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(54) Title: RELEASABLE POLYESTER HIGH GLOSS METAL TRANSFER FILM

(57) Abrégé/Abstract:

A carrier film of thermoplastic polyester has releasable metal adhesive properties suitable for a metal transfer in which the polyester film is metalized and the metal layer is subsequently transferred to a permanent adhesive-coated substrate. The metal layer is in direct contact with the polyester carrier film and no intermediate release layer is present. Desired metal adhesion is provided by dispersing a suitable surfactant, and optionally, a hydrocarbon wax, uniformly into the polyester film. Surfactant on the outer surface of the carrier film modifies metal adhesion to the polyester such that the metal can be removed in a metal transfer operation.

## ABSTRACT OF THE DISCLOSURE

A carrier film of thermoplastic polyester has releasable metal adhesive properties suitable for a metal transfer in which the polyester film is metalized and the metal layer is subsequently transferred to a permanent adhesive-coated substrate. The metal layer is in direct contact with the polyester carrier film and no intermediate release layer is present. Desired metal adhesion is provided by dispersing an suitable surfactant, and optionally, a hydrocarbon wax, uniformly into the polyester film. Surfactant on the outer surface of the carrier film modifies metal adhesion to the polyester such that the metal can be removed in a metal transfer operation.

## RELEASABLE POLYESTER HIGH GLOSS METAL TRANSFER FILM

## FIELD OF THE INVENTION

[001] This invention relates to polyethylene terephthalate (PET) films with release properties suitable for transferring metal to substrates, such as paperboard. More 5 specifically it relates to a metalized PET film able to receive, carry, and transfer onto a substrate a metal layer directly in contact with the PET layer of the film.

## BACKGROUND OF THE INVENTION

[002] Polymeric films such as PET film are commonly used to transfer metal to paperboard and other substrates for use in packaging, greeting cards, and similar product 10 applications where it is desirable to give the product a metallic appearance. The technique of transferring metal from film to another substrate is used where it is not practical to metalize such substrates directly.

[003] One typical metal transfer technique uses a metalized conventional polymeric film and bonds the complete metalized film structure to the substrate. Typical methods for 15 depositing metal onto the polymeric film include vapor and sputter metallization processes. Such deposition techniques typically create strong bonds between the metal and the film. Because metal does not readily separate from the polymeric layer of the film, in the transfer procedure the paperboard substrate becomes permanently bonded to the metalized polymeric film. This can create excessive non-recoverable scrap since the resulting 20 laminate, for example generated by post-consumer packaging disposal, can not be easily recycled.

[004] Another technique that is well known and practiced in industry is to create a carrier film that can be used to transfer a metal layer to paperboard and other substrate materials. The carrier film is created by coating a layer of release material on the base polymeric film 25 in a secondary, separate process from producing the base polymeric film. Subsequently, and in an entirely separate third process, a metal layer is deposited onto the release layer for example by via vapor or sputter metallization. The individual steps may be carried out at different locations by different converters. A disadvantage is that an extra processing step is required, in particular the step of applying a release layer. A need exists for biaxially

oriented polyester films that can transfer metal from a layer deposited onto the carrier film surface to another substrate without the need for costly coatings between the metal layer and the carrier film surface.

[005] The primary function of the release layer is to provide appropriate adhesion between 5 the polymeric film surface and the metal layer. The adhesion of the metal to the film surface should be strong enough to endure handling in manufacture, packaging, shipping, etc. prior to metal transfer. However, adhesion should be sufficiently weak that the metal layer cleanly separates from the carrier film surface when contacted with the substrate.

[006] There is a need for a method of metal transfer from a polymeric film to a substrate in 10 which a metal layer can be applied directly onto the polymeric film and in which the metal layer readily releases and separates from the film. It is desirable to have a carrier film that does not have an added release layer on the surface of the polymeric film. It is further desired to have a carrier film for metal transfer in which the base layer is a single polymeric composition that can be recycled after the metal has been transferred. Still further it is 15 desired to have a polyester-based carrier film and transfer film that is free of a non-polyester release layer.

[007] Basically, metal is transferred by contacting an adhesive-coated substrate with the metal layer side of the polymeric carrier film composite and then peeling the polymer away to leave the metal on the substrate. The ability to make the transferred metal on the 20 substrate highly glossy is very desirable. However, generating a high gloss appearance after removing the polymeric film is made problematic by conventional film "anti-blocking" technology. Polymeric film tends to stick to itself and other surfaces, sometimes referred to as "blocking," during various film handling steps of the metal transfer operations. Typically, blocking is reduced by uniformly dispersing fine inorganic particles in the 25 polymer of the carrier film. The particles give the film a rough surface texture that renders the film less susceptible to blocking. Because the metal layer profile conforms to the carrier film surface, after removal of the polymer the transferred metal exhibits a rough surface texture. Unfortunately, surface roughness reduces gloss such that the transferred metal has a low gloss or even matte finished appearance. A very smooth transferred metal surface, for 30 example as might be formed without particles embedded in the polymer, should have high gloss appearance but is impractical to achieve because friction between adjacent polymer film layers makes film handling unmanageable. Thus there is an important need to have a

polymeric film free of a separate release layer that can transfer metal to a substrate with superior gloss.

#### SUMMARY OF THE INVENTION

[008] The present invention provides a single or multi-layered thermoplastic polyester carrier film for metal transfer that is free of a non-polyester release layer. The composition of the thermoplastic polyester carrier film is preferably polyethylene terephthalate ("PET"). At least one surface of the novel carrier film is intended for receiving, carrying and releasing a metal layer in the process of transferring the metal layer to a substrate, such as paperboard. The metal receiving surface of the polyester carrier film has suitable metal adhesion and release properties that result from the incorporation of one or more release agents into the polyester carrier film metal-bearing layer.

[009] In one aspect, the release agent is a surfactant. The surfactant can be an anionic surfactant, a nonionic surfactant or a combination of anionic and nonionic surfactants. The surfactant is dispersed within the carrier film metal-bearing layer. In another aspect the release agent in the novel polyester-based carrier film is a hydrocarbon composition wax.

[010] Accordingly, the present invention provides a polyester carrier film for use in metal transfer, the film having a total thickness of about 4 - 75  $\mu\text{m}$ , and consisting essentially of polyester and a release agent of composition and amount effective to provide at least one outer surface of the film with metal adhesion of less than 100 g/in. The total thickness of the polyester film of this invention is preferably about 5 - 75  $\mu\text{m}$ , more preferably about 8 - 50  $\mu\text{m}$ , and most preferably about 10 - 25  $\mu\text{m}$ .

[011] The invention also provides a method of transferring metal to a substrate comprising the steps of: (A) providing a polyester carrier film having a total thickness of 4 - 75  $\mu\text{m}$  consisting essentially of polyester and a release agent, and (B) depositing a metal layer of thickness equivalent to an optical density in the range of up to about 4 in direct contact with an outer surface of the polyester carrier film, in which the release agent is of composition and amount effective to provide metal adhesion between the outer surface and the metal layer of about 1-100 g/in. Preferably the optical density of the metal layer is about 0.01 - 4, and more preferably about 0.4 - 3.3. Surface resistivity of the exposed side of the base layer

is not critical, however, it typically is less than  $1 \times 10^{17}$  ohm/square. The carrier film can be a composite of multiple polyester sub-layers.

[012] In another aspect, this invention also provides a polymeric carrier film without a release layer and having a metal side surface of the carrier film polymer suitably smooth to enable transfer of a metal layer onto a substrate with resulting high metal surface gloss. Desired smoothness of the metal side surface of the carrier film polymer is obtained by controlling the size and concentration of anti-block agent particles throughout the carrier film polymer including the region of the carrier film distant from, as well as the region near, the side on which the metal to be transferred is placed.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

[013] Fig. 1 is a schematic cross section view of an embodiment of the novel metal transfer film in proximity to an adhesive coated substrate prior to transferring a metal layer.

[014] Fig. 2A is a surface topography map of the skin layer of the film produced with small size dispersed solid particles as further explained in Example 14.

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[015] Fig. 2B is a surface topography map of the skin layer of the film produced with large size dispersed solid particles as further explained in Example 13.

#### DETAILED DESCRIPTION OF THE INVENTION

[016] In certain aspects this invention relates to biaxially oriented coextruded multilayer polyester films that can be readily fabricated, have ease of handling, and metal release properties on at least one outer layer surface, for use in metal transfer processes. To fabricate this highly specialized film with special surface properties any standard method to fabricate co-extruded biaxially oriented multilayer films may be employed. As used herein, the term "polyester carrier film" refers to a film of polyester and release agent according to this invention prior to deposition of a layer of metal thereon. The term "transfer film" refers to a composite of the polyester carrier film with a metal layer of metal deposited on an outer surface of the polyester carrier film. The primary intended use of the novel polyester carrier film is to receive, carry and transfer some or all of the metal from the metal layer onto a surface of a substrate.

[017] The novel polyester carrier film has two sides and has a base layer B of polyester. The polyester carrier film can be monolithic consisting only of layer B, or a composite of multiple layers of polyester. A preferred embodiment of the invention includes at least a two layer coextruded polyester carrier film, that includes at least one outer layer A adjacent one side of base layer B with an optional opposite outer layer C. Other embodiments may include one or more inner layers I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub>...I<sub>n</sub>, positioned between the outermost and B layers, such as an A/I<sub>1</sub>/I<sub>2</sub>/B/C structure, for example. The outermost layers, whether A, B, or C, are sometimes referred to as skin layers. Any layer may contain reclaimed polyester resin.

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10 [018] In the present invention either or both outer surfaces of the skin layers have metal adhesion of less than 100 g/in, preferably less than 50 g/in, and more preferably less than 20 g/in, measured as described in Test Methods section below. The metal adhesion property is achieved by blending into the polyester of the film surfactants that are either ionic, nonionic or a combination thereof. For cost effectiveness it is preferable that the surfactant component is present only in the outermost layer or layers, which are normally thinner than 15 the total thickness of inner layers, i.e., non-skin layers.

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[019] Some examples of nonionic surfactants may be cetostearyl alcohol, stearyl alcohol, oleyl alcohol, cetyl alcohol, pentaethylene glycol monododecyl ether, polyoxypropylene glycol alkyl ethers, octaethylene glycol monododecyl ether, lauryl glucoside, polyoxyethylene glycol octylphenol ethers, octyl glucoside, and decyl glucoside.

[020] Some examples of anionic surfactant may be perfluorooctanesulfonate, perfluorobutanesulfonate, sodium dodecylbenzenesulfonate, sodium sulphate, alkyl benzene sulfonates, dioctyl sodium sulfosuccinate, alkyl ether phosphate, alkyl aryl ether phosphate, sodium stearate; perfluorononanoate, perfluorooctanoate, sodium lauroyl sarcosinate, 25 sodium myreth sulfate, sodium lauryl sulfate, sodium laureth sulfate, and ammonium lauryl sulfate, and more generally aliphatic and aromatic sulphonates.

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[021] There are a number of companies that produce master batches of surfactant compounds in PET for example, T7910 from Toray Industries, Inc. containing sodium dodecylbenzenesulfonate, Tas1125 from Sukano containing an aliphatic sulphonate, or Elecut® S618-A1 from Takemoto Oil and Fat containing a proprietary mixture of nonionic and anionic surfactants.

[022] As presently understood, the parameter that mainly affects the desired degree of metal adhesion between the metal layer and an outermost polyester layer is the surface density, i.e., mass per unit area, of surfactant on the outermost surface of the polyester skin layer when the metal layer is applied. Surfactant that is initially uniformly dispersed within 5 the polyester resin that forms the skin layer will bloom to the surface during the carrier film manufacturing process. The amount of surfactant incorporated in the polyester resin should take the blooming effect into account. That is, as thickness of the skin layer decreases, less surfactant-bearing polyester resin is used, and therefore, less surfactant at any given surfactant concentration in the polyester is available to migrate to the surface.

10 Accordingly, the concentration of surfactant in the polyester resin to achieve a preselected level of metal adhesion should be increased as the thickness of the corresponding polyester layer decreases. The concentration of surfactant by weight in any outer layer should be at least about 0.01 wt%, preferably at least about 0.05 wt%, and more preferably at least about 0.10 wt%. The concentration of surfactant by weight in any outer layer is preferably less 15 than 10 wt%, more preferably less than 5 wt%, and most preferably less than 3 wt%.

[023] An advantageous feature of this invention is that metal adhesion can be controlled to a preselected value within a narrow range by adjusting the concentration of release agent in the polyester carrier film. Preferably the metal adhesion can be controlled to within a range of  $\pm 10$  g/in of a target metal adhesion value. Pursuant to the guidelines just 20 described, the actual amount of surfactant will be adjusted depending upon the thickness of the skin layer to provide a suitable metal adhesion value and should be determined by one of ordinary skill in the art without undue experimentation.

[024] Juxtaposition of the elements discussed above can be understood with reference to Fig. 1. The figure shows a cross section of an embodiment of a metal transfer film **10** in 25 proximity to a substrate **15** coated with a layer of adhesive **11**. The novel metal transfer film has a multilayer composite polyester carrier film **1** of three substrata **2**, **4** and **6**, in the illustrated embodiment. Base layer **2** is a primary component layer of the multilayer carrier film **1**. Adjacent and directly in contact with the base layer are layers **4** and **6**. Being outermost layers of the composite polyester carrier film, layers **4** and **6** are designated as 30 skin layers.

[025] The figure shows that a metal layer **8** is deposited in direct contact with the side of skin layer **6** opposite the base layer **2**. In traditional metal transfer films, there is an extra

release layer positioned between the metal layer **8** and the outermost layer **6** the function of which has been described above. The novel metal transfer film does not have a separate and distinct release layer.

[026] In use, an adhesive layer 11 coated onto a receiving substrate 15, is brought in contact with the metal layer **8** of the metal transfer film **10**. The metal layer is then bonded to the substrate by the adhesive layer and thereafter the base layer 1 is stripped away from the metal layer. This process leaves the metal layer attached to the receiving substrate by the adhesive layer 11. An advantage of the novel metal transfer film is that all of the layers of the carrier film consist essentially of polyester. By "consists essentially of" is meant that the polymer content of the film is at least about 99 wt% and preferably exclusively polyester. The film can include, usually in small proportion to the polymer, and in addition to the operative surfactants, other non-polymeric ingredients such as stabilizers and additives that do not materially affect the novel aspects of the invention. Only the polymeric film remains after stripping the metal layer. Because the polymeric component of every layer of the carrier film is the same polymer, preferably PET, the residual carrier film can be recovered and recycled as a raw material for use in the same or a different end use application. Additional aspects, features and advantages of the invention will be explained, below.

[027] In a primary aspect, the present invention calls for providing a metal transfer film consisting of a carrier film of predominantly polyester and a metal layer directly in contact with the carrier film. A release layer as used in traditional metal film transfer operations is not present between the carrier film and the metal layer. The normally very high metal adhesion of the polymeric carrier film is adjusted to a preselected lower adhesive strength by incorporating a suitable release agent into the carrier film polymer. In accord with the principles disclosed herein, it is possible to incorporate into a polyester layer an amount of release agent effective to provide a desired degree of metal adhesion called for by a converter in a metal transfer film process. The preferred release agent is a surfactant or combination of surfactants. Preference is given to use of a mixture of anionic and nonionic surfactants. Optionally, hydrocarbon wax, such as paraffin wax, can be added to any or all layers of the film. Generally, the greater amount of release agent incorporated into the metal-contacting layer of the carrier film at a given layer thickness, the lower the metal adhesion and the more easily the metal strips from the transfer film.

[028] The polymeric carrier film can be monolayer or it can be a composite of multiple layers of polyester. In a multilayer structure the carrier film layers are fused adjacent to each other, preferably by a thermal fusion process such as coextrusion such that layers will not delaminate under metal transfer film processing conditions. A so-called A/B multilayer 5 structure with a base layer (layer "B") and a skin layer (layer "A") is preferred. The skin layer is the layer in contact with the metal layer. An A/B/C structure is an alternately preferred structure for the novel polyester-based carrier film in which the "C" layer is a skin layer on the base layer surface opposite the A layer. Preferably the base layer is the predominant layer in thickness and bulk of the whole polyester-based carrier film. In a 10 multilayer composite structure, the surfactant release agent particles should be present at least in the metal-contacting layer, but may also be present in other layers of the carrier film.

[029] The controlled metal release property of the polyester carrier film is obtained by incorporating surfactant into the carrier film, and preferably in only one or more of the outer 15 layers. Preferably the surfactant is an anionic surfactant, a nonionic surfactant or a combination thereof. Metal adhesion of PET without an incorporated surfactant release agent is typically much greater than 150 g/in. Incorporation of surfactant according to this invention can provide metal adhesion of less than 100 g/in, preferably about less than 50 g/in, and more preferably less than 20 g/in.

20 [030] In some end use applications it is desirable to transfer effectively all of the deposited metal whereas in other cases it is desirable to transfer only specific portions of the metal. According to this invention, all or any selected parts of the metal deposited onto the surface of the base layer may be readily transferred to the substrate utilizing well known techniques.

25 [031] Typical schemes for a metal transfer process call for providing carrier films from film "converters", i.e., suppliers and processors of film who provide, treat and/or modify the polyester film in secondary operations that are entirely separate from and subsequent to the manufacture of the polyester film. Such polyester carrier films include a non-polyester composition release layer coating applied to an outer surface of a monolithic polyester film .

30 Those films are in turn metalized on the release layer via a process such as vapor deposition or sputtering. The metal transfer film of polymeric base layer/release layer/metal layer structure is used to apply metal to substrate products such as paperboard that are not directly

metalizable by conventional means. The paperboard converters specify, and the film converters supply, desired degrees of metal adhesion based on the nature of the product and the metal. An advantage of this invention is the ability to control the bond strength of the metal to the PET base layer to a preselected value within the range of metal adhesion 5 normally desired by paperboard converters. The metal transfer film of this invention does not have a special, non-polyester-based release layer between the base layer and the metal. Thus the polyester base film metalizing converter can apply the metal in direct contact with the polyester base layer of the carrier film. An intermediate release layer typically applied as a coating on the base film is not required. This feature provides many productivity 10 enhancing and cost saving benefits. It is especially valuable that the concentration of surfactant and optional wax release agent incorporated into the polymeric base layer can modify the metal adhesion of the carrier film to match the different specifications for diverse metal transfer end use applications of metal transfer converters. This invention further can provide metal adhesion with precision of narrow tolerance limits of the metal 15 transfer converters' target.

[032] Processing of film at commercial scale normally demands moving, rolling and unrolling, among other procedures, of wide webs of the film at high speed. In such unit operations the webs have opportunities to come in contact with each other and with the processing equipment. Friction can cause the contacting webs to stick together or to jam the 20 equipment consequently generating substantial waste product and lost productivity. Stagnant film, for example, when stored on a heavy roll for extended time, can also stick to itself. This condition is known as "blocking" in the industry. Giving a rough texture to the potentially contacting surfaces of the film is a way to control friction and thereby partition the webs from themselves and machinery. A preferred technique for roughening the 25 surface involves embedding fine, solid, anti-blocking agent particles into a layer of the film. The particles at and near the sides of the film form irregularities that make the surface rough.

[033] Texture of the carrier film surface in contact with the metal can shape the metal layer surface transferred onto the substrate. Degree of surface can affect visual appearance 30 of the finished metal-coated substrate product. Usually, rough surface texture gives a dull, matte finish, and conversely, a smooth surface texture gives a shiny, gloss finish. As used herein, a smooth surface is defined as having surface roughness Ra of about 100 – 150 nm.

A more smooth surface has Ra of about 50 – 100 nm, and a very smooth surface has Ra of about 5 – 50 nm. A rough surface typically suitable to produce a matte appearance of the transferred metal, has an Ra of about 200 – 500 nm. The symbol “Ra” means a surface roughness measured with a “surfcoorder” analytical device, for example, a SurfCorder SE 5 500 Surface Roughness Measuring Instrument (Kazaka Laboratory Ltd. Tokyo, Japan).

[034] A problem addressed by this invention is the creation of a very highly glossy surface effect, referred to herein as “high metal surface gloss” of a substrate onto which a metal layer is applied by peeling away the carrier film from a metal transfer film. Thus a high metal surface gloss has a remarkably shiny, bright metallic appearance to the visual 10 observer. The invention provides for producing a high metal surface gloss appearance using a metal transfer film without a release layer between the carrier film and the metal layer being transferred.

[035] Total reflection of light impinging on an object is characterized by the two components of specular reflection and diffuse reflection. Gloss is an optical property of a 15 surface related specular reflection which is mirror-like reflection of light in a specular direction at an angle equal to the incident angle. Diffuse reflection is light reflected at all angles. Factors that affect gloss are the refractive index of the illuminated object, the incident angle of light impinging on the object, and the surface topography (i.e., roughness) of the object. Respecting topography, the fraction of reflection that is specular increases 20 with smoothness. Increased roughness caused by irregularity of the surface topography decreases the fraction of specular reflection. Roughness can contribute to reduced specular reflection in two ways. Firstly, curvature of the irregular surface contour scatters impinging light by reflecting at different angles. Secondly, specularly reflected light from surface locations at different elevations creates a canceling effect due to mutual specular beam 25 interference. The first aspect can make the illuminated object appear dull. The second aspect has a light attenuating effect. The presence of fine, solid particles dispersed in a layer of polymeric film causes localized variations in the thickness of the film and thereby affects surface roughness. Thus incorporation of selected size distributions of particles at selected concentrations is a primary technique for controlling surface roughness of a 30 film. The term “high metal surface gloss” means that the finished, metal-coated surface of the substrate exhibits specular reflection gloss of at least about 830 gloss units (“GU”) by glossmeter measurement at 60° angle. The ability to achieve high metal surface gloss

product is enhanced by utilizing a metal transfer film (i.e., polymeric carrier film with metal coating) that exhibits surface smoothness of at least about 860 gloss units measured at 60° angle and at least about 1300 gloss units measured at 20° angle. Moreover, the smoothness of the metal-contacting side of the polymeric carrier film prior to metal deposition should 5 correspond to specular reflection gloss of at least 160 gloss units measured by glossmeter at 60° angle, more preferably at least about 180 gloss units at 60° angle.

[036] It also has been found that a high metal surface gloss can be obtained by transfer of metal from the novel polymeric carrier film of which the polymer-to-metal surface has a Surfcooler surface roughness, Ra, preferably at most about 50 nm, and more preferably at most 10 about 30 nm, still more preferably at most about 25 nm, and most preferably at most about 15 nm. An Ra value as low as about 0 nm is theoretically suitable to provide the desired gloss but is impracticable to achieve. Preferably Ra can be at low as about 12 nm and more preferably about 15 nm. Similarly acceptable gloss performance is obtained when the polymeric carrier film surface has a stylus surface roughness value, Sra, in the range of about 0-30, preferably 15 about 10-30 and more preferably about 10-15. Stylus surface roughness is determined using a stylus type contact profilometer, for example a Surfcooler ET-30 HK surface topography instrument (Kosaka Laboratory Ltd, Tokyo Japan). Most preferably, the carrier film surface should have both Ra of about 12 nm - 30 nm and an Sra value of about 10-30.

[037] Carrier film surface roughness that provides high metal surface gloss is achieved by 20 controlling the size and concentration of anti-block agent particles dispersed in the polymeric film. Theoretical Ra and Sra values of about 0 should be achieved from a polymeric film having no anti-block agent particles present. This condition is not practicable because substantially complete absence of anti-block agent particles renders surface friction of the carrier film too high for handling the film in commercial scale industrial fabrication and 25 processing equipment. Thus for practical purposes, some anti-block agent particles should be uniformly dispersed in the polymer of the carrier film. Of course, if the particle size and/or concentration of any particles for anti-block or other purposes, such as pigmentation, is too great, the surface of the transferred metal will be too rough and finished appearance will be less glossy than high metal surface gloss.

30 [038] For adequate surface roughness to enable manageable handling of the film and yet to obtain surface smoothness consistent with high metal surface gloss the nominal particle size of anti-block particles suitable for use in this invention is preferably about 0.1  $\mu\text{m}$  to about

2.4  $\mu\text{m}$ , more preferably about 0.1  $\mu\text{m}$  to about 2.0  $\mu\text{m}$  and most preferably about 0.1  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ , and the concentration of the anti-block particles is preferably about 0.01 wt% to about 1.0 wt%, and more preferably about 0.01 wt% to about 0.05 wt%.

[039] As mentioned above, it is contemplated to use multi-layer composites, e.g., A/B/C layered structure, for the polymeric carrier film. Applying a layer of metal, M, to an exposed surface of the carrier film thus provides a metal transfer film with an M/A/B or M/A/B/C structure in which A and C are polymeric skin layers and B is a polymeric core layer. In such situations, it is advantageous to disperse anti-block agent particles of partitioning effective size and concentration only in outermost layers B or C as the case might be. That is, metal-contacting layer A would have no particles and the M/A interfacial surface kept very smooth for highly glossy metal transfer performance.

[040] It can be problematic for obtaining high metal surface gloss after metal transfer if excessively large or high concentrations of particles are present in layers adjacent to, and even distant from, metal contacting skin layer A. Particles are deliberately incorporated into outer layers B or C for anti-blocking purposes. Also particles can be allowed into layer B of an A/B/C structure when all or part of the polymer stream of layer B is scrap or recycled polymer that is contaminated with solid particulate matter. Excessively large particle sizes and concentrations tend to protrude into skin layer A and can adversely affect roughness of the metal contacting surface. Caution should be exercised to avoid too large or concentrated anti-block agent particles in layers B and C that will cause surface of layer A roughness parameters Ra and Sra to exceed the preferred limits specified above.

[041] This invention further advantageously provides the ability to utilize an A/B/A polymeric carrier film. This structure can be produced economically by unit operations equipped with only two extruders, i.e., one for each of layers A and B compositions. This set up can simply and directly make an A/B carrier film. Alternatively, flow from a single skin composition extruder can be split to feed A composition onto both sides of B to yield the A/B/A structure. The surface of the metal-contacting layer A should be smooth enough to enable transferred metal with high metal surface gloss. The surface of the non-metal-contacting layer A should be rough enough to provide manageable film handling. It has been found that an A/B/A composite carrier film suitably satisfying both gloss and film handling criterial can be made when Ra and Sra parameters of layer A are within the ranges specified above.

[042] Preferably according to this invention anti-block agent particles should be smaller than about 1  $\mu\text{m}$ . However, when the core and/or skin layer on the metal-contacting side of the carrier film are suitably thick to mask the effect of large concentrations or large size of particles dispersed in a layer distant from the metal-containing side, larger particles can be used. For effective masking, the total thickness of layers B, and C, preferably should be at least as great as the largest particles in such distant layers. For example, in a metal/skin layer/core layer/skin layer metal transfer film M/A/B/C, larger size particles, i.e. particles nominally bigger than 1  $\mu\text{m}$ , and larger concentrations of particles can be tolerated only in layer C, provided that layers A and B have a combined thickness large enough to smooth perturbations of the M/A interfacial surface that would otherwise result from the particles in layer C.

[043] According to this invention, the overall thickness of the carrier film is preferably about 5  $\mu\text{m}$  to about 75  $\mu\text{m}$ , more preferably about 8  $\mu\text{m}$  to about 50  $\mu\text{m}$  and most preferably about 10  $\mu\text{m}$  to about 25  $\mu\text{m}$ . Thickness of the metal-contacting skin layer A, and, when applicable, skin layer C, should be preferably about 0.5  $\mu\text{m}$  to about 5  $\mu\text{m}$ . Thickness of the core layer is the difference between the total carrier film thickness and the total thicknesses of the skin layers present. Typically, the core layer is the thickest layer of the carrier film. Thickness of the metal layer is typically less than about 4 optical density units that corresponds approximately to 500 angstroms. The metal layer thus adds negligibly to the overall thickness of the metal transfer film. Many types of anti-blocking particles may be used such as silica, calcium carbonate, talc, alumina, or polymeric particles, such as, cross-linked polystyrene, acrylic, polyamide, or combinations thereof.

[044] The smoothness characteristics for a high metal surface gloss quality specified above relate to the surface of the carrier film facing the metal being transferred. The surface of the side of the carrier film opposite the metal-contacting side can be less smooth. The non-metal-contacting side surface can have an Ra of about 5-250 nm, preferably about 5-150 nm, and more preferably about 5-50 nm. The optional wax release agent can be included in one or more film layers to modify the release characteristics of the film provided by the surfactant primary release agent. The wax need not be added to the outer release layer in order to be effective since the wax will migrate from within the film through the outer layers to the surface of the film during stretching and heat setting processes of film making. The wax can be added as a separate additive to the polyester resin when forming a carrier

film layer. A preferred method of adding wax release agent to a specific layer includes recovering a waste or discarded polyester film that originally had a paraffin wax coating. The wax-coated film is recycled by shredding the film to fine particle size, agglomerating the shredded film by use of a bladed centrifuge process, and then re-extruding the wax

5 containing resin into pellets. The resulting recycled resin pellets can be blended with other raw material resin and additional wax, as appropriate to form one or more layers of the polyester carrier film. Typically, the wax is about 0.1-1 wt. % of recycled polyester film. Any wax-containing layer of the novel carrier film can contain up to 100 wt. % of recycled polyester film.

10 [045] Without wishing to be bound by any particular theory, it is contemplated that the primary mechanism for modifying adhesion of the metal layer to polyester of the carrier film is the creation during metalization of a metal oxide layer between the polyester and the pure metal layers. The surfactant at the surface of the polyester carrier film supplies oxygen at this surface. Surfactants containing nitrate ion, sulfate ion, alkyl sulfate ion, sulfonate ion, or alkyl sulfonate ion are very suitable in this regard. Metal deposition methods for metalizing films typically include first evacuating oxygen from vapor, usually air, in the chamber in which metalization is to be carried out. This permits highly pure metal to deposit on and bond with the carrier film polymer. According to this invention, oxygen brought to the polymer surface by the surfactant rapidly (i.e., normally within a few

15 minutes) reacts with the metal to create a layer of metal oxide between the polyester carrier film and the bulk of the deposited metal layer more distant from the surface. The resulting metal oxide layer is less adhesive to the polyester and thus facilitates release of the metal layer during the later metal transfer operation.

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[046] It is thus understood that this invention is particularly well suited to metal transfer operations involving any metals that readily oxidize. Metals commonly used are aluminum, copper, silver, titanium, and a mixture of these.

[047] One preferred embodiment of the novel carrier film is a two layer PET film structure in which one layer is a skin layer with a thickness of preferably about 0.1 - 10 microns, more preferably about 0.2 - 6 microns, and most preferably about 0.3 - 2 microns. The

25 second carrier film layer constitutes most of the the structure thickness that is preferably about 5 - 75 microns, more preferably about 8 - 50 microns, and most preferably 10 - 25 microns. The second carrier film layer optionally contains wax added from ground,

recycled, paraffin wax-coated film. The skin layer has a surface roughness, Ra, of preferably about 5 - 50 nm, more preferably about 5 - 30 nm, and most preferably about 5 - 15 nm.

[048] Another preferred embodiment is a three layer PET film structure in which the non-skin carrier film layer is substantially free of added particles. One or both skin layers have release

5 properties by incorporation of surfactants. The skin layers preferably have a thickness of about 0.1 - 5 microns, more preferably about 0.2 - 3.6 microns, and most preferably about 0.3 - 2 microns. The non-skin carrier film layer can contain wax release agent from addition of recycled paraffin wax coated film. The carrier film has a thickness of about 5 - 75 microns, more preferably about 8 - 50 microns, and most preferably about 10 - 25 microns.

10 [049] The polyester for use in this invention can be prepared by any known method such as by the polycondensation of terephthalic acid or an ester-forming derivative thereof with an alkylene dihydroxyl compound. For example, these polymers can be copolymers of repeating units derived from aromatic dicarboxylic acid aliphatic glycol. Examples of suitable aromatic dicarboxylic acid are terephthalic acid, naphthalenedicarboxyl acid, isophthalic acid and the

15 like. Examples of aliphatic glycol are ethylene glycol, butanediol, neopentyl glycol, trimethylene glycol, cyclohexane dimethanol and the like. Examples of polyesters for use in the invention include copolymers comprising alkylene terephthalate or alkylene naphthalene as the main recurring units in the polymer chain. A preferred polyester is polyethylene terephthalate.

20 [049A] The transferable layer of metal is preferably selected from the group consisting of aluminum, copper, silver, titanium and blends thereof. The transferable layer of metal generally has a thickness equivalent to an optical density of 0.2 to 4. The transferable layer of metal exhibits a specular reflection of at least 830 gloss units measured by glossmeter at a 60° angle.

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## EXAMPLES

[050] This invention is now illustrated by examples of certain representative embodiments thereof, wherein all parts, proportions and percentages are by weight unless otherwise indicated.

[051] Test Methods

30 [052] Thickness: Overall film thicknesses were measured by micrometer using a stack of 10 sheets and dividing the measurement by 10. Measurements were repeated every 9 inches in the transverse direction of the web. The thickness of each coextruded layer of the

multilayer film was calculated by the ratio of the corresponding extrusion flow rate to the total extrusion flow rate of all layers.

[053] Metal Adhesion: Metal adhesion was measured by a 180 degree ethylene acrylic acid polymer peel test consisting of heat sealing an adhesive layer of Dow Primacor® 3300 EAA polymer to the metalized side of the film using a Sentinel Model 12-ASL Sealer at 220°F and 38 psi for 20 seconds. An Instron® 4200-004 tensile test machine was used to measure the peel force to peel away the metal with the adhesive layer at 180 degrees from the metalized surface of the film.

[054] Surface Roughness: Surface roughness ("Ra") was measured by a Surfcoorder Model SE-500 surface roughness measurement instrument. The measurements were repeated 3 times and the average value of Ra was recorded. Surface mapping and Sra roughness analysis was performed according to the HIPOSS (High Precision Optical Surface Sensor) method using a Stylus type surface topography analysis instrument Surfcoorder ET-30 HK, equipped with an SSC Surface Picture Analyzer type SPA-1 and an SSC X-Y chart recorder type RA-XY 4A (all manufactured by Kosaka Laboratory Ltd.)

[055] Surface Resistivity: Surface resistivity was measured with a concentric ring probe from TREK, Inc, Model No. 152 concentric ring probe resistivity meter according to ASTM Standard D 257-99. The testing conditions were 25°C at 50% of relative humidity.

[056] Surface Energy: Surface energy was determined by using the known numerical relationship between surface tension in dynes/ cm of a polymer surface and the contact angle of a pure water drop deposited onto the surface (Zisman correlation). The contact angle was measured using a Contact Angle Meter (from Tantec, Schaumberg, IL) as described in US patent 5,268,733.

[057] Surface gloss: Surface gloss was measured at 60° angle (and at 20° angle where noted) according to ASTM D 523 using a Micro TRI-Gloss Meter from BYK-Gardner. Three individual measurements along the machine direction of film formation (MD) and three along the transverse direction (TD) were conducted. The overall average of all six measurements is reported. The results are expressed in Gloss Units. The measurement results of a gloss meter are related to the amount of reflected light from a black glass standard of defined refractive index that defines a standard gloss measurement value of 100 gloss units. Material to be measured with a higher refractive index than the standard, such

as polymeric film, can have a measurement value above 100 gloss units (GU). Typically, metallic surfaces measure values above about 700 GU at 60° angle and above about 1500 at 20° angle.

[058] Procedure:

5 [059] Three layer PET carrier films having A/B/C layer structure and two layer films having A/B layer structure for the examples were prepared by the following method. PET and ingredients listed in Table I, below, for each layer were blended, dried and then extruded in conventional melt extrusion equipment. To produce base layer B a serial set of single screw extruders was used. Reclaimed PET film was optionally included in this layer. For the  
10 composition of layers A and C, PET plus the other ingredients were mixed and fed through a counter-rotating twin screw extruder and dried via in-line vacuum in the melt zones of the extruder. Extrusion temperatures were in the range of 270°C to 300°C. The melt flow from each extruder was filtered separately and then fed into a melt distributor such that the melt flow from the twin screw extruder was split to form self-supporting film layers A and C that were  
15 overlaid onto opposite sides of the melt flow forming self-supporting film layer B to form an overall A/B/C structure. To produce a two layer A/B structure, the twin screw extruder melt flow was overlaid only on one side of the base layer melt flow. The resulting combined melt flow entered a flat die set at about 270°C. The melt curtain exiting the die dropped and was electro-statically pinned onto a rotating casting roll chilled to about 20°C causing the curtain to  
20 solidify into a continuously moving amorphous sheet. This sheet entered a set of rotating heated rolls of different speeds such that the traveling sheet was oriented about 4 times in the machine direction. Next, this machine-direction oriented sheet traveled into a multi-zone enclosed heated oven, where the film was first preheated to a temperature of about 90°C. In the next zone, at about 165°C, the moving film was oriented about 4 times in the transverse direction, and then heat set at about 240°C. During this orientation or stretching, release agent  
25 blooms to the outer surfaces of the layers A and C of the film. Then the film was relaxed by about 3% in the relaxation zone of the oven. The resulting two layer A/B and three-layer A/B/C films were wound up into rolls as is standard industry practice.

[060] Comparative Example 1

30 [061] A two layer PET carrier film was prepared by coextruding adjacent skin layer A and base layer B. Inert filler particles were dispersed in each of the molten polymer feeds to the film forming unit. Thickness and composition of the layers is shown in Table I. The

concentrations and sizes of the particles gave the outer surfaces of the layers different surface roughnesses. No metal release agent according to this invention was included in the layers. The outer layers had surface resistivity on the order of magnitude of  $10^{16}$  ohms/sq. Analytical results for this and other examples are presented in Table II. The surfaces of 5 layers A and B also had surface energies typical for PET film as indicated by surface tensions of 40 dynes/cm.

[062] The surface of skin layer A was metalized with a layer of aluminum of thickness equal to a measured optical density of 2.5 by metal vapor deposition. Metal adhesion was of the aluminum layer on layer A was measured as 135 g/in. This is a high adhesion 10 strength and would not be suitable for a metal transfer film.

[063] Example 2

[064] A two layer PET carrier film was prepared as in Comp. Ex. 1 with the exception that a release agent surfactant particles of sodium dodecylbenzenesulfonate at concentration 0.48 % was uniformly dispersed into skin layer A. Surface resistivity of layer A was much 15 reduced (order of magnitude of  $10^{11}$  ohms/sq.) and the surface tension increased to surface tension of greater than 53.5 dynes/cm. The carrier film was coated with aluminum to an optical density of 2.5. Metal adhesion was measured to be 45.7 g/in. This represents a significant reduction relative to Comp. Ex. 1. The surface resistivity of layer B lowered slightly (relative to Comp. Ex. 1) but was still at the  $10^{14}$  level.

20 [065] Example 3

[066] The procedure of Ex. 2 was repeated except that a blend of release agent surfactants alkane sulphonate (0.06%) and sodium sulfate (0.003%) was incorporated in skin layer A. Layer A had a surface resistivity on the order of  $10^{16}$ . Following aluminum metalization, 25 metal adhesion was measured to be 26.7 g/in. The transfer film would be suitable for a metal transfer film.

[067] Example 4

[068] The procedure of Ex. 2 was repeated except that aliphatic sulphonate was substituted as the surfactant release agent at 0.015 % in skin layer A. The surface resistivity reduced to a relatively low value of the order of magnitude of  $10^{12}$  ohms/sq. After coating the skin

layer with a 2.5 optical density thickness metal layer of aluminum, the metal adhesion was measured to be a very acceptable value of 11.2 g/in.

[069] Example 5

[070] The procedure of Ex. 4 was repeated except that the concentration of the surfactant release agent was doubled to 0.03 %. Resistivity of layer A dropped to the  $10^{10}$  range. After depositing aluminum to an optical density of 2.5, the metal adhesion was found to also drop to 7.9 g/in. that is very good for many metal transfer operations.

[071] Examples 6 and 8

[072] In these examples the procedure of Ex. 2 was repeated with a mixture of anionic/nonionic surfactants serving as the release agent. In Ex. 6 the concentration of the surfactant was 1.2 % and in Ex. 8 the the concentration was raised to 2.0 %. Again, resistivities of the B layer remained at the  $10^{14}$  level. The surfactant containing layer A showed nearly equal and significant resistivity reduction relative to Ex. 1. After coating with aluminum, metal adhesion of the 1.2 % surfactant sample was well in the range of suitable metal transfer film at 6 g/in. Increasing the concentration to 2.0% surfactant lowered the metal adhesion farther to 5.2 g/in.

[073] Example 7

[074] The procedure of Ex. 2 was repeated except that the polymer of layer A was a blend of 50% virgin PET and 50% Auriga PET resin "8428". The Auriga PET resin contains surfactant. The surface resistivity of layer A did not change from that of Comp. Ex. 1 however, metal adhesion of the carrier film to the aluminum layer did reduce to 33.3 g/in, which is well into the acceptable range for metal transfer films.

[075] Example 9

[076] The procedure of Ex. 2 was repeated with the exception that 0.48% sodium dodecylbenzenesulfonate was added to thicker layer B as well as layer A. Due to the presence of surfactant in both layers, resistivities of both surfaces dropped to the approximate  $10^{11}$  level. After metalization to 2.5 optical density with aluminum, the metal adhesion of layer A was determined to be 6.3 g/in. This result suggests an interaction between the layers in that the effect of the same surfactant at the same level in layer A was much enhanced by the surfactant in the adjacent layer B.

## [077] Example 10

[078] The procedure of Ex. 6 was repeated except that 1.2% mixed anionic/nonionic surfactant was incorporated into thicker layer B as well as in layer A. Comparing this example to Ex. 6, it appears that the analytical results were somewhat analogous to those of Ex. 9. The surface resistivities of both A and B layers dropped by four orders of magnitude relative to Comp. Ex. 1. Additionally, the metal adhesion of layer A of 4.8 g/in. was significantly lower than in Comp. Ex. 1 and slightly lower than 6 g/in. of Ex. 6. Thus there is agreement with the suggestion that some interaction between the layers due to presence of the same release agent surfactant in both on the metal adhesion value of layer A.

## 10 [079] Example 11

[080] The procedure of Ex. 8 was repeated with the exception that the additives composition of layer B was changed. Firstly the 0.3  $\mu\text{m}$  polystyrene particles incorporated into layer B at 0.06% was replaced by 0.3% of 2.4  $\mu\text{m}$  silica particles. Additionally, layer B included 0.05% paraffin wax release agent. Analytical results showed that surface resistivity of layer A dropped similarly as in Ex. 8 to the  $10^{10}$  level and that the metal adhesion reduced to a very low value of 2 g/in. The lower metal adhesion value further supports the suggestion that wax from layer B affects adhesion on the surface of layer A. Example 11 also has a relatively high surface energy of greater than 53.5 dynes/cm.

## [081] Example 12

20 [082] A three layer PET film carrier film is prepared by coextruding an A/B/C composition and structure. Both skin layers A and C have the same calcium carbonate/aluminum oxide particle package for modifying the surface texture and a release agent of mixed anionic/nonionic surfactant at 2.0% concentration. The base layer B includes a silica particle component and 0.013 % paraffin wax release agent. The surface of layer A was metalized with aluminum to a thickness equivalent to 2.5 optical density. The metal adhesion of the carrier film to the metal layer was 5.1 g/in.

## [083] Example 13

[084] A two layer PET carrier film was prepared by coextruding (1) a 1.2  $\mu\text{m}$  thick skin layer A of PET containing 1 wt% mixture of sodium dodecylbenzenesulfonate anionic surfactant a nonionic surfactant, 0.33 wt% of 0.1  $\mu\text{m}$  size alumina particles and 0.11 wt%

of 1.0  $\mu\text{m}$  size calcium carbonate particles, and (2) an adjacent 10.8  $\mu\text{m}$  thick, base layer B of PET containing 0.04 wt% of 2.4  $\mu\text{m}$  size silica particles. The filler particles were dispersed uniformly in each of the molten polymer feeds to the film forming unit. The concentrations and sizes of the particles gave the outer surfaces of the layers different surface roughnesses. The skin layer side of the carrier film was metalized with aluminum to an optical density of 2.2. Metal adhesion to the skin layer was determined to be 1.3 g/cm (3.4 g/in.). A layer of adhesive was coated onto the metal side of the metalized film. A substrate article of paperboard was placed into contact with the adhesive layer and the polymeric carrier film/metal/adhesive/paperboard composite was inserted in the nip between a pair of compression rolls then passed through an oven to cure the adhesive. The polymeric carrier film was peeled from the substrate leaving a metal coating exposed on the paperboard surface. Surface roughness and gloss values of the clear carrier film prior to metalization, the metal transfer film of metalized carrier film, and metal surface of the substrate article after the metal had been transferred to it from the carrier film are presented in Table III. Skin layer A surface topography of the A/B carrier layer film is shown in Fig. 2B.

[085] Example 14

[086] A 1.2  $\mu\text{m}$  thick PET skin layer, A, a 9.6  $\mu\text{m}$  thick PET core layer, B, and a 1.2  $\mu\text{m}$  thick PET skin layer, C, were coextruded to form an A/B/C multilayer carrier film structure. Both skin layers A and C contained 2 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant, 0.11 wt% of 1.0  $\mu\text{m}$  size calcium carbonate particles and 0.33 wt% of 0.10  $\mu\text{m}$  size alumina particles dispersed therein. The core layer B includes 0.01 wt% of 0.1  $\mu\text{m}$  size alumina particles. The surface of layer A was metalized with aluminum to a thickness equivalent to 2.2 optical density. The metal adhesion of the aluminum to the carrier film was 1.2 g/cm (3.1 g/in.). Metal was transferred from the metal transfer film to paperboard as described in Ex 13. Surface roughness and gloss data are presented in Table III. Skin layer A surface topography of the A/B/C carrier film is shown in Fig. 2A.

[087] Example 15

[088] A 1.2  $\mu\text{m}$  thick PET skin layer, A, a 16.1  $\mu\text{m}$  thick PET core layer, B, and a 1.2  $\mu\text{m}$  thick PET skin layer, C, were coextruded to form an A/B/C multilayer carrier film structure. Both skin layers A and C contained 2 wt% mixture of sodium dodecyl-benzenesulfonate

and a nonionic surfactant, 0.17 wt% of 1.0  $\mu\text{m}$  size calcium carbonate particles and 0.33 wt% of 0.10  $\mu\text{m}$  size alumina particles dispersed therein. The core layer B includes 0.01 wt% of 0.1  $\mu\text{m}$  size alumina particles. The surface of layer A was metalized with aluminum to a thickness equivalent to 2.2 optical density. The metal adhesion of the aluminum to the 5 carrier film was 1.2 g/cm (3.1 g/in). Surface roughness and gloss data are presented in Table III.

[089] Example 13 demonstrates a practical implementation of using a release layer-free polymeric carrier film to transfer metal to a commercially useful substrate. Gloss of the transferred metal on the paperboard substrate is about equivalent to a good quality, state of 10 the art gloss finish. Particles in the core layer were relatively large (2.4  $\mu\text{m}$ ). This example shows that such particles in the core layer can affect surface topography of the carrier film metal-contacting layer as seen in Fig. 2B (rougher) compared to Fig. 2A (smoother). Surface roughness likely contributed to slightly muted film and metal gloss values. In Example 14, a release layer-free, polymeric carrier film is able to provide a remarkably 15 bright and shiny finish that is well within the gloss unit range for very desirable, high metal surface gloss. Size of particles in layers distant from the metal-contacting skin layer is reduced compared to Ex. 13 contributing to the smoother surface topography seen in Fig. 2A.

[090] Example 15 is very similar in structure to Ex. 14 with the main exception that high 20 concentration (i.e., 0.17 wt% vs 0.11 wt%) of 1.0  $\mu\text{m}$  size, calcium carbonate particles were used in the metal-contacting skin layer A. The very moderate increase in particle concentration caused the gloss to diminish relative to Ex. 14 while maintaining nearly the same Ra measured surface roughness. Appearance of carrier and metal transfer film was acceptable yet slightly less appealing than the preferred high metal surface gloss evident in 25 Ex. 14. Thus Ex. 15 shows that the high metal surface gloss is importantly sensitive to a number of factors that include concentration of embedded particles, size of the particles in the metal-contacting skin layer and size and concentration of particles in layers distant from the metal-contacting skin layer.

TABLE I

	A/B/C Layer Thickness (μm)	A Layer Polymer	A Layer Other Components	B Layer Polymer	B Layer Other Components	C Layer Composition
Comp.	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub>	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 1						
Ex. 2	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 0.48wt% Sodium dodecyl-benzenesulfonate	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 3	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 0.06 wt% Alkane sulphonate 0.003 wt% Sodium sulphate	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 4	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 0.015 wt% Aliphatic Sulphonate	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 5	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 0.03 wt% Aliphatic Sulphonate	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 6	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 1.2 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 7	5/28/0	50 wt% virgin PET 50 wt% Auriga 8428 PET	0.4 wt% 0.9μm CaCO <sub>3</sub>	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 8	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 2.0 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.06 wt% 0.3 μm polystyrene	none
Ex. 9	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 0.48 wt% Sodium dodecyl-benzenesulfonate	PET	0.06 wt% 0.3 μm polystyrene 0.48wt% Sodium dodecyl-benzenesulfonate	none
Ex. 10	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 1.2 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.06 wt% 0.3 μm polystyrene 1.2 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	none
Ex. 11	5/28/0	PET	0.4 wt% 0.9μm CaCO <sub>3</sub> 2.0wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.3 wt% 2.4 μm silica 0.05wt% paraffin wax	none
Ex. 12	1.2/22/1.2	PET	0.13 wt% 1.0 μm CaCO <sub>3</sub> 0.3 wt% 0.1 μm Al <sub>2</sub> O <sub>3</sub> , 2.0 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.075 wt% of 2.4 μm silica 0.013 wt% paraffin wax	Same as Layer A

TABLE I (continued)

Ex. 13	1,2/10.8/0	PET	0.13 wt% 1.0 $\mu\text{m}$ $\text{CaCO}_3$ 0.3 wt% 0.1 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 1.0 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.04 wt% 2.4 $\mu\text{m}$ $\text{Al}_2\text{O}_3$	none
Ex. 14	1,2/9.6/1.2	PET	0.11 wt% 1.0 $\mu\text{m}$ $\text{CaCO}_3$ 0.33 wt% 0.1 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 2.0 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.01 wt% 0.1 $\mu\text{m}$ $\text{Al}_2\text{O}_3$	Same as Layer A
Ex. 15	1,2/16.1/1. 2	PET	0.17 wt% 1.0 $\mu\text{m}$ $\text{CaCO}_3$ 0.33 wt% 0.1 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 2.0 wt% mixture of sodium dodecyl-benzenesulfonate and a nonionic surfactant	PET	0.01 wt% 0.1 $\mu\text{m}$ $\text{Al}_2\text{O}_3$	Same as Layer A

TABLE II

	A Layer	B Layer	A Layer	B Layer	A Layer	A Layer
	Surface Resistivity at 25 degC, 50% RH (ohms/sq)	Surface Resistivity at 25 degC, 50% RH (ohms/sq)	Surface Tension by contact angle (dynes/cm)	Surface Tension by contact angle (dynes/cm)	Metal Thickness (optical density)	Metal Adhesion (g/in)
Comp. Ex. 1	$1.8 \times 10^{16}$	$3.1 \times 10^{16}$	40	40	2.5	135
Ex. 2	$1.1 \times 10^{11}$	$1.6 \times 10^{14}$	> 53.5	40	2.5	45.7
Ex. 3	$2.2 \times 10^{16}$				2.5	26.7
Ex. 4	$1.1 \times 10^{12}$				2.5	11.2
Ex. 5	$4.3 \times 10^{10}$				2.5	7.9
Ex. 6	$1.4 \times 10^{10}$	$6.5 \times 10^{14}$	> 53.5	41	2.5	6
Ex. 7	$1.9 \times 10^{16}$				2.5	33.3
Ex. 8	$1.2 \times 10^{10}$	$5.7 \times 10^{14}$	> 53.5	41	2.5	5.2
Ex. 9	$8.0 \times 10^{10}$	$1.6 \times 10^{11}$	> 53.5	> 53.5	2.5	6.3
Ex. 10	$1.6 \times 10^{10}$	$1.1 \times 10^{10}$	> 53.5	> 53.5	2.5	4.8
Ex. 11	$1.2 \times 10^{10}$		> 53.5		2.5	2
Ex. 12					2.5	5.1
Ex. 13					2.2	3.4
Ex. 14					2.2	3.1
Ex. 15					2.2	3.1

TABLE III

	Ra (nm)	Sra (nm)	60° Gloss Clear Film	60° Gloss Metalized Film	20° Gloss Metalized Carrier Film	60° Gloss Transferred Metal Surface
Ex. 13	52	32	164	859	1625	795
Ex. 14	26	12	186	878	1775	836
Ex. 15	23		176	864	1683	

[091] Although specific forms of the invention have been selected in the preceding disclosure for illustration in specific terms for the purpose of describing these forms of the invention fully and amply for one of average skill in the pertinent art, it should be understood that various substitutions and modifications which bring about substantially 5 equivalent or superior results and/or performance are deemed to be within the scope of the following claims.

What is claimed is:

1. A carrier film for use in transferring a thin layer of metal onto a substrate, the carrier film having a thickness of 4 - 75  $\mu\text{m}$  and comprising a polymer consisting essentially of polyester and a release agent,

in which the carrier film comprises (i) a core layer with a first side and a second side opposite the first side and (ii) a first skin layer coextensively adjacent in direct contact with the first side of the core layer, the side of the first skin layer opposite the core layer defining a metal-contacting surface for contact with the thin layer of metal,

in which the release agent comprises surfactant selected from the group consisting of anionic surfactant, non-ionic surfactant and a mixture thereof, and is present in the polyester of the film in amount effective to provide the metal-contacting surface with a preselected adhesion value to a metal in the range of 0.4 - 39 g/cm (1 - 100 g/in) measured by a 180 degree ethylene acrylic acid polymer peel test,

in which at least one of the core layer and the first skin layer each independently comprises a heterogeneous mixture of finely divided solid particles uniformly dispersed in a continuous phase of the polyester,

in which the solid particles in the carrier film are present in concentration and size effective to provide the metal-contacting surface with roughness characterized by Ra (roughness average) at most 50 nm and Sra (stylus surface roughness) at most 30, and

in which the metal-contacting surface exhibits a specular reflection of at least 160 gloss units measured by glossmeter at a 60° angle.

2. The carrier film of claim 1 in which the release agent of the carrier film is provided in a concentration that is effective to control the metal adhesion on the surface to within a range of  $\pm 3.9$  g/cm ( $\pm 10$  g/in) of the preselected target metal adhesion value.

3. The carrier film of claim 1 wherein the carrier film is biaxially oriented and in which the polyester is polyethylene terephthalate (PET).

4. The carrier film of claim 1 in which the carrier film further includes 0.1 - 1 wt% paraffin wax.

5. The carrier film of claim 1 which further comprises a second skin layer coextensively adjacent in direct contact with the second side of the core layer opposite the first skin layer,

in which at least one of the core layer and the second skin layer each independently comprises a heterogeneous mixture of finely divided solid particles uniformly dispersed in a continuous phase of the polyester, and

in which the solid particles in the carrier film are present in concentration and size effective to provide the metal-contacting surface with roughness characterized by Ra (roughness average) at most 50 nm and Sra (stylus surface roughness) at most 30.

6. The carrier film of claim 5 in which any solid particles in the core layer are present in the range of 0.01 wt% to 1.0 wt% and have size of 0.1-1.0  $\mu\text{m}$ .

7. The carrier film of claim 5 in which solid particles are present in the second skin layer in the range of 0.01 wt% to 1.0 wt% and have size of 0.1  $\mu\text{m}$  to 2.4  $\mu\text{m}$ .

8. A metal transfer film, comprising the carrier film of claim 6 in combination with a transferable layer of a metal in direct contact with the metal-contacting surface of the first skin layer, the metal being selected from the group consisting of aluminum, copper, silver, titanium and a blend thereof, and the transferable layer having a thickness equivalent to an optical density of 0.2 to 4, and in which the transferable layer of metal on the metal-contacting surface exhibits a specular reflection of at least 830 gloss units measured by glossmeter at a 60° angle.

9. A metal transfer film, comprising the carrier film of claim 1 in combination with a transferable layer of a metal in direct contact with the metal-contacting surface of the first skin layer, the metal being selected from the group consisting of aluminum, copper, silver, titanium and a blend thereof, and the transferable layer having a thickness equivalent to an optical density of 0.2 to 4, and in which the transferable layer on the metal-contacting surface exhibits a specular reflection of at least 830 gloss units measured by glossmeter at a 60° angle.

10. A method of transferring a metal to a substrate comprising the steps of:

(A) providing a metal transfer film consisting of (i) a carrier film having a thickness of 4 - 75  $\mu\text{m}$  and comprising a polymer consisting essentially of polyester and a release agent, in which the film comprises (1) a core layer with a first side and a second side opposite the first side and (2) a first skin layer coextensively adjacent in direct contact with the first side of the core layer, the side of the first skin layer opposite the core

layer defining a metal-contacting surface that exhibits a specular reflection of at least 160 gloss units measured by glossmeter at a 60° angle,

in which at least one of the core layer and the first skin layer each independently comprises a heterogeneous mixture of finely divided solid particles uniformly dispersed in a continuous phase of the polyester,

in which the solid particles in the carrier film are present in concentration and size effective to provide the metal-contacting surface with roughness characterized by Ra (roughness average) at most 50 nm and Sra (stylus surface roughness) at most 30, and

in which the release agent comprises surfactant selected from the group consisting of anionic surfactant, non-ionic surfactant and a mixture thereof, and is present in the polyester of the film in amount effective to provide the metal-contacting surface with a preselected adhesion value to a metal in the range of 0.4 - 39 g/cm (1 - 100 g/in) measured by a 180 degree ethylene acrylic acid polymer peel test, and (ii) a transferable layer of the metal deposited in direct contact with the metal-contacting surface of the first skin layer, the transferable layer having a metal thickness equivalent to an optical density in the range of 0.2 - 4.0,

(B) providing a substrate article having a surface coated with an adhesive layer,

(C) contacting the transferable layer of the metal transfer film with the adhesive layer of the substrate such that the metal transfer film bonds to the adhesive layer of the substrate, and

(D) stripping the carrier film from the metal layer, thereby transferring the metal onto the substrate.

11. The method of claim 10 in which the carrier film further includes 0.1 - 1 wt% paraffin wax.

12. The method of claim 10 in which the step of providing the metal transfer film further comprises obtaining a mixture comprising a thermoplastic polyester resin and release agent, heating the mixture effectively to melt the thermoplastic polyester resin, uniformly dispersing the release agent in the thermoplastic polyester resin, thereby forming a melt dispersion, forming a self-supporting film from a polymeric composition comprising the melt dispersion, and stretching the film in a machine direction about 4x and in the transverse direction about 4x, thereby causing the release agent to bloom to the outer surface of the carrier film.

13. The method of claim 10 in which the carrier film further comprises a second skin layer coextensively adjacent in direct contact with the core layer on the second side of the core layer that is opposite the first skin layer,

in which at least one of the core layer and the second skin layer each independently comprises a heterogeneous mixture of finely divided solid particles uniformly dispersed in a continuous phase of the polyester, and

in which the solid particles in the carrier film are present in concentration and size effective to provide the metal-contacting surface with roughness characterized by Ra (roughness average) at most 50 nm and Sra (stylus surface roughness) at most 30.

14. The method of claim 13 in which any solid particles in the core layer are present in the range of 0.01 wt% to 1.0 wt% and have size of 0.1  $\mu\text{m}$  to 1.0  $\mu\text{m}$ .

15. The method of claim 14 in which solid particles are present in the second skin layer in the range of 0.01 wt% to 1.0 wt% and have size of 0.1  $\mu\text{m}$  to 2.4  $\mu\text{m}$ .

16. The method of claim 13 in which the transferable layer of metal on the metal-contacting surface of the carrier film exhibits a specular reflection of at least 830 gloss units measured by glossmeter at a 60° angle.

17. The method of claim 13 in which after the carrier film is stripped from the metal layer, the metal on the substrate exhibits a specular reflection of at least 860 gloss units measured by glossmeter at a 60° angle.

18. The carrier film of claim 1 in which the solid particles are present only in the core layer.

19. A metal transfer film, comprising the carrier film of claim 5 in combination with a transferable layer of a metal in direct contact with the metal-contacting surface of the first skin layer in which the transferable layer on the metal-contacting surface exhibits a specular reflection of at least 830 gloss units measured by glossmeter at a 60° angle.

20. A carrier film for use in transferring a thin layer of metal onto a substrate, the carrier film having a thickness of 4 - 75  $\mu\text{m}$  and comprising a polymer consisting essentially of polyester and a release agent,

in which the carrier film comprises (i) a core layer with a first side and a second side opposite the first side, (ii) a first skin layer coextensively adjacent in direct contact with the

first side of the core layer, the side of the first skin layer opposite the core layer defining a metal-contacting surface for contact with the thin layer of metal, and (iii) a second skin layer coextensively adjacent in direct contact with the second side of the core layer opposite the first skin layer,

in which the second skin layer comprises a heterogeneous mixture in the range of 0.01 wt% to 0.1 wt% of finely divided solid particles having particle sizes of 0.1  $\mu\text{m}$  to 2.4  $\mu\text{m}$  uniformly dispersed in a continuous phase of the polyester,

in which the release agent comprises surfactant selected from the group consisting of anionic surfactant, non-ionic surfactant and a mixture thereof, and is present in the polyester of the film in amount effective to provide the metal-contacting surface with a preselected adhesion value to a metal in the range of 0.4 - 39 g/cm (1-100 g/in) measured by a 180 degree ethylene acrylic acid polymer peel test,

in which the solid particles in the carrier film are present in concentration and size effective to provide the metal-contacting surface with roughness characterized by Ra (roughness average) at most 50 nm and Sra (stylus surface roughness) at most 30, and

in which the metal-contacting surface exhibits a specular reflection of at least 160 gloss units measured by glossmeter at a 60° angle.

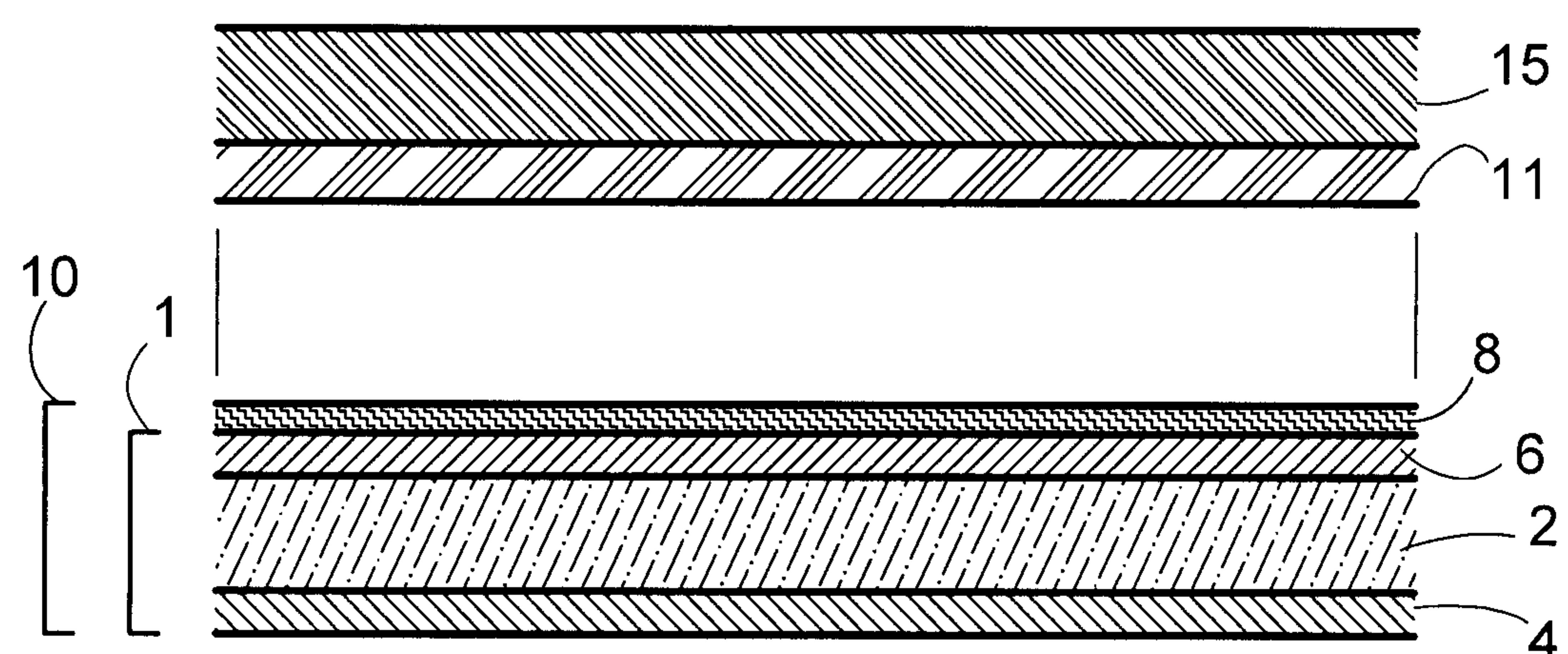


Fig. 1

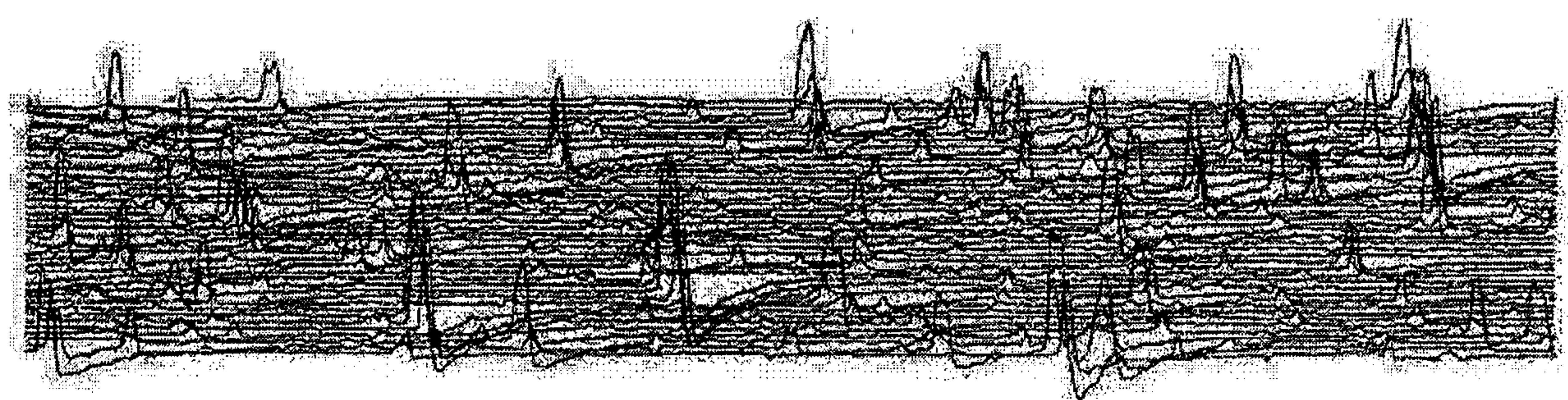


FIG. 2A

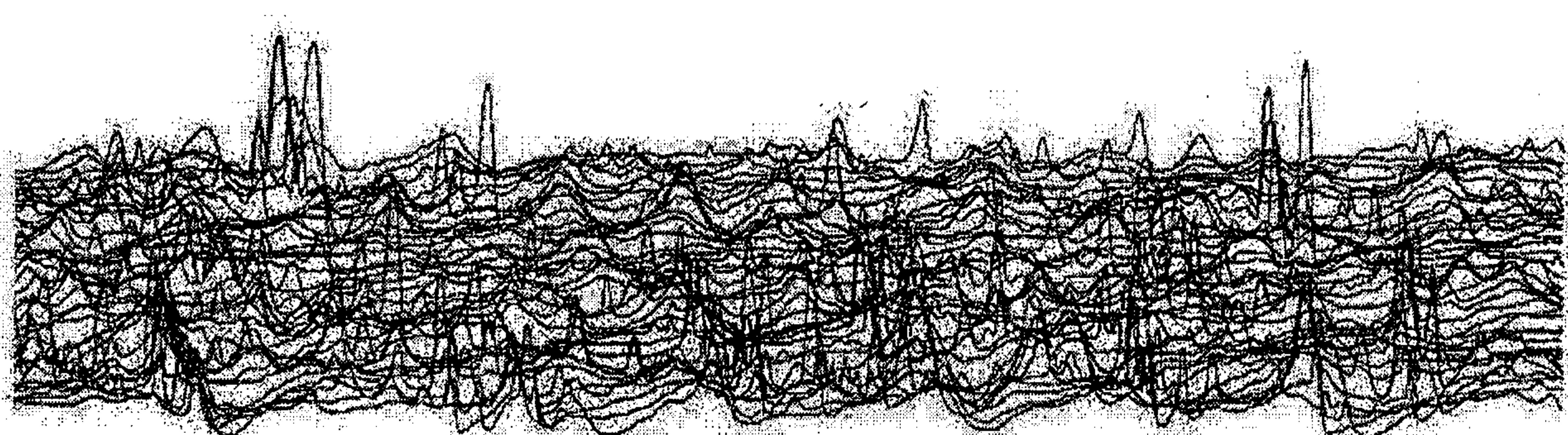


FIG. 2B