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(54) **FLEXIBLE PACKAGING SUBSTRATES COMPRISING THERMALLY-STABLE PRINTS**

FLEXIBLE VERPACKUNGSSUBSTRATE MIT WÄRMESTABILEN AUFDRUCKEN

SUBSTRATS D’EMBALLAGE SOUPLE COMPRENANT DES IMPRESSIONS THERMIQUEMENT STABLES

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Description

Field of the Invention

[0001] The present invention is related to a printed packaging substrates and to a method for the production of flexible packaging substrates comprising thermally-stable digital prints.

State of the Art

[0002] Within the flexible packaging business, decreased time to market deliveries from brand-owner to end-customer has been an on-going trend for years. The customization of packaging and dedicated promotional campaigns towards the consumer require a capability from the converter to respond fast, efficiently and flexibly with short-order printing campaigns. Also during the packaging design phase, the production of mockup samples, with a printed representative for the final product, requires fast and flexible printing technology.

[0003] The term *"flexible packaging"* is intended to refer to thin film or foil materials which are generally supplied in a roll format, printed on, and then rolled up again after printing. Exemplative flexible packaging substrates include plastics and polymer films in general, metallized polymer films, metal foils, laminates thereof, and laminates of polymer films with paper, polymer-coated papers and the like. Flexible packaging substrates can be used, for example, to pack food, pharmaceuticals, cosmetics, or tobacco.

[0004] The art of package printing and decoration is dominated by liquid-ink processes that are based on drying or curing individual ink layers through the evaporation of water or volatile organic compounds. These processes consume high amounts of energy and often negatively affect the environment due to emission of solvent or greenhouse gases in the atmosphere.

[0005] The introduction of radiation-curable inks, such as ultraviolet (UV) and electron beam (EB) curable inks, helps to reduce this kind of emissions.

[0006] Two main technologies are used in radiation-curable inks. The first uses free radical species to initiate the polymerization of reactive functional groups, more particularly ethylenically unsaturated double bonds. The most commonly used reactive groups are (meth)acrylate and more particularly acrylate groups, as disclosed for example in WO 97/31071, US 2015/0116432 and US 2015/0184005.

[0007] One limitation of radical-curable (meth)acrylate based inks is the flexibility of the cured ink. This is generally linked to the shrinkage associated with acrylate materials after curing that renders the ink film brittle and not suitable for applications where high flexibility is required.

[0008] Another technology used in radiation curing is the generation of very strong acids to initiate the cationic polymerization of reactive functional groups such as for example, cyclic ethers such as oxirane or oxethane, preferably alicyclic epoxides, allyl ethers and vinyl ethers, as disclosed for example in US 5,674,922 and US 2010/0136300.

[0009] The benefits of cationic curing over radical curing include low shrinkage and therefore good adhesion and excellent flexibility. Furthermore, cationic systems are not sensitive towards oxygen inhibition, which makes substantially complete (at or about 100%) monomer conversion possible. This means that cationic technology allows the curing of thick pigmented ink films more easily than free radical technology.

[0010] The use of radiation-curable inks for use in flexible packaging has been extensively described in the literature.

[0011] US 2008/0218570 A1 discloses methods and devices for forming high-quality, high throughput, ultraviolet or electron beam curable gel ink images on flexible substrates for packaging applications.

[0012] WO9516572 discloses a process of forming printed indicia upon a substrate which comprises forming patterned indicia upon the substrate of a composition comprising one or more ethylenically unsaturated monomers and an ethylenically unsaturated group comprising polyether; and curing the applied indicia by exposure to a beam of electrons.

[0013] JP S57 11083 discloses a plastic film, with use of an electron-curing printing ink containing a methacryloyl radical-containing compound (e.g. polyester methacrylate methylmethacrylate) and a dyestuff or a pigment. A printed surface is heated at 50-150 °C during radiation of electron beams, to cure the ink with a low absorption dose. Consequently, the printed matter is completely cured even with the radiation of electron beams of 10Mrad or less, and the printed matter is continuously coiled after the radiation of electron beams.

[0014] EP 2 133 210 A1 and EP 2 720 877 A1 disclose a method for printing and decorating packaging materials, such as paper, paper board and various flexible polymer films by electron-beam exposure of plural layers of curable inks and coatings which do not substantially change their viscosity during the printing process. The inks and coating are essentially free of volatile components before, during and after exposure to electron-beam irradiation. The method involves applying multiple layers of ink and an optional coating onto a substrate. Thereafter, these layers are simultaneously exposed with electron-beam radiation to cause ethylenically unsaturated components to polymerize or crosslink such that they become dried.

[0015] US 7,886,665 discloses a method of producing a printed packaging material comprising, in sequence:

- applying an actinic radiation activatable liquid ink to a packaging material,
- exposing the ink to first actinic radiation to activate the ink;

- applying an energy-curable coating over the ink; and

- curing the coating with second actinic radiation;

wherein the ink is substantially free of curable functionality, wherein the exposure to the first actinic radiation and curing with the second actinic radiation is such that the packaging material contains less than 700 ppm total of residual solvent or water, and wherein the exposure to the first actinic radiation and curing with the second actinic radiation is such that the packaging material has a degree of cure of at least 5 MEK rubs.

[0016] US 2006/0000545 discloses process for manufacturing a sterilizable packaging material having one film or foil with printing thereon, the printing, coated with an electron-beam-curable material, preferably an acrylate based material, and the outer layer are radiated with electrons for the purpose of curing the coating material.

[0017] EP 0 741 644 A1 discloses a system and method for the printing of substrates for use in food packaging and, more particularly, a flexographic printing system and method for applying and curing radiation cured inks to a flexible, heat shrinking web employing a combination of UV radiation and EB radiation.

[0018] EP 2 305 758 A1 relates to a laminate comprising a) a substrate comprising a thermoplastic polymer, b) a single- or multi-layer ink film and/or varnish film comprising a printing ink or a printing varnish, comprising a binder with a non-radiation-curing aromatic polycarbonate and a solvent comprising at least one radiation-curing monomer, which is selected from the group consisting of acrylates, methacrylates, vinyl ethers and nitrogen-containing compounds with an ethylenic double bond, wherein the binder is dissolved in the solvent and the solvent is bound in chemically crosslinked form in the printing ink or printing varnish after curing.

[0019] US 2002/119295 A1 discloses an article including a first and second outer surfaces, printing an image on the first outer surface and applying a radiation-curable varnish on the first outer surface so as to cover at least a portion of the image.

[0020] EP 1 159 142 A1 discloses a printed packaging material in which a printed image is disposed on a primary surface. That image includes two primary components. The first is at least one marking containing a pigment. The second is a pigment-free coating which overlies the outermost marking. The coating is made from materials which can polymerize and/or crosslink when exposed to ionizing radiation. After the film is exposed to such radiation, the coating hardens to form a protective layer over the printed markings.

[0021] US 2013/0233189 A1 discloses a flexible substrate whereby a radiation-curable ink is applied to the substrate and an overcoat layer is applied on the cured ink.

[0022] Cationically curable inks have been reported in for example JP 10-324836, US 5,889,084 and US 2005/187309 A1.

[0023] Among the drawbacks of radiation-curable inks, the complication of the printing process and the generation of low molecular weight compounds, jeopardizing their use for food and pharmaceutical packaging, may be cited.

[0024] In addition to the conventional printing technologies applied in the flexible packaging, such as heliogravure and flexographic printing, new technologies emerged in the past decades and became more or less successful. Key-decision parameters for investments, and the determining success of the technology in some markets, are investment costs, machine speeds, attainable web widths, pre-press preparation time, availability of suitable colors, flexibility to change designs, printing quality, ink encourage to the substrates, product safety aspects of the inks, stability of the inks in terms of temperature and UV light.

[0025] Among these new technologies, digital printing such as for example inkjet printing and liquid electrography, is most noticeable.

[0026] Digital printing devices and methods are known in the printing arts and are generally described, for example, in US 6,608,986; US 6,529,288; US 6,539,858; US 6,162,570; US 5,819,667 and US 5,777,576.

[0027] A technology which gained widespread attention in flexible packaging is the digital offset technology or liquid electrography. Digital printing is intrinsically flexible and fast in changing designs because no physical printing plates are applied. The image remains purely digital.

[0028] In general, digital offset technology involves creating an image on a photoconductive surface by means of a laser, applying an ink having charged particles to the photoconductive surface, such that they selectively bind to the image, and then transferring the charged particles in the form of the image to a print substrate.

[0029] The photoconductive surface is typically on a cylinder and is often termed a photo imaging plate (PIP). The photoconductive surface is selectively charged with a latent electrostatic image having image and background areas with different potentials. For example, an electrostatic ink composition comprising charged particles in a carrier liquid can be brought into contact with the selectively charged photoconductive surface. The charged particles adhere to the image areas of the latent image while the background areas remain clean. The image is then transferred to a print substrate directly or, more commonly, by being first transferred to an intermediate transfer member, which can be a soft swelling blanket, and then to the print substrate. Ink transfer is forced by an applied electrical field and carrier ink liquid is evaporated from the blanket. The hot-melted ink is adhered to the substrate by means of pressure and tackiness. The process is repeated for every color. Principally, the ink transfers to the substrate without change and without penetrating into the substrate. Hence, the resulting image quality is very high and appears to be independent from the substrate characteristics.

[0030] Variations of this method utilize different ways for forming the electrostatic latent image on a photoreceptor or on a dielectric material.

[0031] Electrographic printing on plastic, paper or metal is for example disclosed in US 2011/0256478.

[0032] The inks, particularly those developed for liquid electrography, are designed to form high resolution, uniform gloss, sharp image edges and thin image layers and in general comprise carrier liquid, resin and colorant. Typical carrier liquids can include a mixture of a variety of different agents, such as surfactants, dispersants, co-solvents, viscosity modifiers, and/or other possible ingredients.

[0033] A major limitation of flexible substrates, printed by liquid electrography, is the thermal stability of the prints based on the conventional inks. Particularly, in direct contact sealing applications, the print at the surface of the substrate, in direct contact with the sealing jaws of a flexible packaging machine, suffer from the limited thermal stability of the inks. Depending on packaging speeds and applications, typical temperature ranges, on vertical and horizontal form fill seal machines are between 120 and 200°C. Lack of heat resistance of the inks after sealing results in color changes and design deformations due to ink softening and ink flowing under the pressure of the sealing jaws.

[0034] A typical solution to overcome this problem is to apply surface protective coatings as disclosed in for example EP 1 159 142 A1; US 2005/019533 A1; US 2007/085983 A1; US 2008/118746 A1 and US 2013/0233189 A1.

[0035] Limitations to this approach is the lack of intercoat adhesion between the coating and the ink, and the risk of changing the high gloss, high optical quality and aspect of the inks after application of the coating. Moreover, for the particular case of solvent- or water-based protective coatings, solvent and/or water removal require in a heat sensitive operation step.

Aim of the Invention

[0036] The present invention aims to provide a flexible packaging comprising digital prints and a method for the production of the printed flexible packaging, said printed flexible packaging presenting specific advantages over the above-mentioned prior art.

Summary of the invention

[0037] The present invention discloses a flexible packaging substrate comprising one or more digitally-printed electron beam crosslinked ink layers, wherein

- the flexible packaging substrate comprises one or more films selected from the group consisting of natural polymeric material and synthetic polymeric material and,
- the one or more crosslinked ink layers are characterized in that

  ◦ the crosslinks comprise carbon-carbon bonds, wherein each of the carbons independently is a tertiary or quaternary carbon comprising at least two (meth)acrylic copolymer segments,
  ◦ the concentration of ethylenically unsaturated groups and alicyclic epoxides in said ink layers is less than 0.05 meq/g, preferably less than 0.03 meq/g, more preferably less than 0.01 meq/g, most preferably less than 0.005 meq/g,

  the one or more crosslinked ink layers being the top-surface of the flexible packaging substrate.

[0038] Preferred embodiments of the present invention disclose one or more of the following features:

- the flexible packaging substrate is free of an additional layer, protecting the one or more crosslinked ink layers;
- the flexible packaging substrate comprises a primer layer sandwiched between the crosslinked ink layers and the substrate;
- the total layer thickness of primer and ink layer(s) is comprised between 0.4 and 4 μm, preferably between 0.6 and 3.5 μm, more preferably between 0.8 and 3 μm;
- the layer thickness of the primer is comprised between 0.01 and 0.5 μm, preferably between 0.05 and 0.4 μm and most preferably between 0.1 and 0.3 μm.

[0039] The present invention further discloses a method for forming a printed flexible packaging substrate comprising the steps of:

a) providing a flexible packaging substrate;
b) applying at least one digital print by a digital printing process of at least one ink composition, said ink composition :

- comprising a carrier liquid, a resin, a co-resin polymer and a colorant, the resin comprising copolymers of polymerized monomers selected from the group consisting of ethylene, (meth)acrylic acid, alkyl (meth)acrylate and vinyl acetate and
- having a concentration of ethylenically unsaturated groups and a concentration of alicyclic epoxides of less than 0.2 meq/g, preferably less than 0.1 meq/g, more preferably less than 0.05 meq/g, most preferably less than 0.01 meq/g;

c) subjecting the digital print to an electron beam irradiation, wherein:

- electron energies are comprised between 10 and 300 keV;
- the irradiation dose received by the digitally printed ink is comprised between 15 and 100 kGy;
- the electron beam irradiation of the digital ink is performed in an oxygen-poor region, meaning an oxygen concentration less than 300 ppm.

[0040] Preferred embodiments of the method for forming the printed flexible substrate disclose one or more of the following features:

- the at least one ink composition is substantially free of components comprising molecular structures with dangling and/or end-standing ethylenically unsaturated double bonds;
- the flexible packaging substrate of step a) is plasma treated, preferably corona plasma treated, before initiation of step b);
- the method comprises the additional step of applying a primer composition before initiating step b);
- the digital printing process of step b) is liquid electrographic printing;
- the electron beam irradiation dose in step c) is at least 18 kGy, preferably at least 20 kGy;
- the electron beam irradiation dose in step c) is comprised between 20 and 100 kGy, preferably between 25 and 80 kGy, more preferably between 30 and 60 kGy;
- the electron beam irradiation in step c) is performed at an oxygen concentration of less than 250 ppm, preferably less than 200 ppm, more preferably less than 150 ppm;
- the flexible packaging substrate of step a) comprises polyethylene terephthalate, high-density polyethylene, oriented polypropylene, oriented polyamide, polystyrene or paper;
- the primer composition comprises one or more polyacrylamide(s);
- the ink formulation comprises one or more (meth)acrylic (co)polymer(s) resin(s);
- the ink formulation comprises:
  - from 20 to 95% by weight of hydrocarbon carrier liquid,
  - from 5 to 80% by weight of one or more (meth)acrylic (co)polymer(s) resin(s),
  - from 10 to 50% by weight of one or more carboxyl-functional ethylene comprising copolymer(s) co-resin(s) and
  - from 0.1 to 80% by weight of one or more colorants;
- the method comprises an additional lamination step of the flexible packaging substrate to a seal layer;
- the method comprises a step of heat sealing the printed flexible substrate or the laminate in a heat sealing assembly at a temperature comprised between 100 and 250°C, preferably between 110 and 230°C, more preferably between 120 and 220°C.

[0041] The present invention further discloses a flow pack comprising the flexible packaging substrate.

Description of the Invention

[0042] The present invention discloses a flexible packaging substrate comprising thermally-stable digital prints, preferably obtained from liquid electrographic printing, said thermal stability being obtained by subjecting said prints, to electron beam irradiation.

[0043] Thermal stability of the digital prints is a prerequisite for heat-sealing, particularly in direct contact applications wherein the inks, at the surface of the substrate comes in direct contact with the sealing jaws of the packaging machine. Lack of heat resistance of the prints, after sealing results in color changes and design deformations due to ink softening and flowing under influence of the sealing jaws.

[0044] The inventors have surprisingly found that digital prints, preferably obtained from liquid electrographic printing of conventional ink formulations, not qualified as UV or electron beam curable inks, comprising (meth)acrylic copolymer resins and being substantially free of (meth)acrylic double bonds and/or alicyclic epoxides, are rendered thermally-stable through electron beam irradiation.

[0045] The flexible packaging substrates comprising the electron beam irradiated digital ink allow for heat sealing without the need of an additional protective layer on top of said prints.

[0046] The components composing the inks for being used in the present invention are substantially free of dangling or end-standing ethylenically unsaturated functional groups such as (meth)acryl, vinyl-, allyl-, and fumarate functional groups.

[0047] By dangling ethylenically unsaturated groups, the present invention means functional groups not incorporated into the molecular backbone, such as for example in unsaturated polyesters or in butadiene comprising (co)polymers.

[0048] By substantially free of ethylenically unsaturated groups the present invention means that the concentration of ethylenically unsaturated groups is less than 0.2 meq/g, preferably less than 0.1 meq/g, more preferably less than 0.05 meq/g, most preferably less than 0.01 meq/g.

[0049] By substantially free of alicyclic epoxides, the present invention means that the concentration of alicyclic epoxides is less than 0.2 meq/g, preferably less than 0.1 meq/g, more preferably less than 0.05 meq/g, most preferably less than 0.01 meq/g.

[0050] Preferably, the ink formulations for being used in the present invention are free of (meth)acrylic double bonds and/or alicyclic epoxides.

[0051] Preferably, the ink formulations for being used in the present invention do not comprise components comprising dangling and/or end-standing ethylenically unsaturated functional groups such as vinyl-, allyl-, and fumarate functional groups.

[0052] Prior-art resins specially developed for UV and electron beam curing in general are characterized by a concentration of ethylenically unsaturated groups or of alicyclic epoxides higher than 1.0 meq/g and even higher than 1.5 meq/g, the high concentration being sought for reactivity reasons.

[0053] Despite the substantial absence of such ethylenically unsaturated groups and of alicyclic epoxides, in the inks used in the present invention, the electron beam irradiation crosslinks the polymer chains, wherein the crosslinks preferably are carbon - carbon crosslinks.

[0054] The carbon - carbon crosslinks of the electron beam crosslinked ink of the present invention preferably are characterized in that the carbon atoms are tertiary or quaternary carbon atoms.

[0055] More preferably, the carbon - carbon crosslinks are of the type $(R^1)_2R^2C - C(R^1)_2R^3$ wherein:

- R^1 is a (meth)acrylic copolymer segment,
- R^2 is a hydrogen atom or a (meth)acrylic copolymer segment,
- R^3 is a hydrogen atom, a methyl group or a (meth)acrylic copolymer segment,

as determined by Fourier Transformed InfraRed Spectroscopy.

[0056] The concentration of residual ethylenically unsaturated groups or alicyclic epoxides in crosslinked inks, obtained from irradiation of inks designed for crosslinking under influence of UV or EB, and comprising significant concentrations of ethylenically unsaturated groups or alicyclic epoxides, is higher than 0.05 meq/g, more preferably higher than 0.1 meq/g, most preferably higher than 0.2 meq/g.

[0057] Crosslinked conventional UV and EB inks are characterized in that they comprise residual ethylenically unsaturated groups and/or alicyclic epoxides, resulting from an incomplete conversion due to viscosity increase upon increasing the crosslinking degree.

[0058] The concentration of ethylenically unsaturated groups or alicyclic epoxides and the degree of conversion may be determined by combining titrations, such as for example iodometric titrations, with Fourier-transformed infrared spectroscopy.

[0059] The concentration of ethylenically unsaturated groups and alicyclic epoxides in conventional inks crosslinked on a substrate according to the method of the present invention is lower than 0.05 meq/g, preferably lower than 0.03 meq/g, more preferably lower than 0.01 meq/g, most preferably lower than 0.005 meq/g.

[0060] Preferably, the conventional inks crosslinked on a substrate according to the method of the present invention are free of ethylenically unsaturated groups and alicyclic epoxides.

[0061] The liquid inks for being used in the present invention preferably comprise a carrier liquid, a resin, a co-resin polymer and a colorant.

[0062] The co-resin preferably comprises an ethylene acrylic acid co-polymer, a maleic anhydride polymer having polyethylene grafted to the polymer, and combinations thereof. The amount of co-resin is comprised between 10 and 50 % by weight, preferably between 10 and 40 % by weight more preferably between 10 to 20 % by weight of the ink formulation.

[0063] The resin preferably comprises (co)-polymers of (meth)acrylic acid; copolymers of (meth)acrylic acid and alkyl (meth)acrylate; co-polymers of ethylene and (meth)acrylic acid; co-polymers of ethylene and alkyl(meth)acrylate; co-polymers of ethylene, (meth)acrylic acid and alkyl(meth)acrylate; co-polymers of ethylene and vinyl acetate; co-polymers of ethylene, (meth)acrylic acid and vinyl acetate; co-polymers of ethylene, alkyl(meth)acrylate and vinyl acetate; co-polymers of ethylene, (meth)acrylic acid, alkyl(meth)acrylate and vinyl acetate; co-polymers of (meth)acrylic acid and vinyl acetate; co-polymers of alkyl(meth)acrylate and vinyl acetate; co-polymers of (meth)acrylic acid, alkyl(meth)acrylate and vinyl acetate; polymers such as for example polyethylene; polystyrene; isotactic polypropylene; polyesters; polyvinyl toluene; polyamides; styrene/butadiene copolymers; epoxy resins; low molecular weight ethylene-acrylic acid ionomers and combinations thereof.

[0064] The amount of resin is comprised between 5 and 80 % by weight, preferably between 10 and 60 % by weight, more preferably between 15 and 40 % by total weight of the ink formulation.

[0065] The carrier liquid preferably comprises a hydrocarbon selected from the group consisting of an (iso)paraffinic hydrocarbon, an aliphatic hydrocarbon, an isomerized aliphatic hydrocarbon, a branched chain aliphatic hydrocarbon, an aromatic hydrocarbon, a de-aromatized hydrocarbon, a halogenated hydrocarbon, a cyclic hydrocarbon, a functionalized hydrocarbon and combinations thereof. Preferablyn the carrier is 3,5,7-trimethyldecane.

[0066] The amount of carrier liquid is comprised between 20 and 95 % by weight, preferably between 40 and 90 % by weight, more preferably between 60 to 80 % by weight of the ink formulation.

[0067] The colorants are organic and/or inorganic colorants. The colorants may comprise cyan colorants, magenta colorants, yellow colorants, violet colorants, orange colorants, green colorants, black colorants, and combinations thereof. The amount of colorant is comprised between 0.1 and 80 % by weight of the ink formulation.

[0068] The ink formulation further may comprise charge adjuvants, such as for example aluminum tristearate and charge director such as for example sulfonic acids or salts thereof. Charge adjuvants are in general used in amounts comprised between 0.1 and 5 % by weight preferably between 0.5 and 4 % by weight, more preferably between 1 to 3 % by weight of the ink formulation while charge directors in general are used in an amount comprised between 0.001 to 1% by weight of the ink formulation.

[0069] The flexible packaging substrate preferably comprises one or more film(s) of natural polymeric material, e.g. cellulose or synthetic polymeric material e.g. a polymer formed from alkylene monomers such as polyethylene or polypropylene, polyethylene terephthalate (PET), polyvinylchloride, polycarbonate, polystyrene and styrenebutadiene. In some examples, the substrate may comprise or be biaxially orientated polypropylene (BOPP).

[0070] In some examples, the substrate may comprise a cellulosic paper, which may be coated or uncoated cellulosic paper. A coated cellulosic paper includes, but is not limited to, a cellulosic paper coated with a non-cellulosic material.

[0071] The surface intended to receive the digital print first may be subjected to a physical compatibilisation treatment such as a plasma treatment, preferably a corona plasma treatment, a flame treatment or the like in order to modify its surface energy. Another option is the application of a primer on the substrate. This primer application can also be preceded by a physical surface treatment.

[0072] The primer for being used in the present invention may be applied through digital printing. The primer preferably comprises a carrier fluid and a resin wherein the carrier is preferably a hydrocarbon as disclosed above and wherein the resin preferably is selected from the group consisting of cellulose, dextrin, maltose monohydrate, polyacrylic acid, polyvinylalcohol, styrene maleic anhydride copolymer, maleimide copolymer, polyacrylamide, sucrose octaacetate, sucrose benzoate and combinations thereof. Preferably, the primer for being used in the present invention comprises polyacrylamide.

[0073] The term polyacrylamide includes all (alk)acrylamide homopolymers as well as copolymers and functionalized polyacrylamides. The polyacrylamides may be anionic, cationic or nonionic. Various monomers, preferably ethylenically unsaturated monomers may be copolymerized with (alk)acrylamide monomers to form the polyacrylamides.

[0074] The flexible packaging substrate is provided with a digital print preferably obtained from liquid electrographic printing followed by an electron beam irradiation.

[0075] The flexible packaging substrate of the present invention comprises a primer and one or more ink layers, digitally printed on at least one side of at least one layer or film composing said flexible substrate; wherein the crosslinked ink layers form the top-surface of the flexible packaging substrate and the primer layer is sandwiched between the crosslinked ink layers and the substrate; wherein the total layer thickness of primer and ink layer(s) is comprised between 0.4 and 4 μm, preferably between 0.6 and 3.5 μm, more preferably between 0.8 and 3 μm and wherein the layer thickness of the primer is about 0.2 μm.

[0076] In the digital printing machine, the substrate is loaded into the priming unwinder, where it is corona treated, to achieve better wetting and ink adhesion. In a next step, a primer is applied to enable covalent bonding between the substrate and the ink. The primer is dried in the drying station, whereupon it passes into the printing engine. The substrate comprising the digital print subsequently is subjected to electron beam bombardment.

[0077] Electron energies are comprised between 10 and 300 keV, preferably between 20 and 250 keV, preferably between 30 and 200 keV.

[0078] The irradiation dose received by the digitally-printed ink is comprised between 15 and 100 kGy, preferably between 20 and 80 kGy, more preferably between 30 and 60 kGy.

[0079] The electron beam irradiation of the digital print is performed in an oxygen-poor region obtained through the application of a vacuum or through the use of an inert gas blanket such as a nitrogen blanket.

[0080] By oxygen-poor medium, the present invention means an oxygen concentration less than 300 ppm, preferably less than 250 ppm, more preferably less than 200 ppm, most preferably less than 150 ppm or even less than 100 ppm.

[0081] After electron beam bombardment of the digitally-printed substrate, said substrate can be further processed into a laminate, which subsequently is heat-sealed at a temperature comprised between 100 and 250°C, preferably between 110 and 230°C, more preferably between 120 and 220°C at a pressure comprised between 20 and 120 N/cm^2, preferably between 20 and 110 N/cm^2, more preferably between 40 and 100 N/cm^2.

Examples

[0082] The following illustrative examples are merely meant to exemplify the present invention but is not destined to limit or otherwise define the scope of the present invention.

Example 1

[0083] A polyethylene terephthalate (PET) 12 μm film was treated by Corona (400 W) and subsequently introduced into the HP 20000 Indigo digital printing system where it was provided with a colorless digital primer Digiprime® 050 from Michelman at a layer thickness of about 0.2 μm and a cyan ink layer, at a layer thickness of about 1 μm, was printed thereon.

[0084] The digitally-printed PET film was then transferred to a vacuum electron beam processing device.

[0085] The electron beam gun has a deflection system which is computer-controlled and has been programmed in a manner that the gun, was radiating onto the drum, normally used as a coating drum. The printed film, passing over this coating drum, was irradiated by the electron beam gun. The deflection system was programmed to allow the electron beam scanning over an area of 200 mm (winding direction) x 400 mm (cross direction) and therefore radiating this area. By passing the web with a speed of 15m/min through this zone, the ink was irradiated for 0.6 seconds. The electron beam gun was operated at an acceleration voltage of 35 kV, resulting in electrons with an energy of 35 keV. The emission current was 0.42 A, resulting in a total radiation power of 15 kW is scanning over an area.

[0086] The electron beam irradiated digitally-printed PET samples were laminated. The lamination was carried out with the use of an aromatic adhesive UK2640/H6800 against a cast-polypropylene 80 μm thick film as the sealant layer.

[0087] The PET/PP laminates were sealed, outside to outside, at temperatures of 150°C, 180°C, 200°C, 210 and 220°C, respectively at a pressure of 3.5 bar for 0,6 s with two heated jaws.

[0088] At an irradiation dose of 10 kGy, the digital print showed defects, such as ink removal, ink shrinkage and gloss change, at sealing temperatures from 150 to 220°C. Said defects completely disappeared for an irradiation dose of 18 kGy and higher.

Example 2

[0089] Example 1 was repeated, wherein the cyan ink was substituted by respectively black ink, magenta ink, orange ink, violet ink, white ink and yellow ink.

[0090] At an irradiation dose of 10 kGy the digital prints of the respective colors showed similar defects as in example 1. Said defects disappeared once an irradiation dose of 18 kGy or higher was applied.

Example 3 (comparative example)

[0091] Example 2 was repeated, yet omitting electron beam irradiation. For all colors, severe print defects were observed for sealing temperatures of 150°C and higher.

Example 4 (comparative example)

[0092] Example 2 was repeated wherein the respective digital prints were subjected to electron beam irradiation and wherein the irradiation dose was limited to 15 kGy. For all colors, severe print defects were observed for sealing temperatures of 200°C and higher.

Example 5

[0093] Example 1 was repeated wherein the PET film was replaced by a 30 μm-thick polymer coated paper. Similar results as for Example 1 were observed.

Claims

1. A flexible packaging substrate comprising one or more digitally-printed electron-beam crosslinked ink layers, wherein

   - the flexible packaging substrate comprises one or more films selected from the group consisting of natural polymeric material and synthetic polymeric material and
   - the one or more crosslinked ink layers are **characterized in that**:

     ◦ the crosslinks comprise carbon - carbon bonds, wherein each of the carbons independently is a tertiary or quaternary carbon, comprising at least two (meth)acrylic copolymer segments;
     ◦ the concentration of ethylenically unsaturated groups and alicyclic epoxides is less than 0.05 meq/g, preferably less than 0.03 meq/g, more preferably less than 0.01 meq/g, most preferably less than 0.005 meq/g;

   the one or more crosslinked ink layers being the top surface of the flexible packaging substrate.

2. The flexible packaging substrate of claim comprising a primer layer sandwiched between the crosslinked ink layers and the substrate.

3. The flexible packaging substrate of any of the previous claims, wherein the total layer thickness of primer and ink layer(s) is comprised between 0.4 and 4 μm, preferably between 0.6 and 3.5 μm, more preferably between 0.8 and 3 μm.

4. The flexible packaging substrate of any of the previous claims, wherein the layer thickness of the primer is comprised between 0.01 and 0.5 μm, preferably between 0.05 and 0.4 μm and most preferably between 0.1 and 0.3 μm.

5. A method for forming a printed flexible packaging substrate according to any of the previous claims comprising the steps of:

   a. providing a flexible packaging substrate;
   b. applying at least one digital print by a digital printing process of at least one ink composition, said ink composition :

      - comprising a carrier liquid, a resin, a co-resin polymer and a colorant, the resin comprising copolymers of polymerized monomers selected from the group consisting of ethylene, (meth)acrylic acid, alkyl

(meth)acrylate and vinyl acetate, and
- having a concentration of ethylenically unsaturated groups and a concentration of alicyclic epoxides of less than 0.2 meq/g, preferably less than 0.1 meq/g, more preferably less than 0.05 meq/g, most preferably less than 0.01 meq/g;

c. subjecting the digital print to an electron beam irradiation, wherein:

• electron energies are comprised between 10 and 300 keV;
• the irradiation dose received by the digitally printed ink is comprised between 15 and 100kGy;
• the electron beam irradiation of the digital print is performed in an oxygen-poor region, meaning an oxygen concentration less than 300 ppm.

6. The method according to Claim 5, wherein the flexible packaging substrate of step a) is plasma treated, preferably corona plasma treated, before initiating step b).

7. The method according to Claim 5 or 6, comprising the additional step of applying a primer composition before initiating step b).

8. The method according to any of Claims 5 to 7, wherein the digital printing process of step b) is liquid electrographic printing.

9. The method according to any of Claims 5 to 8 wherein the electron beam irradiation dose in step c) is at least 18 kGy, preferably at least 20 kGy.

10. The method according to any of the preceding Claims 5 to 9, wherein the electron beam irradiation dose in step c) is comprised between 20 and 100 kGy, preferably between 25 and 80 kGy, more preferably between 30 and 60 kGy.

11. The method according to any of Claims 5 to 10, wherein the electron beam irradiation in step c) is performed at an oxygen concentration of less than 250 ppm, preferably less than 200 ppm, more preferably less than 150 ppm.

12. The method according to any of Claims 5 to 11, wherein the flexible packaging substrate of step a) comprises polyethylene terephthalate, high density polyethylene, oriented polypropylene, oriented polyamide, polystyrene or paper.

13. The method according to any of Claims 5 to 12, wherein the primer composition comprises one or more polyacrylamide(s).

14. The method according to any of Claims 5 to 13, wherein the ink formulation comprises one or more (meth)acrylic (co)polymer(s) resin(s).

15. The method according to any of Claims 5 to 14, wherein the ink formulation comprises:

- from 20 to 95 % by weight of hydrocarbon carrier liquid,
- from 5 to 80 % by weight of one or more (meth)acrylic (co)polymer(s) resin(s),
- from 10 to 50 % by weight of one or more carboxyl-functional ethylene comprising copolymer(s) co-resin(s) and
- from 0.1 to 80 % by weight of one or more colorants.

16. The method according to any of Claims 5 to 15, comprising the additional lamination step of the flexible packaging substrate to a seal layer.

17. The method according to any of Claims 5 to 16, comprising the step of heat sealing the printed flexible substrate or the laminate in a heat sealing assembly at a temperature comprised between 100 and 250°C, preferably between 110 and 230°C, more preferably between 120 and 220°C.

18. Flow pack comprising the flexible packaging substrate according to any of Claims 1 to 4.

Patentansprüche

1. Flexibles Verpackungssubstrat, umfassend ein oder mehrere digital aufgedruckte, mittels Elektronenstrahl vernetzte Tintenschichten, wobei

- das flexible Verpackungssubstrat eine oder mehrere Folien umfasst, die ausgewählt sind aus der Gruppe bestehend aus natürlichem Polymermaterial und synthetischem Polymermaterial, und
- die eine oder die mehreren vernetzten Tintenschichten **dadurch gekennzeichnet, dass**:

o die Vernetzungen Kohlenstoff-Kohlenstoff-Bindungen umfassen, wobei jedes der Kohlenstoffatome unabhängig ein tertiäres oder quartäres Kohlenstoffatom ist, umfassend mindestens zwei (Meth)acryl-Copolymer-Segmente;
o die Konzentration ethylenisch ungesättigter Gruppen und alicyclischer Epoxide geringer als 0,05 mEq/g, bevorzugt weniger als 0,03 mEq/g, besonders bevorzugt we-

niger als 0,01 mEq/g, ganz besonders bevorzugt weniger als 0,005 mEq/g ist;

wobei es sich bei der einen oder den mehreren vernetzten Tintenschichten um die obere Oberfläche des flexiblen Verpackungssubstrats handelt.

2. Flexibles Verpackungssubstrat nach Anspruch 1, umfassend eine Grundierungsschicht, die zwischen den vernetzten Tintenschichten und dem Substrat liegt.

3. Flexibles Verpackungssubstrat nach einem der vorstehenden Ansprüche, wobei die Gesamtschichtdicke von Grundierung und Tintenschicht(en) zwischen 0,4 und 4 μm, bevorzugt zwischen 0,6 und 3,5 μm, besonders bevorzugt zwischen 0,8 und 3 μm beträgt.

4. Flexibles Verpackungssubstrat nach einem der vorstehenden Ansprüche, wobei die Schichtdicke der Grundierung zwischen 0,01 und 0,5 μm, bevorzugt zwischen 0,05 und 0,4 μm und ganz besonders bevorzugt zwischen 0,1 und 0,3 μm beträgt.

5. Verfahren zum Bilden eines bedruckten flexiblen Verpackungssubstrats nach einem der vorstehenden Ansprüche, umfassend die folgenden Schritte, in denen:

a. ein flexibles Verpackungssubstrat bereitgestellt wird;
b. mindestens ein digitaler Aufdruck aus mindestens einer Tintenzusammensetzung mittels eines digitalen Druckprozesses aufgebracht wird, wobei die Tintenzusammensetzung:

- einen flüssigen Träger, ein Harz, ein Co-Harz-Polymer und ein Färbemittel umfasst, wobei das Harz Copolymere aus polymerisierten Monomeren umfasst, die ausgewählt sind aus der Gruppe bestehend aus Ethylen, (Meth)acrylsäure, Alkyl(meth)acrylat und Vinylacetat, und
- eine Konzentration ethylenisch ungesättigter Gruppen und eine Konzentration alicyclischer Epoxide von weniger als 0,2 mEq/g, bevorzugt weniger als 0,1 mEq/g, besonders bevorzugt weniger als 0,05 mEq/g, ganz besonders bevorzugt weniger als 0,01 mEq/g aufweist;

c. der digitale Aufdruck einer Elektronenstrahlbestrahlung unterzogen wird, wobei:

• die Elektronenenergien zwischen 10 und 300 keV betragen;
• die von der digital aufgedruckten Tinte aufgenommene Bestrahlungsdosis zwischen 15 und 100 kGy beträgt;
• die Elektronenstrahlbestrahlung des digitalen Aufdrucks in einem sauerstoffarmen Bereich, womit eine Sauerstoffkonzentration von weniger als 300 ppm gemeint ist, durchgeführt wird.

6. Verfahren nach Anspruch 5, wobei das flexible Verpackungssubstrat aus Schritt a) plasmabehandelt wird, bevorzugt coronaplasmabehandelt wird, bevor Schritt b) eingeleitet wird.

7. Verfahren nach Anspruch 5 oder 6, umfassend den zusätzlichen Schritt des Aufbringens einer Grundierungszusammensetzung, bevor Schritt b) eingeleitet wird.

8. Verfahren nach einem der Ansprüche 5 bis 7, wobei der digitale Druckprozess aus Schritt b) flüssiges leitfähiges Drucken ist.

9. Verfahren nach einem der Ansprüche 5 bis 8, wobei die Elektronenstrahlbestrahlungsdosis in Schritt c) mindestens 18 kGy, bevorzugt mindestens 20 kGy beträgt.

10. Verfahren nach einem der vorstehenden Ansprüche 5 bis 9, wobei die Elektronenstrahlbestrahlungsdosis in Schritt c) zwischen 20 und 100 kGy, bevorzugt zwischen 25 und 80 kGy, besonders bevorzugt zwischen 30 und 60 kGy beträgt.

11. Verfahren nach einem der Ansprüche 5 bis 10, wobei die Elektronenstrahlbestrahlung in Schritt c) bei einer Sauerstoffkonzentration von weniger als 250 ppm, bevorzugt weniger als 200 ppm, besonders bevorzugt weniger als 150 ppm durchgeführt wird.

12. Verfahren nach einem der Ansprüche 5 bis 11, wobei das flexible Verpackungssubstrat aus Schritt a) Polyethylenterephthalat, Polyethylen von hoher Dichte, orientiertes Polypropylen, orientiertes Polyamid, Polystyrol oder Papier ist.

13. Verfahren nach einem der Ansprüche 5 bis 12, wobei die Grundierungszusammensetzung ein oder mehrere Polyacrylamide umfasst.

14. Verfahren nach einem der Ansprüche 5 bis 13, wobei die Tintenformulierung ein oder mehrere (Meth)acryl-(Co)polymer-Harze umfasst.

15. Verfahren nach einem der Ansprüche 5 bis 14, wobei die Tintenformulierung Folgendes umfasst:

- zu 20 bis 95 Gew.-% Kohlenwasserstoffträger-

flüssigkeit,
- zu 5 bis 80 Gew.-% ein oder mehrere (Meth)acryl-(Co)polymer-Harze,
- zu 10 bis 50 Gew.-% ein oder mehrere carboxylfunktionelles Ethylen umfassende Copolymer-Co-Harze und
- zu 0,1 bis 80 Gew.-% ein oder mehrere Färbemittel.

16. Verfahren nach einem der Ansprüche 5 bis 15, umfassend den zusätzlichen Laminierungsschritt des flexiblen Verpackungssubstrats auf eine Siegelschicht.

17. Verfahren nach einem der Ansprüche 5 bis 16, umfassend den Schritt des Heißsiegelns des bedruckten flexiblen Substrats oder des Laminats in einer Heißsiegelanordnung bei einer Temperatur zwischen 100 und 250 °C, bevorzugt zwischen 110 und 230 °C, besonders bevorzugt zwischen 120 und 220 °C.

18. Flowpack, umfassend das flexible Verpackungssubstrat nach einem der Ansprüche 1 bis 4.

Revendications

1. Substrat d'emballage souple comprenant une ou plusieurs couches d'encre réticulée par faisceau d'électrons imprimée numériquement, dans lequel

- le substrat d'emballage souple comprend un ou plusieurs films choisis dans le groupe constitué par un matériau polymère naturel et un matériau polymère synthétique et
- la ou les couches d'encre réticulée sont **caractérisées en ce que** :

o les liaisons transversales comprennent des liaisons carbone-carbone, dans lesquelles chacun des carbones est indépendamment un carbone tertiaire ou quaternaire, comprenant au moins deux segments de copolymère (méth)acrylique ;
o la concentration de groupes éthyléniquement insaturés et d'époxydes alicycliques est inférieure à 0,05 méq/g, de préférence inférieure à 0,03 méq/g, mieux encore inférieure à 0,01 méq/g, idéalement inférieure à 0,005 méq/g ;

la ou les couches d'encre réticulée constituant la surface supérieure du substrat d'emballage souple.

2. Substrat d'emballage souple de la revendication 1 comprenant une couche de primaire intercalée entre les couches d'encre réticulée et le substrat.

3. Substrat d'emballage souple de l'une quelconque des revendications précédentes, dans lequel l'épaisseur de couche totale de la/des couche (s) de primaire et d'encre est comprise entre 0,4 et 4 μm, de préférence entre 0,6 et 3,5 μm, mieux encore entre 0,8 et 3 μm.

4. Substrat d'emballage souple de l'une quelconque des revendications précédentes, dans lequel l'épaisseur de couche du primaire est compris entre 0,01 et 0,5 μm, de préférence entre 0,05 et 0,4 μm et idéalement entre 0,1 et 0,3 μm.

5. Procédé de formation d'un substrat d'emballage souple imprimé selon l'une quelconque des revendications précédentes comprenant les étapes suivantes :

a. obtention d'un substrat d'emballage souple ;
b. application d'au moins un imprimé numérique par un procédé d'impression numérique d'au moins une composition d'encre, ladite composition d'encre :

- comprenant un liquide de support, une résine, un polymère servant de co-résine et un colorant, la résine comprenant des copolymères de monomères polymérisés choisis dans le groupe constitué par l'éthylène, l'acide (méth)acrylique, un (méth)acrylate d'alkyle et l'acétate de vinyle, et
- ayant une concentration de groupes éthyléniquement insaturés et une concentration d'époxydes alicycliques de moins de 0,2 méq/g, de préférence moins de 0,1 méq/g, mieux encore moins de 0,05 méq/g, idéalement moins de 0,01 méq/g ;

c. soumission de l'imprimé numérique à une irradiation par faisceau d'électrons, dans lequel :

• les énergies électroniques sont comprises entre 10 et 300 keV ;
• la dose d'irradiation reçue par l'encre imprimée numériquement est comprise entre 15 et 100 kGy ;
• l'irradiation par faisceau d'électrons de l'imprimé numérique est effectuée dans une région pauvre en oxygène, c'est-à-dire une concentration d'oxygène inférieure à 300 ppm.

6. Procédé selon la revendication 5, dans lequel le substrat d'emballage souple de l'étape a) est traité par plasma, de préférence traité par plasma corona, avant d'initier l'étape b).

7. Procédé selon la revendication 5 ou 6, comprenant l'étape supplémentaire d'application d'une composition de primaire avant d'initier l'étape b).

8. Procédé selon l'une quelconque des revendications 5 à 7, dans lequel le procédé d'impression numérique de l'étape b) est une impression électrographique liquide.

9. Procédé selon l'une quelconque des revendications 5 à 8 dans lequel la dose d'irradiation par faisceau d'électrons à l'étape c) est d'au moins 18 kGy, de préférence au moins 20 kGy.

10. Procédé selon l'une quelconque des revendications 5 à 9, dans lequel la dose d'irradiation par faisceau d'électrons à l'étape c) est comprise entre 20 et 100 kGy, de préférence entre 25 et 80 kGy, mieux encore entre 30 et 60 kGy.

11. Procédé selon l'une quelconque des revendications 5 à 10, dans lequel l'irradiation par faisceau d'électrons à l'étape c) est effectuée à une concentration d'oxygène de moins de 250 ppm, de préférence moins de 200 ppm, mieux encore moins de 150 ppm.

12. Procédé selon l'une quelconque des revendications 5 à 11, dans lequel le substrat d'emballage souple de l'étape a) comprend du téréphtalate de polyéthylène, du polyéthylène haute densité, du polypropylène orienté, du polyamide orienté, du polystyrène ou du papier.

13. Procédé selon l'une quelconque des revendications 5 à 12, dans lequel la composition de primaire comprend un ou plusieurs polyacrylamide(s).

14. Procédé selon l'une quelconque des revendications 5 à 13, dans lequel la formulation d'encre comprend une ou plusieurs résine(s) de (co)polymère(s) (méth)acrylique(s).

15. Procédé selon l'une quelconque des revendications 5 à 14, dans lequel la formulation d'encre comprend :

- de 20 à 95 % en poids de liquide de support hydrocarboné,
- de 5 à 80 % en poids d'une ou plusieurs résine (s) de (co)polymère(s) (méth)acrylique(s),
- de 10 à 50 % en poids d'une ou plusieurs co-résine(s) de (co)polymère(s) comprenant de l'éthylène carboxyfonctionnel et
- de 0,1 à 80 % en poids d'un ou plusieurs colorants.

16. Procédé selon l'une quelconque des revendications 5 à 15, comprenant l'étape supplémentaire de stratification du substrat d'emballage souple sur une couche de scellage.

17. Procédé selon l'une quelconque des revendications 5 à 16, comprenant l'étape de thermoscellage du substrat souple imprimé ou du stratifié dans un ensemble de thermoscellage à une température comprise entre 100 et 250 °C, de préférence entre 110 et 230 °C, mieux encore entre 120 et 220 °C.

18. Emballage Flow Pack comprenant le substrat d'emballage souple selon l'une quelconque des revendications 1 à 4.

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