Title: DECORATIVE AND/OR INFORMATION CONTAINING LABEL COMPRISING EMBLEMS AND METHOD OF MANUFACTURING IT

Abstract: A precursor (2) of a label (1) comprising a release carrier (6) with a release surface (6a) bearing a polymer layer (3) and a discontinuous emblem layer (4) comprising at least one emblem (5) at the interface between the release surface (6a) and major surface (3a) of the polymer layer (3) is disclosed.
DECORATIVE AND/OR INFORMATION CONTAINING LABEL COMPRISING EMBLEMS AND METHOD OF MANUFACTURING IT

Field

The present disclosure relates to a decorative and/or information containing label comprising one or more emblems and a method for manufacturing it. The present disclosure also relates to a precursor of said label obtained during said method of the present disclosure.

Background

EP 0,911,786 discloses a laser markable label comprising a polymer layer which includes an addition for reversible optical labelling, the additive being made recognizable, and especially visible, by means of electron beams, X-rays, in particular by visible light and, very particularly by IR or UV radiation. The polymer layer may also comprise an additive suitable for reversible magnetic or electrical labelling. Emblems such as logos or bar codes can be introduced into this layer by partially ablating the cover layer with a laser beam. This partially destroys the exposed surface of the layer which tends to make the label less durable and mechanically stable. Also, incorporating the emblems requires an additional laser ablation step which may be less desirable from a manufacturing point of view.

EP 0,688,678 discloses a single-layer laser label comprising
a) a support layer which
b) contains an additive which changes colour under laser irradiation and which
c) is coated on one side with a self-adhesive composition which
d) is optionally covered with a release paper or a release film.

This label requires the use of special pigments such as copper hydroxid phosphate pigments or specific pearlescent pigments which when irradiated with a laser show a colour change. The limited versatility of the label of EP '678 is not acceptable for many applications. The formation of the emblems requires an additional laser irradiation step subsequent to the manufacturing of the label which may not be desirable from a manufacturing point of view. Also, laser
ablation tends to damage the exposed surface of the label which may adversely affect its mechanical properties and durability.

In one aspect, the present disclosure provides a decorative and/or information containing label comprising one or more emblems which is highly versatile and may comprise a broad range of pigments and dyes. In some embodiments, the decorative and/or information containing label does not require an additional laser ablation step to provide one or more emblems and/or which has advantageous mechanical properties and/or provide an aesthetically pleasing surface appearance. In another aspect, the present disclosure provides an advantageous method of manufacturing such label.

Summary
The present disclosure relates to a precursor of a label comprising a release carrier with a release surface bearing a polymer layer and a discontinuous emblem layer comprising at least one emblem at the interface between the release surface and a major surface of the polymer layer. The release surface of the release carrier and/or the materials of the polymer layer and the emblem layer are selected so that the cohesive force of the polymer layer, the cohesive force of the one or more emblems and the bonding force between the one or more emblems and the polymer layer is higher than the interfacial adhesive force between the polymer layer and the emblems, respectively, and the release surface. A surface portion of such emblem(s) contacts the release surface so that such surface portion of the emblem(s) is coplanar with the adjacent exposed surface of the polymer layer. This results in the label which comprises the polymer layer and the emblem layer, being essentially cleanly separatable from the release surface when peeling off the release carrier.

The present disclosure furthermore relates to a label comprising a polymer layer comprising one or more emblems arranged adjacent to one of the major surfaces of said polymer layer, said emblems comprising one or more polymers and one or more colouring agents selected from the group consisting of inorganic pigments
including metal flakes, organic pigments, inks and dyes, and/or one or more inorganic microspheres or beads whereby said colouring agents and/or inorganic microspheres or beads and/or their respective concentration are selected so that the one or more emblem(s) are visually discernible from the polymer layer. In some embodiments, the label bears on its other major surface an adhesive layer such as, in particular, a pressure-sensitive adhesive layer.

The present disclosure further relates to a method of making the precursor of a label comprising the steps of

(i) providing a release carrier,
(ii) applying a discontinuous emblem layer comprising one or more emblems to the release surface of the release carrier, and
(iii) applying the polymer layer onto the release surface and the emblem layer so that the emblem layer is arranged at the interface between the polymer layer and the release surface of the release carrier.

The present disclosure furthermore relates to a method of making a label according to the invention comprising the steps of

(i) providing a precursor of the present invention, and
(ii) removing the release carrier.

**Brief Description of the Drawings**

*Fig. 1* shows one embodiment of a precursor 2 of the present disclosure comprising a release carrier 6, a polymer layer 3 and a discontinuous emblem layer 4 comprising several emblems 5 at the interface between the release surface 6a and the major surface 3a of the polymer layer 3. The surface of the emblem(s) 5 facing the release surface 6a is coplanar with the surface 3a of the polymer layer 3.

*Fig. 1a* shows one embodiment of a label 1 of the present disclosure which is obtainable from the precursor 2 of *Fig. 1* by removing the release carrier 6.
Optionally a protective layer 10 may be applied onto the major surface 3a of the polymer layer 3 (not shown).

*Fig. 2* shows another embodiment of a precursor 2 of the present disclosure which is based on the precursor 2 of *Fig. 1a* but additionally comprises an adhesive layer 7 attached to the surface 3b of the polymer layer 3. The adhesive layer 7 is covered with release liner 9.

*Fig. 2a* shows another embodiment of a label 1 of the present disclosure which is obtainable from the precursors 2 of *Fig. 2* by removing the release carrier 6. Optionally a protective layer 10 may be applied to the major surface 3a of the polymer layer 3 (not shown).

**Detailed Description**

The term "label" as used above and below denotes a spatially limited section of a one- or multilayer continuous polymeric film optionally including an adhesive layer such as, in particular, a pressure-sensitive adhesive layer. The label can be obtained from such polymeric film. The polymeric film may comprise only one polymeric layer 3 comprising one or more emblems 5 arranged adjacent to major surface 3a of the polymer layer 3 and no further polymeric layers, or it may comprise one or more polymeric layers 8 in addition to polymeric layer 3. The label can be obtained from such continuous polymeric film by converting using conventional techniques such as, for example, die-cutting. The label can have different lengths and includes, for example, products with a relative short length such as identification or price tags or decorative and/or information providing tabs but also tape products with a relative great length sufficient for winding them into a roll.

The term "emblem" as used above and below denotes a three-dimensional section which is arranged within the polymer layer 3 adjacent to the surface 3a of the polymer layer 3. In the precursor 2 the one or more emblems 5 are arranged so that a surface portion of such emblem(s) 5 contacts the release surface 6a
whereby such surface portion of the emblem(s) 5 is coplanar with the exposed adjacent surface 3a of the polymer layer 3. This is also referred to above and below as the emblem layer 4 and/or the emblem(s) 5 being arranged at the interface between the surface 3a of the polymer layer 3 and the release surface 6a of release carrier 6. The one or more emblems are visually discernible against the surrounding polymer layer 3, and are preferably arranged to provide a decorative or aesthetical effect such as figures or symbols and/or to deliver information such as, for example, an instruction, warning or identification information.

The precursor 2 of a decorative and/or information containing label 1 of the present disclosure comprises a release carrier 6 which, in some embodiments, comprises a carrier film or layer such as a paper or polymer film bearing a low-adhesion release layer to provide a release surface 6a allowing for an essentially residue-free removal of the release of the polymer layer 3 embedding emblem(s) 5, from the release surface 6a. Representatives of suitable carrier films or layers comprise, for example, high-density papers such as glassine paper, clay-coated paper, kraft paper, polymer-laminated paper such as polyethylene-laminated paper and polymeric films. Useful polymeric films and layers include, for example, polyolefin polymers, monoaxially oriented polypropylene (MOPP), biaxially oriented polypropylene (BOPP), simultaneously biaxially oriented polypropylene (SBOPP), polyethylene, copolymers of polypropylene and polyethylene, polyester polymers, polycarbonate polymers, polymethacrylate polymers, cellulose acetate, polyester (e.g., biaxially oriented polyethylene terephthalate), vinyl acetates, and combinations thereof.

The low-adhesion release layer may, for example, be coated onto the carrier film or layer followed by subsequent drying and/or UV or e-beam curing. Examples of suitable low adhesion coatings are cellulose acetate butyrate, vinyl acetate-dibutyl maleate, vinyl alcohol silicone emulsions, or preferably water-based ethylene acrylic acid or water-based acrylic. The carrier films or layers may also be treated with release agents such as fluorine containing resins or silicone resins.
Alternatively, it is also possible to apply a printable low-adhesion coating as is described, for example, in U.S. Pat. No. 5,496,635.

In case the release carrier 6 itself comprises a release material such as, for example, a highly fluonated polymer it is also possible to omit the low-adhesion release layer and employ the carrier layer alone.

The precursor 2 of the decorative and/or information providing label 1 furthermore comprises a discontinuous emblem layer 4 comprising one or more emblems 5. The term "discontinuous" means in case only one emblem is present, that such emblem 5 covers only part (preferably less than 50 %) of the release surface 6a. In case two or more emblems 5 are present the term "discontinuous" means that the two or more emblems are not linked to each other but form discrete, separate sections. The two or more emblems 5 preferably cover less than 75 % and more preferably less than 50 % of the release surface 6a.

In some embodiments, the emblems layer 4 is applied by printing a printable or coatable precursor of the emblems 5 onto the release surface 6a with subsequent drying and/or curing. The printable or coatable precursor of the emblems preferably has a Brookfield viscosity of between 300 cPoise and 8,000 cPoise and more preferably between 300 and 3,000 cPoise at a temperature of 20 °C. The precursor of the emblems may be applied by any printing method such as, for example, by screen printing, ink-jet printing, electrostatic printing or rotogravure printing, flexo printing, letterpress printing, offset printing or thermal transfer or hot stamping printing.

The printable or coatable precursor of the emblem(s) 5 comprises one or more polymers which are selected to allow for an essentially clean and residue-free removal of the emblems 5 together with the surrounding matrix of polymer layer 3 from the release surface 6a when removing the release carrier 6 to provide the label 1. In some embodiments, the polymers of such precursor of the emblem are selected from a group of polymers consisting of (meth)acrylate polymers,
polyurethane polymers, polyamide polymers, polystyrene polymers, polymers comprising polymerized units derived from one or more olefin monomers, from one or more (meth)acrylic monomers, from one or more vinyl monomers, silicone polymers, and mixtures thereof.

Representative examples include polyolefins such as polyethylenes, polypropylenes and polybutylenes; olefinic copolymers such as ethylene(meth)acrylate copolymers; ethylene/vinyl acetate copolymers; acrylonitrile-butadiene-styrene copolymers; acrylic polymers and copolymers, polyurethanes and copolymers such as acrylic polyurethanes; vinyl polymers and copolymer such as polyvinylchloride, and mixtures thereof. Mixtures or blends of any plastic or plastic and elastomeric materials such as polypropylene/polyethylene, polyurethane/polyolefin, polyurethane/polycarbonate, polyurethane/polyester can also be used.

In some embodiments, the acrylic polyurethane may be the acrylic polyurethane which is disclosed in WO 93/12155 and comprises components A, B and C wherein component A comprises a copolymer of

(i) a monoester of acrylic or methacrylic acid and an aliphatic diol having 2 to 8 carbon atoms, and

(ii) an ester of acrylic or methacrylic acid and an aliphatic alcohol having 1 to 8 carbon atoms, and optionally a vinyl aromatic monomer as well as N-vinylpyrrolidone or N-vinylcaprolactame, said component A having a $T_G$ of $30 \, ^\circ\mathrm{C}$ to $100 \, ^\circ\mathrm{C},$

component B comprises an aliphatic polyester diol with an weight-average molecular weight less than 20,000, and

component C comprises a polyfunctional isocyanate or blocked polyfunctional isocyanate.

This polymer is described in more detail on page 5, line 4 - page 7, line 14 of WO 93/12155 which passage is enclosed herein by reference.
The precursor of the emblem(s) 5 furthermore comprises one or more additives which render the emblem(s) 5 visually discernible from the polymer layer 3. Such additives comprise, in particular, colouring agents such as inorganic pigments including metallic pigments or metallic flakes such as aluminium flakes or particles, organic pigments, water-borne or solvent-borne inks or dyes, and/or inorganic microspheres and/or beads such as, for example, glass beads. These additives may be selected so that the emblem(s) 5 are visually discernible from the surrounding polymer layer 3 by the unaided eye under normal ambient light conditions but it is also possible that the additives are selected so that the emblem(s) 5 are visibly discernible when viewing them through magnifying glasses or a microscope, respectively, or upon irradiating the label 1 with UV light, IR light or viewing it under retroreflective lighting conditions. It was found that emblem(s) comprising partially metallized glass beads or a combination of glass beads which may or may not be metallized, with metal flakes exhibit retroreflective properties. The term "partially metallized glass beads" refers to glass beads 20 - 60 % of the surface of which are coated with a thin metal film which may be applied, for example, by CVD or PVD techniques. The use of glass beads which may or may not be aluminized in combination with aluminium and/or silver flakes or particles is preferred. Glass beads suitable in the present invention are preferably essentially spherical and typically have a diameter of between 40-60 micrometers (µm).

Inorganic pigments which are suitable include, for example, titanium dioxide white, carbon and vegetable black, iron oxide pigments, cadmium pigments, lead chromate pigments, chromium oxide pigments including chromium oxide green, ultramarine blue, chrome green, phthalo chrome green, mixed metal oxide pigments and bi-vanadates.

Organic pigments which are suitable include, for example, azo pigments, polycyclic pigments and metal complex pigments. Suitable azo pigments include, for example, monoazo yellow and orange pigments, disazo pigments, naphthol pigments, benzimidazolone pigments and disazo condensation pigments.
Suitable polycycic pigments include, for example, phthaiocyanine pigments, quinacridone pigments, peryiene and perinone pigments, thioindigo pigments, anthraquinone pigments, dioxazine pigments, isoindoiinone and isoindoiine pigments, diketopyrrolo pyrroie pigments, triarycarbionium pigments and quinophthaione pigments.

Commercially available inorganic pigments which are suitable for use in the emblem(s) include, for example, carbon black available as carbon black paste from Degussa, Germany. As a white coloured pigment, titanium dioxide in silane modified form can be used (Kronos CL 310, Kronos Titan, Leverkusen, Germany). Lead sulfo-chromate pigments and mixed crystal lead sulfo-chromate-molybdate pigments are available from Heubach as Heucotron T and Heucotron T Orange 8010, respectively. Also aluminium particles of 5 µm length in a solvent (STAPA-Off-Set 3000, Eckhart-Werke, Fürth, Germany) can be used as organic pigments.

Commercially available organic pigments include isoindolininone yellow commercially available as Cromophtal Yellow 2RLTS from Ciba; peryiene red commercially available as Irgazin Red BPTN from Ciba; pthalocyanine green, a halogenated Cu-phtalocyanine commercially available as Chomophtal Green GFN from Ciba; quinacridone violet commercially available as Cinquasia Violet RRT-899D from Ciba; C. I. pigment red 178/15 (Paliogen rot L391 0 HD, BASF, Ludwigshafen, Germany); C. I. pigment yellow 110 (Irgazin gelb 3RLT-N, Ciba-Geigy, Marienberg, Germany); and C. I. pigment blue 15 11, Heliogen blau K691 1D, BASF, Ludwigshafen, Germany).

Pearlescent pigments that subtly change colour as the viewing angle is changed can be obtained, for example, from Merck KGaA, Darmstadt, Germany, under the Iriodin trade designation.

Liquid crystal polymer additives which change colour when the viewing angle is changed are also suitable and can be obtained from, for example, Wacker Chemie of Munich, Germany.
It is also possible to use up-converting pigments, down-converting pigments or a combination thereof.

Down-converting pigments are pigments that emit UV light upon absorption of light from the visible spectrum. These may be organic or inorganic. Inorganic as referred to herein means the pigment may be entirely inorganic or it may contain inorganic compounds complexed by organic compounds (e.g. chelates etc). Preferred are down-converting pigments having an average particle size greater than 1 \( \mu m \) or greater than 1.5 \( \mu m \). An example of a down converting additive which is invisible under ambient light but visible under UV light is Black Light Varnish available from Wernecke of St. Paul, MN, USA. It is also possible to use S.A. Other examples are fluorescent or phosphorescent pigments such as rare earth metals or rare earth metal oxides, e.g. neodymium oxides. A suitable fluorescent pigment is available from Honeywell under the trade designation Lumilux® Effect Blue SN. It is also possible to use Examples of phosphorescent pigments include the Lumilux® Phosphorescent pigments series available from Honeywell such as Luminux® green SN-F5, Lumilux® Green N5 or Lumilux® C-Pigments.

Exemplary up-converting (anti-stoke's) pigments are materials capable of emitting electromagnetic radiation of greater energy upon absorption of electromagnetic radiation of lower energy. For example, the up-converting pigments may be capable of absorbing infrared radiation and emitting radiation in the visible spectrum (e.g. from about 400 nm up to less than 700 nm wavelength), e.g. pigments that emit green light upon irradiation with infrared light (e.g. radiation of from about 700 to about 1300 nm wave length). It is also possible to use an up-converting pigment which is excited by electromagnetic radiation of the visible spectrum and emits UV light (e.g. radiation of a less than 400 nm up to less than 250 nm wave length).

Up-converting pigments are typically inorganic materials doped with erbium (Er), ytterbium (Yb) or thulium (Tm), such as for example rare earth metal fluorides.
doped with rare earth metals or metal ions, such as for example Yb\(^{3+}\), Er\(^{3+}\), Tm \(^{3+}\), Nd\(^{3+}\), Ho\(^{3+}\), although crystals doped with ions of some transition metals, e.g. Ti\(^{2+}\), Ni\(^{3+}\), Mo\(^{3+}\) or Re\(^{4+}\) have also been used in the fabrication of up-converting pigments. Typical examples of up-converting pigments correspond to the general formula \(\text{NaI}_n\text{F}_4\): Yb\(^{3+}\), Er\(^{3+}\) with Ln typically being Y, Gd or La. A particular example is NaYO.57,YbO.39, ErO.39F4. Other examples include oxysulfide doped with rare metals corresponding to the general formula M2O2S: Yb, Tm, Er with M being a lanthanoid or Y, Sc such as for example Gd2O2S: Yb, Tm, Er or Y2O2S2: Yb, Tm, Er. Other examples of crystals that may be doped with such ions include manganese halides and tungstate crystals such as RbMnCl\(_3\), CsMnCl\(_3\), CsMnBr\(_3\), Rb2MnCl\(_4\) or NaY(WO\(_4\))2. Examples of suitable up-converting nanopowders include Al2O3 or yttrium aluminium garnet doped with Nd\(^{3+}\) or Ce\(^{3+}\). Preferably, the up-converting pigments are crystalline.

Inks which are suitable in the present invention include 3M Process Colour Series 880I which is commercially available from 3M Company.

The average size of the colouring agents can vary widely. Organic pigments typically have an average size of between 0.03 - 1 \(\mu\)m or between 0.03 - 3 \(\mu\)m or between 0.05 - 0.5 \(\mu\)m. The average size of inorganic pigments can vary between 0.2 \(\mu\)m to 50 \(\mu\)m or even more. Titanium dioxide, for example, has a size of typically between 0.2 - 1 \(\mu\)m whereas red iron oxide has typically has an average size of between 0.3 - 3 \(\mu\)m. The average size of metal particles and flakes typically is between 3 - 25 \(\mu\)m, and glass beads have a typical average size of 40 - 60 \(\mu\)m. The person skilled in the art will easily select the appropriate thickness of the polymer layer 3 and of any additional polymer layers 8, if present, in view of the respective average size of the colouring agents used.

In one embodiment of the invention that has a particular favourable migration behaviour of the pigments even after heat treatment above 80\(^{\circ}\)C for one hour (i.e. low or no migration into adjacent layers), the pigments used have a particle size of
greater than 1 µm or greater than 1.5 µm for the preferred layer thicknesses as
described herein.

In one embodiment the colouring agents and/or inorganic microspheres or beads
used are preferably selected so that the one or more element(s) 5 are visibly
discernible against the polymer layer 3 upon formation of the precursor 2, i.e.
without requiring a further treatment step such as an additional irradiation source
other than visible light.

In another embodiment, the colouring agents and/or inorganic microspheres or
beads used in the present invention, are preferably selected so that the one or
more element(s) 5 are visibly discernible against the polymer layer 3 upon
formation of the precursor 2, that is, without requiring a further treatment step
such as laser irradiation. Therefore the use of colouring agents which exhibit a
colour change upon i.e. upon irradiation with an energy source other than visible
light, e.g. UV light (e.g. down-converting pigments) IR- light (e.g. up-converting
pigments) or laser marking such as the Lazerflair® pearlescent pigments from
Merck.

In some embodiments, the one or more additives included into the precursor of
the emblem(s) 5 to render such emblem(s) visually discernible against the
polymer layer 3 are present in an amount of from 2 - 70 pph, and, in some
embodiments, 2-50 pph (parts per hundred resin) with respect to the mass of such
precursor.

The precursor of emblem(s) 5 may comprise further agents and additives such as,
for example, levelling agents, thickeners, wetting agents, polymerization catalysts,
crosslinking agents and solvents. Levelling agents support the formation of a
uniform and smooth surface without surface defects. Suitable levelling agents are
generally organic silicones and fluorochemicals. Thickeners and solvents may be
added in order to adjust the viscosity of the precursor of the emblem(s) 5 to impart
advantageous phntability properties to it. Polymerization catalysts and, optionally,
crosslinking agents may be added if the precursor is cured subsequent to its application to the release surface.

While the structure of that part of the surface of the emblem(s) 5 which is or has been in contact with the release surface 6a is determined by the surface structure of the release surface 6a and preferably is essentially flat, the shape of the other surface portions of the emblem(s) 5 which are in contact with the polymer layer 3, can vary broadly and can be, for example, essentially polygonic or essentially curved. The average height of the emblem(s) which is defined as the average distance between the release surface 6a and the maximum extension of the emblem(s) 5 in a direction normal to such release surface 6a is, in some embodiments, less than the thickness of the polymer layer 3; in some embodiments, less than 90 %; and in some embodiments, less than 50 % of the thickness of the polymer layer 3. In case of glass beads or pearlescent pigments, for example, which may have an extension of, for example, 40-80 µm the average height of the emblem(s) may exceed the thickness of the polymer layer 3; in such case one or more further polymer layers 8 are required, and the emblem(s) 5 extend in such additional polymer layers 8.

The extension and shape of the emblem(s) 5 in the plane of surface 3a of the polymer layer 3 can vary broadly and is determined by the desired decorative effect or the information to be displayed. Emblem(s) 5 which are visible and discernible with the unaided eye typically have an extension in the plane of surface 3a of at least 1 mm. Emblem(s) 5 with an extension in the plane of surface 3a of, for example, 10 - 500 and, in some embodiments, 25 -250 µm are typically not readily discernible with the unaided eye but require the use of, for example, magnifying glasses or a microscope. Therefore such emblem(s) having an extension in the µm-range, can be used as a security feature which is referred to below in the Example section as "microschpht"-type emblem(s) 5.

The precursor 2 of the decorative and/or information providing label 1 furthermore comprises a polymeric layer 3 which is attached to the release surface 6a of the
release carrier thereby enclosing the one or more emblem(s) 5. In some embodiments, a precursor of the polymer layer 3 is laid down onto the release surface 6a by printing or coating or casting methods such as, for example, screen printing, spraying, rotogravure or knife coating. It is also possible to apply the polymer layer 3 by extrusion, lamination, calendaring, or thermal transfer printing or hot film stamping. The printable and/or coatable precursor of the polymer layer 3 preferably has a Brookfield viscosity of between 300 cPoise and 8,000 cPoise and more preferably of between 300 and 3,000 cPoise at 20 °C. Subsequent to its application to the release surface 6a and the emblem(s) 5, the precursor of the polymer layer may be dried and/or cured. Drying may be applied, in particular, to waterborne precursors of the polymer layer using a drying temperature of, for example, 20 - 200 °C. Curing may be effected, for example, by irradiating the precursor of the polymer layer 3 with UV light or by increasing its temperature to accelerate curing.

The printable or coatable precursor of the polymer layer 3 comprises one or more polymers which are selected

• to provide a sufficiently strong bond to the emblem(s) 5, and
• to allow for an essentially clean removal of the polymer 3, together with the emblem(s) 5, from the release surface 6a when removing the release carrier 6

so that the label 1 can be separated essentially intact and cleanly from the release surface 6a of the release carrier. The precursor of the polymer layer 3, the precursor of the emblem(s) 5 and/or the release surface 6a are therefore selected so that the interfacial adhesive force between the polymer layer 3 enclosing the emblem(s) 5 and the release surface 6a is less than the cohesive strength of the polymer layer 3, the cohesive strength of the emblem(s) 5 and the bonding strength between the polymer layer 3 and the emblem(s) 5.
The requirement of a sufficient bonding strength between the polymer layer 3 and the emblem(s) 5 can usually be met by selecting the precursor of the polymer layer 3 so that it is compatible with the polymer of the emblem(s) 5 and its precursor. The term "compatible" means that the precursors of the polymer layer 3 and of the emblem(s) are selected so that they are chemically similar to each other and can react to form a chemical bond. If the precursor of the polymer layer 3 comprises, for example, a polymer comprising unsaturated carbon-carbon double bonds or acrylic groups the precursor of the emblem(s) 5 preferably also comprises a polymer comprising such groups. Such a choice can be made easily and does not require any inventive input from the person skilled in the part.

The precursor of polymer layer 3 comprises one or more polymers which are preferably selected from the group of polymers given above for the polymers suitable to use in the emblems. Especially preferable are acrylic based and polyvinyl based polymers.

In some embodiments, the precursors of the polymer layer 3 and the one or more emblem(s) 5 each comprise at least one polymer which is essentially the same.

In some embodiments, the polymers used on the precursors of the polymer layer 3 and the emblem(s) 5 are selected so that the polymer layer 3 of the label 1 with the emblem(s) 5 enclosed therein, has a tensile strength at break of about 1,000 N/cm² to about 5,000 N/cm² and, in some embodiments, from about 1,250 N/cm² to 4,000 N/cm². The elongation at break of the polymer layer 3 preferably is between 2 - 50 %. The polymer layer 3 preferably has a thickness of between 5 - 500 µm and more preferably between 20 - 250 µm.

The precursor of the polymer layer 3 may comprise further additives such as colouring agents such as inorganic and organic pigments, inks and dyes, inorganic or organic microspheres, glass beads, levelling agents, thixotropic agents, thickeners, wetting agents, polymerization catalysts, crosslinking agents and solvents.

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If colouring agents and/or microspheres are added to the precursor of the polymer layer 3 these additives and/or their concentration are selected to be different from the colouring agents and/or microspheres or their concentration, respectively, used in the emblem(s) 5 so that the emblem(s) 5 are visually discernible against the polymer layer 3 enclosing such emblem(s) 5. For the purposes of the present disclosure colouring agents such as the Lazerflair® pearlescent pigments from Merck which change their colour upon laser irradiation, are considered to be the same pigment before and after the laser irradiation. In one embodiment of the invention the labels 1 of the present disclosure preferably comprise a colouring agent which exhibits a colour change when irradiated with an IR-light source, (such as an IR laser beam) or a UV light source under conditions which essentially do not result in damaging the surface 3a of the polymer layer. In another embodiment of the invention the labels 1 of the present invention preferably comprise a colouring agent which exhibits a colour change without irradiation with an IR-light source, (such as an IR laser beam) or a UV light source.

In the label of the present invention the total concentration of the colouring agents in the emblem(s) 5 is different from the total concentration of the colouring agents in the polymer layer (3).

In some embodiments, the precursor of the polymer layers 3 comprises partially metallized glass beads or optionally non-metallized glass beads in combination with metal flakes or particles to impart retroreflective properties to the polymer layer.

The variation of the colourants and/or microspheres and/or their concentration, respectively, in and adjacent to the surface 3a of the polymer layer 3 is a unique feature of some embodiments of the precursor 2 and the corresponding label 1 obtainable from such precursor. This construction allows for a broad variety of
design possibilities without placing restrictions on the nature of the colourants and/or microspheres used which is required, for example, in EP 0,688,678.

In some embodiments, the precursor 2 of label 1 comprises an adhesive layer 7 so that the label 1 can be adhesively attached to substrates. The adhesive layer may be attached to the surface 3b of the polymer layer 3 (i.e., to the major surface of the polymer layer which is opposite to the major surface 3a and to the emblem layer 4) or, if the precursor 2 and the corresponding label 1 comprise further polymer layers 8 which are attached to the surface 3b of the polymer layer, to the exposed surface of such layer or stack of layers.

The adhesive layer 7 may be applied onto the polymer layer 3 (or the exposed outside layer of the precursor) by casting from an organic solution or an aqueous dispersion or by such techniques as hot melt coating. The adhesive layer 7 may also be obtained by laminating an adhesive film onto the polymer layer 3 or the outside layer of the precursor, respectively. Examples of suitable adhesive films include 3M Transfer Tape 9458 (thickness 25.4 µm, suitable for application to smooth surfaces) and 3M VHB 4918, clear (thickness 2.0 µm, suitable for application to rough surfaces). To promote adhesion between the polymer layer 3 (or the outside layer of the precursor) and the adhesive layer 7, surface 3b of the polymer layer 3 (or the outside layer of the precursor) can be treated before the adhesive is applied. This treatment can comprise the application of a chemical primer or preferably include corona discharge treatment.

For making the adhesive layer 7, it may be preferred to use pressure-sensitive adhesives or heat-activatable adhesives. These may comprise polyacrylates, polyesters, polyimides, polyolefins, polyamides, polyurethanes, silicone polymers, polybutadiene and copolymers, polyisoprenes and copolymers, natural and synthetic rubbers as well as hydrogenated derivates thereof with and without resins, fillers and crosslinking agents.
Polyacrylates have also proven to be useful, particularly those which have been modified for use on a variety of surfaces exhibiting very different surface energies, such as steel and polyethylene. Useful alkyl acrylates (i.e., acrylic acid alkyl ester monomers) for the preparation of polyacrylates include linear or branched monofunctional unsaturated acrylates or methacrylates of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to 14 and, in particular, from 4 to 12 carbon atoms. Examples of these lower alkyl acrylates include but are not limited to, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, n-octyl acrylate, n-octyl methacrylate, 2-methylbutyl acrylate, isononyl acrylate, n-nonyl acrylate, isoamylacrylate, n-decyl acrylate, isodecyl acrylate, isodecyl methacrylate, isobornyl acrylate, 4-methyl-2-pentyl acrylate and dodecyl acrylate.

In some embodiments, acrylate-based pressure-sensitive adhesive materials such as copolymers of isooctyl acrylate and acrylic acid like those disclosed in U.S. Pat. No. 2,884,126 (U.S. Pat. No. Re: 24,906) may be used. The adhesive layer 7 can have a thickness of 10 to 2,000 µm, in some embodiments, 10 to 1,000 µm.

In some embodiments, the pressure-sensitive adhesives are tackified or non-tackified isooctyl acrylate and acrylic acid copolymers. The copolymers may be employed in amounts ranging from 50 to 70 % and, in some embodiments, in an amount of about 60 % by weight. As tackifying resin, there may be used, for example, Foral 85 (company Hercules), a hydrogenated rosin or its glycerol or pentaerythritol esters in amounts of preferably 30 to 50 % and particularly preferred of about 40 % by weight. In the mixture of adhesive, typically antioxidants in amounts of about 0.5 - 2 wt. % and cross-linkers such as for example aziridine compounds may be added.

The adhesive layer 7 can be protected by a release liner 9. The release liner is generally adhesive-repellant and may comprise paper or film which has been coated or modified with compounds of low surface energy relative to the adhesive applied. Organo silicone compounds, fluoropolymers, polyurethanes,
polyethylene naphthalate and polyolefins can serve this purpose. The release liner can also be a polymeric sheet produced from polyethylene, polypropylene, PVC, polyesters with or without the addition of adhesive-repellant compounds. The release liner can have a thickness of 25 to 250 µm, preferably 30 to 200 µm.

The one or more additional layers 8 which may be attached to the surface 3b of polymer layer 3 may be polymer layers each comprising one or more polymers which may be selected from a group of thermoplastic polymers consisting of polyesters, polycarbonates (e.g. acrylonitrile butadiene styrene polycarbonate), polyarylates, polyamides, polyimides, polyamide-imides, polyether-amides, polyetherimides, polyaryl ethers, polyarylether ketones, aliphatic polyketones, polyphenylene sulphide, polysulfones, polystyrenes and their derivatives, polyacrylates, polymethacrylates, cellulose derivatives, polyethylenes, polyolefins, copolymers having a predominant olefin monomer, fluorinated polymers and copolymers, chlorinated polymers, polyacrylonitrile (e.g. acrylonitrile styrene acrylate), vinyl polymers such as polyvinylacetate, polyvinylchloride or polyvinylalcohol, polyethers, ionomeric resins, elastomers, silicone resins, epoxy resins, and polyurethanes. The layer 8 may have a thickness of from 10 to 500 µm.

In some embodiments, such additional polymer layer(s) 8 comprises one or more polymers selected from the group of polymers identified above for use in polymer layer 3 and in the emblem layer 4.

The additional layers 8 may be applied to surface 3b of polymer layer 3 by any conventional technique including lamination, coating, printing or the like. The additional polymer layers may comprise further additives such as colouring agents including inorganic and organic pigments, inks and dyes, organic and inorganic microspheres and beads, levelling agents, thixotropic agents, thickeners, wetting agents, polymerization catalysts, crosslinking agents and solvents.
In one embodiment, precursor 2 and the corresponding label 1 comprise one or more additional polymer layers. These one or more additional polymer layers 8 may comprise one or more colouring agents (or colourants) which are different from and/or used in a different concentration than the colourants used in the polymer layer 3 and/or the one or more emblem(s) 5. This allows for specific decorative and/or aesthetical effects including laser ablation of the polymer layer 3 to display the one or more polymer layers 8 beneath layer 3. While this broadens the design possibilities made available, laser ablation may not be preferred for any application because it damages the surface of the label 1 which makes such label less mechanically durable.

In some embodiments, label 1, which is obtainable from the precursor 2 by removing the release carrier 6, offers several advantages and unique properties.

The exposed surface of the label 1 may be formed by surface 3a of the polymer layer 3. The roughness and structure of surface layer 3a including the exposed surface of the emblem(s) 5 is determined by the roughness and structure of the release surface 6a to which the polymer layer 3 and the emblem(s) 5 had been applied in the precursor 2.

Generally, the release surface 6a is essentially smooth resulting in an essentially smooth surface 3a of the label 1. The term "essentially smooth" means that the release surface 6a exhibits an average roughness Rz of less than 5 µm and in some embodiments, of less than 3 µm. In some embodiments, the average surface roughness Rz is between 0.5 - 2.5 µm; and, in some embodiments, between 0.7 - 1.5 µm. Label 1 does not require a laser after-treatment to render the emblem(s) 5 visually discernible against the polymer layer 3. Consequently, the surface portion of the emblem(s) 5 within such surface 3a is not damaged by any laser treatment, and the surface roughness of the surface 3a and the surface portion of the emblem(s) 5 within such surface 3a is preferably essentially the same.
For specific applications where the surface of the label should have, for example, a leather-like look/surface appearance, the release surface 6a may be modified to have a higher roughness \( R_z \) of, for example, between 5 \( \mu \)m and 1,000 \( \mu \)m.

If desired, the release layer is structured and exhibits a regular or irregular pattern of indentations and/or elevations as is described, for example, in EP 0,951,518.

A protective layer 10 may be attached to the surface 3a of the polymer layer 3 of the label to protect the label 1 and to impart, for example, scratch resistance to it. In some embodiments, the protective layer 10 is transparent. Examples of suitable materials for the protective layer of the invention include primed or unprimed polyethylene terephthalate (polyester), polyvinylchlohe, polyolefins, or cellulose acetate films. While these protective films 10 are intended to protect the label permanently it is also possible to apply, for example, a masking tape to the exposed surface of the polymer layer for temporary protection.

Label 1 comprises a polymer layer 3 with emblem(s) 5 arranged adjacent to the surface 3a of such polymer layer 3 as is described above. In such label the polymer layer 3 and/or the emblem(s) 5 comprise one or more colourants and/or microspheres so that the colourants and/or microspheres and/or their concentration, respectively, in the polymer layer 3 on the one hand and in the emblem(s) 5 on the other hand are different from each other. In other words, there is a variation of colourants and/or microspheres and/or their respective concentration in the area of surface 3a of the polymer layer 3 and the emblem(s) 5 enclosed therein so that the emblem(s) 5 are visually discernible against the polymer layer 3.

Label 1 is preferably made by manufacturing precursor 2 and removing the release carrier 6. Removal of release carrier 6 is preferably obtained by peeling off the release carrier.
If desired, a protective layer 10 may additionally be applied to the polymer layer 3 as was described above.

In some embodiments, the precursor is made by providing a release carrier 6 in the first step. Then the emblem layer 4 comprising one or more emblems 5 is attached to the release surface 6a, for example, by printing the precursor of emblem(s) 5 onto the release surface 6a. The emblem(s) 5 may be dried and/or cured subsequent to such printing step. Then the precursor of the polymer layer 3 is applied onto the release surface 6a and the emblem(s) 5 so that the polymer layer 3 encloses the emblems. The precursor of the polymer layer may be applied by coating, casting or printing using any known coating and/or printing method. It is also possible to apply the polymer layer 3 or its precursor, respectively, by extrusion, lamination, hot stamping or thermal transfer printing. Then the precursor of the polymer layer 3 is dried and/or cured. If desired, the precursor may be further modified by attaching one or more further polymer layers and an adhesive layer 7 such as a pressure-sensitive adhesive layer.

The present disclosure will be further illustrated in the following examples which are to exemplify embodiments of the present disclosure without restricting them.

List of Materials

**Component A:**

Acrylate polyol comprising 2-hydroxyethyl methacrylate (2-HEMA), methylmethacrylate (MMA), ethylmethacrylate (EMA) and iso-butylmethacrylate (IBMA), was prepared according to the following procedure: 50 parts toluene and 50 parts butylacetate were charged to a reaction vessel equipped with a nitrogen purge, stirrer, thermometer and addition funnel. 2.5 parts di-t-butyl peroxide was added to the solvents at 60 °C. 100 parts monomer mixture, comprising 16 parts 2-HEMA, 55 parts MMA, 17 parts EMA and 12 parts IBMA, was mixed with 2.5 parts azobisisobutyronitrile. The monomer mixture was added to the contents of the vessel with stirring in three equal portions: one portion initially, one portion after 1 hour and one portion after 2 hours. After the exotherm was complete, the
reaction mixture was stirred at 60 °C for 8 hours. Final solids content was about 50 weight%.

**Component B:**
Aliphatic polyesterdiol: Epsilon-carpolactonediol, available under the trade-name TONE® 230 (Union Carbide, USA)

**Component C:**
Blocked multifunctional isocyanate, adduct of 1,6-hexamethylene diisocyanate and 2-butanone oxime available under the trade name Desmodur BL 3175 (Bayer Leverkussen, Germany)

**Colouring agents (Component D):**
D1: titanium dioxide silane modified, commercially available under the trade name Kronos CL310 (Kronos Titan, Germany)
D2: Aluminum particles in solvent, 5µ available under the trade name STAPA-Off-Set 3000 (Eckhart-Werke, Germany)
D3: Carbon black paste in soya alkyd resin available under the trade name TACK 1 (Degussa, Germany)

**Component E (levelling agent):**
3M Novec™ Fluorosurfactant FC 4434

**Acrylic coating mixture-1 (white):**
The solution of acrylate polyol (component A; 59 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 15 weight %) in toluene. Component D1 (30 parts per hundred resin pph) was added. The resulting mixture was rendered homogeneous by mixing on a ball mill for eight hours at room temperature.
Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 26 weight %) was added as well as dibutyltindilaurate catalyst (0.2 pph) and component E (0.6 pph).

**Acrylic coating mixture-2 (silver):**

The solution of acrylate polyol (component A; 56 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 17 weight %) in toluene. Component D2 (8 pph) was added. The resulting mixture was rendered homogeneous by mixing on a ball mill for eight hours at room temperature.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 27 weight %) was added as well as dibutyltindilaurate catalyst (0.2 pph) and component E (0.6 pph).

**Acrylic coating mixture-3 (black):2a (silver)**

The solution of acrylate polyol (component A; 57 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 9.8 weight %) in toluene. Component D1 (8 weight %), component D2 (3 weight %) and 1 weight % SP-green (Secure Products, NJ, USA) were added. The resulting mixture was rendered homogeneous by mixing on a ball mill at room temperature for eight hours.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 19 weight %) was added as well as tin(II) 2-ethylhexanoate catalyst (0.1 pph) and component E (0.1 pph).

**Acrylic coating mixture-3 (black)**

The solution of acrylate polyol (component A; 56 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B;
17 weight %) in toluene. Component D3 (7.5 pph) was added. The resulting mixture was rendered homogeneous by mixing on a ball mill for eight hours at room temperature.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 27 weight %) was added as well as dibutyltindilaurate catalyst (0.2 pph) and component E (0.6 pph).

**Acrylic coating mixture-4 (clear):**

The solution of acrylate polyol (component A; 59 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 15 weight %) in toluene. Glass beads were added (5 weight %). The resulting mixture was rendered homogeneous by mixing on a ball mill for eight hours at room temperature.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 26 weight %) was added as well as dibutyltindilaurate catalyst (0.2 pph) and component E (0.6 pph).

**Acrylic coating mixture-4a (clear)**

The solution of acrylate polyol (component A; 59 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 9 weight %) in toluene. 0.5 weight % of SP green was then added. The resulting mixture was rendered homogeneous by mixing on a ball mill for eight hours at room temperature.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 19 weight %) was added as well as tin(II) 2-ethylhexanoate catalyst (0.1 pph) and component E (0.1 pph).
**Acrylic coating mixture-4b (clear)**

The solution of acrylate polyol (component A; 59 weight %) as prepared above was mixed with a 50 % by weight solution of aliphatic polyester diol (component B; 9 weight %) in toluene. 0.1 weight % of SP green and 0.5 weight % of Lumilux® C- Red CD 168 (Honeywell Europe, Seelze Germany) were then added. The resulting mixture was rendered homogeneous by mixing on a ball mixer at room temperature for eight hours.

Directly preceding the coating in the Examples (see below), blocked isocyanate (component C; 19 weight %) was added as well as tin(II) 2-ethylhexanoate (0.1 pph) and component E (0.1 pph).

**Glass beads:**

Glass beads having an average diameter of about 50um and a refractive index of 2.3

**Adhesive:**

3M Transfer Tape 9458: acrylic pressure sensitive adhesive, having a thickness of 25.4 urn

**Examples**

**Preparation of films or labels**

**Preparation of release carrier 6**

A casting release carrier comprising a polymer-coated paper was prepared by taking a 108 g HIFI Kraft paper (available from Chem Tenero AG) and coating it with a solution of acrylic release material. The paper was then dried to give a dry coating weight of 30 g/cm². The surface was smooth and glossy and exhibited an average roughness \( R_z \) of approximately 1.0 \( \mu m \). This release carrier is denoted below as release carrier 6/sample 1.
For screen printed films, a double side siliconized PET-release liner having a thickness of 76 µm and quality 1876, commercially available from Huhtamaki, was used. This release carrier is denoted below as release carrier 6/sample 2.

**Example 1**

In a first step acrylic coating mixture-1 was printed as an emblem layer onto release carrier 6/sample 1 using rotogravure method. The emblem layer was dried at 180 °C for 1 minute.

Then acrylic coating mixture-2 was coated as polymer layer 3 onto the release carrier 6/sample 1 and oven dried at 180 °C during 2 min. Dry polymer layer 3, having a smooth surface, was about 10 µm in thickness.

A polymer layer 8 comprising acrylic coating mixture-3 was coated onto the first layer and dried at 200 °C during 2 min. The coating thickness of this second layer was about 50 µm after drying.

In a next step, 3M Transfer Tape 9458 was laminated onto the polymer layer 8 to provide pressure-sensitive adhesive layer 7 and the release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 1 used in the first step of the production was removed.

**Example 2**

In Example 2, a multilayer film was produced essentially according to the method as described in Example 1, except that the emblem layer 4 was printed onto the release carrier 6/sample 1 through screen printing. The emblem layer 4 was screen-printed with the 3M™ Process Colour 889I (red) and oven dried at 80 °C during 3 min.

A high cohesive bond between the emblem layer 4 and the polymer layer 3 was observed by a cross-cut test with the 3M Scotch Tape 610, according to the test method EN ISO 2409.
**Example 3**

In Example 3, a multilayer film from which labels 1 can be cut was produced using screen printing method.

In a first step, an emblem layer was printed onto Huhtamaki’s release liner (release carrier 6/sample 2) using 3M™ Process Colour 889I (red). The emblem layer was dried at 80 °C for 3 minutes.

In a second step, the polymer layer 3 was screen printed onto the pre-printed release carrier 6/sample 2 using 3M™ Process Colour 844I (yellow) and oven dried at 80 °C during 5 min. The dried polymer layer 3 was about 15 µm in thickness.

In a third step, a polymer layer 8 was screen printed onto the polymer layer 3 using 3M™ Process Colour 885I (black) and dried at 80 °C during 10 min. The coating thickness of this additional polymer layer 8 was about 50 µm after drying.

In a next step, 3M Transfer Tape 9458 was laminated onto polymer layer 8 to provide adhesive layer 7 and release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, release carrier 6/sample 2 used in the first step of the production was removed.

**Example 4**

In Example 4, a multilayer film from which labels 1 can be cut was made with a retro-reflective emblem layer 4, using a screen-printing method.

In a first step acrylic coating mixture-4 was screen-printed onto release carrier 6/sample 2 in a pattern or a logo to provide the emblem layer 4, which was then dried at 180 °C for 1 minute.
Then acrylic coating mixture-2 was coated as polymer layer 3 onto the pre-printed release carrier 6/sample 2 bearing the emblem layer 4, and was oven dried at 160 °C during 2 min. The dry polymer layer 3 was about 15 µm in thickness.

A layer 8 was coated onto polymer layer 3, using acrylic coating mixture-3. The coating was dried at 200 °C during 2 min. The coating thickness of this additional layer 8 was about 50 µm after drying.

In a next step, 3M Transfer Tape 9458 was laminated onto the additional layer 8 to provide adhesive layer 7 and release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 2 used in the first step of the production was removed.

**Example 5**

In Example 5, a multilayer film from which labels 1 can be cut was made.

In a first step a modified acrylic coating mixture-1 comprising, instead of silane modified titanium dioxide (component D1), 5 wt.% of glass based (average size of 40-60 µm) was printed onto release carrier 6/sample 1 in a pattern or a logo using rotogravure method to provide the emblem layer 4 which was then dried at 180 °C for 1 minute. The composition of acrylic coating mixture-1 was otherwise as indicated above.

In a second step acrylic coating mixture-4 was coated onto the pre-printed release carrier 6/sample 1, bearing the emblem layer 4, to form polymer layer 3. Layer 3 was oven dried at 180 °C during 2 min. The dried polymer layer 3 was about 15 µm in thickness.

A polymer layer 8 comprising an acrylic coating mixture as disclosed in Example 1 above was coated onto polymer layer 3 and oven dried at 180 °C during 2 min. The dried additional polymer layer 8 was about 15 µm in thickness.
A further additional polymer layer 8a was coated onto the first additional polymer layer 8 using acrylic coating mixture-3. The coating was dried at 200 °C for 2 min. The coating thickness of this further additional polymer layer 8a was about 50 µm after drying.

In a next step, 3M Transfer Tape 9458 was laminated onto the further additional polymer layer 8a to provide adhesive layer 7 and release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 1 used in the first step of the production was removed.

Example 6
In Example 6, a multilayer film from which labels 1 can be cut is made which comprises a clear retro-reflective additional polymer layer 8 next to polymer layer 3. This construction offers the advantage that in case polymer layer 3 is laser-marked this retro-reflective layer will be seen as a retro-reflective background by lighting.

In a first step emblem layer 4 was made by printing acrylic coating mixture-1 in a pattern or a logo onto release carrier 6/sample 1 using rotogravure method. The printed emblem layer 4 was dried at 180 °C for 2 minutes.

Then acrylic coating mixture-2 was coated onto the pre-printed release carrier 6/sample 1 bearing emblem layer 4, to make polymer layer 3 which was oven dried at 180 °C during 2 min. The dried polymer layer 3 was about 15 µm in thickness.

In a next step an additional polymer layer 8 was obtained by coating acrylic coating mixture-4 onto the polymer layer 3. The additional polymer layer 8 was oven dried at 180 °C during 2 min. The dried polymer layer 8 was about 15 µm in thickness.
A further additional polymer layer 8a was coated onto the first additional polymer layer 8 using acrylic coating mixture-3. The coating was dried at 200 °C for 2 min. The coating thickness of this further additional polymer layer 8a was about 50 µm after drying.

In a next step, 3M Transfer Tape 9458 was laminated onto the further additional polymer layer 8a to provide adhesive layer 7 and release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier/sample 1 used in the first step of the production was removed.

**Example 7**

In Example 7, a multilayer film was produced essentially according to the method as described in Example 1, except that a micro-script with a height between 100 - 500 µm was printed in addition to the logo to form the emblem layer 4. This adds an added security feature to prove the authenticity of the film. This micro script is legible clearly by use of a magnifying glass.

**Example 8**

In Example 8, a single layer film was produced.

In a first step acrylic coating mixture-2a was printed as an emblem layer onto release carrier 6/sample 1 using rotogravure method. The emblem layer was dried at 180 °C for 1 minute.

Then acrylic coating mixture-2 was coated as polymer layer 3 onto the release carrier 6/sample 1 and oven dried at 180 °C during 2 min. Dry polymer layer 3, having a smooth surface, was about 53 µm in thickness.

In a next step, 3M Transfer Tape 9458 was laminated onto the polymer layer 8 to provide pressure-sensitive adhesive layer 7 and the release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 1 used in the first step of the production was removed.
**Example 9**

In Example 9, a single layer film was produced. In a first step acrylic coating mixture-4a was printed as an emblem layer onto release carrier 6/sample 1 using rotogravure method. The emblem layer was dried at 180 °C for 1 minute.

Then acrylic coating mixture-2 was coated as polymer layer 3 onto the release carrier 6/sample 1 and oven dried at 180 °C during 2 min. Dry polymer layer 3, having a smooth surface, was about 53 µm in thickness.

In a next step, 3M Transfer Tape 9458 was laminated onto the polymer layer 8 to provide pressure-sensitive adhesive layer 7 and the release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 1 used in the first step of the production was removed.

**Example 10**

In Example 10, a single layer film was produced. In a first step acrylic coating mixture-4b was printed as an emblem layer onto release carrier 6/sample 1 using rotogravure method. The emblem layer was dried at 180 °C for 1 minute.

Then acrylic coating mixture-2 was coated as polymer layer 3 onto the release carrier 6/sample 1 and oven dried at 180 °C during 2 min. Dry polymer layer 3, having a smooth surface, was about 52 µm in thickness.

In a next step, 3M Transfer Tape 9458 was laminated onto the polymer layer 8 to provide pressure-sensitive adhesive layer 7 and the release liner 9. The coating thickness of the adhesive layer 7 was 25.4 µm. Finally, the release carrier 6/sample 1 used in the first step of the production was removed.
Test methods
The labels obtained from the films by cutting were tested according to the following test methods.

The results are given in Tables 1 - 3.

Abrasion resistance
The abrasion resistance was tested according to the CSA-test method C22.2 No. 0.15-M95, using a Teledyne Taber Abrasion Tester, CS-10 Abrasion wheel, 250 gr. weight. The test was run on 40 x 40 mm test samples (100 cycles).

The results of abrasion resistance as given in Table 1 are determined by visual inspection of the abraded surface (after the 100th cycle) using following standard:
+ = good
++ = very good (no change)

Chemical and water resistance
The resistance to chemicals or water was tested by immersing the sample into the respective test liquid for a period of 10 seconds, following by drying for 20 seconds. This procedure was repeated five times. Test liquids used were n-heptane, n-iso-propanol, diesel, drinking water.

The legibility of logo was determined by visual inspection using following standard:
+ = logo good legible
++ = logo very good legible (no change)

The results are recorded in Table 1.
Heat resistance
100 mm x 25 mm samples, adhered to an aluminium plate were exposed to a
temperature of 120 °C and 180 °C for a period of one hour in a forced air oven.
Each sample was visually evaluated with respect to shrinkage, adhesion and
colour changes.

The evaluation symbols given in Table 1 have the following meaning:
+ = good
++ = very good (no change)

Smear resistance - Rub test
The smear resistance of the printed logo, adhesion strength at the edges as well
as the adhesive oozing were tested according to the test method DIN 57700 (or
VDE 700) and using several test liquids like water, n-heptane, iso-propanol and
diesel.

The samples were adhered to an aluminium plate. The samples were rubbed
during 15 seconds using a square of white tissue, soaked with water. This
procedure was repeated with each of the test liquids. For all samples a rating ++
was obtained, indicating no visible change was detected.

Cross-cut test
The bonding of the logo to the top layer was tested accordingly to EN ISO 2409,
using 3M Scotch Tape 610. All examples showed a very good bond between logo
and top layer. 0 % of printed logo was removed during the test.

Reflection measurement
The reflection R' was measured according to DIN 67520-2, using an illumination
angle of +5° and an observation angle of 0.33°. The results, recorded in
cd/(m².lux) are given in Table 2.

Tensile strength and elongation
The tensile strength and elongation of the labels was measured according to AFERA 4004 and AFERA 4005 test methods respectively. The tests were done on specimen of 1 inch width. Testing conditions were 22 °C and 50 % relative humidity.

The tensile strength at break (N/cm²) and the elongation (%) are recorded in Table 2.

**Roughness measurement Rz**

The roughness of the polymer layer 3 was measured according to Test Method DIN EN ISO 1302 (06/02) using a Perthometer M2 testing equipment, available from Mahr. The results, recorded in µm are given in Table 2.

**Table 1: Performance result**

<table>
<thead>
<tr>
<th>Ex.-No.</th>
<th>Thickness (µm) of label (without adhesive)</th>
<th>Resistance rating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Abrasion</td>
</tr>
<tr>
<td>1</td>
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<td>++</td>
</tr>
<tr>
<td>2</td>
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<td>+</td>
</tr>
</tbody>
</table>

**Table 2: Performance**

<table>
<thead>
<tr>
<th>Ex.-No.</th>
<th>Tensile Strength at break (N/cm²)</th>
<th>Elongation (%)</th>
<th>Reflection R² [cd/(m².lux)]</th>
<th>Roughness Rz (µm)</th>
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</thead>
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</tr>
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</tr>
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</table>
The pigment detection was carried out after performing the tests listed below. A 3M Laser Reveal Verifier commercially available from 3M Deutschland GmbH, Germany was used for examples 8 to 10. In example 10 also a Money Detector from Conrad GmbH, Germany was used. In all examples, the pigments were clearly detected. Additionally, the sample of example 10 was inspected visually after oven aging at 120°C for 1h. No migration of the pigments to the reverse side the label/emblem construction was observed.

### Table 3:

<table>
<thead>
<tr>
<th>Ex.-No.</th>
<th>Tensile Strength at break (N/cm²)</th>
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List of reference numbers

1. Label
2. Precursor of label 1
3. Polymer layer
3a. Major surface of polymer layer 3 facing release surface 6a
3b. Major surface of polymer layer 3 opposite to major surface 3a
4. Emblem layer
5. Emblem(s)
6. Release carrier
6a. Release surface
7. Adhesive layer
8. Further polymer layer
9. Release liner
10. Protective layer
What is claimed is:

1. Precursor (2) of a label (1) comprising a release carrier (6) with a release
surface (6a) bearing a polymer layer (3) and a discontinuous emblem layer (4) comprising at least one emblem (5) at the interface between the release surface (6a) and a first major surface (3a) of the polymer layer (3).

2. Precursor (2) according to claim 1 wherein the polymer layer (3) comprises one or more polymers selected from the group consisting of (meth)acrylate polymers, polyurethane polymers, polyester polymers, polymers comprising polymerized units derived from one or more olefin monomers, one or more acrylic monomers and/or or more vinyl monomers, silicone polymers, polyimide polymers and mixtures thereof.

3. Precursor (2) according to claim 2 wherein the polymer layer (3) comprises one or more colouring agents selected from the group consisting of inorganic pigments including metal flakes, organic pigments, inks and dyes, up-converting pigments, down-converting pigments, a combination of up- and down-converting pigments and/or one or more inorganic microspheres or beads.

4. Precursor (2) according to any of the preceding claims wherein the emblem (5) comprises one or more polymers selected from the group consisting of (meth)acrylate polymers, polyurethane polymers, polymers comprising polymerized units derived from one or more olefin monomers, from one or more acrylic monomers, from one or more vinyl monomers, silicone polymers, and mixtures thereof.

5. Precursor (2) according to claim 4 wherein the emblem (5) comprises one or more colouring agents selected from the group consisting of inorganic pigments including metal flakes, organic pigments, inks and dyes, inorganic up-converting pigments, down-converting pigments, a combination of up-
and down-converting pigments and/or one or more inorganic microspheres or beads.

6. Precursor according to claim 5 wherein the additives comprised in the polymer layer (3) and in the emblem (5), respectively, and/or their concentration are different from each other so that the emblem (5) is visually discernible from the polymer layer (3).

7. Precursor (2) according to any of the preceding claims wherein the polymer layer (3) has a thickness of between 5 and 500 µm.

8. Precursor (2) according to any of the preceding claims wherein the precursor (2) further comprises an adhesive layer (7) which is attached to a second major surface (3b) of the polymer layer (3).

9. Precursor (2) according to claim 8 wherein the adhesive layer (7) comprises a pressure-sensitive adhesive.

10. Precursor (2) according to claim 9 wherein the pressure-sensitive adhesive is selected from the group consisting of acrylic, block copolymer, rubber resin, poly(alpha) olefin and silicone pressure-sensitive adhesives.

11. Precursor (2) according to any of claims 8 - 10 wherein the adhesive layer (7) is covered with a release liner (9).

12. Precursor (2) according to any one of claims 8 - 11 further comprising one or more further polymer layers (8) between the polymer layer (3) and the adhesive layer (7).

13. Label (1) comprising a polymer layer (3) comprising one or more emblems (5) arranged adjacent to a first major surface of said polymer layer (3), said emblems (5) comprising one or more polymers and a material selected from
the group consisting of (a) one or more colouring agents selected from the group consisting of inorganic pigments including metal flakes, organic pigments, inks and dyes; (b) up-converting pigments, down-converting pigments, a combination of up- and down-converting pigments, and/or one or more inorganic microspheres; (c) beads; and (d) combinations thereof; whereby said matehal(s) and/or their respective concentration are selected so that the one or more emblem(s) (5) are visually discernible from the polymer layer (3).

14. Label according to claim 13 wherein the polymer layer (3) and the one or more emblem(s) (5) do not comprise any colouring agent which exhibits a colour change when subjecting the label to laser irradiation.

15. Label according to claim 13 wherein the polymer layer (3) and the one or more emblem(s) (5) comprise at least one colouring agent which exhibits a colour change or becomes visible when subjecting the label to an IR-light source or an UV light source.

16. Label according to any of claims 13-15 wherein the total concentration of the colouring agents in the emblem(s) 5 is different from a total concentration of the colouring agents in the polymer layer (3).

17. Label according to any of claim 13-16 wherein a second major surface (3b) of the polymer layer (3) bears an adhesive layer (7).

18. Label according to any of claims 13-17 comprising one or more additional polymer layers on the polymer surface (3b) or between the polymer surface (3b) and adhesive layer (7), respectively.

19. Method of making the precursor (2) of a label (1) according to any of claims 1-12 comprising the steps of

(i) providing a release carrier (6),
(ii) applying a discontinuous emblem layer (4) comprising one or more emblems (5) to the release surface (6a) of the release carrier (6), and

(iii) applying the polymer layer (3) onto the release surface (6a) and the emblem layer (4) so that the emblem layer (4) is arranged at the interface between the polymer layer (3) and the release surface (6a) of the release carrier (6a).

20. Method according to claim 19 wherein the polymer layer (3) is applied by coating, casting, printing, extrusion, calendering or lamination.

21. Method according to any of claims 18-20 wherein the emblem layer (4) is applied by printing, imaging or rotogravure coating, thermo-transfer printing, film printing, flexo printing, offset printing, digital printing and letter press printing, optionally with subsequent drying and/or curing.

22. Method according to claim 21 wherein printing is effected by screen printing, electrostatic printing, ink jet printing and the like.

23. Method of making a label (1) comprising the steps of

(i) providing a precursor (2) of a label (1) according to any of claims 1 - 12, and

(ii) removing the release carrier (6).
INTERNATIONAL SEARCH REPORT

PCT/US2007/076267

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/28(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC B32B 27/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal) "precursor" "label" "polymer" "emblem"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US 6254970 Bl. (International Playing Card &amp; Label Co.), 03 M 2001 (03 07 2001) see claim 1 and Figure 1</td>
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<td>US 6537651 B2, (Avery Dennison Corporation), 25 Mar 2003 (25 03 2003) see Figure 3 and claim 1</td>
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See patent family annex

Date of the actual completion of the international search

24 DECEMBER 2007 (24 12 2007)

Date of mailing of the international search report

24 DECEMBER 2007 (24.12.2007)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No 82-42-472-7140

Authorized officer

LEE, Young Jae
Telephone No 82-42-481-8305

Form PCT/ISA/210 (second sheet) (April 2007)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons.

1. Claims Nos because they relate to subject matter not required to be searched by this Authority, namely

2. Claims Nos because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically

3. Claims Nos 4-12 and 17-23 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims. It is covered by claims Nos.

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.
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