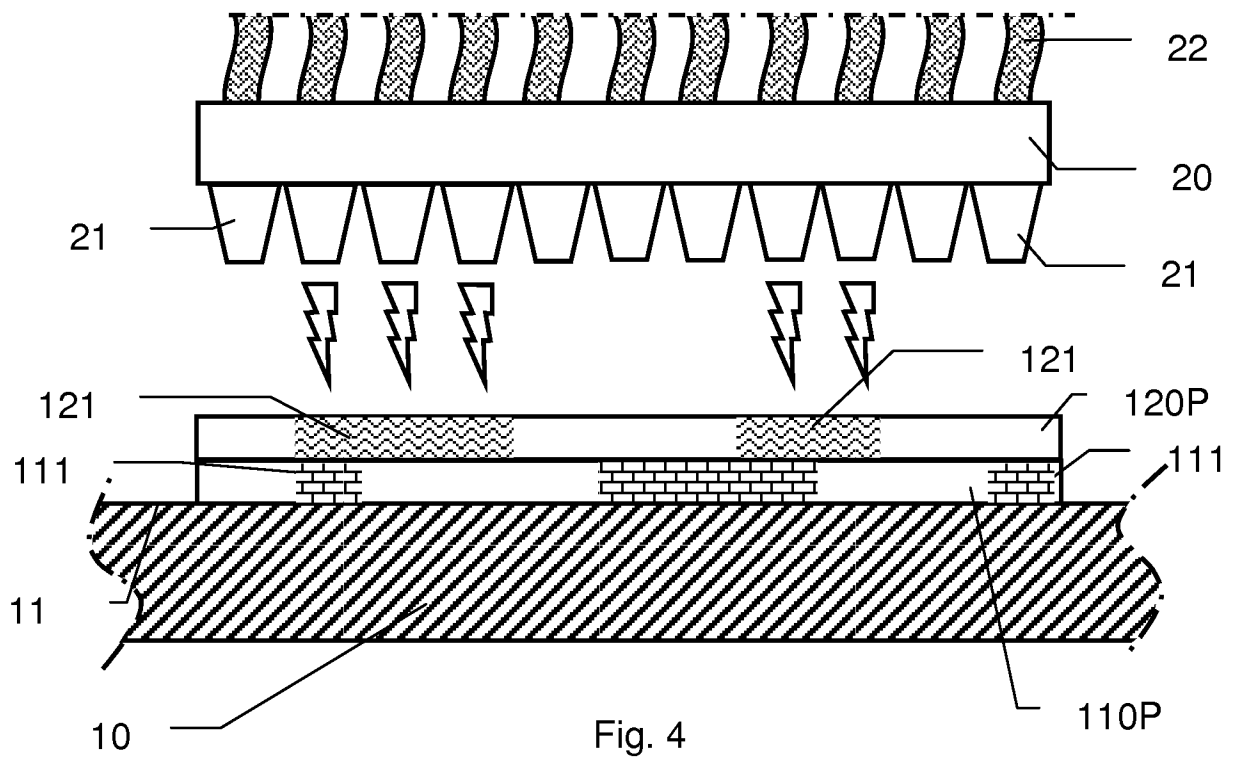


Fig. 4

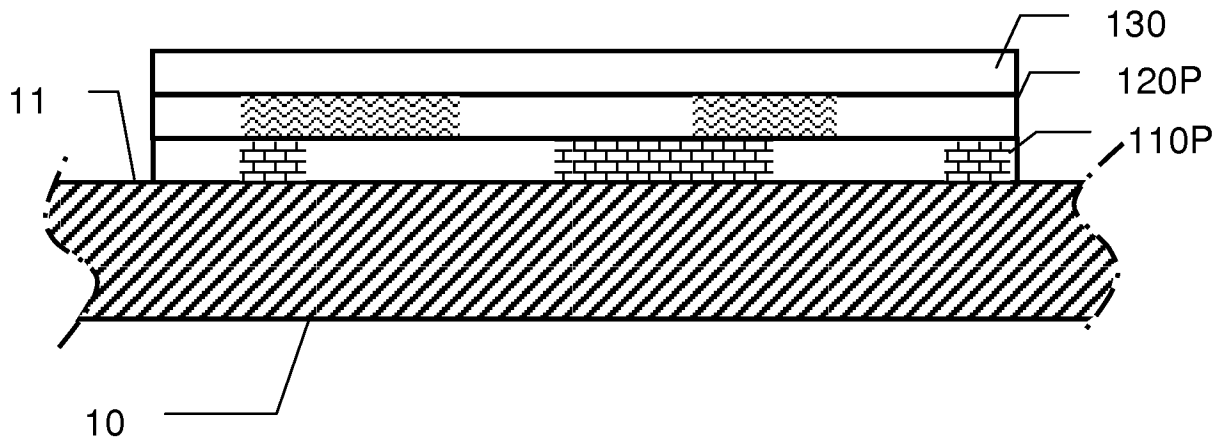


Fig. 5

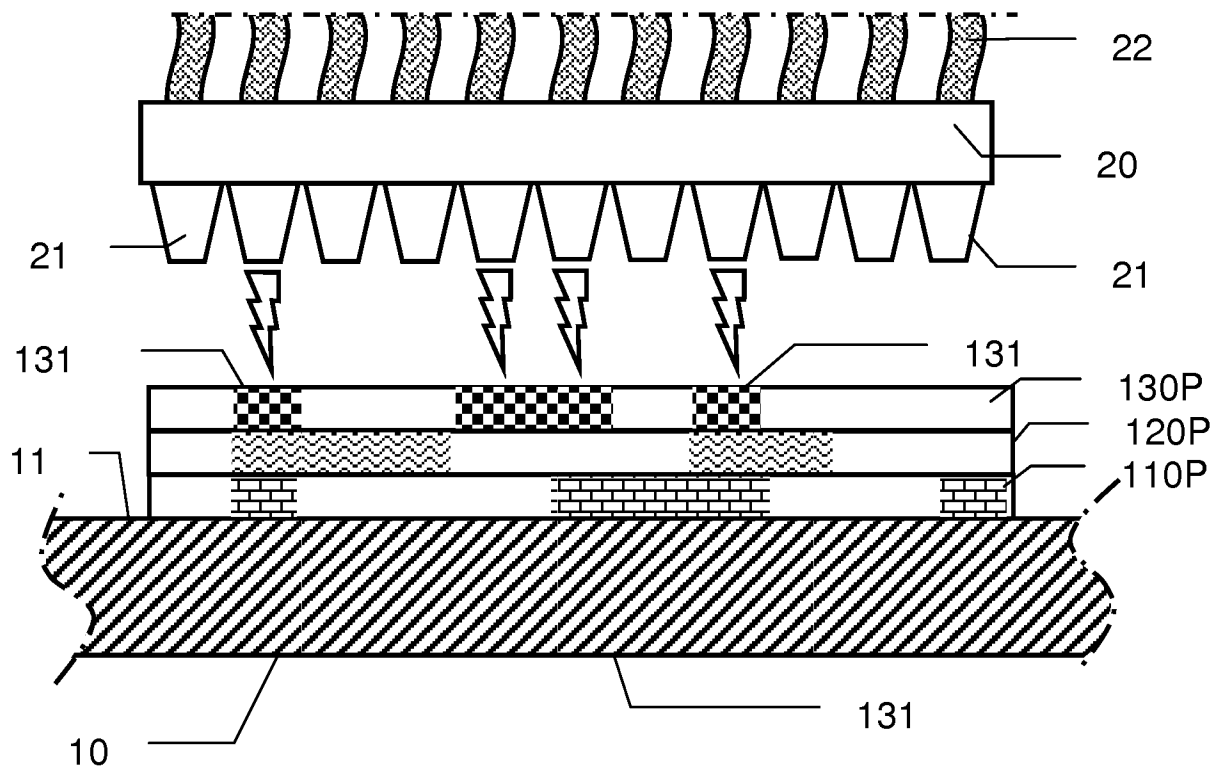


Fig. 6

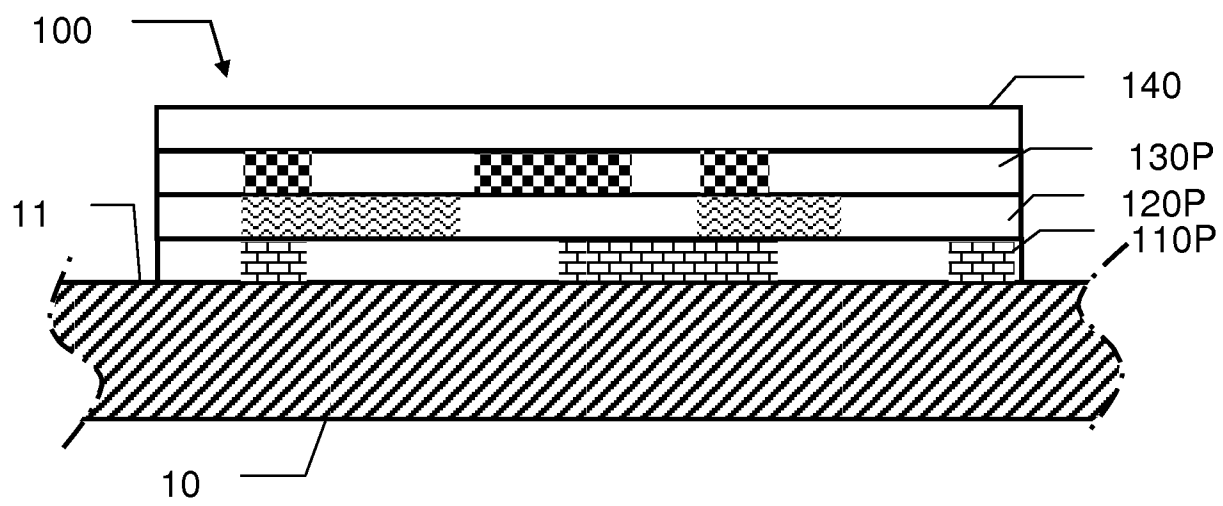
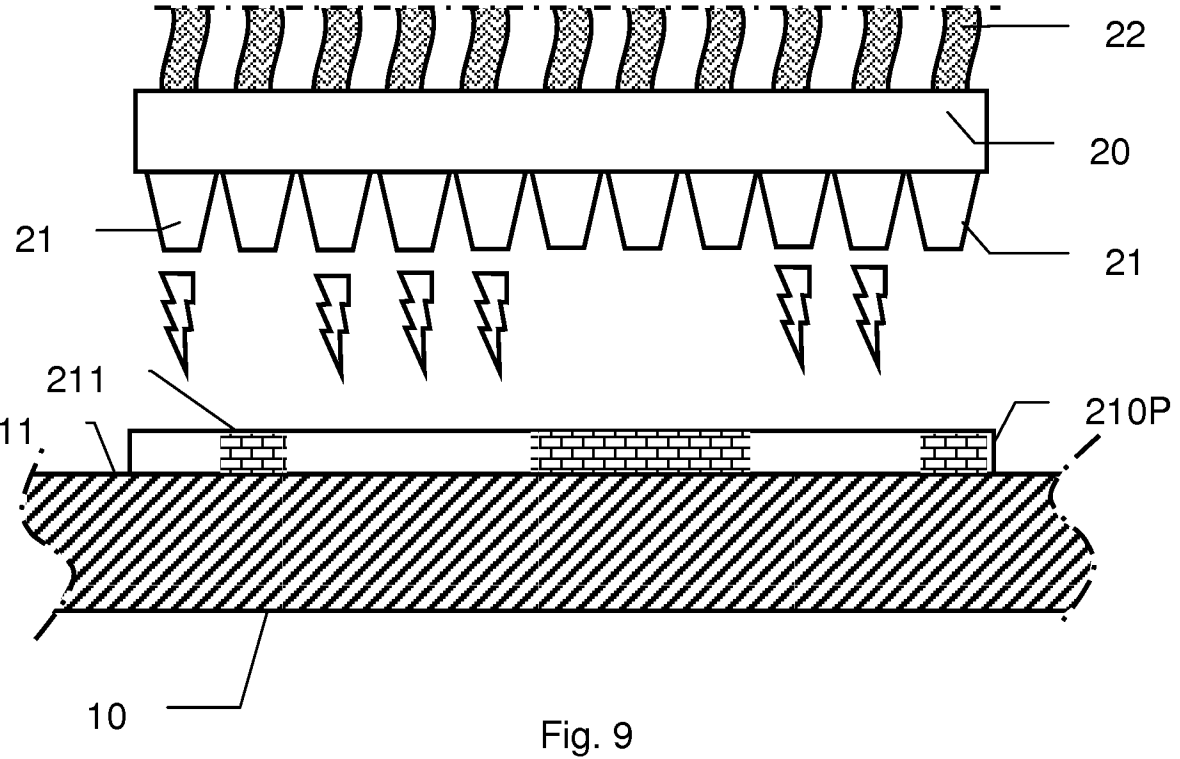
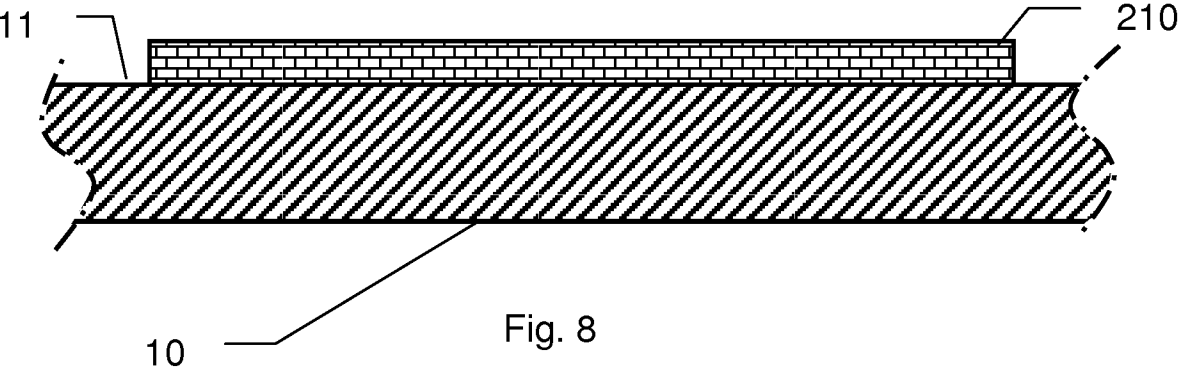
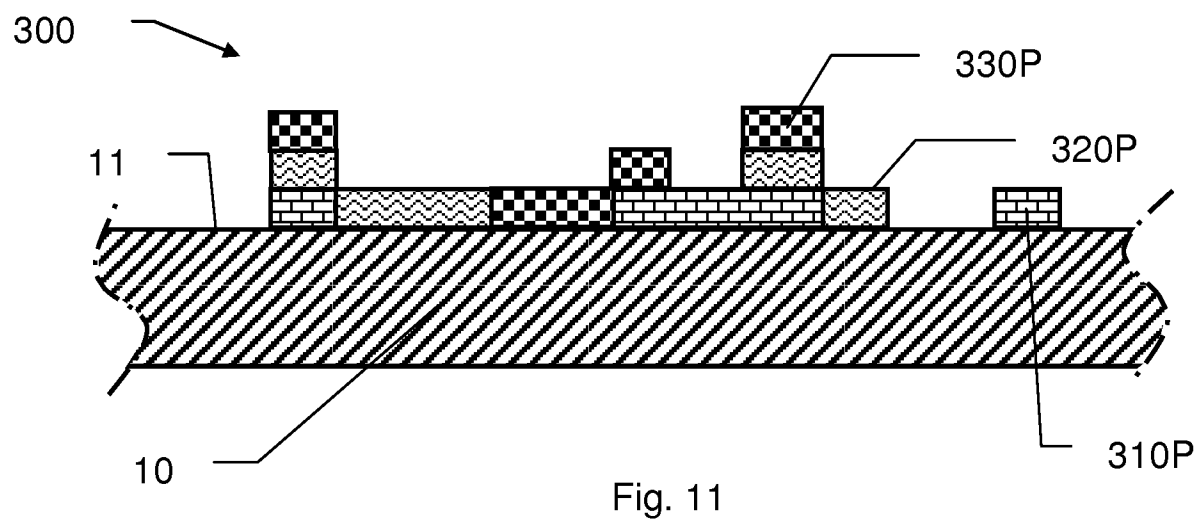
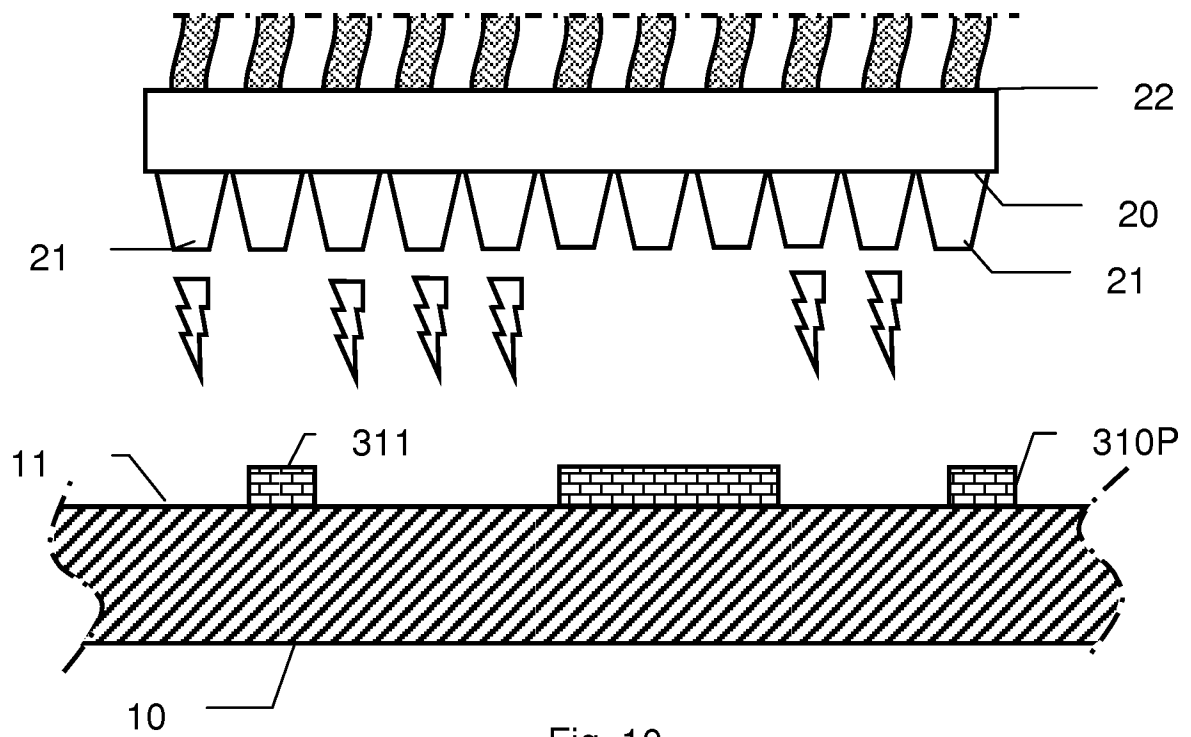
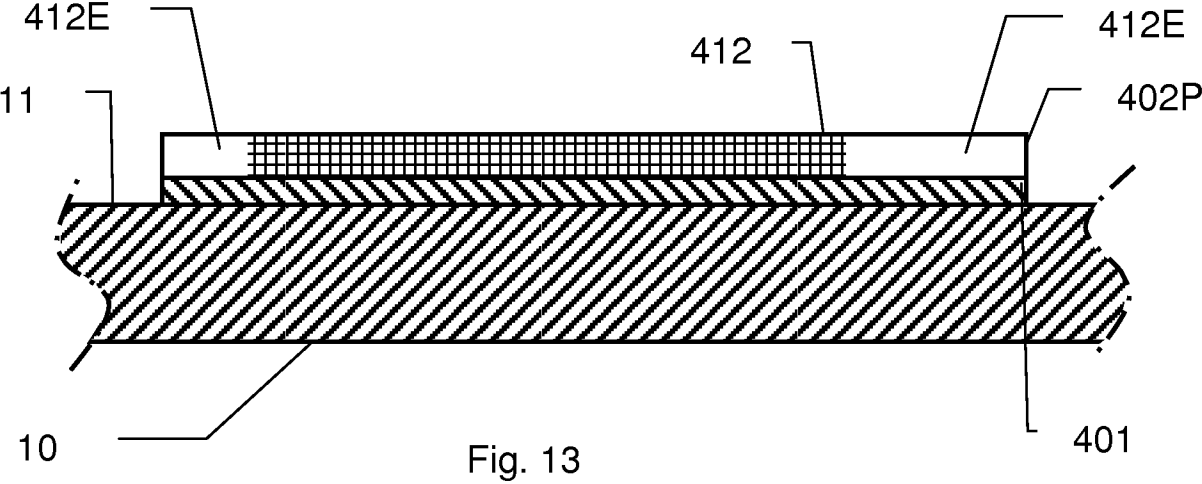
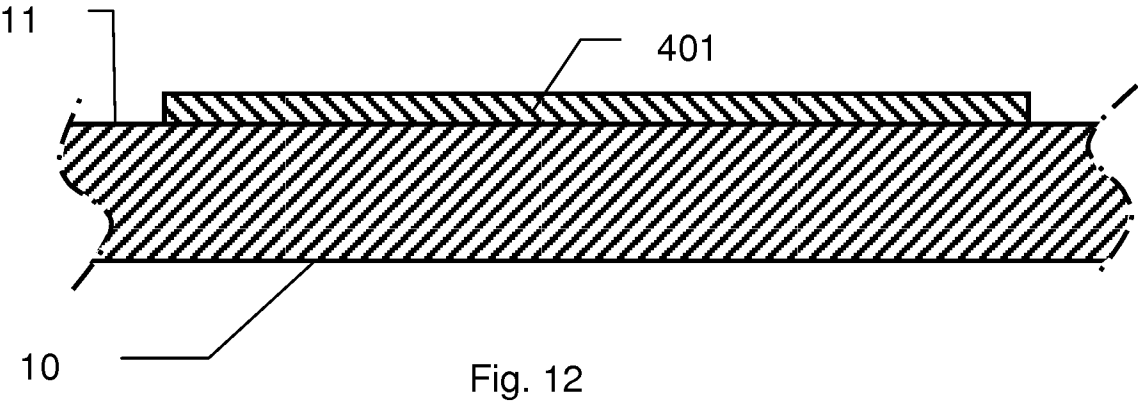
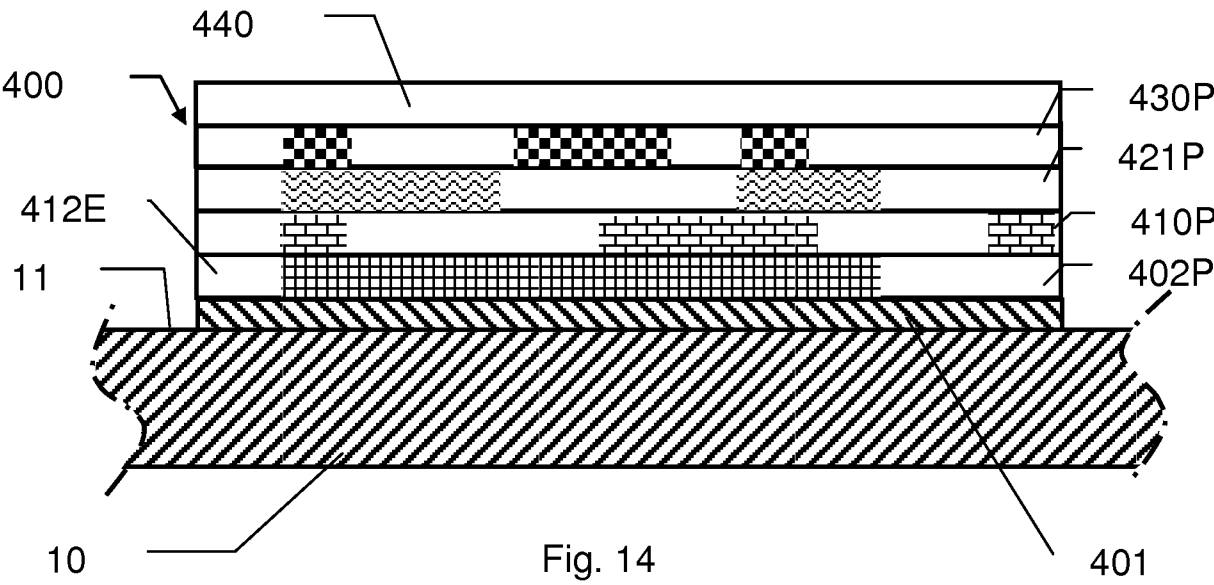


Fig. 7









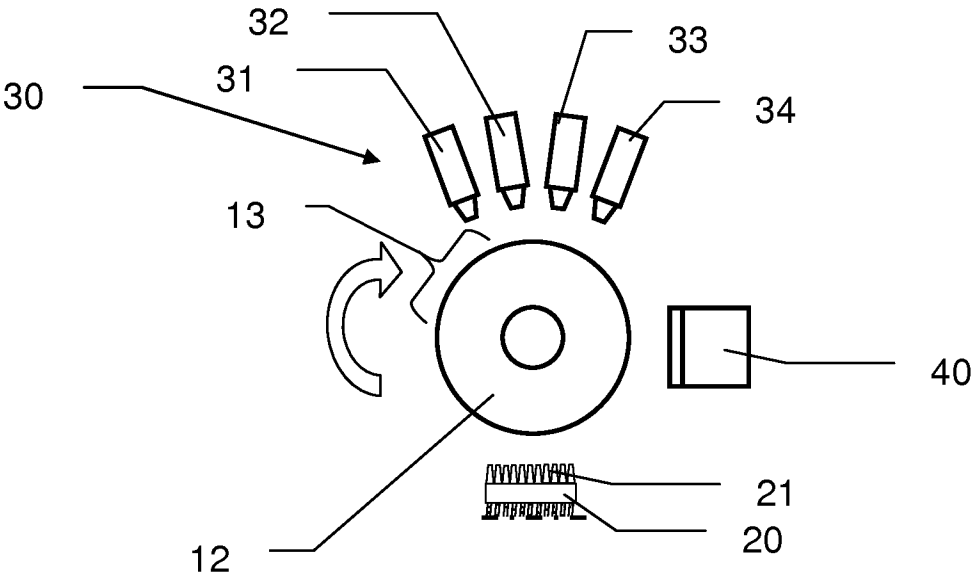


Fig. 15