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(54) Intermediate ink-receiver sheet for transfer printing

(57) A transferable image media having, a carrier support; a release layer including a matting agent, an

optional hydrophobic protection layer and an ink receptive layer.

Description

[0001] This invention relates to a transfer media for transferring an image to a permanent substrate.

[0002] Ink-jet printing is a non-impact method for recording information in response to an electronic signal, such as that generated by a computer. In the printer, the electronic signal produces droplets of ink that are deposited on a media, such as paper or transparent film. Ink-jet printers have found broad commercial acceptance due to their reliability, relatively quiet operation, graphic capability, print quality, and low cost.

[0003] In current ink-jet printing applications, several inks (typically having colors of black, cyan, magenta and yellow) are used to print textual and graphic information on a printing media, typically ordinary paper. The inks primarily are composed of water, and contain a colorant that may be a dye or pigment dispersion. The inks generally also contain

a polyhydric alcohol to prevent nozzle clogging, and may contain various adjuvants. Such inks and ordinary paper are well suited for desk-top publishing, as currently practiced, wherein only a small portion of the paper receives printed text and graphic information.

- [0004] It also is desired to reproduce high quality colored pictoral information (such as photographs and the like) ¹⁵ using ink-jet technologies for applications such as commercial printing and desk-top publishing. In these applications, however, the printing media will receive substantially more of the black and colored inks in order to accurately reproduce the various hues, tints, and colors contained in a typical colored picture. For example, the printing media will be expected to receive up to 200% or more coverage in conventional commercial printing applications.
- [0005] Ordinary paper stock is usually not suitable for such high quality applications for a number of reasons. Water disrupts the paper structure, causing "cockle" that affects appearance of the paper and, in extreme cases, may actually cause the paper to distort to the extent that it contacts the ink-jet pen, disrupting the printing process. Also, the paper may not absorb water sufficiently quickly to achieve the desired printing speed, or may cause flooding of the paper surface, which adversely affects image quality. Moreover, wicking of ink into the paper may cause the paper to "show through" into the printed image, detracting from image quality. There is a need for the printed text and pictures to be more robust: e.g., exhibit better bandleability water fastness, and smear resistance after printing.
- ²⁵ more robust; e.g., exhibit better handleability, water fastness, and smear resistance after printing.
 [0006] Special ink-jet media have been developed to achieve high quality images in ink jet printing. In applications such as proofing, an image is printed on an image receptor element and then transferred to a permanent substrate.
 [0007] There is still a need for development of transfer media that improves the appearance of the final imaged article.
- [0008] The present invention provides a transfer media for receiving printed images involving an ink, particularly an aqueous ink-jet ink containing a dye or pigment colorant, and more particularly a dye-based ink jet ink. The printed image is readily transferred to a permanent substrate, which may be paper, plastic, glass, aluminum foil, etc., due to the components contained in the ink receptive layer of the media and the presence of a matting agent in the release layer. This media has improved gloss characteristics, and therefore exhibits reduced image distortion.

[0009] Accordingly, in one embodiment, the invention provides a transferable image media comprising, in order:

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(a) a carrier support;

(b) a release layer comprising at least one release agent selected from the group consisting of thermoplastic polyamide polymers and polyamide copolymers and combinations thereof; cellulose ethers; polyethylene oxides; and blends of water-soluble polymers with polyethylene oxide; and at least one matting agent in an amount of from about 3 to about 30% by weight, based upon the weight of the release layer;

- (c) a hydrophobic protection layer having a surface adjacent the release layer, said protection layer comprising at least one compound selected from acrylate or methacrylate polymers, epoxy resins, diene rubbers, polyolefin elastomers, polyurethane elastomers, polyvinyl chloride, polyvinyl butyral, polycarbonates, cellulose esters, and combinations thereof; and
- (d) an ink receptive layer comprising at least 15% of a water soluble binder and a hydrophilic thermoplastic polymer having at least one carboxylic acid group and a molecular weight of at least 6000.

[0010] The media and process provide special utility in applications involving printing of pictoral information, particularly in demanding ink-jet printing applications which require more ink than normally used in printing text.

[0011] In another embodiment of the invention the transferable image media excludes a protection layer.

[0012] Another aspect of the invention relates to the process for preparing an inked image by using the transferable image media described above.

[0013] In a preferred application, the media has, in order, an ink receptive layer, a hydrophobic protection layer, a release layer, and a carrier support.

⁵⁵ **[0014]** The carrier support is a material having sufficient stiffness and dimensional stability to support a printed image without having the image distort or misalign, and sufficient water resistance that it can be exposed to an aqueous ink without warping or shrinkage. The material also should withstand heat and pressure applied during the lamination steps described below. The support typically has a thickness of about 25 to about 250 microns (1.0 to 10 mils), preferably

about 50 to 200 microns (2 to 8 mils). Suitable materials include polymeric films, such as polyethylene terephthalate and polyethylene naphthanate, polyamides, polycarbonates, fluoropolymers, polyacetals, and polyolefins. Thin metal sheets may be selected, as well as natural or synthetic paper treated to be water resistant. The substrate may be transparent, translucent, or opaque. It may be colored and can have components, such as antihalation dyes, incorporated therein to meet the needs of specific applications. Polyethylene terephthalate films are a preferred support ma-

rated therein to meet the nee terial.

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[0015] Conventional antistat coatings may be present on one or both sides of the support to reduce static if the support is later separated by "peeling", as discussed below. The antistatic coatings may also contain materials such as colorants, antihalation dyes, optical brighteners, surfactants, plasticizers, coating aids, and the like.

- ¹⁰ **[0016]** Conventional back-coating on carrier support may be applied to the media carrier support in order to reduce curl. Additionally, the carrier support may have a backing layer, to improve transport properties of the media in the inkjet printer, if the material selected as the first substrate does not possess the desired handling properties. The backing layer may have antistatic agents, matting agents, and the like that are commonly employed in the art. For example, the carrier support may have an abrasion resistant coating as disclosed in U.S. Patent No. 5,069,942.
- ¹⁵ **[0017]** An anchor layer may be used to ensure adequate adhesion of the release layer to the carrier support. The term "anchor layer", as employed in the art, means a layer that is adhesively bonded to the layers on both sides of it. Adhesive materials for bonding different types of materials are well known in the art and are discussed in <u>Handbook of Adhesives</u>, <u>2nd Edition</u>, Irving Skeist, Ed. (Van Nostrand Reinhold Co., New York, 1977). Any conventional adhesive material can be used in the anchor layer or layers so long as it is not adversely affected by the printing step. Examples
- 20 include ethylene/vinyl acetate copolymers, vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers, thermoplastic polyamides, and the like. The choice of adhesive will depend on the compositions of the release layer and the support. The anchor layer or layers may contain materials such as antistats, colorants, antihalation dyes, optical brighteners, surfactants, plasticizers, coating aids, and the like. The anchor layer(s) generally has a thickness in the range of 0.01 to 10 microns, preferably 0.05 to 5 microns.
- ²⁵ **[0018]** The release layer facilitates removal of the carrier support from the rest of the transfer media component layers after imaging.

[0019] The release layer includes a release agent selected from cellulose ethers; polyethylene oxides; and blends of water-soluble polymers with polyethylene oxide; thermoplastic polyamides and copolymers thereof such as Ultramid®1C. Examples of water soluble polymers include polyvinyl alcohol, polyvinyl pyrrolidone, polysaccharides, cellu-

³⁰ losic compounds like hydroxy methyl cellulose, starch and gum. An example of cellulose ether include ethyl cellulose. [0020] It has been found that matting agents added to release layer can be used to adjust the gloss characteristics of the layer adjacent to the release layer (i.e., the image reception layer or, where the media contains a protection layer, the protection layer).

[0021] Preferably, the release layer contains a matting agent having a preferred particles size of from about 3 to about 45 microns, preferably from about 8 to about 20 microns, in an amount of from about 3 to about 30 percent by weight, preferably from about 5 to about 10 percent by weight, based on the weight of the release layer.

[0022] The matting agent used should be chemically inert and may be either inorganic or organic. Some suitable matting agents for use in the release layer include inorganic fillers such as silica or silicates, zeolites, calcined kaolin, diatomaceous earth, barium sulfate, aluminum hydroxide or calcium carbonate, glass beads, mica, tin oxide and tita-

- ⁴⁰ nium dioxide and organic matting agents such as polymeric particles, for example, particles of homo- or copolymers of styrene or styrene derivatives such as divinyl benzene, fluorcarbon polymers, and crosslinked polyacrylates and other materials that would be readily apparent to one skilled in the art. The preferred matting agent is silica. [0023] The release layer may also contain other components such as antistats, colorants, antihalation dyes, surfactants, plasticizers, coating aids, and the like.
- ⁴⁵ **[0024]** The release layer generally has a thickness in the range of from about 2 to about 20 microns, preferably from about 3 to about 6 microns. In other words, the dry coating weight of the release range from about 20 to about 200 mg/dm², preferably from about 30 to about 60 mg/dm².

[0025] The hydrophobic layer includes at least one compound selected from acrylate or methacrylate polymers such butyl methacrylates having a glass transition temperature (Tg.) of 15°C and 35°C; epoxy resins, diene rubbers such

- as polyisoprene, polybutadiene, styrene-butadiene rubbers, chloroprene rubber; polyolefin elastomers; polyurethane elastomers; polyvinyl chloride; polyvinyl butyral; polycarbonates; cellulose esters. The preferred compounds include butyl methacrylates having Tgs. of 15°C and 35°C, or mixtures thereof.
 [0026] Preferably, the hydrophobic protection layer may also contain UV absorbers. Suitable UV absorbers often
- ⁵⁵ contain groups such as, for example, benzoates, benzophenones, salicylates, cinnamates, dithiocarbamates, benzo ⁵⁵ triazoles, propenoic esters, diphenylaccrylates and combinations thereof. Examples of suitable UV absorbers include:
 ⁵⁶ propoxylated ethyl para-aminobenzoate; propoxylated ethyl para-aminobenzoate; dipropylene glycol salicylate; 4-do ⁵⁷ decylox-2-hydroxybenzophenone; 2-ethylhexyl para-dimethylaminobenzoate; 2-ethylhexyl-p-methoxycinnamate; 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-4-n-octoxybenzophenone; hydroxybenzoate type; nickel dibutyl dithi-

ocarbamate; N-(p-ethoxycarbon-ylphenyl)-N'-ethyl-N'-phenylformamidine; blends of benzophenone and 1-hydroxycyclohexyl phenyl ketone; 2-methyl-1-(4-methylthio)phenyl)-2-morpholinopropanone-1; 2-ethylhexyl-p-methoxy cinnamate; 2-hydroxy-4-methoxybenzo-phenone; dihydroxybenzo-phenone; 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid; 2-hydroxy-4-n-octoxybenzophenone; 2-(2' hydroxy-5-'-methylphenyl)benzotriazole; 2,2',4,4'-tetrahydroxy ben-

- zophenone; Sodium 2,2'-dihydroxy-4,4' dimethoxy-5-sulfobenzophenone; 2-hydroxy-4-methoxy benzophenone; 2-hydroxy-4-methoxy benzophenone-5-sulfonic acid; ethyl-2-cyano-3,3-diphenylacrylate; ethylhexyl-2-cyano-3,3-diphenylacrylate; 2,4-dihydroxy benzophenone; 2-propenoic acid, 2-cyano-3,3-diphenyl-2-ethyl hexyl ester.
 [0027] The hydrophobic protection layer may contain conventional ingredients such as matte agents. Since the print-
- ed image is viewed through the hydrophobic protection layer, the layer is transparent and preferably has no yellowness that might shift color balance of the printed image.

[0028] The hydrophobic protection layer generally has a thickness in the range of from about 3 to about 40 microns, preferably from about 7 to about 20 microns.

[0029] The ink-receptive layer is constructed of a composition having a balance of properties. The ink-receptive layer is releasably affixed to the hydrophobic protection layer where present or the adjacent layer release layer in order that is many her readily approach after being imaged and the image transformed preferable by lemination.

¹⁵ it may be readily separated after being imaged and the image transferred, preferably by lamination, to a permanent substrate. Since the printed image is viewed through the ink receptive layer, the layer is transparent and preferably has no yellowness that might shift color balance of the printed image.

[0030] It is desirable that the ink receptive layer not be so tacky at ambient temperatures that it presents a handling problem. However, materials should be avoided that are so slippery that the material presents a registration problem during lamination to the permanent substrate. For many applications, it will be desirable to employ an ink receptive layer that is scratch and abrasion resistant when wet or dry, and is resistant to cracking or creasing from folding.

[0031] The ink receptive layer typically has a thickness of from about 3 to about 40 microns, preferably from about 5 to about 20 microns. It contains at least 15% of a water soluble binder, preferably selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, cellulose compounds such as polyhydroxymethyl cellulose, polyhydroxyethyl cellulos

25 cellulose, polyhydroxypropyl cellulose, polyhydroxypropyl methyl cellulose, starch, gelatin, gum arabic, and combinations thereof; and a hydrophilic thermoplastic polymer having at least one carboxylic acid group, preferably in an amount of from 15 to 85%, and a molecular weight of at least 6000.

[0032] The polymer-containing carboxylic acid groups conveniently is a copolymer of (1) at least one monomer selected-from the group consisting of acrylic acid, methacrylic acid, and olefinic dicarboxylic acid (e.g., maleic or itaconic

- ³⁰ acid), and an olefinic dicarboxylic anhydride (e.g., maleic or itaconic anhydride), and (2) at least one monomer selected from the group consisting of an acrylate or methacrylate ester having 1 to 6 carbon atoms, a dialkylamine acrylate or methacrylate, styrene, vinyl acetate, vinyl methyl or ethyl ether, vinyl pyrrolidone, ethylene oxide, or the like. Some copolymers that may be selected are methyl methacrylate (37%)/ethyl acrylate (56%)/acrylic acid (7%) terpolymer, acid no. 76-85, molecular weight 260,000; methyl methacrylate (61.75%)/ethyl acrylate (25.75%)/acrylic acid (12.5%)
- terpolymer, acid no. 100, molecular weight 200,000; styrene/maleic anhydride half ester copolymers, having styrene to maleic anhydride ratios of 1.4/1 to 1.0/1 and molecular weights from 60,000 to 215,000 and poly(methyl vinyl ether/ maleic acid).

[0033] Some useful hydrophilic thermoplastic polymers having at least one carboxylic acid group and a molecular weight of at least 6000 include methyl vinyl ether/maleic acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; the dense function acid or anhydride; acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; acid

- 40 ethylene/maleic acid or anhydride; styrene/maleic acid or anhydride; polymethacrylic acid and polyacrylic acid. [0034] Where a pigment-based ink is used, the ink receptive layer may also contain a neutralizing component to minimize or avoid cracking of the coating. Neutralizing agents, for example, ammonia; N,N-dimethylethanolamine; triethanolamine and 2-amino-2-methyl propanol, may be selected to adjust the pH of the solution to approximately 4.0, which has been found to be advantageous in minimizing the cracking of the inked image formed by a pigment-based ink.
- [0035] The coating may also contain conventional ingredients such as inorganic fillers, humectants, UV absorbers, polymeric dispersants, defoamers, mold inhibitors, antioxidants, latex, dye mordants, optical brighteners, etc.
 [0036] The ink receptive layer generally has a thickness in the range of 3 to 40 microns, preferably 10 to 20 microns.
 [0037] In one embodiment, the, ink receptive layer may be placed directly on the release layer containing a matting agent wherein the matting agent has a specified size and is present in a specified amount. Accordingly, the invention
- ⁵⁰ provides a transferable image media comprising, in order:
 - (a) a carrier support;
 - (b) a release layer; and
 - (c) an ink receptive layer.

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[0038] The hydrophobic protection layer and the ink receptive layer are sequentially applied to the carrier support having thereon a release layer. For high coverage images, the hydrophobic protection layer has a dry coating weight of about 30 mg/dm² (milligram per square decimeter) to about 400 mg/dm²; similarly, the ink receptive layer has a

coating weight from about 30 mg/dm² to about 400 mg/dm². Appropriate coating weight is needed to provide sufficient ink vehicle absorbing capacity to prevent ink spread or puddling and to minimize cockle with porous substrates. The layers are applied to the carrier support by conventional coating methods such as roller coating or knife coating methods (e.g., air knife, trailing blade). All the ingredients can be premixed to form the compositions that are applied to the surface of the release layer at the dry coating weights set out above.

[0039] In a different embodiment the hydrophobic protection layer and the ink receptive layer may be laminated, in order, to a release layer that is coated on a carrier support.

[0040] The adhesion balance between the various media layers is important if the media is to function as a transfer media. The adhesion force at the point of separation should be lower than the adhesion forces between all other layers

10 remaining at separation. Anchor layers may be present between layers, other than at the point of separation, to increase the adhesion force between layers.

[0041] The permanent support for the colored image can be chosen from almost any material desired. For most applications a paper permanent support is used. Other materials which can be used as the permanent support include cloth; wood; glass; china; polymeric films such as polyethylene terephthalate, polyethylene, polypropylene, etc.; syn-

thetic papers; thin metal sheets or foils; cardboard, etc. An adhesive may be employed to achieve desired bonding strength between the ink receptive layer and the permanent support.
 [0042] The transfer media provided by this invention may receive ink printed by conventional ink-jet printers, such as thermal or bubble jet printers, piezoelectric printers, continuous flow printers, or valve jet printers. After the ink is

as thermal or bubble jet printers, piezoelectric printers, continuous flow printers, or valve jet printers. After the ink is printed on the media, the printed.

- 20 [0043] A transfer process may be used to produce a single or multi-colored image on a permanent substrate. For example, a media may be printed with one or more colored inks, and then transferred to a permanent substrate, which may have been primed or have an adhesive layer to ensure durable bonding. Then, the media substrate and release layer are readily removed by stripping or peeling, leaving the ink receptive layer and the hydrophobic layer (if present) on the permanent substrate. In a variation, this process may be repeated with the ink receptive layer containing various
- ²⁵ colors of ink dispersions to build up a multi-colored image. In these applications, it is important that the ink receptive layer have the desired degree of transparency because the colorant is viewed through the layer.
 [0044] The media and processes of the invention have utility for ink-jet printing technologies, with aqueous ink dispersions, to provide high quality printed images on a broad variety of substrates. Pictorial as well as textured information may be printed. For multicolored images, yellow, cyan, magenta and black inks may be used to advantage. Applications
- ³⁰ include desktop publishing, as well as wide format applications such as the printing of signs, banners, and the like. Applications further include applying ink jet images to objects having non-planar topography.
 [0045] In accordance to the present invention, the gloss reading of the transfer media can be adjusted to match the gloss reading of the permanent substrate. Matched gloss readings improves the appearance of the final imaged article.
- 35 EXAMPLES

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[0046] Table 1 below lists the name and chemical description of the ingredients used in the Examples.

40		Glossary	
40 45 50	Name	Available From	General Chemical Description
	Ultramid® 1C	BASF Corporation, Charlotte, NC	co-polyamide of nylon 6 and nylon 66
45	Syloid® ED2	W. R. Grace and Company, Baltimore, MD	silica particles having particle size of 10-15 microns (μ)
	Syloid® ED5	W. R. Grace and Company, Baltimore, MD	silica particles having a particle size of 25-30 microns
50	Cronar® 471	E. I. du Pont de Nemours and Co., Wilmington, DE	polyester resin
	Elvacite® 2044 Elvacite® 2046	E. I. du Pont de Nemours and Co., Wilmington, DE	acrylic polymer
55	Gantrez® AN119	ISP, Wayne, NJ	poly(methyl vinyl ether/maleic anhydride)

Table 1:

	Glossary						
Name	Available From	General Chemical Description					
Elvanol® 52-22	E. I. du Pont de Nemours and Co., Wilmington, DE	poly vinyl alcohol					
Zelec® ECP3010 XC	E. I. du Pont de Nemours and Co., Wilmington, DE	particles consisting of mica and tin oxide having particle size of 3 to 5 microns					
PVP-K90	ISP, Wayne, NJ	polyvinyl pyrrolidone					
Epon® 1101	Shell Chemical, Houston, TX	epoxy resin					
Bakelite® VAGH	Union Carbide Corp., Danbury, CT	vinyl chloride resin					
Scripset®	Monsanto Co., St. Louis, MO	poly(styrene)maleic anhydride					
Gantrez® S97	ISP, Wayne, NJ	poly(methyl vinyl ether/maleic acid)					

Table 1: (continued)

PRINTING AND LAMINATION 20

[0047] Unless otherwise stated, each of the transfer media in the Examples was printed using a HP2000C printer (available from Hewlett-Packard, Palo Alto, CA) using commercial inks (Cyan HP-C4841A; Yellow HP-C4842A;Magenta HP-C4843A; Black HP-4844A) for this printer to form a four-color image. The printed media was then transferred to a permanent substrate, which is Reflection® paper (Consolidated Papers Inc., Wisconsin Rapids, WI), by lamination.

25 The lamination equipment was a WaterProof® Laminator (E. I. du Pont de Nemours and Company, Wilmington, DE), at a lamination temperature was 110°C.and a pressure of 400 psi (2.758 x 10⁶ Pa).

GLOSS AND OPTICAL DENSITY MEASUREMENTS

- 30 [0048] Gloss reading of the image transferred to the permanent substrate in the Examples was measured using a Novo-Gloss™ reading meter(Gardco®, Paul N. Gardner Company, Inc., Pompano Beach, FL) at 60° angle. [0049] Optical density of the image after it has been transferred to the permanent substrate in the Examples was measured using a Macbeth® RD918 densitometer (Kollmorgen Corp, Newburgh, NY).
- [0050] Unless otherwise stated, the amount of ingredients in the various component layers are listed in parts by 35 weight, based upon the weight of the component layer.

EXAMPLE 1

Effect Of Matte Agent Particle Size On Release Layer Properties 40

[0051] Two transfer media(Samples A and B), each containing the following components layers were made: a support, a release layer, a hydrophobic protective layer and an ink receiving layer. [0052] The component layers were prepared as described below:

Release Laver: 45

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Sample A: A 13% coating solution was prepared by adding 24 gms (grams) of Ultramid® 1C into a solvent mixture of 149.6 gms of N-propyl alcohol and 26.4 gms of water. The mixture was stirred with high RPM for 3 hrs. 2.4 gms of Syloid® ED2 were added to the above solution followed by stirring for 20 min. The Sample A coating solution was coated on a sheet of Cronar® 471, with a 4 mil (101.16 microns (U)) knife to form a release layer having a dry thickness of 58 mg/dm² with the drying weight composition listed in Table 2 below:

Table 2.

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Sample A Release Layer Composition							
INGREDIENT AMOUNT (PARTS BY WEIGHT							
Ultramid® 1C	1.0						
Syloid® ED2	0.1						

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<u>Sample B</u>: A second release layer was prepared using the same procedure for making Sample A release layer, as described above, with the following exception: Syloid® ED5 was used. The dry weight composition of Sample B is listed in Table 3 below:

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	Table 3:			
Sample B	Release Layer Composition			
INGREDIENT AMOUNT (PARTS BY WEIG				
Ultramid® 1C	1.0			
Syloid® EDS	0.5			

Hydrophobic Layer:

15 [0053] A 30% coating solution of Elvacite® 2044 was prepared by adding 60 gms (grams) of Elvacite® 2044 into 140 gms of acetone. The mixture was stirred for approximately 3 hrs. The coating solution was coated onto each of Samples A and B, using a 6 mil (152 micron) knife to obtain a dry coating weight of 192 mg/dm².

Ink Receptive Layer:

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[0054] A 7% Gantrez® AN119 coating solution was prepared by adding 14 gms of Gantrez® AN119 into 186 gms of deionized water, stirring for 30 minutes with high RPM and heating up to 80°C for 3 hours. 14 gms of triethanolamine (Ashland Chemical Co. Industrial Chemicals and Solvents Div., Columbus, OH) were then added. A 7% solution of Elvanol® 52-22 was prepared by adding 14 gms of Elvanol® 52-22 into 186 gms of cold water, then heating up to 85°C for 3 hrs until the solution became clear and homogeneous. 20 gms of Gantrez® AN119 solution containing trieth-

for 3 hrs until the solution became clear and homogeneous. 20 gms of Gantrez® AN119 solution containing triethanolamine and 80 gms of Elvanol® 52-22 solution were then mixed. This coating solution was coated with a 12-mil (0.3 micron) thick knife onto the dried hydrophobic protection layers in Samples A and B to form ink receptive layers with a dry weight of 190 mg/dm². The composition of the ink receptive layer is listed in Table 4 below:

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Ink Receptive Layer Composition for Samples A and B					
INGREDIENT AMOUNT (PARTS BY WEIGHT)					
Gantrez® AN 119	1				
Elvanol® 52-22	3				
Triethanolamine	1				

Table 4:

[0055] An image was printed on each of Samples A and B using an HP2000C printer and to form a four color image. The printed media were then laminated to Reflection® paper (Consolidated Papers Inc., Wisconsin Rapids, WI), using a WaterProof® Laminator (E. I. du Pont de Nemours and Company, Wilmington, DE) at a lamination temperature of 110°C. and a laminating pressure of 400 psi (2,758 kPa). Results of the gloss and optical density measurements are shown in Table 5 below:

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Gloss and Optical Density of Image Printed By HP2000C on Samples A and B										
Sample	Matte Agent Particle Size (μ)		Optical Density					Gloss		
		К	С	М	Y	R	G	В	60°	
А	10-15	1.42	0.83	1.37	1.43	1.25	1.22	0.91	6.9	
В	25-35	1.35	0.80	1.32	1.40	1.20	1.18	0.87	8.4	

TABLE 5:

[0056] The Sample A media was also printed with a continuous flow ink jet printer, AX4 (E. I. du Pont de Nemours and Company, Wilmington, DE) with a standard commercial ink, and then transferred to Reflection® paper. Results of the gloss and optical density measurements are shown in Table 6 below:

Gloss and Ontical Density of Image Printed By AX4 Printer on Sample A									
01000 0110		Densit	y or inta	gernn	cu by A				
Sample			Opt	ical Den	isity			Gloss	
	К	С	М	Y	R	G	В	60°	
А	1.94	1.63	1.71	1.24	1.77	1.50	1.54	10.2	

TABLE 6:

EXAMPLE 2 10

Effect Of Amount Of Matte Agent On Gloss

[0057] Five transfer media (Samples C, D, E, F and G) were prepared as described below.

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Release layer coatings were prepared as follows:

[0058] A 13% solution (Sample C release layer) was prepared by adding 24 gms of Ultramid® 1C into a solvent mixture of 149.6 gms of N-propyl alcohol and 26.4 gms of water. The mixture was stirred with high RPM for 8 hrs. The solution was coated on Cronar® 471 with a 4 mil (0.1 micron) knife to have the dry thickness of 61 mg/dm². Samples 20 D, E, F and G release layers were prepared following the same procedure used to prepare Sample C release layer, with the following exception: the level of Syloid® ED2 was varied as shown in Table 7 below.

	Table 7:								
25	Release Layer Compositions for Samples C-G								
		Release Layer Ingredient		Amount (% by weight)					
	Sample		С	D	Е	F	G		
30		Ultramid® IC	99	97	95	92	90		
		Syloid® ED2	1	3	5	8	10		

[0059] A hydrophobic protection layer and an ink receptive layer were then coated over each of the release layers as described in Example 1 above.

35 [0060] Each of the media C through G were printed with an HP2000C printer (Hewlett Packard Co, Palo Alto, CA) to form a four color image on each of the samples. The printed media were then laminated to Reflection® paper using a WaterProof® laminator at 110°C and 400 psi (2758 kPa). Optical density and gloss level were measured and the results are shown in Table 8 below:

40		IABLE 8							
	Sample			Opt	ical Der	sity			Gloss
		К	С	М	Y	R	G	В	60°
	С	2.50	1.02	0.92	0.87	0.98	1.65	1.25	62.4
45	D	2.25	0.95	0.87	0.82	0.88	1.43	1.13	50.7
	E	2.12	0.88	0.82	0.77	0.85	1.38	1.06	41.2
	F	1.93	0.85	0.76	0.74	0.80	1.32	1.01	25.6
50	G	1.57	0.90	0.74	0.72	0.74	1.29	0.95	14.5

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[0061] As shown in Table 8 above, the gloss decreases with increased dosage of the matte agent, Syloid® ED2.

EXAMPLE 3

Effect of Release Layer Thickness On Gloss

[0062] Four transfer media (Samples H, I, J and K) were prepared following the procedure for preparing Sample A

media with the exception of the release layer thickness: Release layer having the composition of Table 2 above were coated with a 3, 6, 8 and 15 mil (76, 152, 203, 381 microns) knife onto a Cronar® 471 to obtain the different thicknesses of release layer shown in Table 9 below. The gloss measurements of Samples H-K are also listed in Table 9 below.

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Table 9					
Sample	Thickness of Release Layer	Gloss (at 60° angle)			
Н	38 mg/dm ²	9.7			
I	75 mg/dm ²	7.2			
J	112 mg/dm ²	7.3			
K	190 mg/dm ²	12.1			

[0063] The optical density of Samples H-K were essentially the same.

15 **EXAMPLE 4**

Transfer Media Including An Alternate Matte Agent

[0064] A three layer transfer media (Sample L) was prepared as described in Example 2 with the following exceptions: 20 Zelec® ECP3010 XC was used in place of Syloid® ED2; and PVP-K90, which dissolves in cold water was used in place of the Elvanol® 52-22, and Elvacite® 2044 is replaced with a blend of Elvacite® 2044 and 2046 in a 50/50 weight ratio. The media had the component layers and composition listed in Table 10 below:

Table 10.

Sample L					
Component Layer	Dry Weight (mg/dm ²)	Composition	Amount (parts by weight)		
ink receptive layer	195	Gantrez® AN119	1		
		PVP K-90	3		
		triethanolamine	1		
hydrophobic layer	185	Elvacite® 2044	1		
		Elvacite® 2046	1		
release layer	35	Ultramid® 1C	1		
		Zelec® ECP3010CX 0.1 part	0.1		
	Component Layer ink receptive layer hydrophobic layer release layer	Component LayerDry Weight (mg/dm²)ink receptive layer195hydrophobic layer185release layer35	Table 10.Sample LComponent LayerDry Weight (mg/dm²)Compositionink receptive layer195Gantrez® AN119PVP K-90triethanolaminehydrophobic layer185Elvacite® 2044Elvacite® 2046Elvacite® 2046release layer35Ultramid® 1CZelec® ECP3010CX 0.1 part		

[0065] The media was printed using an HP2000C printer, and the printed media was laminated to Reflection® paper, 40 using a WaterProof® laminator at 115°C and 400 psi (2758 kPa). Gloss and optical density measurements are shown in Table 11 below:

ΤА	B	F	1	1
1/ 1				

Sample		Optical Density Gloss						Gloss
	К	K C M Y R G B					60°	
L	2.23	0.87	1.76	2.01	1.40	1.39	0.93	61.3

EXAMPLE 5 50

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Alternate Hydrophobic Protection Layer

[0066] A transfer media (Samples M) was prepared as described below. A release layer was prepared as follows: [0067] A 13% Ultramid® 1 C solution with Syloid® ED2 was prepared as described in Example 2 and a 4 mil (101 55 micron) knife was used to coat the solution on 4 mil (101 micron) Cronar® 471 (DuPont) to obtain the matte release layer with a dry coating weight of 55 mg/dm².

A hydrophobic layer was prepared as follows:

[0068] 30 gms of Elvacite® 2044 and 30 gms of Epon® 1101 were added to 140 gms of acetone. The mixture was stirred for 3 hrs. A 6 mil (152 micron) knife used to overcoat the solution on top of the release layer to obtain a hydrophobic layer having a coating wieght of 54 mg/dm² with the composition shown in Table 12 below:

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Table 12:				
Sample M Protection Layer Composition				
Ingredient Amount (parts by weight)				
Elvacite® 2044	3 part			
Epon® 1101	1 part			

An ink receptive layer was prepared as follows:

[0069] A 7% Poly(vinylpyrrolidone) K-90 (ISP Wayne, NJ) solution was prepared by adding 14 gms of the polymer into 186 gms of cold water, and stirring for approximately 1 hour. 150 gms of 7% PVP K-90 solution, 150 gm of 7% Elvanol® 52-22 solution, 100 gms of 7% Gantrez® AN119 solution prepared as described in Example 2, and 7 gms of triethanolamine were mixed and stirred for 20 min. 12 mil (305 microns) knife was used to overcoat the solution on top of hydrophobic layer to obtain 190 mg/dm² ink receptive layer with the dry weight composition as

	Table 13:				
Sample M Ink R	Sample M Ink Receptive Layer Composition				
Ingredient	Amount (parts by weight)				
PVP K-90	1.5				
Elvanol® 52-22	1.5				
Gantrez® AN119	1.0				
Triethanolamine	1.0				

[0070] The media was printed and then the image was laminated on to Reflection® paper. The gloss and optical density measurements are shown in Table 14 below.

TABLE 14

Sample M Measurements							
Optical Density						Gloss	
К	С	М	Y	R	G	В	At 60° angle
1.33	0.75	0.73	0.70	0.79	1.09	0.86	13.8

40 EXAMPLE 6

Alternate Hydrophobic Protection Layer

[0071] A three layer transfer media (Sample N) was prepared by repeating the steps of Example 5 above with the following exceptions: the ink receptive and hydrophobic layers prepared as described below were used.

[0072] The hydrophobic protection layer had the composition shown in Table 15 below:

Sample N Protection Layer Composition				
Ingredient Amount (parts by weigh				
Elvacite® 2044	3			
Bakelite® VAGH	1			

Table 15

⁵⁵ The ink receptive layer was prepared by the following procedure:

[0073] A 13% Scripset® solution was prepared by adding 14 gms of Scripset® and 7 gms dimethanolamine (DMEA) into 186 gms of water and stirring for approximately 3 hrs. The dry weight composition is shown Table 16 below:

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Sample N Ink Receptive Layer Composition				
Ingredient Amount (parts by weight)				
Scripset® 640	1			
Elvanol® 52-22	3			
DMEA	1			

¹⁰ **[0074]** The transfer media was printed and laminated. Gloss and optical density were measured. Results are shown in Table 17 below.

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IABL	 17

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Optical Density					Gloss		
К	С	М	Y	R	G	В	At 60° angle
1.31	0.71	0.72	0.70	0.76	1.08	0.83	12.6

20 EXAMPLE 7

Transfer Media Without Protection Layer

[0075] A three-layer transfer media (Sample O) was prepared as follows:

25 A release layer was prepared as follows:

[0076] A 10% Elvacite® 2046 solution was prepared by adding 20 gins of Elvacite® 2046 to 180 gms of acetone and stirring for 3 hrs until dissolved. 2 gms of Syloid® ED2 were then added into the solution and the mixture stirred for 1 hr. until the ingredients were well dispersed. This dispersion was then coated using a 4 mil (101 microns) knife onto a gel-subbed Mylar® (DuPont) at a coating weight of 55 gm/dm². The composition is shown in Table 18 below:

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TABLE 18:			
Sample O Release Layer Composition			
Ingredient	Amount (parts by weight)		
Elvacite® 2046	1.0		
Syloid® ED2	0.1		

[0077] An ink receptive layer similar to that described in Example 1 was prepared and coated onto the release layer using a 12 mil (304 microns) knife to obtain a coating weight of 190 mg/dm².

⁴⁰ **[0078]** The transfer media was printed and laminated. Gloss and optical density were measured. Results are shown in Table 19 below.

TABLE 19							
Optical Density						Gloss	
К	С	М	Y	R	G	В	At 60° angle
1.30	0.80	0.75	0.70	0.73	1.05	0.86	12.5

50 Claims

- **1.** A transferable image media comprising, in order:
 - (a) a carrier support;

(b) a release layer comprising at least one release agent selected from polyamide polymers and polyamide copolymers and combinations thereof; cellulose ethers; polyethylene oxides; and blends of water-soluble polymers with polyethylene oxide; and at least one matting agent in an amount of from about 3 to about 30% by

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weight, based upon the weight of the release layer;

(c) optionally, a hydrophobic protection layer having a surface adjacent the release layer, said protection layer comprising at least one compound selected from acrylate or methacrylate polymers, epoxy resins, diene rubbers, polyolefin elastomers, polyurethane elastomers, polyvinyl chloride, polyvinyl butyral, polycarbonates, cellulose esters, and combinations thereof; and

(d) an ink receptive layer comprising at least 15% of a water soluble binder selected from polyvinyl alcohol, polyvinyl pyrrolidone, polysaccharides, cellulosic compounds, gelatin, starch, gum arabic and combinations thereof; and a hydrophilic thermoplastic polymer having at least one carboxylic acid group and a molecular weight of at least 6000.

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- 2. The media of Claim 1 wherein the matting agent has a particle size of 3 to 45 microns (µm).
- 3. The media of Claim 1 or Claim 2 wherein the matting agent has a particle size of 8 to 20 microns (µm).
- 15 4. The media of Claim 1, 2 or 3 wherein the matting agent is selected from silica, silicates, zeolites, calcined kaolin, diatomaceous earth, barium sulfate, aluminum hydroxide or calcium carbonate, glass beads, mica, tin oxide, titanium dioxide, particles of homo- or copolymers of styrene or styrene derivatives, fluorcarbon polymers particles, crosslinked polyacrylates, and combinations thereof.
- **5.** The media of Claim 1, 2, 3 or 4 wherein the acrylate or methacrylate polymer is a butyl methacrylate having Tg of 15°C, a butyl methacrylate having Tg of 35°C or mixtures thereof.
 - 6. The media of Claim 1, 2, 3, 4 or 5 wherein the hydrophobic protection layer further comprises UV absorbers selected from 2-propenoic acid, 2-cyano-3,3-diphenyl-2-ethyl hexyl ester; propoxylated ethyl para-aminobenzoate; propoxylated ethyl para-aminobenzoate; dipropylene glycol salicylate; 4-dodecylox-2-hydroxybenzophenone; 2-ethyl-hexyl para-dimethylaminobenzoate; 2-ethylhexyl-p-methoxycknanate; 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-4-n-octoxybenzophenone; hydroxybenzoate type; nickel dibutyl dithiocarbamate; N-(p-ethoxycarbon-ylphenyl)-N'-ethyl-N'-phenylformamidine; blends of benzophenone and 1-hydroxycyclohexyl phenyl ketone; 2-methyl-1-(4-methylthio)phenyl)-2-morpholinopropanone-1; 2-ethylhexyl-p-methoxy cinnamate; 2-hydroxy-4-methoxyben-
- 30 zo-phenone; dihydroxybenzo-phenone; 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid; 2-hydroxy-4-n-octoxybenzophenone; 2-(2' hydroxy-5'-methyl-phenyl)benzotriazole; 2,2',4,4'-tetrahydroxy benzophenone; Sodium 2,2'-dihydroxy-4,4' dimethoxy-5-sulfobenzophenone; 2-hydroxy-4-methoxy benzophenone; 2-hydroxy-4-methoxy benzophenone-5-sulfonic acid; ethyl-2-cyano-3,3-diphonyluzylate; ethylhexyl-2-cyano-3,3-diphenylacrylate; 2,4-dihydroxy benzophenone.

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7. The media of Claim 1, 2, 3, 4, 5, or 6, wherein the hydrophilic thermoplastic polymer having at least one carboxylic acid group and a molecular weight of at least 6000 is selected from the group consisting of methyl vinyl ether/ maleic acid or anhydride; methyl vinyl ether/itaconic acid or anhydride; ethylene/maleic acid or anhydride; styrene/ maleic acid or anhydride; polymethacrylic acid and polyacrylic acid.

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