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THERMAL TRANSFER PRINTING INCORPORATING A COATING FOR PRINTABLE PLASTIC FILMS

This invention relates to a coating composition which enhances the printability of plastic surfaces, particularly plastic films. More particularly, the present invention relates to a method of thermal transfer printing which incorporates the use of a coating composition to improve such printing on plastic films.

5 Thermal transfer printing processes have been developed to satisfy "on-demand" type printing requirements. Thermal transfer printing, however, has also typically been limited to print surfaces composed of paper as opposed to plastic surfaces. This is primarily due to the poor print quality and poor durability of plastic surfaces in thermal transfer printing processes. In thermal transfer printing processes, a print surface
10 substrate is provided for printing thereon, and a thermal element in the form of a printing head is provided for transferring the image to the substrate. A thermographic ribbon which includes a solid ink thereon is disposed between the print surface substrate and the print head. The print head includes a plurality of heating elements which can be individually heated in the desired image for printing. In operation, the thermographic
15 ribbon is sandwiched between the print head and the print surface substrate, causing the print head to contact the thermographic ribbon which in turn contacts the print surface substrate. The individual heating elements of the print head are heated in the image desired to be printed. Such sandwiching and heating simultaneously applies pressure and heat to the thermographic ribbon, which causes the solid ink contained on the
20 thermographic ribbon to be melted or liquefied at the portions of the print head which are being heated. Since the thermographic ribbon is in contact with the print surface substrate, the melted ink is transferred from the thermographic ribbon to the print surface substrate in the form of the image desired.

25 While thermal transfer printing processes have become popular, such processes have traditionally been used mainly with paper substrates, due to the difficulty in printing on plastic films and the high cost associated with such films. For example, commercial products such as product numbers 01-180 and 01-181 marketed by Madico Graphic Films, Woburn, Mass., and Kimdura K-100 marketed by Kimberly Clark are printable polymer films useful in thermal transfer printing processes. While such films have proved

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to be useful alternatives to paper, they are significantly more expensive than paper, and are therefore inefficient in "on-demand" type printing use due to cost considerations.

U. S. Patent No. 5,233,924 to Ohba et al. describes a "synthetic paper" type product which is an example of an alternative substrate described as useful in thermal transfer printin processes. This patent discloses a finely porous opaque polyolefin film layer incorporating an inorganic fine powder, with an ethylene-vinyl alcohol copolymer film layer on one or both sides of the polyolefin film layer, and further including a coat layer such as an inorganic material. While such films have proven to provide adequate print quality in thermal transfer printing, the high cost of these materials results in a significant downside to their use. Additionally, the smooth surface of the ethylene-vinyl alcohol copolymer appears to be a hinderance in many printing applications.

The invention is directed to a printable coating composition which comprises an acrylic-based emulsion which includes inorganic particulates and a surfactant. In one embodiment, the invention includes an ultra violet light stabilizer additive. The special coating formulation of this invention overcomes prior difficulties in the printing, especially lithographic and thermal transfer printing, of plastic films.

The acrylic binder contemplated comprises a thermoplastic polymer or copolymer of a carboxylic acid containing vinylic unsaturation such as acrylic acid or methacrylic acid or ester of those acids. The acrylates contemplated contain lower alkyl groups such as those ranging from about 1 to about 16 carbon atoms, specific examples include methyl, ethyl, butyl, lauryl and stearyl. Useful acrylic resins may be modified with non-acrylic monomers such as acrylonitrile, butadiene and/or styrene.

Acrylic polymer binders are well known in the art and are described in U.S. Patent Nos. 3,753,769; 4,058,645 and 4,749,616.

A particularly useful thermoplastic copolymer is ethylene-acrylic acid available commercially under the trade name Michem, particularly Michem-4983, by Michelman Corporation. Ethylene-acrylic acid is, typically, produced by high pressure copolymerization of ethylene and acrylic acid. When ethylene is copolymerized with acrylic acid, the molecular structure is significantly altered by the random inclusion of bulky carboxylic acid groups along the backbone and side chains of the copolymer. The carboxyl groups are free to form bonds and interact with any poly substrate.

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Commercially available ethylene-acrylic acid copolymers are Primacor 4983 sold by Dow Chemical Co., an aqueous dispersion having 25% solids content and obtained from a reaction between 15 mole % acrylic and 85 mol % ethylene. Other acrylic emulsions that may be employed are those sold under the name of Acrylic, particularly Acrylic
5 79XW318A, 89XWO55 and 90XW067 by Valspar Corporation.

The total amount of the binder can range from about 20% to about 80%, specifically about 30% to about 60% by weight based on the entire weight of the coating composition.

The binder can be entirely acrylic polymer or it can be entirely ethylene-acrylic acid copolymer. For some applications a combination of acrylic polymer and ethylene-
10 acrylic copolymer is preferred. Usually, when there is no acrylic polymer, pigment dispersion is poor and so is adhesion of the coating to the substrate. If there is no ethylene-acrylic acid copolymer, the coating tends to be moisture sensitive. Thus, a balance between the acrylic polymer and the ethylene-acrylic acid copolymer is preferred.
15 When a combination is employed, the preferred amount is 5 to 50% by weight of acrylic polymer and 95 to 50% by weight of ethylene-acrylic acid copolymer. A typical formulation includes 5 to 20 wt. % acrylic polymer and 95 to 80 wt. % ethylene-acrylic acid copolymer based on the entire weight of the combination.

Another component of the formulation comprises at least one ink receptivity
20 enhancing particulate additive.

The particulate additive, often referred to as filler, comprises finely divided inorganic solid materials such as silica, including fumed silica, talc, diatomaceous earth, calcium silicate, bentonite and clay. The amount of filler comprises a substantial percentage of the weight of the coating, typically, about 20% to about 80%, specifically
25 from about 30% to about 60% based on the entire weight of the coating. The particulates are generally small in size, typically ranging from about 1 μ m to about 10 μ m, specifically from about 3 μ m to about 7 μ m. Specific examples of fillers include kaolin, silica (also known for antiblocking properties), aluminum silicates, clay and talc. Pulp may also be employed.

30 Opacity enhancing particulates which will possibly enhance the ink receptivity of the coating may also be employed. These are relatively inert substances. Calcium

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carbonate is extensively used in thermoplastics, it is relatively inexpensive and easy to use. It can be used in its natural form but "precipitated calcium carbonate" which is prepared by chemical processes can be employed. Sometimes, particulates of calcium carbonate are coated with a resin to reduce plasticizer absorption and this form can also be employed.

Particulates which provide pigmentation may also be used. Pigments contemplated are organic and inorganic substances with particle sizes which are rarely less than 1 micron in diameter. Typical pigments include carbon black and titanium dioxide. Calcium carbonate can also act as a pigment. Other pigments not to be excluded by this invention are metallic pigments such as particles of aluminum, copper, gold, bronze or zinc. These pigments are usually flake shaped particles which reflect light when incorporated into the coating vehicle.

The ink absorbing material, opacifying particulates and/or pigment are usually used in combination, depending upon the desired degree of translucency or opacity. Typically the opacifying particulates and /or pigment concentration ranges from about 5% to about 70% of the total particulate concentration of the coating, specifically about 10% to about 45% of the total particulate concentration of the coating.

Further specific examples of particulates which may be employed in addition to those noted above include acetylene black, alpha cellulose, aluminum silicates, barium sulfate, calcium silicate, calcium sulphate, cellulose, clays, diatomite, glass flake, keratin, lignin, lithophone, mica, microballoons, molybdenum disulfide, nepheline syonite, paper, pulp, quartz, shell flour, talc, vermiculite and wood.

The invention further comprises an optional ultra violet stabilizer additive. This is a chemical agent which absorbs or screens out radiation beyond the violet end of the spectrum of visible radiations to prevent radiation catalyzed reactions which degrade plastic. Typical UV absorbers are benzophenone, benzotriazoles, including hydroxyphenyl-benzotriazole, substituted acrylonitriles, salicylic derivatives and nickel complexes. Care must be taken with certain UV stabilizers, such as benzophenone, which may act as a thickening agent. A contemplated UV stabilizer is commercially available benzotriazole "Tinoven 1130" available from Ciba-Geigy, "UV5411" available from Cytec, and "Mixxim BB/200" available from Fairmont. Commercially available

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benzophenone can be obtained from BASF under the name "Uvinul 3048" or from Great Lakes Chemical under the name "Syntase 230". Another commercially available UV absorber is an oxalanilide sold under the name "VP Sanduvor VSU" by Sandoz. The UV absorber is, typically, used in combination with a free-radical scavenger which halts any UV catalyst reactions. Typical free-radical scavengers include hindered amines including hindered aminoether light stabilizers. Contemplated commercially available hindered amines include "Tinuven 123" sold by Ciba-Geigy, "Uvasil 299" sold by Enichem and "BLS 1770" sold by Mayzo. Commercially prepared UV absorber/free radical scavenger packages are available such as "VP Sanduvor 3225" sold by Sandoz. Typically, when using a UV absorber and a free-radical scavenger in combination, the concentration of free-radical scavenger ranges from about 10% to about 60%, preferably about 20% to about 40% by weight based on the entire amount of UV stabilizer additive employed. The total amount of UV stabilizer additive package that is useful in the coating compositions of this invention comprises about 1 to 15%, specifically 2 to 8% by weight of the entire coating composition. Usually, the UV stabilizers are blended in an hydrocarbon solvent, specifically, alcohol solvent which is miscible with water. Typically, the amount of alcohol employed is sufficient to solubilize the UV stabilizer additives, the amount ranging from about 0.5% to about 5% by weight based on the entire weight of the coating.

The coating composition further comprises, in relatively minor amounts, a surface active agent which facilitates dispersion of the particulates. This component is especially important to disperse the UV stabilizer. Any suitable surface active agent which promotes coating stability can be employed. Anionic emulsifiers are contemplated. They include alkali metal and ammonium salts of the sulfates of alcohols having from 8 to 18 carbon atoms such as sodium lauryl sulfate, alkali metal and ammonium salts of aromatic sulfonic acids such as dodecane-1-sulfonic acid and octadiene 1-sulfonic acid, aralkylsulfonates such as sodium isopropyl benzene sulfonate, sodium dodecyl benzene sulfonate and sodium isobutyl naphthalene sulfonate, alkali metal and ammonium salts of sulfonated dicarboxylic acid esters such as sodium dioctyl sulfosuccinate and disodium N-octadecylsulfosuccinamate, alkali metal or ammonium salts of free acids of complex organic mono and diphosphate esters, and the like. Non-ionic emulsifiers such as octyl or

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nonylphenyl polyethoxyethanol, and the like, may also be used. Mixtures of the forgoing are also contemplated. A specific emulsifier is the disodium ethoxylated alcohol (C_{10} - C_{12}) half ester of sulfosuccinic acid available from American Cyanamide Company sold under the tradename Aerosol A-102 or the disodium ethoxylated nonylphenol half esters of sulfosuccinic acid (Aerosol A-103). Another specific emulsifier is the sodium salt of an alkylaryl polyether sulfonate available from Rohm and Haas Company under the tradename "Triton X-200" or "Triton X-405" an ethylene oxide derivative. Another useful emulsifier is "Tergitol 15-5-9".

An effective amount of surface active agent, sufficient to disperse the UV stabilizer and particulates may be used. This amount can range from about 0.5 wt. % to about 10 wt. % of the total weight of the coating, specifically about 1 wt. % to about 7 wt. % of the total weight of the coating.

Traditional coating additives can also be included in the coating of this invention. Typically such materials include modifiers to improve the coefficient of friction, surface slip and antiblocking properties. Specific examples of such modifiers include natural waxes such as paraffin wax, microcrystalline wax, beeswax, carnauba wax, montan wax (lignite wax), etc. and synthetic waxes such as hydrogenated castor oil, chlorinated hydrocarbon waxes, long chain fatty acid amides and the like. Other modifiers that can be added to the coating mixture include one or more wetting agents, crosslinking agents, stabilizers, catalysts, plasticizers, defoamers, slip agents, anti-static agents and antioxidants.

The coating is made by combining all the ingredients sequentially or at the same time and mixing or blending them at room temperature and atmospheric pressure conditions in a conventional mixing apparatus. Typically, the coating is in an aqueous media having a solid content of about 10 to 80%, typically 25 to 60% based on the entire weight of the final coating composition.

Typically the film to be treated with the coating of this inventions is formed by extruding a polyolefin resin, such as polypropylene, through a flat sheet extruder die at a temperature ranging from between about 200 to about 250°C, casting the film onto a cooling drum and quenching the film. The sheet is then stretched about 3 to 7 times in the machine direction (MD) orienter followed by stretching about 5 to about 10 times in

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the transverse direction (TD) orienter.

The film to be treated with the coating of this invention can include any single or multi-layer thermoplastic material that can be formed into a thin film. Contemplated materials include any polyolefin such as polypropylene, polyethylene, polybutene, polystyrene, polyvinyl chloride, copolymers and blends thereof. Other film materials contemplated include polyethyleneterephthalate and nylon. In multilayer films there are one or more skin layers located on at least one surface of the thermoplastic core layer. The skin layer can comprise polyethylene, including medium and high density polyethylene, polypropylene, copolymer or terpolymer of C₂-C₃ alpha olefins or blends thereof. At least one side of the film can comprise a heat seal or pressure seal surface. Typical heat seal materials comprise ethylene and propylene homopolymers, copolymers or terpolymers such as ethylene-propylene, ethylene-propylene-butene-1, and polyvinylidenechloride polymers. Any of the materials can contain inorganic particulates such as titanium dioxide to enhance the whiteness or color of the substrate or to enhance antiblocking properties.

A primer enhances binding of the coating of this invention to the uncoated film. Typical primers are polymers with good adhesion to the uncoated films such as polyethyleneimine and epoxy resins.

In one embodiment of the invention, the final printed film is adhered to an object. Any conventional glue can be employed to adhere the film. Glues contemplated are pressure sealable, hot melt or water-based. The coating of this invention will not interfere with the adhesive. Thus, the adhesive can be applied to the print side of the film so that the printed surface will face the object to which it is applied. This is useful when it is desirable to read the print through the object, e.g. a glass window or a clear plastic container.

Typically, prior to coating the film with the final formulated composition of this invention, the film surface is treated to create a high energy surface environment sufficient for the adhesion of a primer or other coating such as by flame or corona treatment or other method which can oxidize the film surfaces. Corona treatment is accomplished by exposing the film surface to a high voltage corona discharge while passing the film between spaced electrodes. After electronic treatment of the film

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surface, the coating can be applied.

Alternatively, the coating can be applied off-line, by any conventional method. For example, the film can be coated by roller coating, spray coating, slot coating or immersion coating. Gravure roll coating or reverse direct gravure coating are acceptable methods. The excess coating solution can be removed by squeeze rolls or doctor knives.

Regardless of the method by which the coating is applied, the amount should be such that upon drying a smooth, evenly distributed layer is obtained. A preferred coating weight ranges from about 3 to 9 g/m².

The substrate can be of any desired thickness, although thicknesses will typically range from about 20 to about 100 microns for high speed equipment.

In one aspect of the invention, the coating is employed on labels for stretch wrap packaging film.

In any event, the coating composition of this invention may be applied to both surfaces of the film. Alternatively, one surface may have another coating composition applied to it or a substrate such as another polymer film or laminate, a metal foil such as aluminum foil, cellulosic webs, paper, spunbonded polyolefin fiber, a suitable adhesive such as a hot melt or room temperature sealable adhesive or water based adhesive.

Thus, the present invention contemplates a method for forming a thermal transfer print image. Typically, thermal transfer printing has been used to print onto paper substrates, due to the difficulty in providing an image having clear resolution onto a plastic film using thermal transfer printing processes. By incorporating the coating composition of the present invention, a method for forming a thermal transfer print image on a plastic substrate can be easily accomplished.

The present invention can be used for thermal transfer printing processes in a number of applications, including "on-demand" type digital printing, and is particularly useful for pressure-sensitive decals, bar coding, point application identification labeling such as airline luggage tags, visitor identification badges and the like. Since the present invention accomplishes thermal transfer printing onto plastic films, a variety of applications are contemplated which are not limited by the previously shortcomings in using paper as a printing surface. For example, water resistant substrates for outdoor use are contemplated by the present invention.

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The present invention contemplates the use of any known process for accomplishing thermal transfer printing. A typical thermal transfer printing process is discussed in "Materials for Thermal Transfer Printing" by Anczurowski and Sanders in the Journal of Imaging Technology 13: 97-102 (1987).

5 In preferred processes, a thermographic element such as a thermographic ribbon is provided, including a support having a dye or ink layer thereon. The ink layer has a melting temperature below that of the ribbon substrate and compatible with the heating temperature of the print head. When the print head is heated, the ink layer should be capable of melting on the ribbon, without causing degradation of the ribbon support.

10 Preferably, the ink layer has a melting temperature from about 60 °C to about 80 °C. Alternately, a subliminal-type dye or ink can be used. An example of a commercially available thermographic ribbon is 4065-manufactured by Sony. The thermographic ribbon is disposed between the thermoplastic substrate having the coating composition thereon and a print head containing a plurality of thermal heating elements. The heating

15 elements of the print head can be image-wise heated, such that specific elements of the print head are individually heated in the desired image for printing. The image-wise heating of the thermographic ribbon melts the solid ink component of the thermographic ribbon in the form of the desired image. The thus-melted ink is transferred to the thermoplastic substrate having the coating thereon. Since the thermographic ribbon is

20 image-wise heated, only the solid ink on that portion of the thermographic element which is being heated in the image is caused to melt.

 In dye sublimation-type thermal transfer printing processes, it is not necessary to directly contact the substrate surface with the thermographic element in order to transfer the image. Instead, the thermographic ribbon includes a subliminal dye thereon. When

25 the print head heats the thermographic ribbon according to the image desired, the subliminal dye sublimates into a gas. The printing surface substrate having the coating composition coated thereon is positioned adjacent the thermographic ribbon, and is maintained at a temperature below that of the thermographic element. The dye which has been sublimed into a gas transfers to the cold substrate where it condenses and the dye is

30 transferred to the print surface substrate in the form of the image transferred from the thermographic ribbon.

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Color printing onto plastic films using thermal transfer printing processes according to the present invention incorporating coating compositions for the plastic films is also contemplated by the present invention.

Examples

5 The following Examples 1-3 compare uncoated polypropylene film and prior art synthetic paper with polypropylene film coated with various coating compositions according to the present invention, for use in thermal transfer printing processes.

Example 1

10 This Example represents a plastic film known in the art, without any coating composition according to the present invention. The film consists of a biaxially oriented polypropylene film, sold commercially as 160LL302 by Mobil Chemical Company.

Example 2

15 This Example represents an expensive synthetic paper product of the prior art, sold commercially under the name Kimdura by Kimberly Clark. The Kimdura product is a biaxially oriented polypropylene film having mineral filled skins, and a clay-based top coating. The film is believed to be produced in accordance with Process (4) disclosed in U.S. Patent No. 5,233,924. The film is believed to be a finely porous polyolefin type synthetic paper coated on either side with an ethylene-vinyl alcohol copolymer, having a clay filled top coating thereover.

20 Example 3

 This Example represents a plastic film incorporating the coating composition of the present invention to provide a high quality, low cost thermal transfer print surface.

25 A print enhancing coating is prepared by combining 19.9% ethylene-acrylic acid co-polymer, 10.3% acrylic polymer, 32.4% clay, 25.8% talc, 6.4% titanium dioxide and 5.2% commercial antistatic, suspension aid and defoamer additives in aqueous solution. The mixture is prepared to a solids concentration of 46-48%.

30 A biaxially oriented polypropylene film sold commercially as 260LLG202 by Mobil Chemical Company is treated to a dyne level of 38 dynes/cm. The film is coated with a polyethyleneimine primer sold by Daubert Chemical, which contains 1.9% polyethyleneimine, 0.5% hexocellosolve and 97.6% water. The print enhancing coating is applied to the primed surface using a reverse gravure coater to a coat weight of 3.75

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g/m³. The coating composition is air dried at a temperature of 93° C.

The print surface substrates can be printed using a Zebra 140Xi printer manufactured by Zebra Corp., incorporating the following ribbons:

- I I-21 ribbon manufactured by Iimak Corp., representing a ribbon
5 incorporating a hard wax carrier.
- II I-28 ribbon manufactured by Iimak Corp., representing a ribbon
incorporating a fast wax carrier.
- III R2 Prime ribbon manufactured by Iimak Corp., representing a ribbon
incorporating a resin carrier.
- 10 IV SP330 ribbon manufactured by Iimak Corp., representing a ribbon
incorporating a resin carrier.
- V PM260 ribbon manufactured by Iimak Corp., representing a ribbon
incorporating a premium resin carrier.
- 15 VI 4065 ribbon manufactured by Sony Corp., representing a ribbon
incorporating a wax/resin carrier.
- VII 4075 ribbon manufactured by Sony Corp., representing a ribbon
incorporating a resin carrier.
- VIII 4080 ribbon manufactured by Sony Corp., representing a ribbon
incorporating a wax/resin carrier.



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WHAT IS CLAIMED IS:

1. A method for forming a thermal transfer print image comprising:

(a) providing a thermoplastic substrate having a coating composition on at least one surface thereof, said coating comprising:

5 (i) about 20 to about 80 weight percent, based on the entire weight of the coating of at least one binder selected from the group consisting of a polymer of carboxylic acid containing vinylic unsaturation, a copolymer of carboxylic acid containing vinylic unsaturation and mixtures thereof;

10 (ii) about 20 to about 80 weight percent, based on the entire weight of the coating, of at least one finely divided particulate filler; and

(iii) about 0.5 to about 10 weight percent, based on the entire weight of the coating, of a surface active agent;

(b) imagewise-heating a thermographic element comprising a support including a dye layer, and

15 (c) transferring a dye image to said surface of said substrate having said coating thereon.

2. A method as in claim 1, wherein said image-wise heating step (b) causes said dye layer to melt and said transferring step (c) is accomplished by directly contacting said print surface with said thermographic element including said melted dye layer.

20 3. A method as in claim 1, wherein said image-wise heating step (b) causes said dye layer to sublime, and said transferring step (c) is accomplished by positioning said print surface adjacent said thermographic element, thereby causing said sublimated dye-layer to condense on said print surface.

25 4. A method as in claim 1, wherein said polymer of carboxylic acid is derived from acrylic acid, methacrylic acid or ester thereof.

5. A method as in claim 1, wherein said copolymer of carboxylic acid is ethylene acrylic acid copolymer.



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6. A method as in claim 1, wherein said binder comprises a mixture of about 5 to about 50% by weight acrylic polymer and about 95 to about 50% by weight ethylene acrylic acid copolymer based on the entire weight of the mixture.
7. A method as in claim 1, wherein said surface active agent is an anionic emulsifier or a non-ionic emulsifier.
8. A method as in claim 7, wherein said surface active agent is selected from the group consisting of sodium salt of an alkylaryl polyether sulfonate, ethylene oxide derivative and mixtures thereof.
9. A method as in claim 1, wherein said particulate filler is selected from the group consisting of silica, talc, diatomaceous earth, calcium silicate, bentonite, clay and mixtures thereof.
10. A thermal transfer print image comprising:
a polyolefin substrate treated on at least one surface with a coating composition comprising:
(a) about 20 to about 80 weight percent, based on the entire weight of the coating of at least one binder selected from the group consisting of a polymer of carboxylic acid containing vinylic unsaturation, a copolymer of carboxylic acid containing vinylic unsaturation and mixtures thereof,
(b) about 20 to about 80 weight percent, based on the entire weight of the coating, of at least one finely divided particulate filler, and
(c) about 0.5 to about 10 weight percent, based on the entire weight of the coating, of a surface active agent; and
a thermal transfer dye image on said surface coated with said composition, said dye image transferred to said polyolefin substrate by thermal transfer printing.