



(11) **EP 2 353 881 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.08.2011 Bulletin 2011/32

(51) Int Cl.:
B41M 5/52^(2006.01) B41M 5/00^(2006.01)

(21) Application number: **10152940.2**

(22) Date of filing: **08.02.2010**

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

(71) Applicant: **3M Innovative Properties Company
Saint Paul, MN 55133-3427 (US)**

(72) Inventors:
• **Johannsen, Heiner
41748 Viersen (DE)**

• **Kinnbacher, Ralf
41453 Neuss (DE)**
• **Schappert, Klaus
41453 Neuss (DE)**

(74) Representative: **Voortmans, Gilbert J.L.
3M Europe S.A./N.V.
Office of Intellectual Property Counsel
Hermeslaan 7
1831 Diegem (BE)**

(54) **Printable film**

(57) The present application discloses a printable film comprising a polymeric film having opposite first and second major sides, the surface of the polymeric film on the first major side defining an ink receptive surface on one side of the printable film and the second major side having an adhesive layer, wherein the ink receptive sur-

face is defined by an ink receptive layer comprising (a) a copolymer of an olefin and a hydrocarbon ester of an acrylic acid and (b) an inorganic filler and wherein the ink receptive layer is oriented only along its machine direction or is not oriented.

EP 2 353 881 A1

Description

[0001] The present invention relates to printable films that are receptive to solvent-based inkjet inks and methods of printing onto such films. More specifically, the present invention relates to melt-processed films that are receptive to solvent-based inkjet inks and methods of printing onto such films to make a graphic suitable for application on vehicles or buildings. A variety of graphics for advertising and promotional displays may be produced. The invention further relates to a method of applying a graphic.

[0002] A variety of print methods have been employed for imaging various sheet materials. Commonly employed print methods include gravure, off-set, flexographic, lithographic, electrographic, electrophotographic (including laser printing and xerography), ion deposition (also referred to as electron beam imaging (EBI)), magnetographics, inkjet printing, screen printing, and thermal mass transfer. More detailed information concerning such methods is available in standard printing textbooks.

[0003] One of ordinary skill in the art appreciates the differences in these various print methods and recognizes that a combination of ink and receiving substrate that results in high image quality in one printing method often exhibits an entirely different image quality with another print method. For example, in contact printing methods such as screen-printing, a blade forces the ink to advance and wet the receiving substrate. Image defects are typically due to a subsequent recession of the ink contact angle with the substrate. In the case of non-contact printing methods, such as inkjet printing, the individual ink drops are merely deposited on the surface. In order to achieve good image quality, the ink drops need to spread, join together, and form a substantially uniform, leveled film. This process requires a low advancing contact angle between the ink and the substrate. For any given ink/substrate combination, the advancing contact angle is typically significantly greater than the receding contact angle. Accordingly, ink/substrate combinations that result in good image quality when printed with contact methods such as screen printing, often exhibit insufficient wetting when imaged with non-contact printing methods such as inkjet printing. Insufficient wetting results in low radial diffusion of the individual ink drops on the surface of the substrate (also referred to as "dot gain"), low color density, and banding effects (e.g., gaps between rows of drops).

[0004] Another important difference between screen-printing and inkjet printing is the physical properties of the ink. Screen printing ink compositions typically contain over 40% solids and have a viscosity of at least two orders of magnitude greater than the viscosity of inkjet printing inks. It is not generally feasible to dilute a screen printing ink to make it suitable for inkjet printing. The addition of large amounts of low viscosity diluents drastically deteriorates the ink performance and properties, particularly the durability. Further, the polymers employed in screen printing inks are typically high in molecular weight and exhibit significant elasticity. In contrast, inkjet ink compositions are typically Newtonian.

[0005] Inkjet printing is emerging as the digital printing method of choice due to its good resolution, flexibility, high speed, and affordability. Inkjet printers operate by ejecting, onto a receiving substrate, controlled patterns of closely spaced ink droplets. By selectively regulating the pattern of ink droplets, inkjet printers can produce a wide variety of printed features, including text, graphics, holograms, and the like. The inks most commonly used in inkjet printers are water-based or solvent-based. Water-based inks require porous substrates or substrates with special coatings that absorb water.

[0006] Ink receptive media, in particular media receptive to solvent based inks used for example in inkjet printers have been disclosed in for example US 20030235681, WO 03/002353, US 20030224150 and US 20030107635.

[0007] It would now be desirable to find a further printable film that can in particular be printed with solvent based inks and in particular that can be printed with solvent based inks in inkjet printers including piezo inkjet printers. Desirably, such a film is a non-PVC based printable film and is of low cost, yet providing good to excellent printing properties. It would further be desirable to find a film that can be used for producing graphics, such as for example large graphics, that can be applied to vehicles or buildings for purposes of advertisement for example. Desirably, the graphic adheres well to these substrates yet can be easily and cleanly be removed. In particular, a printable film would be desired that has good or excellent mechanical properties including high elongation at break allowing the film to be removed cleanly and easily even with a stronger adhesive as may be necessary to allow the film to adhere well in outdoor applications and in particular allow use of the film on vehicles and buildings. Desirably, the printable films can be easily printed and can be handled easily and conveniently.

[0008] In accordance with one aspect of the present invention, there is provided a printable film comprising a polymeric film having opposite first and second major sides, the surface of the polymeric film on the first major side defining an ink receptive surface on one side of the printable film and the second major side having an adhesive layer, wherein the ink receptive surface is defined by an ink receptive layer comprising (a) a copolymer of an olefin and a hydrocarbon ester of an acrylic acid and (b) an inorganic filler and wherein the ink receptive layer is oriented only along its machine direction or is not oriented, ie the ink receptive layer is not oriented along any of the machine direction and transverse direction perpendicular to the machine direction.

[0009] The printable film is typically of low cost, yet provides good to excellent printability, in particular by solvent based inks. Also, the printable film can be printed well with inkjet printers including piezo inkjet printers using solvent

based inks. In a particular aspect of the present invention, the ink receptive layer may be a self-supported layer and thus the polymeric film may consist of a single layer formed by the ink receptive layer. Hence, the first major side of the ink receptive layer defines the printable surface of the printable film and the surface on the opposite second major side of the ink receptive layer may be provided directly with the adhesive layer. Optionally, one or more primer layers may be provided between the surface of the ink receptive layer and the adhesive layer or the surface may be corona treated for improving adherence of the adhesive layer thereto.

[0010] In a further aspect, there is provided a method of making a graphic suitable for application on vehicles or buildings, the method comprising printing of an ink composition on the printable film.

[0011] In yet a further aspect, there is provided a graphic comprising an ink composition printed on the ink receptive surface of the printable film.

[0012] In a still further aspect of the invention there is provided a method of applying a graphic comprising adhering the graphic to a vehicle or a building.

[0013] The following is a summary of embodiments according to the invention:

1. A printable film comprising a polymeric film having opposite first and second major sides, the surface of the polymeric film on the first major side defining an ink receptive surface on one side of the printable film and the second major side having an adhesive layer, wherein the ink receptive surface is defined by a ink receptive layer comprising (a) a copolymer of an olefin and a hydrocarbon ester of an acrylic acid and (b) an inorganic filler and wherein the ink receptive layer is oriented only along its machine direction or is not oriented in any of the machine direction and transverse direction perpendicular to the machine direction.

2. A printable film according to embodiment 1 wherein the ink receptive layer defining the ink receptive surface further comprises a polyolefin.

3. A printable film according to embodiment 2 wherein said polyolefin is selected from polyethylene, polypropylene and copolymers of ethylene and propylene.

4. A printable film according to any of the previous embodiments wherein the amount of said copolymer is at least 30% by weight of the total weight of the ink receptive layer.

5. A printable film according to embodiment 4 wherein the amount of said copolymer is between 40% and 80% by weight of the total weight of the ink receptive layer.

6. A printable film according to embodiment 2 or 3 wherein the weight ratio of said polyolefin to said copolymer of an olefin and a hydrocarbon ester of an acrylic acid is between 1:10 to 1:2

7. A printable film according to any of the previous embodiments wherein said hydrocarbon ester of an acrylic acid is selected from the group consisting of alkyl acrylates and alkyl methacrylates.

8. A printable film according to embodiment 7 wherein said hydrocarbon ester of an acrylic acid is an alkyl acrylate wherein the alkyl group has 1 to 8 carbon atoms.

9. A printable film according to any of the previous embodiments wherein the inorganic filler is selected from solid and hollow glass, ceramic or metal particles, zeolite particles, metal oxides, metal, alkali- alkaline earth carbonates silicates, metasilicates, aluminates or sulfates, kaolin, talc, clays, titanium dioxide and mixtures thereof.

10. A printable film according to embodiment 9 wherein the inorganic filler comprises calcium carbonate, titanium dioxide or a mixture thereof.

11. A printable film according to any of the previous embodiments wherein the amount of inorganic filler is between 10 and 50 % by weight based on the total weight of the ink receptive layer.

12. A printable film according to any of the previous embodiments wherein said ink receptive layer also defines the surface of the polymeric film on the second major side thereof and wherein said adhesive layer is provided directly on the ink receptive layer or wherein one or more primer layers are provided between the ink receptive layer and the adhesive layer.

13. A printable film according to any of the previous embodiments wherein said adhesive layer comprises a rubber

based adhesive.

14. A printable film according to embodiment 13 wherein said rubber based adhesive comprises an elastomeric resin, a tackifier and optionally a plasticizer.

15. A printable film according to embodiment 14 wherein said tackifier is an aliphatic hydrocarbon resin.

16. A printable film according to any of the previous embodiments wherein the polymeric film has a thickness between 0.1 and 0.5 mm.

17. A method of making a graphic suitable for application on vehicles or buildings, the method comprising printing of an ink composition on a printable film as defined in any of embodiments 1 to 16.

18. A method according to embodiment 17 wherein said ink composition comprises organic solvent.

19. A method according to any of embodiments 17 or 18 wherein an image is printed.

20. A graphic comprising an ink composition printed on the ink receptive surface of a printable film as defined in any of embodiments 1 to 16.

21. A method of applying a graphic comprising adhering a graphic as defined in embodiment 20 to a vehicle or a building.

[0014] The ink receptive layer of the polymeric film includes a copolymer of an olefin and a hydrocarbon ester of an acrylic acid. Within the context of this invention, the term 'acrylic' should be understood to include methacrylic. The hydrocarbon ester is typically an aliphatic ester and includes in particular, linear or branched alkyl esters. Included therein are also alkyl esters that include one or more aliphatic rings, ie that include a cyclic moiety. In a particular embodiment, the hydrocarbon ester of the acrylic acid is an alkyl ester of acrylic or methacrylic acid for example a linear or branched alkyl ester of acrylic or methacrylic acid having 1 to 12 carbon atoms in the alkyl group such as for example 1 to 8 carbon atoms or 1 to 5 carbon atoms. Examples of hydrocarbon esters of an acrylic acid include methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl acrylate and n-hexyl acrylate.

[0015] The olefin component of the copolymer is typically an alpha-olefin. Examples of olefins include ethylene, propylene, butene, isobutylene, hexane and octane. Typically, the olefin will be selected from ethylene and propylene. Also, the copolymer may include units derived from different olefins. The copolymer can be a random copolymer as well as block-copolymer. Typically, the amount of repeating units in the copolymer derived from the hydrocarbon ester of an acrylic acid is between 5% by weight and 40% by weight, for example between 10% by weight and 35% by weight.

[0016] Particular examples of copolymers include a copolymer of ethylene and methyl acrylate, a copolymer of ethylene and ethyl acrylate, a copolymer of ethylene and butyl acrylate. Commercially available copolymers that can be used include Lotryl™ 30BA02, Lotryl™ 29MA03 and Lotryl™ 24MA005 all available from Arkema.

[0017] In a particular embodiment, the copolymer is used in an amount of at least 30% by weight of the total weight of the ink receptive layer. For example, the amount may be at least 35% or at least 40% or at least 45%. In one embodiment, the amount of the copolymer in the ink receptive layer is at least 50% by weight or preferably at least 55% by weight or at least 60% by weight. In one embodiment, the copolymer may constitute all of the polymeric component of the ink receptive layer. Preferably though, the copolymer will be used in a blend with a polyolefin. Suitable polyolefins for blending with the copolymer include polyalpha olefins including polyethylene, polypropylene and copolymers of ethylene and propylene. Low and/or high density polyethylene may be used in admixture with the copolymer in the ink receptive layer. Generally, the weight ratio of the polyolefin to the copolymer of an olefin and a hydrocarbon ester of an acrylic acid is between 1:10 and 1:2, for example between 1:8 and 1:4. In a particular embodiment, the amount of the copolymer in the ink receptive layer is between 40 and 80% of the total weight of the ink receptive layer.

[0018] The ink receptive layer further includes inorganic filler. The inorganic filler may be chosen to have an average particle size of from about 0.1 to 25 microns and may be any shape including amorphous shapes, spindles, plates, diamonds, cubes, needles, fibers and spheres. Generally, the inorganic filler will be spherical. Examples of inorganic filler components include solid or hollow glass, ceramic or metal particles, microspheres or beads; zeolite particles; inorganic compounds including, but not limited to metal oxides such as titanium dioxide, alumina and silicon dioxide; metal, alkali- or alkaline earth carbonates, silicates, metasilicates or sulfates; kaolin, talc, clays, carbon black and the like.

[0019] Particularly useful inorganic fillers include crystalline and amorphous silica, clay particles, aluminum silicate, titanium dioxide and calcium carbonate. Preferably such fillers are coated to reduce agglomeration and improve dispersability. Preferred inorganic fillers include calcium carbonate, titanium dioxide and mixtures thereof. The amount of

inorganic fillers in the ink receptive layer typically range from about 10% to about 50% by weight, relative to the total weight of ink receptive layer. Preferably, the total amount of fillers is at least about 25%, for example at least 30% or at least 40% by weight.

[0020] To enhance durability of the ink receptive layer, especially in outdoor environments exposed to sunlight, a variety of commercially available stabilizing chemicals can be added optionally to the primer compositions. In particular, UV light stabilizers may be added. Ultraviolet light stabilizers can be present in amounts ranging from about 0.1 to about 5 weight percent of the total primer or ink receptive layer.

[0021] In general, the ink receptive layer is typically substantially free of colorant. However, it may also contain colorants to provide a uniform background colored film.

[0022] The thickness of the ink receptive layer of the polymeric film is typically between 0.1 and 0.5 mm, for example 0.125 to 0.3 mm. The ink receptive layer can be used on its own without the need of a supporting film or co-extruded layer. Hence, the ink receptive layer may be used as a self-supported polymeric film or in other words, the ink receptive layer may define the polymeric film. It has been found that the ink receptive layer can provide good to excellent printability combined with excellent mechanical properties, including high elongation at break without the need for a supporting film. Accordingly, the thickness of the polymeric film is generally between 0.1 and 0.5 mm, for example between 0.125 and 0.3 mm.

[0023] The printable film includes an adhesive layer on the second major side, ie the side opposite to the side containing the ink receptive layer. As the ink receptive layer can readily be used as a self supporting layer, the adhesive layer may be provided directly to the ink receptive layer. The adhesive may be applied by any means known in the art including melt-coating, transfer coating, solvent coating, lamination and extrusion or coextrusion. The adhesive layer may be activated by pressure, heat, solvent or any combination thereof and may be of any type based on a poly(α -olefin), a block copolymer, an acrylate, a rubber/resin, or a silicone. The adhesive may be applied at conventional coating weights (e.g., 0.0001 to 0.02 g/cm²) using any conventional coating means such a slot die or a gravure roll. Where necessary or desired to improve the adhesion of the adhesive layer to the polymeric film and in particular to the ink receptive layer, the polymeric film or ink receptive layer may be corona treated or conventional primer coating may be provided.

[0024] In a particular embodiment, a pressure sensitive adhesive is used. Pressure sensitive adhesives useful in the present invention can be self-tacky or require the addition of a tackifier. Such materials include, but are not limited to, tackified natural rubbers, tackified synthetic rubbers, tackified styrene block copolymers, self-tacky or tackified acrylate or methacrylate copolymers, self-tacky or tackified poly- α -olefins, and tackified silicones. Examples of suitable pressure sensitive adhesives are described in U.S. Pat. Nos. Re 24,906 (Ulrich), 4,833,179 (Young et al.), 5,209,971 (Babu et al.), 2,736,721 (Dexter), 5,461,134 (Leir et al.), 4,391,687 (Vesley), 4,330,590 (Vesley) and 5,112,882 (Babu), the entire disclosure of which is incorporated herein by reference. Others are described in the Encyclopedia of Polymer Science and Engineering, vol. 13, Wiley-Interscience Publishers, New York, 1988, the Encyclopedia of Polymer Science and Technology, vol. 1, Interscience Publishers, New York, 1964 and Handbook of Pressure-Sensitive Adhesives, D. Satas, Editor, 2nd Edition, Von Nostrand Reinhold, New York, 1989..

[0025] In a particular embodiment, the adhesive layer comprises a pressure sensitive adhesive comprising an elastomeric resin and a tackifier and optionally further a plasticizer. Suitable elastomers include in particular thermoplastic block copolymers having a linear, graft or radial configuration and having the A blocks and B blocks formed predominantly in what is termed an ABA block copolymer. The A block being a monoalkenyl arene, for example polystyrene, having a molecular weight between 2,000 and 125,000, preferably between 7,000 and 30,000. The A block content being from about 10 to 50 percent, more preferably between 10 and 30 percent. Other suitable A blocks may be formed from alphasubstituted styrene, t-butyl styrene and other ring alkylated styrenes as well as mixtures thereof. B is an elastomeric conjugated diene, for example isoprene, having an average molecular weight of from about 5,000 to about 1,000,000, preferably between about 15,000 to about 300,000 and most preferably from 50,000 to 180,000. Although preferably ABA and AB block copolymers will comprise the majority of the elastomer of the adhesive other conventional diene elastomers may be used to a minor extent, i.e., up to 25 percent of the elastomer, such as natural rubber; butadiene, isoprene or butadiene-styrene rubber; butadiene-acrylonitrile; butyl rubber or block copolymers of these diene elastomers. The block copolymer is typically used in an amount ranging from 33 to 50 weight percent, preferably at least 38 weight percent of the adhesive composition.

[0026] Examples of tackifying resins that can be used include those that are compatible with the elastomer and is preferably a tackifying resin having a softening point between 80 and 115° C., such as is produced from polymerization of a stream of aliphatic petroleum derivatives of dienes and monoolefins having 5 carbon atoms as is disclosed in U.S. Pat. Nos. 3,939,328 and 3,954,692, the substance of which are incorporated herein by reference. Preferred are tackifying resins resulting from the copolymerization of a feed comprised predominately of piperylene and 2-methyl-2-butene or isoprene, commercially available as Wingtack™ 95 and Wingtack™ Plus, respectively, from Goodyear Chemical Co. These resins generally have a minimal amount of aromatic hydrocarbons if any and preferably not more than about 7 percent by weight of aromatic hydrocarbons.

[0027] Plasticizers that may be used in the adhesive layer include plasticizing oil such as for example an essentially

aliphatic extending oil, preferably containing more than 5 and less than 45% aromatic hydrocarbons. The plasticizing oil can be aliphatic oils such as paraffinic or naphthenic oils.

[0028] For example in an embodiment, the pressure sensitive adhesive comprises

- (a) 33 to 50 weight percent of an A-B block copolymer of at least one polystyrene block A and at least one polyisoprene block B, wherein in a particular embodiment the A blocks comprise from 10% to 30% of the copolymer,
- (b) an aliphatic tackifying resin,
- (c) a plasticizing oil, which may in a particular embodiment have from 5 to 45 percent aromatic content, and
- (d) a ratio of plasticizing oil to tackifying resin of about at least 0.01 to 0.45,

[0029] In a particular embodiment the oil to resin ratio is such as to give a composite midblock glass transition temperature (CMTg) of from about 245 to 261 K at 50 weight percent elastomer and from about 254 to 265 K at 33 weight percent elastomer wherein the composition of this embodiment comprises all formulations within the area defined by these CMTg defined oil to resin ratio points on a cartesian system where the CMTg defined oil to tackifier resin ratios are on the x-axis and the percent elastomer is on the y-axis.

[0030] Suitable examples of rubber based pressure sensitive adhesives are disclosed in for example US 5019071.

[0031] It has been found that a printable film including a rubber based pressure sensitive adhesive as set out above can be applied to a large variety of different substrates including low surface energy substrates, polycarbonate, polypropylene, aluminium and glass providing excellent adhesion thereto. Further, printable films with these adhesives can be easily and cleanly be removed from the substrates, with no or little adhesive residue and without film breakage, even when the polymeric film of the printable film is constituted only of the ink receptive layer. Hence, these pressure sensitive adhesives adhere well to the ink receptive layer.

[0032] Generally, the ink receptive layer is prepared from a melt-blend obtained by feeding a mixture of the components of a desired composition of the ink receptive layer into a hopper of an extruder. In a particular embodiment, the mixture will include the inorganic filler(s), the copolymer and further components, in particular a polyolefin. In an embodiment where a polyolefin is used, a masterbatch or pre-mixture of the polyolefin and an inorganic filler such as calcium carbonate may be prepared in advance and then fed into the hopper together with the copolymer. The mixture is conveyed through the extruder that is heated, preferably with individually controlled temperature zones heated at increasing temperatures toward the extruder exit to a slot die. It is typically preferred to utilize a suitable mixing device such as a static mixer between the extruder exit and the slot die. In passing through the extruder, and, where used, the static mixer, the mixture of copolymer and additional components are heated to a temperature at or above the glass transition temperature of the copolymer (but below the thermal degradation temperature of the polymer) and mixed to form a melt-blend solution that is extruded through a slot die as a film layer onto a chill role, for example a chrome plated role, maintained at a suitable temperature below the glass transition temperature of the copolymer. In a particular embodiment, a rubber role may be pressing against the chill role defining a nip between the chill role and the rubber role into which the film can be extruded. This particular embodiment may be useful to impart a glossy appearance to the ink receptive layer when desired.

[0033] In a preferred embodiment, the ink receptive layer will be extruded as a self-supported film. An adhesive may be co-extruded with the ink receptive layer but is preferably applied after extrusion of the ink receptive layer into a self-supported film. In another embodiment, the ink receptive layer may also be co-extruded with a supporting layer if desired but this will generally not be preferred as a more cost effective printable film can be obtained by extruding the ink receptive layer as a self-supported film.

[0034] Generally, the ink receptive layer will not be oriented. That is, the ink receptive layer will not be subjected to an orientation device intended to orient the ink receptive layer in the longitudinal (machine) direction or in the transverse direction perpendicular thereto. Hence, in a particular embodiment, the ink receptive layer will be an unoriented layer. Accordingly, the ink receptive layer will be substantially free of voids and be nonporous. As a result, mechanical strength and in particular elongation at break of the printable film, in particular where the ink receptive layer is used as a self-supported film, can be obtained. Typically, the ink receptive layer obtained will have an elongation at break in the machine direction as well as in the transverse direction of at least 100%, typically at least 200% or at least 300%. In a particular embodiment in accordance with the present invention, the ink receptive layer has an elongation at break in both the machine and transverse direction of at least 500%. Hence, the ink receptive layer conveniently has substantially improved mechanical properties compared to voided layers that will typically have elongation at break of 10% or less. As a result excellent mechanical properties may be combined with good printing properties even without the need to use a support layer. In another embodiment, the ink receptive layer may be oriented in the longitudinal or machine direction. Typically, such orientation may be caused in the extrusion process of making the ink receptive layer where following extrusion and conveying of the extruded layer to a take-up roller, the layer may be stretched somewhat while its temperature is still near the glass temperature of the ink receptive layer.

[0035] In accordance with the present invention, the printable film is used to make graphics, in particular graphics for application on vehicles or buildings, either to the exterior of the building for example a glass pane or a wall or in the

interior thereof such as on floors or walls. Vehicles to which the graphic might be applied include any transportation vehicle including cars, trucks, busses, metros and trains as well as airplanes. Generally, the graphic is used for purposes of advertisement and will typically include an advertisement message.

[0036] In an embodiment, the graphic may be obtained by printing an ink composition on the printable film. Generally, an image such as an advertisement message may be printed on the printable film. Typically, printing will be done by inkjet printing including piezo inkjet printing.

[0037] Suitable inks include those that have a viscosity ranging from about 3 to about 30 centipoise at the printhead operating temperature. Such inks preferably have a viscosity below about 25 centipoise, and more preferably below about 20 centipoise at the desired ink jetting temperature (typically from ambient temperature up to about 65°C).

[0038] The ink compositions typically comprise a binder, plasticizer, organic solvent, pigment particles and optional additives such as surfactants (e.g. fluorochemical), antifoaming agent (e.g. silica and silicone oil), stabilizers, etc. Piezo ink jet compositions characteristically have moderate to low surface tension properties. Preferred formulations have a surface tension in the range of from about 20 mN/m to about 50 mN/m and more preferably in the range of from about 22 mN/m to about 40 mN/m at the printhead operating temperature. Further, piezo ink compositions typically have Newtonian or substantially Newtonian viscosity properties. A Newtonian fluid has a viscosity that is at least substantially independent of shear rate. As used herein, the viscosity of a fluid will be deemed to be substantially independent of shear rate, and hence at least substantially Newtonian, if the fluid has a power law index of 0.95 or greater. The power law index of a fluid is given by the expression

$$\eta = m \dot{\gamma}^{n-1}$$

wherein η is the shear viscosity, $\dot{\gamma}$ is the shear rate in s^{-1} , m is a constant, and n is the power law index. The principles of the power law index are further described in C.W. Macosko, *Rheology: Principles, Measurements, and Applications*, ISBN #1-56081-579-5, p. 85.

[0039] In a typical embodiment, the inks employed in the method of making the graphic are non-aqueous, meaning that the ink is substantially free of water. In the case of non-aqueous solvent-based inks, the solvent of the ink composition may be a single solvent or a blend of solvents. Suitable solvents include alcohols such as isopropyl alcohol (IPA) or ethanol; ketones such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK); cyclohexanone, or acetone; aromatic hydrocarbons such as toluene; isophorone; butyrolactone; N-methylpyrrolidone; tetrahydrofuran; esters such as lactates, acetates, including propylene glycol monomethyl ether acetate such as commercially available from 3M under the trade designation "3M Scotchcal Thinner CGS10" ("CGS10"), 2-butoxyethyl acetate such as commercially available from 3M under the trade designation "3M Scotchcal Thinner CGS50" ("CGS50"), ethyl-3-ethoxy propionate such as commercially available from 3M under the trade designation "3M Scotchcal Thinner CGS30" ("CGS30"), diethylene glycol ethyl ether acetate (DE acetate), ethylene glycol butyl ether acetate (EB acetate), dipropylene glycol monomethyl ether acetate (DPMA), iso-alkyl esters such as isohexyl acetate, isoheptyl acetate, isooctyl acetate, isononyl acetate, isodecyl acetate, isododecyl acetate, isotridecyl acetate or other iso-alkyl esters; combinations of these and the like.

[0040] In general, organic solvents tend to dry more readily and thus are preferred solvents for inkjet compositions. As used herein, "organic solvent" refers to a liquid having a solubility parameter greater than 7 $(cal/cm^3)^{1/2}$. Further, organic solvents typically have a boiling point of less than 250°C and a vapor pressure of greater than 5 mm of mercury at 200°F (93°C). Highly volatile solvents, such as MEK and acetone, are typically avoided, as such solvents dry too quickly resulting in nozzle clogging at the print heads. Further, highly polar solvents, such as low molecular weight alcohols and glycols, tend to have too high of a solubility parameter for adequate ink uptake.

[0041] In a particular embodiment, the ink may comprise radiation curable ink. Radiation curable ink compositions comprise one or more radiation curable monomer(s), oligomer(s), macromonomer(s), polymer(s) or various mixtures of such components. "Radiation curable" refers to functionality directly or indirectly pendant from the backbone that reacts (e.g. crosslinks) upon exposure to a suitable source of curing energy. Suitable radiation crosslinkable groups include epoxy groups, (meth)acrylate groups, olefinic carbon-carbon double bonds, allyloxy groups, alpha-methyl styrene groups, (meth)acrylamide groups, cyanate ester groups, vinyl ethers groups, combinations of these, and the like. Free radically polymerizable groups are typically preferred. Of these, (meth)acryl moieties are most preferred. The term "(meth)acryl", as used herein, encompasses acryl and/or methacryl.

[0042] The energy source used for achieving crosslinking of the radiation curable functionality may be actinic (e.g., radiation having a wavelength in the ultraviolet (UV) or visible region of the spectrum), accelerated particles (e.g., electron beam (EB) radiation), thermal (e.g., heat or infrared radiation), or the like with UV and EB being preferred. Suitable sources of actinic radiation include mercury lamps, xenon lamps, carbon arc lamps, tungsten filament lamps, lasers, electron beam energy, sunlight, and the like.

[0043] The radiation curable ingredient may be mono-, di-, tri-, tetra- or otherwise multifunctional in terms of radiation curable moieties. The oligomers, macromonomers, and polymers may be straight-chained, branched, and/or cyclic with branched materials tending to have lower viscosity than straight-chain counterparts of comparable molecular weight.

[0044] A preferred radiation curable ink composition comprises a radiation curable reactive diluent, one or more oligomers(s), macromonomer(s) and polymer(s), and one or more optional adjuvants. For outdoor applications, polyurethane and acrylic-containing monomer(s), macromonomer(s), oligomer(s) and polymer(s) are preferred. The higher molecular weight species also tend to be readily soluble in reactive diluents.

[0045] Examples of commercially available (meth)acrylated urethanes and polyesters include those commercially available from Henkel Corp., Hoboken, NJ under the trade designation "Photomer"; commercially available from UCB Radcure Inc., Smyrna, GA under the trade designation "Ebecryl"; commercially available from Sartomer Co., Exton, PA under the trade designation "Sartomer CN"; commercially available from Akcross Chemicals, New Brunswick, NJ under the trade designation "Actilane"; and commercially available from Morton International, Chicago, IL under the trade designation "Uvithane".

[0046] Provided that at least one of the ingredients is radiation curable, the radiation curable ink may comprise non-radiation curable ingredients as well. For example, polymers such as polyurethanes, acrylic material, polyesters, polyimides, polyamides, epoxies, polystyrene as well as substituted polystyrene containing materials, silicone containing materials, fluorinated materials, combinations thereof, and the like, may be combined with reactive diluents (e.g. monomers).

[0047] Suitable inks for use in the invention include piezo ink compositions commercially available from 3M Company ("3M"), St. Paul, MN under the trade designations "3M Scotchcal 3700 Series Inks", "3M Scotchcal 1600 Series Inks" "3M Scotchcal 6700 Series Inks" and ink compositions available from Ultraview Inkware of VUTEk, Meredith, NH under the trade designation "UltraVu". A preferred piezo ink jet composition is described in U.S. Patent No. 6,113,679 (Adkins), incorporated herein by reference. Radiation curable inks are commercially available from 3M under the trade designations "3M Scotchcal 5000UV Series Inks" and commercially available from SunJet of Sun Chemicals, For Lee, NJ under the trade designation "CrystalUFX Series".

[0048] The graphic produced with the printing method comprise the printable film with ink printed on the ink receptive surface of the printable film. The ink will typically be printed as an image and the image may be text, graphics, coding (e.g. bar coding), etc., being comprised of a single color, multi-colored or being unapparent in the visible light spectrum.

[0049] The graphic is typically adhered to a suitable substrate such as a building or a vehicle through the adhesive layer of the printable film. The nature of the substrate may vary widely and include such substrates as glass, polycarbonate, low energy surfaces including low energy surface paints and metal such as steel or aluminium.

[0050] The invention is further described with reference to the following examples without however the intention to limit the invention thereto.

EXAMPLES

[0051] In the following example all parts and percentages are by weight unless otherwise stated.

Table 1: Materials used

Component	Composition	Trade Name	Supplier
Polymer A	Random copolymer of Ethylene and Butyl Acrylate with content of 27-32% Butyl Acrylate	Lotryl 30BA02	Arkema
Polymer B	Random copolymer of Ethylene and Methyl Acrylate with content of 27-31 % Methyl Acrylate	Lotryl 29MA03	Arkema
Pigment	Titanium Dioxide compounded with LDPE / ratio: 70:30	Remafin Type E	Clariant
Filler A	Calcium Carbonate compounded with LDPE / ratio: 72,5:27,5	MultiBatch ME 50004	Multibase
Filler B	Calcium Carbonate compounded with LDPE / ratio: 70:30	MultiBatch ME 50009	Multibase
Polymer C	Polypropylene Homopolymer	FINA PPH7060	FINA
Filler C	CaCO ₃ PP masterbatch Filler content 72%	Multibatch MP52206	Multibase
Polymer D	Polyvinylacetate Acid Acrylate modified	Bynel 3101	DuPont
In the above table, PP means polypropylene and LDPE means Low Density Polyethylene.			

Printing method

Test file:

[0052] Image quality was evaluated by using a test pattern consist of filled squares printed up to 250% of ink.
 [0053] These pattern was downweb oriented and composed out of individual color squares of the primary colors cyan, magenta, yellow, black and of the secondary colors red (magenta /yellow), green (cyan / yellow) and blue (cyan / magenta), all starting from 5% up to 100% color fill.
 [0054] The red, green and blue rows were printed twice in counterrotated order. This was to print one time the 100% color fills at the end and one time at the start of the printing process.
 [0055] In addition 3 color lines of tertiary colors were printed composed of red, green and blue starting from 5 up to 100% color fill combined with a fix addition of 50% from the not in this ink formulation used primary color (i.e. red is the combination of yellow and magenta, so into this color line 50% of cyan is added to each square).
 [0056] At front at end of the test file the word "Test" was printed with text heights from 1.5 mm up to 7 mm. One time the text was 100% of black on white color and one time white on 100% of black color.

Test printers:

[0057] Two common solvent based piezo ink jet printers were used for printing the described file onto the test substrate.

1) Mutoh Blizzard, filled with 3M Piezo Ink Jet Ink Series 600. Printer had 2 x CMYK ink configuration.
 The Ink Series 600 is a so called mild-solvent ink with using as major solvent 2-butoxyethylacetate (>80%) and smaller quantities of 2-methoxy-2-propylacetate and Cyclohexanone (<10%). The flash point (open cup method) is 68°C.

2) Roland XC-540, filled with Roland Eco-solvent Max inks. Printer had CMYKlcm ink configuration.

[0058] The Eco-solvent Max inks are so called Eco-solvent inks using as major solvent Diethlyene-glycol-diethylether (55%-65%) and smaller quantities of Gamma-bulyrolacetone (10%-20%) and Tetraethylene-glycol-dimetyhlether. The flash point (closed cup method) is 71 °C.

RIP Software:

[0059] To process the test file for printing Onyx PosterShop Version 7.3 was used.

[0060] Ripping was done with a so called IJ Master profile we standardize for lab test prints. This master file is printing without ink restrictions, linearization or ICC profile. Therefore prints done with this profile showing the pure ink flow on top of the media without adjustments.

[0061] Settings used for the test printers:

1) Mutoh Blizzard: FAST540x720 dpi, bidirectional, using 4 pass with picture/speed weaving method. Heater settings used: pre-heater 40°C, print heater 37°C, fixing heater 45°C and post heater 50°C.
 2) Roland XC-540: 360x720 dpi, bidirectional, using 4 pass; heat speed 1000 mm/s. Heater settings used: pre-heater 50°C, print heater 50°C and post heater 55°C. The light colors were reduced to be printed maximum to 30% of ink fills only.

Ink flow/image quality evaluation:

[0062] The ink flow respectively the image quality was evaluated by using the test file described above by observing characteristics such as color uniformity, edge sharpness, color bleed and overall appearance of the test print. The dryness of the ink after printing was noted by lightly touching a cotton bud or lint-free cloth to the test pattern and observing if any ink was transferred from the substrate to the cotton/cloth. All of this was evaluated on a scale of 0 to 5 with 0 being worst and 5 being best.

Making of the ink receptive films

[0063] The film composition detailed in the examples below were obtained by blending the constituents thereof for 10 minutes in a tumbling container. The obtained mixture was then extruded to a film thickness of 0.1 mm using a single screw extruder having 45mm screw, an L/D of 30 and 3 screw zones at a temperature of 160°C for zone 1, 175°C for

EP 2 353 881 A1

zone 2 and 190°C for the third zone. The die was at 190°C and the film was extruded on a chrome plated role maintained at a temperature of 40°C. The extrusion speed was 7 m/min.

[0064] The following films were produced with the above method:

5 Example 1:

50 parts by weight of Base polymer A
50 parts by weight of Filler A
5 parts by weight of Pigment

10

Example 2:

60 parts by weight of Polymer A
40 parts by weight of Filler A
5 parts by weight of Pigment

15

Example 3:

70 parts by weight of Polymer A
30 parts by weight of Filler A
5 parts by weight of Pigment

20

Example 4:

50 parts by weight of Polymer A
50 parts by weight of Filler B
5 parts by weight of Pigment

25

Example 5:

80 parts by weight of Polymer A
20 parts by weight of Polymer B
5 parts by weight of Pigment

30

Example 6:

70 parts by weight of Polymer A
30 parts by weight of Polymer B
5 parts by weight of Pigment

35

40

Example 7:

50 parts by weight of Polymer B
50 parts by weight of Filler A
5 parts by weight of Pigment

45

Example 8:

50 parts by weight of Polymer B
50 parts by weight of Filler B
5 parts by weight of Pigment

50

Example 9:

60 parts by weight of Polymer B
40 parts by weight of Filler B
5 parts by weight of Pigment

55

Example 10:

70 parts by weight of Polymer B
30 parts by weight of Filler B
5 parts by weight of Pigment

Example C1:

40 parts by weight of Polymer D
28 parts by weight of Filler C
32 parts by weight of Polymer C

Example C2:

56 parts by weight of Polymer D
28 parts by weight of Filler C
16 parts by weight of Polymer C

[0065] The printing results obtained with each of these films was as follows:

Ex. No.	Uniformity	Sharpness	Bleed	Overall appearance	Dryness
1	2	1	0	1	1
2	4	4	3	4	3
3	2	2	1	2	2
4	1	1	0	1	1
5	2	2	1	2	1
6	2	2	1	2	1
7	2	2	1	2	1
8	4	4	3	4	3
9	2	2	1	2	1
10	4	5	4	4	4
C1	0	0	0	0	0
C2	0	0	0	0	0

Claims

1. A printable film comprising a polymeric film having opposite first and second major sides, the surface of the polymeric film on the first major side defining an ink receptive surface on one side of the printable film and the second major side having an adhesive layer, wherein the ink receptive surface is defined by a ink receptive layer comprising (a) a copolymer of an olefin and a hydrocarbon ester of an acrylic acid and (b) an inorganic filler and wherein the ink receptive layer is oriented only along its machine direction or is not oriented in any of the machine direction and transverse direction perpendicular to the machine direction.
2. A printable film according to claim 1 wherein the ink receptive layer defining the ink receptive surface further comprises a polyolefin.
3. A printable film according to any of the previous claims wherein the amount of said copolymer is at least 30% by weight of the total weight of the ink receptive layer.
4. A printable film according to claim 2 or 3 wherein the weight ratio of said polyolefin to said copolymer of an olefin and a hydrocarbon ester of an acrylic acid is between 1:10 to 1:2

5. A printable film according to any of the previous claims wherein said hydrocarbon ester of an acrylic acid is selected from the group consisting of alkyl acrylates and alkyl methacrylates.
- 5 6. A printable film according to any of the previous claims wherein the inorganic filler comprises calcium carbonate, titanium dioxide or a mixture thereof.
7. A printable film according to any of the previous claims wherein the amount of inorganic filler is between 10 and 50 % by weight based on the total weight of the ink receptive layer.
- 10 8. A printable film according to any of the previous claims wherein said ink receptive layer also defines the surface of the polymeric film on the second major side thereof and wherein said adhesive layer is provided directly on the ink receptive layer or wherein one or more primer layers are provided between the ink receptive layer and the adhesive layer.
- 15 9. A printable film according to any of the previous claims wherein said adhesive layer comprises a rubber based adhesive.
10. A printable film according to claim 9 wherein said rubber based adhesive comprises an elastomeric resin, a tackifier and optionally a plasticizer.
- 20 11. A printable film according to any of the previous claims wherein the polymeric film has a thickness between 0.1 and 0.5 mm.
- 25 12. A method of making a graphic suitable for application on vehicles or buildings, the method comprising printing of an ink composition on a printable film as defined in any of claims 1 to 11.
13. A method according to claim 12 wherein an image is printed.
- 30 14. A graphic comprising an ink composition printed on the ink receptive surface of a printable film as defined in any of claims 1 to 11.
15. A method of applying a graphic comprising adhering a graphic as defined in claim 14 to a vehicle or a building.



EUROPEAN SEARCH REPORT

Application Number
EP 10 15 2940

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	WO 03/002352 A1 (3M INNOVATIVE PROPERTIES CO [US]) 9 January 2003 (2003-01-09) * page 4, lines 1-29 * * page 7, lines 3-15 * * page 8, line 17 - page 9, line 5 * * page 9, line 23 - page 10, line 2 * * page 12, lines 15-16 * * example 10 *	1-15	INV. B41M5/52 B41M5/00
Y	US 2002/001697 A1 (XING LINLIN [US] ET AL XING LINLIN [US] ET AL) 3 January 2002 (2002-01-03) * paragraphs [0027], [0038] - [0039], [0044], [0047] *	1-15	
Y	US 5 908 723 A (MALHOTRA SHADI L [CA] ET AL) 1 June 1999 (1999-06-01) * column 12, line 46 - column 13, line 21 * * column 14, lines 39-43 * * column 15, lines 1-9 * * column 16, lines 42-45 *	1-15	
Y,D	US 2003/235681 A1 (SEBASTIAN JOHN M [US] ET AL) 25 December 2003 (2003-12-25) * paragraphs [0032], [0046] - [0048], [0055] - [0061], [0067] *	1-15	
A	WO 00/73082 A1 (3M INNOVATIVE PROPERTIES CO [US]) 7 December 2000 (2000-12-07) * page 12, line 1 - page 19, line 30 *	1-15	
A	US 2008/105371 A1 (SMITH REBECCA L [US] ET AL) 8 May 2008 (2008-05-08) * paragraph [0007] - paragraph [0010] * * paragraph [0019] - paragraph [0021] * * paragraph [0024] *	1-15	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 24 June 2010	Examiner Patosuo, Susanna
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

 1
EPO FORM 1503 03.02 (P04C01)

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

EP 10 15 2940

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

24-06-2010

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 03002352	A1	09-01-2003	AT	316006 T		15-02-2006
			BR	0210710 A		20-07-2004
			CA	2449116 A1		09-01-2003
			CN	1620369 A		25-05-2005
			DE	60208785 T2		02-11-2006
			DK	1399317 T3		12-06-2006
			EP	1399317 A1		24-03-2004
			ES	2257542 T3		01-08-2006
			JP	2004531416 T		14-10-2004
			US	2003207025 A1		06-11-2003
			US	2003203135 A1		30-10-2003
			US	2003107635 A1		12-06-2003

US 2002001697	A1	03-01-2002	NONE			

US 5908723	A	01-06-1999	NONE			

US 2003235681	A1	25-12-2003	AU	2003228636 A1		06-01-2004
			CN	1675049 A		28-09-2005
			EP	1515831 A1		23-03-2005
			JP	2005530635 T		13-10-2005
			WO	2004000531 A1		31-12-2003
			US	2005042397 A1		24-02-2005

WO 0073082	A1	07-12-2000	AT	246096 T		15-08-2003
			AU	5452500 A		18-12-2000
			CN	1353647 A		12-06-2002
			DE	60004229 D1		04-09-2003
			DE	60004229 T2		22-04-2004
			EP	1189758 A1		27-03-2002
			JP	2003500262 T		07-01-2003
			US	6649249 B1		18-11-2003

US 2008105371	A1	08-05-2008	NONE			

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 20030235681 A [0006]
- WO 03002353 A [0006]
- US 20030224150 A [0006]
- US 20030107635 A [0006]
- US RE24906 E, Ulrich [0024]
- US 4833179 A, Young [0024]
- US 5209971 A, Babu [0024]
- US 2736721 A, Dexter [0024]
- US 5461134 A, Leir [0024]
- US 4391687 A, Vesley [0024]
- US 4330590 A, Vesley [0024]
- US 5112882 A, Babu [0024]
- US 3939328 A [0026]
- US 3954692 A [0026]
- US 5019071 A [0030]
- US 6113679 A, Adkins [0047]

Non-patent literature cited in the description

- Encyclopedia of Polymer Science and Engineering. Wiley-Interscience Publishers, 1988, vol. 13 [0024]
- Encyclopedia of Polymer Science and Technology. Interscience Publishers, 1964, vol. 1 [0024]
- Handbook of Pressure-Sensitive Adhesives. 1989 [0024]
- **C.W. MACOSKO.** *Rheology: Principles, Measurements, and Applications*, ISBN 1-56081-579-5, 85 [0038]