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(54) **Method of manufacture of highly reflective metallized paper.**

(57) Coated paper substrates having a high gloss suitable for vacuum metallization are manufactured by a direct coating method which comprises laminating an interleaving film and the thermoplastic resin-coated surface of a paper substrate employing suitable temperatures and pressure to render the thermoplastic flowable and thereafter nonflowable. The interleaving film is than stripped away leaving the resin-coated paper substrate with a high specular gloss which can thereafter be vacuum metallized.

Similar high gloss paper substrates are also provided by a transfer coating process which comprises laminating a paper substrate and the thermoplastic resin-coated surface of a transfer film employing sufficient temperatures and pressure to first render the thermoplastic resin flowable and then nonflowable and thereafter stripping away the transfer film.

Paper substrates having 75° specular gloss readings of at least 85 prepared by a process of this invention are then vacuum metallized resulting in the manufacture of highly reflective metallized paper.

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METHOD OF MANUFACTURE OF HIGHLY REFLECTIVE METALLIZED PAPER

BACKGROUND OF THE INVENTION

The present invention is directed to the manufacture of a high gloss coating onto a paper substrate and to the highly reflective vacuum metallized paper produced therefrom.

As used herein, the term "paper" includes sheet-like masses made from fibrous cellulosic materials which may be derived from both natural sources as well as from synthetics such as polyamides, polyesters, and polyacrylic resins, and from mineral fibers such as asbestos and glass. In addition, papers made from combinations of cellulosic and synthetic materials are applicable herein. Paperboard is also included within the broad term "paper".

Various processes have been used for the metallization of paper. In one process, metal foils have been laminated to paper using solvent-based or curing adhesives. The process requires that the metal foil be of a thickness of more than 1 micron (0.0001 mil). The foil laminates are glossy since the finish of the final product is not dependent upon the paper surface but only on the gloss and finish of the foil itself. Foil laminates, even using very thin foils, are expensive. The foil/paper laminates also present handling and application problems (i.e. they tend to curl and crease).

Metallized papers have also been prepared by the direct metallization method where a metallic laden, high solids coating composition is employed. Useful compositions have included ultraviolet curing coatings, electron beam or radiation curing coatings, and high solids aqueous emulsion coatings. By employing high solids coatings, penetration into the porous paper stock is prevented. The gloss and finish of the metallized surface are dependent upon the smoothness of the paper as well as the smoothness of the coating that has been applied.

Another commonly used process is vacuum evaporation or metallization, a process in which an "ultra-thin" layer of metal is deposited on a substrate such as plastic, glass, paper, and the like to achieve a metallic surface appearance. The bright, glossy appearance of metallized papers have lead to their use as decorative wraps and labels. Metallizing directly on paper, however, results in a totally unacceptable material, i.e., a paper with a dull surface. This is due to the rough texture of the paper surface, and even the most highly finished papers have microscopically rough surfaces. Since the deposited metal adheres directly to the surface of the substrate being metallized and also since the resulting metal coating thickness is about 250-300 Angstroms, it isn't surprising that direct metal deposition on paper yields an unacceptable product. Hence, the paper's surface is typically pre-coated with a base coating which fills minor surface imperfections and provides a smooth surface to receive the metal deposit. As a vacuum metallized paper substrate will have a Specular gloss which is very similar to that of the substrate prior to metallization, it is generally understood that the smoother the surface is of the paper substrate employed, the better the resultant gloss will be of the substrate after metallization. Typically substrates having a 75° Specular gloss of at least 80 are required for vacuum metallization.

Glossy coated paper suitable for subsequent vacuum metallization has been prepared by the wet casting method which involves pressing a paper substrate carrying a layer of wet coating against the surface of a heated drum having a highly polished finishing surface. This method is slow and, as such, is not advantagous for economic reasons. Moreover, the critical balance of useful temperatures, pressures and speeds which may be employed in order to prevent a coating from sticking to the casting drum is difficult to maintain during manufacture.

Transfer metallization processes, which are independent of the smoothness of the substrate, are disclosed in U.S. Pat. No. 3,235,395 (issued Feb. 15, 1966 to W.G. Scharf); Brit. Pat. No. 1,536,413 (issued Dec. 20, 1978 to E.V. Oliva); U.S. Pat. Nos. 4,153,494 and 4,215,170 (issued May 8, 1979 and July 29, 1980 respectively to E.V. Oliva) and U.S. Pat. No. 4,382,831 (issued May 10, 1983 to P. Clough et al.).

The process described in the British patent involves coating a backing (e.g. a plastic film or sheet) with a carrier vehicle having a metallic powder dispersed therein, applying an adhesive to the surface of the substrate, combining the backing and substrate, and maintaining the laminated combination at ambient temperature for a time sufficient to permit the adhesive to cure (i.e. absorb the metallic powder and bond it to the surface of the substrate) before the backing is separated.

In U.S. Pat. No. 3,235,395, the transfer technique involves coating a carrier web of a synthetic plastic material with a release layer, forming a metal film on the release layer using vacuum deposition techniques, coating either the surface of the substrate or the metallized layer with an adhesive, combining the substrate and web, conveying the substrate/web combination through hot or cold pressure rollers (depending upon the nature of the adhesive layer) to effect bonding, and then stripping away the carrier. Since the metallic particles are embedded in the release coating and since the release layer only superficially adheres to the carrier web, the carrier web can be readily stripped away without disturbing the metallic particles. The metallic surface, after transfer, is smooth and glossy and covered with a top coating of the plastic used to form the release layer. The transfer technique of this patent, due to the multiplicity of steps and coatings required to achieve a glossy surface, is not recognized as being economically advantageous.

U.S. Pat. Nos. 4,153,494 and 4,215,170 disclose a transfer technique which involves depositing a metal film onto a transfer agent (i.e. carrier) which does not contain a release coating. The transfer agent (e.g. untreated polypropylene) must be smooth since it imparts the final surface to the metallized substrate, and it must have an adherence to the metallic particles less than that of the varnish employed to transfer the metallic particles to the substrate. The transfer agent is metallized by any known method; the substrate or metallized transfer agent is coated with the varnish (e.g. polyurethane varnish); and, before the varnish can cure, the transfer agent and substrate are laminated together by conventional means (a single roll under slight pressure). The varnish absorbs the metallic particles and takes on the smooth surface characteristics of the transfer agent once exceed. The laminate must be cured prior to stripping away the transfer agent. The curing step may be natural or accelerated by heat or exposure to radiation. Due to the cure times required, this process has the economic disadvantage that significant quantities of unacceptable product may be manufactured without any means for determining the cureability of the varnish employed prior to stripping away the transfer agent.

The similar transfer metallization process of U.S. Pat. No. 4,382,831 involves forming a metal film onto a plastic transfer agent (e.g. polyester or polyolefin), coating either the surface of a paper support member or the metallized layer with an aqueous-based thermoplastic adhesive and combining the paper support number and transfer agent. By application of pressure and/or heat the thermoplastic layer is caused to flow. The plastic transfer agent is subsequently removed from the composite leaving a transferred metallic film of high reflectivity on the paper.

There is currently a need in the metallized paper coating industry for an economical means of providing highly reflective metallized paper.

Accordingly, it is an objective of the present invention to provide a process for the manufacture of a high gloss coated paper which upon subsequent vacuum metallization provides a paper product with a highly reflective metallized surface.

SUMMARY OF THE INVENTION

The present invention provides an improved process for the manufacture of paper having high gloss which is suitable for vacuum metallization comprising the steps of:

a) laminating an interleaving film and a coated surface of a paper substrate, said substrate being coated with a thermal resin coating, wherein during the lamination sufficient heat and pressure are employed to first render the resin flowable and thereafter nonflowable; and

b) separating the interleaving film from the resin-coated paper substrate.

The thermal resin adhesives useful herein comprise a thermoplastic resin having a Tg of greater than 0 to less than +50°C. The resin-coated paper substrate prepared have a 75° specular gloss of at least about 85, and preferably have a gloss of 90 or above.

As another aspect of the present invention, paper having similarly high gloss may also be manufactured by the process comprising the steps of:

a) laminating a paper substrate and a coated surface of a transfer film, said transfer film being coated with the thermal resin coating, wherein during said lamination sufficient heat and pressure are employed to first render the resin flowable and thereafter nonflowable whereby transfering the thermal resin coating to the paper substrate; and

b) separating the transfer film from the resin-coated paper substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one process of the present invention, a paper substrate is directly coated with a thin layer of a thermal resin coating using a medium suitable for the particular resin selected (e.g. aqueous emulsion or aqueous solution or organic solvent solution.) After drying the resin-coated paper substrate (e.g. by forced or hot air, over heated drying cans, etc.) the lamination step takes place. In this step, the resin-coated surface of the paper substrate is brought in contact with a suitable interleaving film and laminated through a nip roller at a temperature and pressure sufficient to render the thermal resin flowable. Thereafter, the interleaving film may be immediately stripped. Cooling to ambient temperature prior to stripping is not required because the slight temperature drop which occurs in the period between laminating and stripping is adequate to harden the thermal resin adhesives used herein.

While a coating of the thermal resin adhesive will serve to fill the surface imperfections of the paper substrate and thus increase the overall gloss of the substrate, we have found that by thereafter subjecting the coated substrate to lamination with a suitable interleaving film, paper substrates of significantly improved gloss suitable for metallization may be obtained. The interleaving film, which possesses a smooth, high gloss surface, acts as a template for the thermal resin once it is rendered flowable. The interleaving film, unaffected by the above process, may be employed in web form or in the form of a reuseable continuous loop.

In an alternate process of the present invention, a transfer film is coated with the thermal resin coating. The resin-coated surface (either wet or dried) is thereafter similarly laminated with a paper substrate. The thermal resin coating will adhere to the paper substrate such that subsequent to lamination, the transfer film (which is also suitable for reuse) may be stripped away leaving a paper substrate coated with the resin which exhibits a significantly high gloss suitable for metallization. When practicing the wet transfer process, if the laminant has a moisture content above about 4-6% subsequent to lamination, it may be necessary to further dry it prior to stripping away the transfer film. The dry transfer process is particularly useful for coating light weight porous base paper stock such as tissue, while the wet transfer process is not generally suitable for such light weight materials.

The thermal resin coatings useful herein contain a thermoplastic resin capable of forming a continuous, smooth, hard but flexible film having good block resistance. Thermoplastic resins are those which require no cure (i.e. hardening or crosslinking at room temperature or with heat or irradiation). Moderately hard resins are preferred; however, those which have a slight tack may be used herein. Useful resins herein have a theoretical Tg (glass transition temperature) within the range of greater than 0 to less than +50°C., preferably +3 to +45°C, and most preferably +10 to +40°C. Resins having a theoretical Tg less than 0°C provide coated papers with soft coatings and poor block resistance making them unsuitable for metallization. Resins having a theoretical Tg greater than about +50°C provide coated surfaces which are generally brittle, an undesirable property making such coated paper also unsuitable for metallization.

Among the thermoplastic resins particularly useful herein include the following: polymers and copolymers of styrenes, acrylates and methacrylates, vinyl acetate, maleates, acrylonitrile, acrylamides, acrylic acid and methacrylic acid, and ethylene. The useful concentrations of the comonomers employed in order to provide a thermoplastic resin within the useful Tg range may be easily determined by one skilled in the art. One preferred coating is a blend of styrene/butyl acrylate and styrene/acrylic acid resins having a theoretical Tg of +40°C. Another preferred coating comprises a modified polyvinyl acetate copolymer described in U.S. 4,434,259 (issued February 28, 1984 to S. Gold et al.), the disclosure of which is incorporated herein by reference. While not necessary, crosslinking agents may be employed in the coating composition in order to provide improved water or chemical resistance to the paper substrate. Other optional coating components include, for example, viscosity modifiers, defoamers, and non-blocking additives.

When practicing the wet transfer process, the use of a coalescing solvent may in some instances be advantageously employed to solvate a resin employed in aqueous emulsion in order to provide improved film formation. Generally, practice of the wet transfer process with an aqueous emulsion of a resin having a Tg above about +32°C will necessitate the use of one of many coalescing solvents typically used and well known in the art. Examples of coalescing solvents include, in general, hydrocarbons, alcohols, esters, ethers and ketones. Specific examples of useful coalescents include ethylene glycol monoethylether, ethylene glycol monobutylether, diethylene glycol monobutylether, ethylene glycol monohexylether and the acetates thereof, ethanol, and isopropanol.

The thermoplastic resins may be applied directly onto the paper substrate or onto the transfer film (depending on whether the direct or transfer coating process is employed) by any conventional technique capable of depositing a continuous film. Suitable coating techniques include rotogravure, reverse roll, wire-wound bar, and the like. The coating weight required to form a suitable resin film will vary depending on the paper substrate which is to be employed. Typically for an uncoated paper substrate from 1-4 lbs. (.45-1.81 kg.) dry resin per ream (3000 ft.^{2} or 278.7 m.^{2}) is required, with the optimum being about 1.5-2.5 lbs. (.68-1.13 kg.) per ream for a light weight, machine glazed paper substrate. The useful percent solids of the resin medium employed will typically range from about 20-50%, preferably 20-40% solids and will vary depending on the resin composition employed, the resin medium (aqueous or organic solvent), the desired coating weight, coating viscosity and the paper coating process employed.

The interleaving films useful in the direct coating method are also generally useful as transfer films when practicing the transfer coating methods herein. Generally the films should be heat resistant, dimensionally stable, and exhibit low adhesion to the resin coating employed for easy stripability. Due to the low adhesion of the film to the coating, the film is capable of being reused one or more times in the absence of a buildup of coating on the film. Suitable materials useful for the films include, for example, coated and uncoated polyolefins, coated and uncoated polyesters, and cellulose esters. Films which have been treated (e.g. corona dischared) have found some utility in the practice of the processes herein. However, untreated films are generally preferred. The usefulness of a particular film will vary depending, for example, on the coating process (direct v.s. transfer) and lamination temperature as well as on the thermal resin coating employed. Particularly preferred interleaving films for the direct coating process as well as transfer films used in the dry or wet transfer processes include cellulose acetate and a polyester film obtained from Dupont referred to as 92A Mylar.

The lamination of the combined paper and film may be achieved by conventional lamination techniques. The nip roller employed may consist of one or more pairs of heated metal/pressure rubber roller combinations. Generally only one pair is necessary to effect satisfactory lamination with the paper substrate preferably in contact with the rubber roller. The metal roller is heated to about 160-270°F (71-132°C), preferably 180-250°F (82-121°C), and most preferably 210°F (99°C), the temperature used depending upon the resin selected. The pressure applied by the rubber roller should be sufficient to bring the surfaces into intimate contact (at least about 40-200 psi). The minimum amount of pressure required will also vary depending on the resin and lamination temperature employed. As shown herein, one may be able to employ lower lamination temperatures as the pressure is increased. Other suitable lamination apparatus for practicing the present invention include calendar rolls.

Suitable paper substrate for use herein include both heavy and thin paper stocks, for example, bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical and chemical groundwood, groundwood and the like. The preferred substrates for metallized bottle labels include those with a clay coating or wet strength. The paper substrate does not need to be pre-coated prior to practicing the present invention; however, depending on the ultimate end use of the paper after metallization, a pre-coating may advantageously be employed in order to provide improved water resistance or strength to the paper.

The dried, coated paper substrate is then vacuum metallized. Vacuum metallization is well-known and the detailed procedures will be apparent to those skilled in the art. A review of vapor deposition techniques may be found in Vapor Deposition, C. F. Powell, J. H. Oxley, and J. M. Blocker, Jr., eds., John Wiley and Sons, Inc., New York (1966). Typically the coated paper substrate is unwound, exposed to the metallizing source under high vacuum, and rewound. The optimum vacuum level will depend upon the coating material and most often is 10^{-4} Toor or less. The particular metal chosen will vary with the requirements of the practitioner. Suitable metals include zinc, cadmium, copper, silver, gold, and for bottle labels preferably aluminum. Evaporation sources which can be used in single or multiple chambers include an oven with indirectly heated crucibles, an intermetallic boat heated by direct current inductive evaporation, electron beam evaporation, and sputtering.

In the following examples, which will more fully illustrate the embodiments of this invention, all parts and percentages are given by weight, all temperatures are in degrees Celsius, and all resin or resin blend Tg °C values are theoretical unless otherwise noted.

As used herein, "ream" denotes 3000 ft.^{2} (278.7 m.^{2}). All resins exemplified were employed as 20-40% solids solutions or dispersions unless otherwise noted and were applied directly to a paper substrate or transfer film with a #6 or #8 wire-wound rod.

The test used to measure the gloss of the resin-coated paper substrates before and after metallization was the ASTM Standard Test Method For Specular Gloss (ASTM D 523 - 80) using the 75° geometry. Higher readings indicate better gloss which is the ratio of reflected light to incident light.

EXAMPLE 1

This example describes the preparation of a high gloss paper substrate by the direct coating method of the present invention employing an interleaving film.

Part A

One surface of a paper substrate was coated with various solvent-borne or aqueous-borne thermoplastic resins. The coating weight was 2.5 pounds (1.13 kg.) of resin per ream. The coated surface was dried for 2 minutes at 200°F (93°C). A 1.0 mil (.025 mm.) thick interleaving film of polyester having a basis weight of 12 lb. (5.44 kg.)/ream (92A Mylar obtained from DuPont and referred to herein as PES) was placed on top of the resin coated surface of the paper substrate. The paper/film laminate was run through a nip roller set at 210°F (99°C). The nip roller consisted of a metal/rubber nip with the metal roller being heated to the indicated temperature. During passage through the nip, the interleaving film was in contact with the heated steel roller and the paper substrate was in contact with the rubber roller. After exit from the nip, the interleaving film was subsequently peeled away.

The following resins were used:

Resin A -Blend of 100 parts styrene/butyl acrylate resin and 33 parts styrene/acrylic acid resin in an aqueous emulsion (Tg + 40°C).

Resin B -Nitrocellulose modified vinyl acetate/monoethyl maleate (Tg + 29°C) resin in ethyl acetate/toluene.

Resin C -Vinyl acetate/crotonic acid resin (Tg + 29°C) in ethyl acetate/toluene.

Resin D -Methyl methacrylate/butyl acrylate/acrylic acid resin in toluene/alcohol (Tg + 30°C).

The following paper substrates were used:

38# Paper - 38 lb. (17.23 kg.)/ream two-sided clay coated ground wood (#5 Publication grade).

60# Paper - 60 lb. (27.22 kg.)/ream litho stock paper obtained from Champion International.

In all cases the polyester interleaving film was easily peeled off the coated paper. The 75° specular gloss readings of the coated substrates are given in Table I.

TABLE I

Paper Substrate	Resin Coated on Paper	75° Specular Gloss
38# Paper (uncoated control)	—	58
38# Paper	A	94
38# Paper	B	91
38# Paper	C	96
38# Paper	D	94
60# Paper (uncoated control)	—	70
60# Paper	A	93
60# Paper	B	92
60# Paper	C	92
60# Paper	D	93

The results of Table I show the excellent gloss provided to the paper substrates by the direct coating method employing the PES interleaving film.

Part B.

-The above process was repeated by coating Resins A-D onto the 38# paper. The following interleaving films were evaluated:

PVD/PES - 0.5 mil (.012 mm.) thick polyvinylidene chloride coated polyester having a basis weight of 19 lb. (8.62 kg.)/ream obtained from DuPont (24 M).

CA - 3.5 mil (.088 mm.) thick cellulose acetate having a basis weight of 42 lb. (19.05 kg.)/ream.

LSPP - 1.0 mil (.025 nm.) thick low slip polypropylene having a basis weight of 12 lb. (5.44 kg.)/ream obtained from St. Regis (BF 103).

HSPP - 1.0 mil (.025 nm.) thick high slip polypropylene having a basis weight of 11 lb. (5 kg.)/ream obtained from Hercules (EK 500).

HSPP-CD - Corona discharged HSPP.

In all cases except where indicated the interleaving films were very easy to peel off the coated paper. The gloss results are given in Table II.

TABLE II

Resin Coated on 38# Paper	Interleaving Film	75° Specular Gloss
A	PVD/PES	93
A	CA	87
A	LSPP	80
A	HSPP	81
A	HSPP-CD	84
B	PVD/PES	90
B	CA	98
B	LSPP[a]	—
B	HSPP	94
B	HSPP-CD	92
C	PVD/PES	92
C	CA	96
C	LSPP[b]	90
C	HSPP	96
C	HSPP-CD	95
D	PVD/PES	96
D	CA	95
D	LSPP	90
D	HSPP	94
D	HSPP-CD[b]	90

a - interleaving film could not be removed.
b - interleaving film was very difficult to remove.

The results of Table II show that PVD/PES, CA, and HSPP were useful as interleaving films for all the resin coatings exemplified. The LSPP was found to be unsatisfactory in conjunction with Resins B and C due to the difficulty experienced during film removal.

The gloss results for some of the paper samples coated with Resin A were slightly low for their advantageous use in the preparation of high gloss vacuum metallized substrates (typically a 75° Spectral gloss of at least about 85 is preferred). It should be understood, however, that in many instances one may improve the overall gloss of the paper substate by increasing the coating weight of the resin adhesive or altering the temperature and/or pressure of the laminating nip.

Part C.

The process of Part A was repeated by coating Resins A and B onto the 60# Paper or the clay coated side of 279# Paper (279 lb. (126.55 kg.)/ream clay coated news back board having a 75° Specular gloss of 24). The interleaving films employed during lamination were:

PE - 1.0 mil (.025 mm.) thick polyethylene having a basis weight of 19 lb. (8.62 kg.)/ream obtained from Visqueen.

PE/PES - 0.5 mil (.012 mm.) thick polyethylene-coated polyester having a basis weight of 19 lb. (8.62 kg.)/ream obtained from DuPont (500 L).

The gloss results are given in Table III. Unless otherwise indicated, the interleaving films were easy to very easy to peel off the coated paper.

TABLE III

Resin Coated on Paper Substrate	Interleaving Film	75° Specular Gloss	
		60# Paper	279# Paper
A	PE	58[a]	90
A	PE/PES	89	93[a]
B	PE	88	55
B	PE/PES	85	40

a - interleaving film was resistant to peeling.

The results of Table III show that PE and PE/PES are useful as interleaving films and that in order to obtain a paper substrate with a high specular gloss, the useful interleaving films and resin coatings employed will differ depending on the paper substrate to be coated. Higher basis weight papers will generally require higher nip temperatures than those needed to provide high gloss to lower basis weight papers.

EXAMPLE 2

In this example, the direct coating method employing an interleaving film is illustrated.

The 38# Paper described in Example 1 having an initial gloss of 58 was coated with Resin A (described above) or Resin A' (Resin A containing 3% polyfunctional aziridine, a crosslinker obtained from Cordova Chemical as XAMA-2). The crosslinking additive in Resin A' aids in providing water resistance to the coated paper substrate. The coating weight was 2.5 lbs. (1.13 kg.) resin per ream. The coated surfaces were oven dried for two minutes at 200°F. (93°C). The 75° Spectral gloss of the coated papers measured 76-78.

An interleaving film of PES was placed on top of the resin-coated surface of each paper substrate. The paper film laminates were run through a steel on felt-covered steel nip roller set at 200°F (93°C) and 6000 psi with the interleaving film in contact with the heated steel roll. After exit from the nip, the interleaving film was immediately peeled away. In both cases, the polyester film peeled away very easily. The resultant coated papers each had a gloss reading of 94.

The results indicate that while the resin coatings provided improved gloss over that of the coated paper substrate (76-78 v.s. 58), the direct coating method of the present invention employing an interleaving film provided the coated papers with significantly higher gloss.

Similar results are expected with other thermoplastic resins within the useful Tg range of greater than 0 to less than 50°C. Suitable laminating temperatures and pressures will depend on the Tg of the resin employed.

EXAMPLE 3

This example describes the preparation of a high gloss paper substrate by the dry transfer method of the present invention.

Part A

One surface of a transfer film was coated with one of the thermoplastic resins (A-D) described in Example 1. The coating weight was 2.5 lbs. (1.13 kg.) of resin per ream. The coated surface was dried 2 minutes at 200°F (93°C). A paper substrate was placed on top of the resin-coated surface of the transfer film. The paper/film laminate was run through a nip roller described in Part A of Example 1 which was set at 210°F (99°C). During passage through the nip the uncoated surface of the transfer film was in contact with the heated steel roller and the paper substrate was in contact with the rubber. After exit from the nip, the transfer film was easily peeled away.

The three paper substrates employed are described in Example 1. The transfer films employed were PES, CA, LSPP, HSPP and HSPP-CD. The gloss results are given in Table IV. In all cases, except where indicated, the transfer film was easily peeled from the paper substrate.

TABLE IV

Resin Coated on Transfer Film	Transfer Film	75° Specular Gloss of Paper 38#	60#	279#
A	PES	90	87	91
A	CA	99	100	100
A	LSPP	40[a]	86[a]	71[a]
A	HSPP	96	98	97
A	HSPP-CD	38[a]	84[a]	88[a]
B	PES	92	97	88
B	CA	94	94	92
B	LSPP	74	73	74
B	HSPP	93	90	90
B	HSPP-CD	93	93	89
C	PES	94	96	89
C	CA	96	92	90
C	LSPP	90[a]	10[a]	45[a]
C	HSPP	90	96	58
C	HSPP-CD	90[a]	85[a]	80[a]
D	PES	96	94	90

TABLE IV (cont'd)

Resin Coated on Transfer Film	Transfer Film	75° Specular Gloss of Paper 38#	60#	279#
D	CA	94	98	91
D	LSPP	88	90	80
D	HSPP	90	88	78
D	HSPP-CD	92	90	86

a - difficult pull

The results of Table IV show the excellent gloss provided in general to the paper substrates by the transfer coating method employing the exemplified resins and the PES, CA, and untreated HSPP transfer films. While unsatisfactory gloss and/or difficult pull was exhibited when LSPP was employed as a transfer film, LSPP was shown to be useful when employed in conjunction with Resin D on the two lower basis weight paper stocks. Varying results were also obtained when corona discharged HSPP was employed as a transfer film. The treated film was as useful as the untreated film in some instances providing excellent transfer and gloss with Resins B and D; poor transfer was exhibited with Resins A and C.

Part B.

The process of Part A was repeated by transferring Resins B and D onto the paper substrates, with the exception that the transfer films evaluated were PVD/PES, PE/PES, and PE. In all cases, except where indicated, the transfer film was easily peeled from the paper substrate. The gloss results are given in Table V.

TABLE V

Resin Coated on Transfer Film	Transfer Film	75° Specular Gloss of Paper		
		38#	60#	279#
B	PVD/PES	96	96	90
D	PVD/PES	96	98	92
B	PE/PES	7[a]	15[a]	18[a]
D	PE/PES	96	98	94

TABLE V (cont'd)

Resin Coated on Transfer Film	Transfer Film	75° Specular Gloss of Paper		
		38#	60#	279#
B	PE	20[a]	11[a]	24[a]
D	PE	—[b]	0[a]	0[a]

a - transfer film was very difficult to remove
b - transfer film was fused

The results of Table V show that PVD/PES was a useful transfer film for all paper substrates in conjunction with both resin coatings while PE was not useful in the transfer of the resins at the lamination temperature employed and PE/PES was only useful in the transfer of Resin D.

Part C.

The process of Part A was repeated by transferring various resins from polyester (coated at 2.5 lb. (1.13 kg.)/ream) to the 38# ground wood paper. Unless otherwise noted the coatings were transferred employing a nip temperature of 225°F (107°C). The gloss results are given in Table VI.

TABLE VI

Resin Coated on PES Transfer Film	Resin Description	Tg°C of Resin	75° Specular Gloss of Paper
Resin E	Vinyl acetate/maleic acid resin in aqueous emulsion	+29	89
Resin F	Polyvinyl acetate homopolymer in aqueous emulsion containing a dextrin stabilizer.	+37	90
Resin G	Vinyl acetate/butyl acrylate resin in aqueous emulsion	+ 3	94[a]
Resin H	Vinyl acetate/butyl acrylate/N-methylol acrylamide resin in aqueous emulsion.	- 2	77
Resin I	Vinyl acetate/N-methylol acrylamide resin in aqueous emulsion.	+29	84[b]

TABLE VI (cont'd)

Resin Coated on PES Transfer Film	Resin Description	Tg°C of Resin	75° Specular Gloss of Paper
Resin J	Vinyl acetate/dimethyl maleate/N-methylol acrylamide resin in aqueous emulsion. . .	+42	76
Resin K	Butyl acrylate/styrene/methyl methacrylate/methacrylic acid resin in aqueous emulsion.	+15	95
Resin L	Butyl acrylate/acrylonitrile/methyl methacrylate/N-methylol acrylamide/itaconic acid resin in aqueous emulsion. .	+ 7	82
Resin M	Blend of methyl methacrylate/styrene/butyl acrylate and styrene/acrylic acid resins in aqueous emulsion	+55	102[c]
Resin N	Blend of 100 parts methyl methacrylate/butyl acrylate resin and 30 parts methylmethacrylate/butyl acrylate/acrylic acid resin in aqueous emulsion	+25	96
Resin O	Blend of butyl acrylate/styrene and styrene/acrylic acid resins in aqueous emulsion	−15	—[d]
Resin P	Ethylene/vinyl acetate resin in aqueous emulsion.	0	67
Resin Q	Ethylene/vinyl acetate resin in aqueous emulsion.	+18	87
Resin R	Methyl methacrylate/butyl acrylate/acrylic acid resin in toluene/alcohol . .	+27	89

a - no transfer obtained at 225°F, however 100% transfer obtained at 160°F (71°C.).
b - partial transfer obtained at 225°F (107°C.), however 100% transfer obtained at 200°F (93°C.).
c - paper was unacceptably brittle.
d - no transfer obtained at 225° and 160°F. (107° and 71°C.).

The results show that the transfer process may be conducted with thermoplastic resins of varying Tg's. Resin M (Tg +55°C) provided excellent gloss but was unacceptably brittle. Lower Tg (0° or less) resins H and P were transferrable, however the gloss values provided were low. Such low Tg resins also provide poor block resistance. Resins I and J provided unacceptable gloss, however, by adjusting the coating weight and/or nip temperature, acceptably high gloss may be obtained.

EXAMPLE 4

This example illustrates the correlation which exists between the gloss of a paper substrate before and after metallization.

The dry transfer method described in Part A of Example 3 was repeated by transferring a thermoplastic resin from polyester (coated with 2.5 lb. (1.13 kg.)/ream of the resin) to the 38# ground wood paper. Thereafter the coated papers were vacuum metallized by conventional laboratory methods. The resins employed were Resin A (previously described) and Resin S (described below):

Resin S -Styrene/butyl acrylate/N-methylol acrylamide/methacrylic acid resin (Tg +40 C.) in aqueous emulsion .

The gloss results of the paper after resin transfer and after subsequent metallization are found in Table VII.

TABLE VII

Resin Coated on PES Transfer Film	75° Specular Gloss of Paper After Resin Transfer	After Metallization
A	99	>100
S	98	>100

The results show that papers having high gloss will provide highly reflective papers after metallization.

Example 5

This example illustrates the effect the Tg of the resin coating to be transferred has on the temperatures and pressures required for lamination in order to practice the dry transfer method of the present invention.

Resins having Tg's of +5 to +40°C were coated at 2.5 lb (1.13 kg.)/ream on polyester, dried for 2 minutes at 200 F (93°C) and then laminated with 18# paper (18 lb. (8.2 kg.)/ream machine glazed bleached groundwood) employing a Faustel laminator at varying temperatures and pressures. After lamination the polyester transfer film was pulled away from the paper. The transfer efficiency was then evaluated as follows:

NT - no transfer
PT - partial transfer
T - complete transfer

The results may be found in Table VIII.

TABLE VIII

Temperature °C	Pressure (psi)	Resin (Tg°C) G (+3)	K (+15)	A (+40)
60°	40	NT	NT	NT
	100	NT	NT	NT
77°	100	NT	PT	NT
82°	100	NT	T	NT
93°	100	T	T	PT
99°	40	PT	T	PT
	80	T	T	T
107°	40	PT	T	PT
	60	T	T	PT
	80	T	T	T
116°	40	T	T	T

The results show that laminations with resins having lower Tg values may be accomplished at lower temperatures in comparison to the temperatures required when higher Tg resins are employed. Moreover, lower lamination temperatures may be employed at higher pressures.

Similar variations are expected for the useful lamination temperatures and pressures necessary to practice the wet transfer coating process as well as the direct coating method employing an interleaving film.

EXAMPLE 6

This example illustrates the recyclable use of a transfer film in the dry transfer process of the present invention.

PES was coated with 2 lb. (.91 kg.)/ream of Resin A and laminated with the 38# paper at 210°F (99°C) according to the dry transfer process of Example 3. The process was repeated ten times with the same piece of PES used each time. After 10 recycles, no appreciable build up of coating residue was present on the PES and the papers all exhibited acceptably high gloss.

Similar results are expected with other transfer films which satisfactorily act as transfer agents for a given resin. The recyclability of transfer films employed in the wet transfer coating process as well as that of interleaving films employed in the direct coating process is expected with similar results.

EXAMPLE 7

This example describes the preparation of a high gloss paper substrate by the wet transfer method of the present invention.

One surface of a transfer film was coated with Resin A" (Resin A containing 7% ethylene glycol momobutyl ether acetate obtained from Union Carbide as Butyl Cellosolve® Acetate). The coating weight was 2.5 dry lb. (1.13 kg.) resin/ream. A paper substrate was placed on top of the wet resin-coated surface of the transfer film. The paper/film laminate was run through a nip roller at 210°F (99°C) according to the procedure of Example 3. The three paper substrates as well as the seven transfer films employed are described in Example 1. In all cases the resin coatings were not dried prior to or subsequent to lamination. The gloss results are given in Table IX. In all cases, except where indicated, the transfer film was easily peeled from the paper substrate.

TABLE IX

Resin Coated on Transfer Film	Transfer Film	75° Specular Gloss of Paper		
		38#	60#	279#
A"	PES	94	96	86
A"	PVD/PES	98	96	92
A"	LSPP	86[b]	92	81[b]
A"	CA	95	97	92
A"	PE	82[b]	7[b]	84[a]
A"	PE/PES	—[c]	80	60
A"	HSPP	90	94	63
A"	HSPP-CD	96[a]	70[a]	62

a - difficult to peel
b - very difficult to peel
c - no release

The results show that in general, excellent results were obtained when the transfer film was PES, PVD/PES and CA.

The transfer film, nip temperature and basis weight of the paper will all affect the optimimum conditions for obtaining a high gloss paper. Given that the process was successful for a resin and one basis weight paper would indicate that by adjusting the lamination conditions, other paper substrates may be successfully coated.

EXAMPLE 8

This example directly compares the gloss of paper substrates coated by the dry and wet transfer coating methods with a given resin.

One surface of transfer film (PES) was coated with a resin at a coating weight of 2 lb. (0.91 kg.)/ream. The 38# paper substrate was placed on top of the resin-coated PES immediately or after the coating had dried for 2 minutes at 200°F (93°C). The paper/film laminate was run through a steel on felt-covered steel nip roller set at 270°F (132°C) and 5000 psi with the uncoated side of the transfer film in contact with the heated steel roll. After exit from the nip, the transfer film was immediately peeled away.

In addition to Resins A, B, and S (described above), Resin T was also evaluated:

Resin T -Vinyl acetate/vinyl alcohol (Tg +32°C) resin in aqueous emulsion.

In the wet transfer of aqueous resin A, the coating contained 7% of the coalescent Butyl Cellosolve® Acetate.

The gloss results obtained by both methods may be found in Table X.

TABLE X

Resin Coated on PES Transfer Film	75° Specular Gloss of Paper: Dry Transfer Method	75° Specular Gloss of Paper: Wet Transfer Method
A	98	96
B	93	93
S	97	95
T	94	82

The results show that both transfer methods provided papers with excellent gloss.

Summarizing, this invention is seen to provide high gloss papers suitable for vacuum metallization.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Claims

1. A direct coating process for the manufacture of a high gloss paper suitable for vacuum metallizing comprising the steps of:

a) laminating an interleaving film and a coated surface of a paper substrate, said substrate being coated with a thermal resin coating comprising a thermoplastic resin having a Tg of greater than 0 to less than +50°C, wherein during said lamination sufficient heat and pressure are employed to first render the thermoplastic resin flowable and thereafter nonflowable; and

b) separating the interleaving film from the resin-coated paper substrate whereby providing the high gloss resin-coated paper substrate having a 75° specular gloss of at least about 85, said gloss after lamination being higher than the gloss of the coated paper substrate prior to lamination.

2. The direct coating process of Claim 1, wherein the paper substrate is coated with about 1 to 4 pounds of thermoplastic resin per 3000 ft.^{2}.

3. The direct coating process of Claim 1, wherein the thermoplastic resin is a polymer or blend of polymers consisting essentially of monomers selected from the group consisting of styrene, butyl acrylate, ethyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, vinyl acetate, N-methylol acrylamide, acrylonitrile, ethylene, and vinyl alcohol, maleic acid, dimethyl maleate, and monoethyl maleate.

4. The direct coating process of Claim 1, wherein the thermoplastic resin has a Tg of about +3 to +45°C.

5. The direct coating process of Claim 1, wherein the interleaving film is selected from the group consisting of a coated or uncoated polyester, a coated or uncoated polyolefin, and a cellulose ester.

6. The direct coating process of Claim 5, wherein the interleaving film is selected from the group consisting of polyester, polyvinylidene chloride-coated polyester, polyethylene coated polyester, polypropylene, polyethylene, and cellulose acetate.

7. The direct coating process of Claim 5, wherein the interleaving film is capable of reuse.

8. A highly reflective metallized paper substrate prepared by vacuum metallizing the high gloss resin-coated paper substrate of Claim 1.

9. A transfer coating process for the manufacture of a high gloss paper suitable for vacuum metallizing comprising the steps of:

a) laminating a paper substrate and a coated surface of a transfer film, said transfer film being coated with a thermal resin coating comprising a thermoplastic resin having a Tg of greater than 0 to less than +50°C, wherein during said lamination sufficient heat and pressure are employed to first render the thermoplastic resin flowable and thereafter nonflowable whereby transferring the thermal resin to the paper substrate; and

b) separating the transfer film from the resin-coated paper substrate whereby providing the high gloss resin-coated paper substrate having a 75° specular gloss of at least about 85.

10. The transfer coating process of Claim 9, wherein the transfer film is coated with about 1 to 4 pounds of thermoplastic resin per 3000 ft.^{2}.

11. The transfer coating process of Claim 9, wherein the thermoplastic resin has a Tg of about +3 to +45°C.

12. The transfer coating process of Claim 9, wherein the thermoplastic resin is a polymer or blend of polymers consisting essentially of monomers selected from the group consisting of styrene, butyl acrylate, ethyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, vinyl acetate, N-methylol acrylamide, acrylonitrile, ethylene, vinyl alcohol, maleic acid, dimethyl maleate, and monoethyl maleate.

13. The transfer coating process of Claim 9, further comprising prior to the laminating step, coating the transfer film with the thermal resin coating in solution or dispersion and drying the surface of the coated transfer film.

14. The transfer coating process of Claim 9, wherein the transfer film is selected from the group consisting of a coated or uncoated polyester, a coated or uncoated polyolefin, and a cellulose ester.

15. The transfer coating process of Claim 14, wherein the transfer film is selected from the group consisting of polyester, polyvinylidene chloride-coated polyester, polyethylene coated polyester, polypropylene, polyethylene, and cellulose acetate.

16. The transfer coating process of Claim 14, wherein the transfer film is capable of reuse.

17. A highly reflective metallized paper substrate prepared by vacuum metallizing the resin-coated paper substrate of Claim 10.

18. A process for the manufacture of a highly reflective metallized paper comprising the step of vacuum metallizing a resin-coated paper substrate having a 75° Specular gloss of at least 85, said resin-coated paper substrate being prepared by

a. a direct coating method wherein an interleaving film and the resin-coated surface of the paper substrate are laminated employing sufficient heat and pressure to first render the thermoplastic resin flowable and thereafter nonflowable, the interleaving film being removed prior to vacuum metallization; or by

b) a transfer coating method wherein a resin-coated surface of a transfer film and a paper substrate are laminated employing sufficient heat and pressure to first render the thermoplastic resin flowable and thereafter nonflowable whereby the thermoplastic resin is transferred to the paper substrate, the transfer film being removed prior to vacuum metallization; wherein a thermal resin coating comprising a thermoplastic resin having a Tg of greater than 0 to less than +50°C. is employed as the resin-coating.

19. The process of Claim 18, wherein the thermoplastic resin has a Tg of about +3 to +45°C and is applied at a basis weight of 1 to 4 pounds per 3000 ft^2; wherein the interleaving and transfer film are selected from the group consisting of a coated or uncoated polyester, a coated or uncoated polyolefin and a cellulose ester.

20. The process of Claim 19, wherein the thermoplastic resin is a polymer or blend of polymers consisting essentially of monomers selected from the group consisting of styrene, butyl acrylate, ethyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, vinyl acetate, N-methylol acrylamide, acrylonitrile, ethylene, vinyl alcohol, maleic acid, dimethyl maleate, and monoethyl maleate.