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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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(54) Title: PRIMER COATING FOR USE ON SUBSTRATES

(57) Abstract: A primer coating is provided for use on a variety of substrates which provides enhanced liquid toner or ink adhesion when applied to substrates which are printed using high speed electrophotographic printing devices. The primer coating includes a natural rosin dispersion including a hydrogenated hydrocarbon rosin or rosin ester and a colloid forming material which is blended with a dispersion of a copolymer of ethylene and acrylic or methacrylic acid.

PRIMER COATING FOR USE ON SUBSTRATES

This application claims the benefit of U.S. Patent Applications Serial No. 61/303,821, filed February 12, 2010; and Ser. No. 13/023,826 filed February 9, 2011, entitled PRIMER COATING FOR USE ON SUBSTRATES . The entire contents of said applications are hereby incorporated by reference.

Embodiments described herein relate to a primer coating for use on substrates, and more particularly, to a primer coating for enhancing the adhesion of liquid toner to a variety of substrates which are designed to be printed using an electrophotographic printing device.

In recent years, the use of on-demand, high-speed digital printing machines utilizing liquid or dry toners or inks in electrophotographic systems has become widespread. In such systems, toner images are formed on a photosensitive drum and then electrically transferred onto an intermediate transfer blanket or belt for printing on a paper or polymeric film sheet or web. Printers using such toners or inks are commercially available from Hewlett-Packard Company under the trade name HP Indigo. However, as liquid toners do not transfer well and/or adhere well to the films or paper substrates printed on such presses, the substrates are typically treated with a coating or primer to enhance the adhesion of liquid toners thereto.

A number of coatings or primers have been developed for use on substrates such as polymeric films which render the surface of the films more receptive to liquid toners. Typical coatings currently in use have been developed based on ethylene-acrylic acid copolymers. As described in commonly-assigned U.S. Patent No. 7,470,736, one such primer coating includes a copolymer of ethylene and acrylic or methacrylic acid and a

compatible adhesion enhancer selected from an aliphatic polyurethane dispersion, a hydrogenated hydrocarbon rosin or rosin ester dispersion, and an amorphous acrylic polymer dispersion. The coating is used to enhance the adhesion of liquid toner to a number of polymeric substrates.

However, the development of newer, high speed digital presses presents new challenges to the use of such primer coatings with regard to ink transfer and adhesion to the substrate. For example, the more recently developed HP Indigo 6000 series of digital presses offer higher speed printing at about twice the speed of previous Indigo presses, resulting in shorter ink transfer times and requiring lower activation temperatures for the primer of about 105°C to 110°C. As a result, substrates coated with typical primers may encounter poor ink transfer as the heat energy at the ink-substrate interface is less than in previous press systems. While it is possible to add heating apparatus to the processing equipment at the point of ink transfer, difficulties remain with the use of thicker substrates such as pressure sensitive label substrates, which comprise many layers.

Accordingly, there is still a need in the art for a primer coating which provides good liquid toner transfer and adhesion to a variety of substrates when used in conjunction with high speed digital presses.

Embodiments of the present invention meet those needs by providing a primer coating for use on a variety of substrates including polymers, metal and paper. The coating provides enhanced liquid toner or ink transfer and adhesion to such substrates, especially those which are printed using high speed electrophotographic printing devices. The coating is also moisture resistant.

According to one embodiment of the invention, a primer coating for enhancing adhesion of liquid toner to a substrate is provided. The primer coating comprises a natural rosin dispersion comprised of a hydrogenated hydrocarbon rosin or rosin ester and a protective colloid forming material, and a dispersion of a copolymer of ethylene and acrylic or methacrylic acid.

The protective colloid forming material is selected from casein, shellac, gum Arabic, xanthum gum, starches, and polyvinylpyrrolidone. The natural rosin dispersion optionally further includes an ethylene acrylic acid copolymer, a metal hydroxide, aqueous ammonia, an amine, or a combination thereof.

The primer coating preferably further includes a wetting agent selected from the group consisting of alcohols and surfactants.

Preferably, the natural rosin dispersion comprises from about 35 to 85% by weight solids and the ethylene acrylic acid copolymer dispersion comprises from about 5 to 60% by weight solids.

The primer coating may be applied to a number of substrates including polymers, biopolymers, metal and paper. The primer coating is preferably applied to a substrate by applying the coating to at least one major surface of the substrate and then preferably drying the coating. Prior to applying the primer coating, it is preferable to use a flame treatment or corona discharge treatment on the substrate, particularly where the substrate has a low surface energy (less than 45 dynes/cm).

Typically, the primer coating is applied to a substrate such that, when dried, it forms a coating having a thickness to provide sufficient print receptivity, which will typically be from about 0.1 to about 2 microns, and more preferably, from about 0.3 to

about 0.5 microns to provide sufficient print receptivity. The coated substrate may then be overprinted by applying, e.g., liquid toner from a digital printing apparatus to the primed surface of the substrate.

Accordingly, it is a feature of embodiments of the invention to provide a primer coating and a method of applying the coating to substrates which provides enhanced toner adhesion to the coated substrates when printed with liquid toner inks using high speed electrophotographic printing devices. These, and other features and advantages of the invention will become apparent from the following detailed description and appended claims.

Embodiments of the primer coating provide a number of advantages over prior primer coatings in that enhanced liquid toner adhesion is provided even at high speed digital press operation. By high speed, we mean a linear speed of from about 15 up to about 30 meters/min. In addition, the coating does not require the use of any additional primers or precoatings to achieve proper adhesion to the substrate. The coating may be used in high speed printing operations, particularly in conjunction with the Indigo WS 6000 digital press. The coating provides good ink transfer and adhesion, and a non-blocking surface. By non-blocking, we mean that the coated material can be wound after coating on one surface and can be unwound without causing feeding problems in the printing press.

The coating is environmentally friendly as it is aqueous-based and about 48% of active raw material in the coating comes from renewal resources. The coating may be used for label printing on food packaging as it complies with current FDA regulations for indirect food contact. The coating will also act as a print receptive coating when used to

prime substrates which are printed on other well known Indigo presses such as the WS 4000, WS 4500, and the like.

The primer coating comprises a natural rosin dispersion which includes a hydrogenated rosin or rosin ester and a protective colloid forming material such as casein or shellac which is then blended with the dispersion of a copolymer of ethylene and acrylic or methacrylic acid. Use of the natural rosin dispersion provides low temperature activation properties to the coating, which is advantageous for use in the Indigo WS 6000 series of presses. For example, the activation temperature in conventional Indigo WS 4000 series presses is typically between about 140°C and 150°C, while the WS 6000 series of presses have an activation temperature of about 105°C to 110°C.

The protective colloid forming material also provides anti-blocking properties to the coating without detracting from the print receptivity. While casein or shellac are preferred colloid forming materials for use, additional suitable colloid forming materials include, but are not limited to, gum Arabic, xanthum gum, starches, and polyvinylpyrrolidone.

We have found that by combining the natural rosin dispersion with the ethylene acrylic acid dispersion, a high surface energy print receptive thermoplastic coating results which is suitable for heat sealability and is print receptive with regard to waterbased inks, offset lithographic inks, and dry and liquid toners for use in electrostatic printing.

Prior conventional primer formulations have required the use of mineral fillers and/or migratory waxes to overcome the blocking tendency resulting from low activation temperatures. However, the migratory waxes tend to compromise ink adhesion, and the mineral fillers increase the activation temperature significantly. By including a colloid

forming material in the coating, the blocking problem is overcome and the coating provides effective print receptivity even at low activation temperatures.

We have also found that dispersions of high density polyethylene materials (such as A-C316 from Honeywell) can also be used as anti-block materials in the formulation (up to about 5% by weight on a solids basis) without affecting the printability of the coated substrate. It should be appreciated that amounts of greater than 5% by weight may adversely affect printability and toner adhesion.

The natural rosin dispersion may further include one or more metal hydroxides for use as antiblocking agents. The coating may include from about 0.05 to 5% by weight metal hydroxides. The metal hydroxides may be added to the formulation as metal ions selected from Group IA, IIA, or IIB of the periodic table. Preferred for use are potassium ions in the form of their hydroxides.

Alternatively, the rosin dispersion may include the use of ammonia as well as primary, secondary or tertiary amines. Preferred for use is ammonia or 2-amino-2-methyl-1 propanol (commercially available from Dow under the designation AMP-95) in amounts of about 0.05% to 5% by weight.

The hydrogenated hydrocarbon rosin or rosin ester in the natural rosin dispersion should preferably have a ring and ball softening point in the range of from about 70°C to 105°C. Suitable rosins for use include natural rosins, which typically include mixtures of resin acids or resin acid derivatives and esters. Examples of resin acids include tricyclic diterpenoids, including pimaranes such as pimaric acid, sandaracopimaric acid, isopimacric acid, *delta*^{8}-isopimaric acid, 7,15-pimaradienoic acid, and *delta*^{8}-pimaric acid, abietanes such as abietic acid, levopimaric acid, palustric acid, neoabietic acid,

dehydroabietic acid, dihydroabietic acid, and tetrahydroabietic acid. Examples of resin acid derivatives include, but are not limited to, rosin esters (such as glycerol ester of rosin acid and pentaerythritol ester of rosin acid), rosin fumarics, rosin maleics, rosin phenolics, fortified rosins, and hydrogenated rosins.

Suitable natural rosins include, but are not limited to, oleoresins, tall oil, wood or gum rosins from tree and plant extrudates, wood extracts, and some tackifying resins. Wood extracts include, but are not limited to, terpenoids including polymers made from monoterpenoids (such as α-pinene, ß-pinene, and dipentenes), sesquiterpenoids, diterpenoids (including labdanes), sesterpenoids, triterpenoids, tetraterpenoids, and polyterpenoids.

A preferred hydrogenated rosin for use is a thermoplastic acidic resin which is produced by hydrogenating wood rosin. An example of such a hydrogenated rosin is Foral® AX rosin, available from Eastman, which is suitable for indirect food contact applications. The natural rosin dispersion is preferably prepared by heating the rosin in a pressure vessel under constant agitation together with the other components such that the base reacts with the acid groups on the rosin and upon melting the rosin, forms a colloidal dispersion. The mixture can then be cooled to ambient temperature prior to discharging the dispersion.

Preferably, the natural rosin dispersion comprises about 2 to 5% by weight casein or shellac, from about 30 to 40% by weight of a hydrogenated hydrocarbon rosin or rosin ester, from about 0 to 0.30% by weight sodium chloride, from about 1 to 5% by weight ammonium hydroxide, and the balance water. A preferred casein for use is Casecoat BL330, available from American Casein Co. A preferred shellac is SSB 4560 from

Strover Shellaek Bremen. In embodiments where the natural rosin dispersion includes ethylene acrylic acid, preferred for use is Primacor® 5990I, available from Dow Chemical Company. The ethylene acrylic acid may be included in the natural rosin dispersion in amounts of from about 5 to 50% by weight.

Preferably, the ethylene acrylic acid copolymer dispersion comprises from about 65 to 95 wt% ethylene and from about 5 to 35 wt% acrylic or methacrylic acid. The copolymer may have a number average molecular weight of about 2,000 to 180,000. The copolymer is preferably prepared as a dispersion by heating the solid polymer with a water phase in a pressure reactor in the presence of a base such as ammonia such that the base reacts with the acid groups on the polymer, and upon melting, the polymer forms a colloidal dispersion. The primer coating preferably contains from about 30 to 45 wt% of the copolymer dispersion containing 35% by weight total solids. A suitable ethylene acrylic acid dispersion for use in the present invention is commercially available from Michelman under the designation Michem®Prime 4990R.E.

The ethylene acrylic acid dispersion preferably further contains from about 0 to 1% by weight of a wetting agent for reducing the surface tension of the coating to wet out the substrate and to promote flow or leveling of the coating prior to drying. Suitable wetting agents include surfactants and alcohols, such as propylene glycol. A preferred surfactant is Surfynol® 104PG-50, available from Air Products.

Water (preferably soft water) may also be added to the natural rosin and ethylene acrylic acid dispersions to lower the viscosity of the coating and aid in the flow of the coating. The coating may contain from about 0 to 30 wt% of soft water.

Preferably, the natural rosin dispersion and copolymer dispersion are combined by mixing the rosin dispersion with the copolymer dispersion at ambient temperature with a slow speed stirrer.

The resulting primer coating is applied to a substrate in any suitable manner including gravure coating, roll coating, wire rod coating, flexographic printing, spray coating, screen printing, and the like. Preferably, in instances where the substrate has a low surface energy (less than about 45 dynes/cm), the substrate surface should be treated with a flame treatment or corona discharge treatment prior to coating.

The coating composition is preferably applied such that upon drying, the coating forms a smooth, evenly distributed layer of about 0.1 to 2 microns in thickness, and more preferably, from about 0.3 to 0.5 microns in thickness, which provides the desired printability and adhesion properties to the liquid toner ink and the substrate. After the coating is applied, it may be dried by hot air, radiant heat, or any other suitable means which provides a clear, adherent coated film. The dried coating comprises from about 2 to 5 wt% of the colloid forming material, from about 40 to 50 wt% fully hydrogenated rosin, and from about 45 to 55 wt% ethylene acrylic acid copolymer.

The coating demonstrates excellent adhesion of HP Indigo Electroinks® when applied to embossed and/or heavily textured pressure-sensitive paper label substrates as well as polyethylene label stock. By "excellent adhesion," we mean that at least 85% of the printed ink adheres to the substrate when subjected to standard adhesive tape testing.

In order that the invention may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention, but are not to be taken as limiting the scope thereof.

Example 1

The following rosin dispersion was prepared in a pressure reactor by adding all components and then heating to 140°C under constant agitation until the rosin melted and reacted.

Rosin Dispersion

Component	Parts by Weight
casein[1]	3.56
hydrogenated rosin[2]	36.44
sodium chloride	0.25
30% ammonium hydroxide solution	3.36
soft water	47.39

[1] Casecoat BL330 from American Casein Co.
[2] Foral® AX rosin from Eastman

30.87 parts by weight of the rosin dispersion was blended with the following ethylene acrylic acid dispersion.

Ethylene acrylic acid dispersion

Component	Parts by Weight
ethylene acrylic acid dispersion[1]	37.55
propylene glycol	5.0
surfactant[2]	0.50
soft water	26.8

[1] Michem®Prime 4990R from Michelman, Inc.
[2] Surfynol® 104PG from Air Products

Example 2

A rosin dispersion was made by adding the following components to a pressure reactor which was sealed and heated to 140°C under constant agitation until the materials melted

and reacted with the base. The pressure vessel was then brought to ambient temperature and 14.28 parts by weight of additional soft water were added to the mixture.

Rosin Dispersion

Component	Parts by Weight
ethylene acrylic acid[1]	25.71
hydrogenated rosin[2]	23.14
30% ammonium hydroxide solution	3.61
soft water	56.39

[1]Primacor® 5990I (Dow Chemical)
[2]Foral® AX rosin (Eastman)

20 parts by weight shellac (Shellac 4560 from Strover Shellaek Bremen) was dissolved by the addition of 3.7 parts by weight of a 30% ammonium hydroxide solution to obtain a 20% solids content. 84.03 parts of the rosin dispersion was then added to 4 parts by weight of the shellac mixture, 10.97 parts by weight of an ethylene acrylic acid dispersion (Michem®Prime 4990R from Michelman, Inc.) and 1 part by weight of a surfactant (Surfynol® 104PG from Air Products).

Example 3

The primer formulations of Examples 1 and 2 were applied to a pressure sensitive label stock with a polyethylene face (PE 100 available from Nirotec) at a coat weight of approximately 0.3 to 0.5 dry gsm. For comparison purposes, a conventional ethylene acrylic acid (EAA) coating was applied at the same coat weight. (DigiPrime 2000 from Michelman Inc.) The three samples were then tested for ink adhesion after printing with a HP Indigo WS 6000 digital printer. Adhesion testing was carried out immediately after printing by applying a 3M 610 adhesive tape to the inked surface and then removing. The results are shown below in Table 1. The % of adhesion is recorded as 100% when no ink is removed by the tape and 0% when all the ink is removed. The tests were performed with the preheater temperature on the WS 6000 press set at the following

temperature settings: 45°C, 55 °C, and off. The higher the percent adhesion at the lowest temperature, the better the product performance.

Table 1

Coating	Preheater Temp. (°C)	Percent (%) ink adhesion					
		Black	Cyan	Magenta	Yellow	CMYK	Average
EAA	45	99	20	70	60	95	69
EAA	55	100	93	98	80	99	94
Example1	off	80	0	0	0	97	35
Example 1	45	98	97	96	73	98	92
Example 1	55	99	99	99	100	99	99
Example 2	off	100	99	99	100	99	99
Example 2	45						
Example 2	55	100	100	100	100	100	100

The normal pass/fail mark on these tests is a minimum of 85% adhesion. Thus, based on these tests, the conventional EAA coating on the label stock failed at 45°C preheater settings and failed on yellow ink at the maximum preheater settings. With older generation HP Indigo machines, this is not the case and the conventional coating normally performs without any problems. Both Example 1 and Example 2 demonstrated better adhesion results compared to the conventional EAA coating. Example 1 at a preheater temperature of 55° performed above the pass/fail criteria and Example 2 performed at the same level with the preheater turned off.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention.

CLAIMS

1. A primer coating for enhancing adhesion of liquid toner to a substrate comprising:

a natural rosin dispersion comprising a hydrogenated hydrocarbon rosin or rosin ester and a protective colloid forming material; and

a dispersion of a copolymer of ethylene and acrylic or methacrylic acid.

2. The primer coating of claim 1 wherein said natural rosin dispersion further includes ethylene acrylic acid, a metal hydroxide, aqueous ammonia, an amine, or a combination thereof.

3. The primer coating of claim 1 wherein said protective colloid forming material is selected from casein, shellac, gum Arabic, xanthum gum, starches, and polyvinylpyrrolidone.

4. The primer coating of claim 1 wherein said copolymer dispersion further includes a wetting agent selected from the group consisting of alcohols and surfactants.

5. The primer coating of claim 1 wherein said natural rosin dispersion comprises from about 35 to 85% by weight solids.

6. The primer coating of claim 1 wherein said ethylene acrylic acid copolymer dispersion comprises from about 5 to 60% by weight solids.

7. A method of applying a primer coating for enhancing adhesion of liquid toner to a substrate comprising:

providing a substrate having first and second major surfaces;

providing a primer coating comprising a natural rosin dispersion comprising a hydrogenated hydrocarbon rosin or rosin ester and a protective colloid forming material; and a dispersion of a copolymer of ethylene and acrylic or methacrylic acid; and

applying said coating to at least one major surface of said substrate.

8. The method of claim 7 including treating said at least one major surface of said substrate by a flame treatment or corona discharge treatment prior to applying said primer coating.

9. The method of claim 7 including drying said primer coating after application to said substrate.

10. A coated substrate having first and second major surfaces, with at least one of said major surfaces having coated thereon a primer coating for enhancing adhesion of liquid toner thereto, said coating comprising a blend of a natural rosin dispersion comprising a hydrogenated hydrocarbon rosin or rosin ester and a colloid forming material; and a dispersion of a copolymer of ethylene and acrylic or methacrylic acid.

11. The coated substrate of claim 10 wherein said primer coating is about 0.1 to about 2 microns thick.

12. The coated substrate of claim 10 wherein said primer coating is from about 0.3 to about 0.5 microns thick.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/024267

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D133/00 C09J133/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C09J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 459 129 A (GOODING LEON B [US] ET AL) 10 July 1984 (1984-07-10) examples 2,3	1-12
X	EP 0 347 657 A2 (COLON HERMAN [US]; MALETSKY ALBERT [US]) 27 December 1989 (1989-12-27) the whole document	1-12
A	US 7 470 736 B2 (COOPER ROBIN [BE]) 30 December 2008 (2008-12-30) cited in the application the whole document	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/024267

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