

MULTILAYER FILM STRUCTURE

This invention relates to a multilayer packaging-
or label stock film structure having excellent
printability and non-blocking characteristics.

5 The standard commercial approach to achieve
wetting and adhesion of printing inks on certain
packaging and label stock film is to subject the film
to a surface modifying treatment, especially with
corona discharge or a gas flame. This type of
10 treatment does not always provide for sufficient ink
adhesion for many applications. Excellent adhesion
can be obtained by applying a primer layer to the
film before application of the ink. While this may
provide an excellent surface for wetting and adhering
15 printing inks, preprimed film cannot be sold in roll
form: the primer layer will cause destructive
blocking between the primed surface and the reverse
side of the film after it is rolled up and stored for
any length of time.

20 The present invention seeks to provide a film
which has excellent printability and which is not
subject to destructive blocking.

 The present invention provides a printable film
structure comprising a polymeric film substrate
25 having at least one surface adherently incompatible
with printing ink and having a primer coating thereon
of a type which can cause destructive blocking
between contacting layers of such coated films
wherein the primer coating has thereon a polyester or
30 coating of a water dissipatable printing ink base,
with or without pigment, to prevent blocking.

 In one aspect of the present invention, the
printing ink base is a coating of a water-
dissipatable copolyester having an inherent viscosity
35 of at least 0.1 as measured in a 60/40 parts by

weight solution of phenol/tetrachloroethane at 25°C and at a concentration of 0.5 gm. of polyester in 100 ml. solvent, especially wherein the copolyester comprises the condensation product of the following monomers (or their polyester forming equivalents):

- a) from 90 to 97 mole % isophthalic acid; and, correspondingly,
- b) from 3 to 10 mole % of 5-sulfrisophthalic acid;
- 10 c) from 70 to 85 mole % of 1,4-cyclohexane-dimethanol; and, correspondingly,
- d) from 15 to 30 mole % of diethylene glycol.

In another aspect of the present invention the copolyester comprises the condensation product of the following monomers (or their polyester forming equivalents) :

- a) from 60 to 75 mole % terephthalic acid;
- b) from 15 to 25 mole % of at least one dicarboxylic acid of the formula :
20 $\text{HOOC}(\text{CH}_2)_n\text{COOH}$
wherein n is from 1 to 11;
- c) more than 6 to 15 mole % of at least one sulfomonomer containing an alkali metal sulfonate group attached to a dicarboxylic aromatic nucleus; and
- 25 d) a stoichiometric quantity of about 100 mole % of at least one copolymerisable aliphatic or cycloaliphatic alkylene glycol having from 2 to 11 carbon atoms.

30 In the film structure described above the primer coating can be a coating of a member selected from the group consisting of (A) the reaction product of acidified aminoethylated vinyl polymer and an epoxy resin, (B) poly(ethyleneimine), and (C) mixtures
35 thereof.

The substrates contemplated herein include any polymeric film substrate that can be employed for packaging purposes; for a label stock film; or for decorative purposes. Included within this class of materials are nylon; polyethylene terephthalate; polycarbonate; and polyolefins. The contemplated structures also include coextrudates of the recited materials, laminates of any two or more of these materials or interblends of any of the materials extruded as a single base film. A particularly preferred class of films are the polyolefins. Within the polyolefin class, homopolymers and copolymers of propylene are preferred. Particularly preferred are isotactic polypropylenes containing at least 80% by weight of isotactic polypropylene. The preferred base substrate layer can be homopolymer polypropylene having a melting point from 161°C (321°F) to 169°C (336°F). Commercially available materials of this description include Exxon 4252 and FINA 3371. When the preferred substrate is employed it can be employed as is or with coextruded or laminated thin skin layers which each amount to from 2 to 18% of the total thickness. The skin material can be a copolymer of propylene and another olefin, e.g., ethylene and/or butene-1. The other olefin can be present in the copolymer in an amount from 1 to 7 wt. %. White opaque, cavitated polypropylene is also a substrate film of choice. Polyethylene film in all of its forms and densities, oriented or unoriented is also contemplated.

The films employed can be uniaxially or biaxially oriented. The preferred range of orientation can be from 1.3 to 7 times in the machine direction and from 5 to 10 times in the transverse direction.

Before primer coating any of these materials they may be corona discharge treated to 38 to 42 dynes/cm by standard commercial techniques. They may also be flame treated by means known in the art.

5 The primer coating material contemplated, as indicated above, is the type which inherently causes destructive film blocking between contacting layers of such a coated film when the film is convolutely rolled up and store for at least a number of days.
10 As indicated above, the primer coating comprises a reaction product of an acidified aminoethylated vinyl polymer and an epoxy resin; a poly(ethyleneimine); or a mixture thereof.

15 The primer coating (A) is described in U.S. Patent 5,066,434.

As disclosed the primer materials include the reaction product of an epoxy resin and an acidified aminoethylated vinyl polymer. The contemplated epoxy resins are glycidyl ethers of polyhydroxy compounds.
20 Typical polyhydroxy compounds which may be used include bisphenol A, ring substituted bisphenol A, resorcinol, hydroquinone, phenol-formaldehyde, novolac resins, aliphatic diols, such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-
25 hexanediol, glycerol, lower alkyl hydantoins and mixtures thereof.

The preferred epoxy resins of the present invention are those made by the glycidation reaction between epichlorohydrin and bisphenol A. Epoxy
30 resins of this type are commonly classified by their epoxy equivalent weight (EEW) which is defined as the weight of resin in grams which contains one gram equivalent of epoxy groups. Resins with an EEW from 170 to 280 may be used in the present invention, but
35 the preferred range is from 180 to 210.

A variation in the composition of the epoxy resin component is one in which a hydantoin compound is substituted for the bisphenol A. For example, 1,1-dimethyl hydantoin may be employed in a low molecular weight epoxy resin since resins based on this material are completely water soluble thereby eliminating the necessity for emulsification.

Although the specific structure of the epoxy resin is not critical to the primer employed in the present invention, important considerations in the selection of the epoxy resin depend upon its physical state. For example, it must be liquid and capable of being readily dispersed or dissolved with the second component or curing agent as described hereinbelow. If the epoxy resin is of low viscosity, it may be stirred directly into the second component, i.e., curing agent, however, it is preferred to employ the epoxy resin in an aqueous emulsion.

The second component in the epoxy primer compositions of the present invention is an amino modified acrylic polymer which is water soluble. This polymer is a curing agent for the epoxy compound. The preferred material is described in the U.S. Patent No. 3,719,629 and may be generically described as an acidified amino-ethylated interpolymer having pendant amino alkylate groups. This material is produced by polymerizing acrylate, methacrylate, styrene or other suitable monomers with sufficient methacrylic or acrylic acid to give a - COOH content of 7.5 to 12.5%. Solvent polymerization techniques are preferred. The polymer is then reacted with ethyleneimine monomer and acidified with hydrochloric acid to render the polymer water soluble.

5 The primer coating may be applied to the substrate as a dispersion or as a solution, from an organic vehicle, for example, an alcohol or an aromatic hydrocarbon, such as xylene or a mixture thereof.

10 In one embodiment of the present invention, a liquid epoxy resin is emulsified in a solution of the curing agent by rapid stirring. Thereafter, the resultant dispersion is diluted with water to the desired concentration for coating, which typically includes from about 2 to about 25% solids.

15 When mixing the epoxy resin with the curing agent, it is generally preferred to use a stoichiometric equivalent balance of epoxy and amine groups. However, it has been found that the stoichiometric ratio may be varied over a wide range, for instance, from about one epoxy group to about three amine groups through three epoxy groups to one amine group and, preferably, from about one epoxy group to two amine groups through about two epoxy groups to about one amine group, without seriously affecting the product's usefulness as a primer coating.

25 It is to be understood that the solution or dispersion of epoxy resin and curing agent can contain small amounts of wetting agents in order to facilitate the application of the primer material to the surface of layer (b). Conventional non-ionic wetting agents which can be employed include the hexyl or benzyl ether of ethylene glycol, the hexyl ether of diethylene glycol, butyl alcohol, hexyl alcohol, octyl alcohol and diacetone alcohol.

35 Although mixtures of the epoxy resin and the curing agents will cross-link or cure without the necessary addition of a catalyst, it has been found

advantageous, in certain instances, to use an amine catalyst. Such catalysts include propylene diamine and hexamethylene diamine.

The alternative primer coating material (B)
5 poly(ethyleneimine) is also known as PEI. The use of PEI as a primer material for polymeric coatings on film substrates such as cellophane or polyolefins is well known in the art as disclosed in British Patent Nos. 766,827 & 910,875. This material is also
10 described in U.S Patent No. 3,230,175. A commercially available material of this type is known as EPOMIN L50 a product of Nippon Shogubi. This material can be applied from either aqueous or organic solvent media, such as ethanol in a solution
15 comprising from 0.1 to 0.6% by weight of the poly(ethyleneimine) when a mixture of A and B are employed any ratio is contemplated.

The above described primer coating materials when applied to any of the defined substrate film
20 structures have the draw back of causing destructive blocking when such films are convolutedly wound for shipment to a converter. The essence of the present invention involves the discovery that a certain class of water-dispersible polyester ink bases can be
25 coated onto the surface of these primers and, thereafter, the film structures can be convolutedly wound without any danger of destructive blocking. In addition, it has been discovered that these polyesters can withstand extremely high (93°C;
30 200°F.+) temperatures. Further, these polyester surfaces permit an exceptionally strong bonding to result when printed indicia or design is printed thereon. As will be shown, the multilayer structure and the printed information and/or design can
35 withstand water temperatures of 200°F. alone or in

combination with moderate abrasive action in contact with the printed surface. These polyesters have been described as linear, water-dissipatable polyesters having inherent viscosities as disclosed above and
5 having the equimolar proportions of acid and hydroxy moieties referred to above. The polyesters comprise repeating units of components (a), (b), (c) and (d), as follows:

- (a) 90 to 97 mole % isophthalic acid,
- 10 (b) 3 to 10 mole % 5-sulfoisophthalic acid,
- (c) 70 to 85 mole % 1,4-cyclohexanedimethanol, and
- (d) 15 to 30 mole % diethylene glycol.

Component (b) can be in the form of a sodium salt.

15 These polyesters are described in detail in U.S. Patent 5,006,598.

The following Examples illustrate the invention.

EXAMPLE 1

20 Biaxially oriented homopolypropylene of a thickness of about 1.9 mils is corona discharge treated to about 38 dynes/cm and is one-side prime coated with the reaction product of an acidified aminoethylated vinyl polymer and an epoxy resin as described in Example 3 of U.S. Patent No. 4,214,039.
25 After drying in hot air to a weight of 0.05 gms/msi, the film is convolutely wound and stored at 70°F for about 7 days. On attempting to uncoil the film it will be found to have destructive blocking and be unusable for subsequent conversions.

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EXAMPLE 2

A film as in Example 1, before being rolled up is top-coated with the polyester composition described in Example 13 of U.S. Patent No. 5,006,598. This top-coat is applied to a dry weight of just less

than 0.06 gms/msi. The film is convolutely wound and stored at 70°F for about 7 days. This film can be unrolled and re-rolled with no evidence of blocking.

EXAMPLE 3

5 The film of Example 2 is printed with a water-based flexographic ink known as "No. WR30007, from Environmental Inks and Coating Corp.. Employing #610 Scotch Tape R from 3M Co. as an adherence test, the printing can not be removed.

EXAMPLE 4

10 The printed film of Example 3 is coated with a pressure sensitive adhesive on the reverse side thereof and applied as a label to a glass container. The label and glass are submerged in 200°F. water for
15 10 minutes and then scraped in an attempt to remove the ink. The ink will be found to be firmly bonded to the polyester coated epoxy primed oriented polypropylene substrate. The flexographic ink will not wet corona treated polypropylene film alone and
20 the ink can be easily lifted off by the tape.

EXAMPLE 5

 Biaxially oriented homopolypropylene of a thickness of about 1.9 mils is corona discharge treated to about 38 dynes/cm and is one-side prime
25 coated with the reaction product of an acidified aminoethylated vinyl polymer and an epoxy resin as described in Example 3 of U.S. Patent No. 4,214,039. After drying in hot air to a weight of 0.05 gms/msi, the film is convolutely wound and stored at 70°F for
30 about 7 days. On attempting to uncoil the film it will be found to have destructive blocking and be unusable for subsequent conversions.

EXAMPLE 6

A film as in Example 5, before being rolled up is top-coated with the polyester composition described in Example 28 of U.S. Patent No. 4,525,419. This top-coat is applied to a dry weight of just less than 0.06 gms/msi. The film is convolutedly wound and stored at 70°F for about 7 days. This film can be unrolled and re-rolled with no evidence of blocking.

EXAMPLE 7

The film of Example 6 is printed with a water-based flexographic ink known as "No. WR30007, from Environmental Inks and Coating Corp.. Employing #610 Scotch Tape R from 3M Co. as an adherence test, the printing can not be removed.

EXAMPLE 8

The printed film of Example 7 is coated with a pressure sensitive adhesive on the reverse side thereof and applied as a label to a glass container. The label and glass are submerged in 200°F. water for 10 minutes and then scraped in an attempt to remove the ink. The ink will be found to be firmly bonded to the polyester coated epoxy primed oriented polypropylene substrate. The flexographic ink will not wet corona treated polypropylene film alone and the ink can be easily lifted off by the tape.

The foregoing examples demonstrate that oriented polypropylene film can be prime coated with a primer material which leads to destructive blocking between adjacent layers. This blocking can be eliminated by top coating the prime coating with a polyester composition within the scope of U.S. Patent 4,525,419 or 5,006,598. This polyester coating not only prevents the destructive blocking of the film but also provides a surface to which conventional label printing inks will aggressively adhere and even

withstand the rigors of hot-water applied in an agitating manner to the film in label form applied to a container surface. The same effect will be experienced if the prime coating is

5 poly(ethyleneimine) alone or in combination with the epoxy prime coating material.

The polyesters of the present invention are fundamentally an ink without any pigment. If commercial pigments were added to polyester, they

10 indeed could be employed as a printing ink composition. When the primed substrate is coated with the proper amount of the polyester, blocking between films is prevented. This would be true whether the polyester contained an ink pigment or

15 not. Thus, in its broadest sense the present invention overcomes the tendency of primed substrate films to block by applying a pigment or non-pigmented polyester uniformly over the primed surface. As indicated, since the polyester is fundamentally an

20 ink without pigment and a necessary attribute of an ink is that it has good adhesion to itself, the primed and polyester coated film has excellent print characteristics. It has been found however, that the ink base polyester compositions must not be coated to

25 an extent greater than 0.06 gms/msi. As a lower limit the polyester can be coated to that extent which effectively prevents blocking of the primed substrate film.

**CLAIMS:**

1. A printable film structure comprising a polymeric film substrate having at least one surface adherently incompatible with printing ink and having a primer coating thereon of a type which can cause destructive blocking between contacting layers of such coated films wherein the primer coating has thereon a polyester or coating of a water dissipatable printing ink base, with or without pigment, to prevent blocking.
2. A film structure according to claim 1 wherein the printing ink base is a coating of a water-dissipatable copolyester having an inherent viscosity of at least 0.1 as measured in a 60/40 parts by weight solution of phenol/tetrachloroethane at 25°C and at a concentration of 0.5 gm. of polyester in 100 ml. solvent.
3. A film structure according to claim 1 or 2 wherein the copolyester comprises the condensation product of the following monomers (or their polyester forming equivalents) :
- a) from 60 to 75 mole % terephthalic acid;
 - b) from 15 to 25 mole % of at least one dicarboxylic acid of the formula :
$$\text{HOOC}(\text{CH}_2)_n\text{COOH}$$

wherein n is from 1 to 11;
 - c) more than 6 to 15 mole % of at least one sulfomonomer containing an alkali metal sulfonate group attached to a dicarboxylic aromatic nucleus; and

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- d) a stoichiometric quantity of about 100 mole % of at least one copolymerisable aliphatic or cycloaliphatic alkylene glycol having from 2 to 11 carbon atoms.
- 5 4. A film structure according to claim 1 or 2 wherein the copolyester comprises the condensation product of the following monomers (or their polyester forming equivalents):
- 10 a) from 90 to 97 mole % isophthalic acid; and, correspondingly,
- b) from 3 to 10 mole % of 5-sulfrisophthalic acid;
- c) from 70 to 85 mole % of 1,4-cyclohexane-dimethanol; and, correspondingly,
- 15 d) from 15 to 30 mole % of diethylene glycol.
5. A film structure according to any preceding claim wherein the primer coating comprises a coating of a reaction product of acidified aminoethylated vinyl polymer and an epoxy resin;
- 20 a poly(ethyleneimine); or a mixture thereof.
6. A film structure according to any preceding claim wherein the film substrate comprises nylon; polyethylene terephthalate; polycarbonate; polyethylene; polypropylene; or a
- 25 coextrudate or a laminate of any two or more thereof.



7. A film structure according to claim 6 wherein the substrate comprises polypropylene with or without the same or different skin layers comprising polyethylene; a copolymer of ethylene and another olefin; a copolymer of propylene and another olefin; a terpolymer of olefins; a maleic anhydride modified polymer or a mixture thereof.
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8. A film structure according to claim 6 or 7 wherein the substrate comprises polypropylene interblended with a minor proportion of polyethylene; a copolymer of ethylene and another olefin; a copolymer of propylene and another olefin; a terpolymer of olefins; a maleic anhydride modified polymer or a mixture thereof.
- 10
- 15
9. A film structure according to any preceding claim having a pressure sensitive adhesive on the surface opposite to the copolyester or ink base carrying surface.
- 20
10. Use of a coating of a water dissipatable copolyester or printing ink base to prevent blocking of a printable film structure comprising a polymeric film substrate having at least one surface adherently incompatible with printing ink and having a primer coating thereon of the type which can cause destructive blocking between contacting layers of such coated films.
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