



## POLYESTERS FOR METAL LAMINATION

### Technical Field

This invention concerns poly(ethylene-co-diethylene  
5 terephthalate) polyesters useful for making thin films.  
More specifically, this invention concerns  
poly(ethylene-co-diethylene terephthalate) polyesters  
where the diethylene glycol (DEG) repeat unit component  
10 is 10-30 mol %. These polymers can be converted into  
thin films and are useful as protective barrier films,  
especially in packaging applications. These  
compositions can be used to make biaxially oriented  
films for metal lamination. The metal/polymer  
15 laminations have many uses including precoated metal  
stock for aluminum and steel can manufacturing.

### Background of the Invention

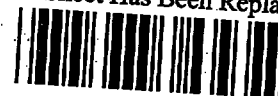
Polyesters made from terephthalic acid (or dimethyl  
terephthalate), ethylene glycol (EG), and diethylene  
20 glycol are well known in the art but it is believed that  
the critical ranges of the monomers used in making the  
polyester for thin film applications which require  
adequate strength and tear properties are novel. U.S.  
Patent 2,698,239 discloses photographic film supports  
25 coated with polyesters selected from terephthalate  
polyesters which contain a polymethylene glycol of 2-10  
methylene groups. This patent discloses the broad range  
of ethylene terephthalate copolyesters containing  
20-100% diethylene glycol. U.S. Patent 4,048,253  
30 discloses ethylene terephthalate copolyesters containing  
30-100 mol % diethylene glycol. U.S. Patent 4,154,918  
discloses ethylene terephthalate copolyesters containing  
5-30 mol % isophthalic acid and 40-80 mol % diethylene  
glycol.

U.S. Patent 5,132,391 discloses the use of diethylene glycol containing ethylene terephthalate copolyesters wherein the acid component contains at least 75 mol % terephthalic acid and the diol component consists of ethylene glycol and diethylene glycol in the ratios 9:1 to 1:1 and contains a copolymerizable phosphorus containing compound. U.S. Patent 4,418,116 discloses ethylene terephthalate copolyesters with 20-45% diethylene glycol and U.S. Patent 4,352,925 teaches the use of ethylene terephthalate copolyesters with 30-50 mol % diethylene glycol as adhesives. U.S. Patent 4,352,925 also contains a summary of diethylene glycol containing polyesters.

There exists a need for a polyester thin film which can be laminated to either aluminum or steel, on one or both sides, and then subsequently drawn into a beverage or food can. This is in part due to increasing environmental pressure on can makers to get away from organic solvents that are used to dissolve or disperse the epoxy coatings that are conventionally used to coat most cans made today. A metal/plastic laminate allows one to make a can in the complete absence of organic solvents. There have been several disclosures in this area of the art.

European Patent Application 402,004A1 discloses laminates of aluminum and ethylene terephthalate copolyester films. The disclosed copolyester contains 0-40 mol % comonomers that can include isophthalic acid and diethylene glycol. The copolyester must have a melting point of 200-260°C.

U.S. Patent 5,149,389 discloses a laminated metal sheet which is useful for can making. The polymeric film is an ethylene terephthalate copolyester with a melting point of 200-270°C. The comonomers of use listed in this disclosure include isophthalic acid,



diethylene glycol, and 1,4-cyclohexanedimethanol at levels of 0-40 mol %. Polyethylene terephthalate (PET) copolymers containing greater than 15 mol % isophthalic acid are slow to crystallize and are thus difficult to manufacture on a large scale. PET copolymers containing greater than 30 mol % diethylene glycol are also slow to crystallize and difficult to handle on a manufacturing scale.

Great Britain Patent Application 2,238,981A discloses a process for making draw-redraw cans. This process uses metal/polymer laminate for drawing into cans. The polymers mentioned are ethylene terephthalate copolymers with at least 75 mol % of the acid component being terephthalic acid and at least 75 mol % of the diol component being ethylene glycol. Diethylene glycol was mentioned in the list of possible glycol-modifying agents. Also disclosed is the need for this polymer to have a melting point of 210-252°C to allow for optimal laminating conditions. Isophthalic acid was the dominant comonomer in this art.

European Patent Application 415,345A2 discloses the use of diethylene glycol in ethylene terephthalate copolymers for steel lamination. The steel/copolyester laminates can be used for can making.

#### Description of the Invention

This invention provides poly(ethylene-co-diethylene terephthalate) copolyesters that can be formed into biaxially oriented films for various applications. Particularly, this invention describes PET copolyesters with 10-30 mol % diethylene glycol. These films are good for various packaging applications including coatings for metals, paper, paperboard, various plastics, wood, ceramics, woven and nonwoven fabrics, leather, and the like. In addition to being useful as



coatings or adhesives for the above-described substrates, the free films are also useful for wrapping and packaging applications involving food and other articles such as clothing, tools, records, toys, toilet  
5 articles, gift items, and the like. In the packaging of foods, the good moisture barrier properties of the films are important. Oriented, heat-set films may be used for standard wrapping applications. Oriented films which have not been heatset are generally used for shrink wrap  
10 applications.

The polymers of this invention are particularly useful for laminating or coating of various metals used in the manufacture of cans. Such cans are useful as containers for beverages, food, and the like. Typical  
15 metals used for the manufacture of cans include aluminum, steel, tin coated steel, zinc coated steel, chrome coated steel, nickel coated steel, blackplate, or phosphated blackplate which is preferably chromate rinsed after phosphating and the like. It has been  
20 found that the composition of the copolyester is quite critical with regard to can coating or can lamination procedures. For example, the tin coating on tin coated steel melts at 230°C. Therefore, coatings or adhesives with melting points higher than 230°C are not suitable  
25 for this application. It has been found that PET copolyesters containing 10 mol % diethylene glycol have a melting temperature of 230°C and they provide good adhesion to aluminum, steel, and the various coated steels used in can making. Also, these copolyesters  
30 have good moisture vapor barrier properties. This is important in steel cans to prevent iron from being leached out of the metal walls of steel cans by beverages or food products containing water. PET or PET copolyesters containing less than 10 mol % modification  
35 are not useful because they do not melt or form bonds

with the metal substrates under the preferred bonding conditions. PET copolyesters containing 30 mol % diethylene glycol represent the upper range of diethylene glycol-modified PET polymers operable for this application. Such copolyesters have a melting temperature of 185°C, are crystallizable in air at temperatures of 60°C to 130°C, have adequate moisture vapor barrier resistance, and provide good coatings or bonds on the various metal can stocks at temperatures of 230°C or less.

PET copolyesters with greater than 30 mol % diethylene glycol cannot be readily crystallized in air because the optimum crystallization temperature in air is high enough to cause the polymer to flow and stick together. This becomes a major problem in large scale manufacturing of copolymers containing high concentrations of diethylene glycol. Also, the moisture vapor transmission rate of the copolyesters increases rapidly as the concentration of diethylene glycol in the copolyesters is increased above 30 mol %. Thus, operable copolyesters in this invention contain 10 to 30 mol % diethylene glycol. Preferred copolyesters contain 15 to 25 mol % diethylene glycol.

This invention is useful for various packaging and adhesive applications. Examples include, but are not limited to, aluminum and steel laminates for can making, wood laminates, adhesive applications, coextrusion structures, coated substrates and the like.

The copolymer must have at least 85 mol % of the acid component as terephthalic acid, preferably at least 95 mol %. The glycol component must be 70-90 mol % ethylene glycol and 10-30 mol % diethylene glycol. The total mole percents for ethylene glycol and diethylene glycol must be at least 90 mol %, preferably greater than 95 mol %. This poly(ethylene-co-diethylene

terephthalate) copolymer may contain small amounts of other comonomers. Comonomers may include 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 4,4'-biphenyl-  
5 dicarboxylic acid, p-hydroxybenzoic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, and aliphatic diacids or diols containing 2 to 20 carbon atoms, and other polyester forming diacids and diols generally known in the art. The comonomers may also include the  
10 diesters of any of the aforementioned diacids. The copolymer may also contain small amounts of chain branching agents and/or chain termination agents.

The polyesters described in this invention are prepared by conventional polymerization methods which  
15 are well known in the art. The polyester is prepared from either terephthalic acid or dimethyl terephthalate with ethylene glycol and diethylene glycol in the presence of catalyst metals. The polymer is prepared by melt phase polycondensation methods and may optionally  
20 be subjected to solid-state polymerization methods to provide polymers with high molecular weights. The copolymers are readily prepared by either batch or continuous processes.

The polyester can have an inherent viscosity of 0.3  
25 to 1.5 dL/g, preferably 0.5-1.1 dL/g.

The polyester compositions described in this invention may contain additives generally known in the  
-art. These include nucleation or crystallization aids, surface lubricants, denesting agents, stabilizers,  
30 antioxidants, ultraviolet light absorbing agents, pigments, colorants, and the like.

The polyesters described herein may also contain inorganic materials such as black iron oxide.

The copolyesters of this invention are readily  
35 extruded into flat or tubular films. Such films can be

readily biaxially oriented and heatset using conventional techniques. These oriented films are valuable shrink-wrap film for the packaging of foods and other items. The copolyester films may also be

5 laminated to one or both sides of metal strips and the laminates can be further processed into metal cans used for beverages and foods. In making such copolyester/metal and copolyester/metal/copolyester

10 laminates, preheated metal sheeting and copolyester film from feed rolls are fed to lamination rolls. Uniform, intimate, and wrinkle-free contact between the preheated metal sheet and the polymer films is made in the lamination nip. Such laminations are generally made at temperatures in the range of 180°C up to 260°C;

15 depending on the metal used and the melting point of the copolyester. By means of flame, induction, infrared, or oven heating, the laminates are reheated to temperatures in the range of 225°C to 280°C and the laminates are then quenched (usually in water) to a temperature below

20 the glass transition temperature of the copolyester to insure that the copolyester coating is in an amorphous state. Can blanks cut from the copolyester/metal or copolyester/metal/copolyester laminates are readily drawn and wall ironed (DWI) or drawn and redrawn (DRD)

25 into cans. Generally, the exterior copolyester layer will contain pigments such as  $\text{TiO}_2$  in order to be able to print and/or decorate the exterior surface of the can. The copolyester films produced in accordance with this invention have a thickness of 5 to 50 microns,

30 preferably 9 to 25 microns.

The thickness of the metal used to make cans is 0.05 to 0.5 mm for steel and 0.02 to 0.5 mm for aluminum can stock.

In addition to the coating of metal can sheeting,

35 it is also possible to laminate the copolyesters of the

present invention to aluminum or tin foil for subsequent use in food pouches, such as potato chips, cookies, and the like. The coating on the foil makes it possible to heat seal the packages. As in the beverage/food can application, the exterior layers of the food pouch laminates generally contain pigments such as  $\text{TiO}_2$  for printing and decoration purposes.

### Examples

The following examples are submitted for a better understanding of the invention.

The analytical data provided in these examples were determined by the following methods.

Tensile Strength, Elongation at Break, Tangent Modulus: ASTM method D882

Elmendorf Tear Resistance: ASTM method D1922

T-peel Strength: ASTM method D1876 (modified as described in Example 18)

Water Vapor Transmission Rate: ASTM method F372

Density Measurements: In a density gradient column

Thermal Analysis (DSC): Measured at a scan rate of  $20^\circ\text{C}/\text{min}$ . after the sample was heated above its melting temperature and rapidly quenched below its glass transition temperature

Inherent Viscosity: Determined at  $25^\circ\text{C}$  with a 0.50 gram sample in 100 mL of 60/40 by weight solution of phenol/tetrachloroethane

Examples 1-5 - Poly(ethylene-co-diethylene terephthalate) copolyesters are prepared using conventional techniques well known in the art, such as

described in U.S. Patent No. 4,352,925, incorporated herein by reference. These copolyesters are prepared so as to have repeat units from 100 mol % terephthalic acid, and repeat units from ethylene glycol and diethylene glycol. The mol % of ethylene glycol (EG) and diethylene glycol (DEG) are given below. Example 5 is comparative, and uses a combination of terephthalic and isophthalic acids.

10     Example 1

90 mol % EG, 10 mol % DEG  
Inherent Viscosity: 0.708 dL/g  
DSC data: Tg = 71.6°C; Tm = 230.1°C  
NMR data: 10.4 mol % DEG  
15     Density: 1.371 g/cm<sup>3</sup>

Example 2

82 mol % EG, 18 mol % DEG  
Inherent Viscosity: 0.713 dL/g  
20     DSC data: Tg = 71.1°C; Tm = 226.2°C  
NMR data: 18.9 mol % DEG  
Density: 1.368 g/cm<sup>3</sup>

Example 3

74 mol % EG, 26 mol % DEG  
25     Inherent Viscosity: 0.747 dL/g  
DSC data: Tg = 59.7°C; Tm = 202.8°C  
NMR data: 25.6 mol % DEG  
Density: 1.365 g/cm<sup>3</sup>

30     Example 4

68 mol % EG, 32 mol % DEG  
Inherent Viscosity: 0.748 dL/g  
DSC data: Tg = 56.5°C; Tm = 183.7°C  
NMR data: 31.5 mol % DEG  
35     Density: 1.362 g/cm<sup>3</sup>

Example 5 (Comparative Example)

82 mol % terephthalic acid, 18 mol %

isophthalic acid, 100 mol % EG

Inherent Viscosity: 0.721 dL/g

5 DSC data:  $T_g = 76.7^\circ\text{C}$ ;  $T_m = 196.0^\circ\text{C}$

NMR data: 18.0 mol % dimethyl isophthalate

Density:  $1.361\text{ g/cm}^3$

Example 6

10 Melt cast (amorphous) film from poly(ethylene-co-diethylene terephthalate) [10 mol % DEG] was produced using a laboratory scale cast film line which consisted of a Killian extruder having a 1 inch diameter, a single flight screw, a 6 inch wide die, and a 500 micron die  
15 opening. The film passed over a chill roll and was collected on a tubular, cardboard roll. All heater zones were set between  $262^\circ\text{C}$  and  $270^\circ\text{C}$ . The die was set at  $268^\circ\text{C}$  with a screw RPM of 65. This produced a measured melt temperature of  $267^\circ\text{C}$ , and an amperage  
20 reading of 3.5. The average thickness of the cast film was 250 microns. Prior to processing, the polymer was dried overnight at  $120^\circ\text{C}$  in a dehumidified air dryer.

Example 7

25 Melt cast (amorphous) film from poly(ethylene-co-diethylene terephthalate) [18 mol % DEG] was produced using a laboratory scale cast film line as described in Example 6. All heater zones were set between  $249^\circ\text{C}$  and  $255^\circ\text{C}$ . The die was set at  $255^\circ\text{C}$  with a screw RPM of 65.  
30 This produced a measured melt temperature of  $250^\circ\text{C}$ , and an amperage reading of 4.5. The average thickness of the cast film was 250 microns. Prior to processing, the polymer was dried overnight at  $120^\circ\text{C}$  in a dehumidified air dryer.

Example 8

Melt cast (amorphous) film from poly(ethylene-co-diethylene terephthalate) [26 mol % DEG] was produced using a laboratory scale cast film line as described in Example 6. All heater zones were set between 240°C and 243°C. The die was set at 248°C with a screw RPM of 65. This produced a measured melt temperature of 241°C, and an amperage reading of 4.5. The average thickness of the cast film was 250 microns. Prior to processing, the polymer was dried overnight at 120°C in a dehumidified air dryer.

Example 9

Melt cast (amorphous) film from poly(ethylene-co-diethylene terephthalate) [32 mol % DEG] was produced using a laboratory scale cast film line as described in Example 6. All heater zones were set between 230°C and 232°C. The die was set at 243°C with a screw RPM of 65. This produced a measured melt temperature of 231°C, and an amperage reading of 4.5. The average thickness of the cast film was 250 microns. Prior to processing, the polymer was dried overnight at 120°C in a dehumidified air dryer.

Example 10 (Comparative Example)

Melt cast (amorphous) film from poly(ethylene isophthalate-co-terephthalate) [18 mol % isophthalate] was produced using a laboratory scale cast film line as described in Example 6. All heater zones were set between 231°C and 237°C. The die was set at 242°C with a screw RPM of 65. This produced a measured melt temperature of 230°C, and an amperage reading of 5. The average thickness of the cast film was 250 microns. Prior to processing, the polymer was dried overnight at 120°C in a dehumidified air dryer.

Example 11

Biaxially oriented film was produced from poly(ethylene-co-diethylene terephthalate) [10 mol % DEG] 250 micron melt cast film using a T.M. Long orienting machine. The film was stretched 4 X 4 at a temperature of 92°C (T<sub>g</sub> + 20°C) at a rate of 28.8 cm/sec. in the X direction and 31.1 cm/sec. in the Y direction. The final stress was 8.31 mPa in the X direction and 6.69 mPa in the Y direction. Immediately after the film was stretched, it was rapidly air cooled below its glass transition temperature. The final thickness averaged 19 microns.

The biaxially oriented sheet was then heatset while being secured in a metal frame for 1 minute at 140°C. The film was then allowed to cool before removing from the heatset frame. The inherent viscosity of the film was 0.652 dL/g and the percent crystallinity was 36.8% based on DSC data. The physical properties of the film are listed below.

| <u>Property of Film</u>          | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
|----------------------------------|----------------------------------|-------------------------------------|
| Tensile Strength (mPa)           | 252                              | 274                                 |
| Tangent Modulus (mPa)            | 3,762                            | 4,237                               |
| Elongation at Break (%)          | 96                               | 101                                 |
| Elmendorf Tear Resistance (g/mm) | 1,300                            | 1,200                               |

Example 12

Biaxially oriented film was produced from poly(ethylene-co-diethylene terephthalate) [18 mol % DEG] 250 micron melt cast film using a T.M. Long

orienting machine. The film was stretched 4 X 4 at a temperature of 90°C (T<sub>g</sub> + 20°C) at a rate of 29.3 cm/sec. in the X direction and 31.0 cm/sec. in the Y direction. The final stress was 3.45 mPa in the X direction and 1.81 mPa in the Y direction. Immediately after the film was stretched, it was rapidly air cooled below its glass transition temperature. The final thickness averaged 16 microns.

The biaxially oriented sheet was then heatset while being secured in a metal frame for 1 minute at 140°C. The film was then allowed to cool before removing from the heat-set frame. The inherent viscosity of the film was 0.693 dL/g and the percent crystallinity was 30.3% based on DSC. The physical properties of the film are listed below.

| <u>Property of Film</u>          | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
|----------------------------------|----------------------------------|-------------------------------------|
| Tensile Strength (mPa)           | 156                              | 251                                 |
| Tangent Modulus (mPa)            | 3,548                            | 3,762                               |
| Elongation at Break (%)          | 59                               | 109                                 |
| Elmendorf Tear Resistance (g/mm) | 3,600                            | 3,600                               |

### Example 13

Biaxially oriented film was produced from poly(ethylene-co-diethylene terephthalate) [26 mol % DEG] 250 micron melt cast film using a T.M. Long orienting machine. The film was stretched 4 X 4 at a temperature of 80°C (T<sub>g</sub> + 20°C) at a rate of 29.7 cm/sec. in the X direction and 31.0 cm/sec. in the Y direction. The final stress was 3.00 mPa in the X direction and 1.74 mPa in the Y direction. Immediately after the film was stretched, it was rapidly air cooled

below its glass transition temperature. The final thickness averaged 15 microns.

The biaxially oriented sheet was then heatset while being secured in a metal frame for 1 minute at 140°C.

5 The film was then allowed to cool before removing from the heatset frame. The inherent viscosity of the film was 0.731 dL/g and the percent crystallinity was 23.0% based on DSC. The physical properties of the film are listed below.

|    |                                     |                                  |                                     |
|----|-------------------------------------|----------------------------------|-------------------------------------|
| 10 | <u>Property of Film</u>             | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
|    | Tensile Strength<br>(mPa)           | 192                              | 223                                 |
| 15 | Tangent Modulus<br>(mPa)            | 3,307                            | 3,659                               |
|    | <u>Property of Film</u>             | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
| 20 | Elongation at<br>Break (%)          | 106                              | 93                                  |
| 25 | Elmendorf Tear<br>Resistance (g/mm) | 2,800                            | 2,800                               |

#### Example 14

30 Biaxially oriented film was produced from poly(ethylene-co-diethylene terephthalate) [32 mol % DEG] 250 micron melt cast film using a T.M. Long orienting machine. The film was stretched 4 X 4 at a temperature of 77°C (T<sub>g</sub> + 20°C) at a rate of 29.1 cm/sec. in the X direction and 31.3 cm/sec. in the Y direction. The final stress was 2.1 mPa in the X direction and 1.0 mPa in the Y direction. Immediately after the film was stretched, it was rapidly air cooled below its glass transition temperature. The final thickness averaged 14 microns.

40 The biaxially oriented sheet was then heatset while being secured in a metal frame for 1 minute at 140°C.

The film was then allowed to cool before removing from the heatset frame. The inherent viscosity of the film was 0.715 dL/g and the percent crystallinity was 15.1% based on DSC. The physical properties of the film are listed below.

|    | <u>Property of Film</u>             | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
|----|-------------------------------------|----------------------------------|-------------------------------------|
| 10 | Tensile Strength<br>(mPa)           | 205                              | 207                                 |
|    | Tangent Modulus<br>(mPa)            | 3,397                            | 3,452                               |
| 15 | Elongation at<br>Break (%)          | 128                              | 104                                 |
| 20 | Elmendorf Tear<br>Resistance (g/mm) | 3,000                            | 3,200                               |

Example 15

Biaxially oriented film was produced from poly(ethylene isophthalate-co-terephthalate) [18 mol % isophthalate] 250 micron melt cast film using a T.M. Long orienting machine. The film was stretched 4 X 4 at a temperature of 97°C (T<sub>g</sub> + 20°C) at a rate of 29.8 cm/sec. in the X direction and 31.5 cm/sec. in the Y direction. The final stress was 4.25 mPa in the X direction and 2.74 mPa in the Y direction. Immediately after the film was stretched, it was rapidly air cooled below its glass transition temperature. The final thickness averaged 15 microns.

The biaxially oriented sheet was then heatset while being secured in a metal frame for 1 minute at 140°C. The film was then allowed to cool before removing from the heatset frame. The inherent viscosity of the film was 0.695 dL/g and the percent crystallinity was 24.0%

based on DSC. The physical properties of the film are listed below.

|    | <u>Property of Film</u>             | <u>Machine (X)<br/>Direction</u> | <u>Transverse (Y)<br/>Direction</u> |
|----|-------------------------------------|----------------------------------|-------------------------------------|
| 5  | Tensile Strength<br>(mPa)           | 243                              | 263                                 |
| 10 | Tangent Modulus<br>(mPa)            | 3,934                            | 4,644                               |
|    | Elongation at<br>Break (%)          | 104                              | 74                                  |
| 15 | Elmendorf Tear<br>Resistance (g/mm) | 2,800                            | 3,100                               |

Example 16

20 The following table shows examples of the relationship between mole percent DEG in poly(ethylene-co-diethylene terephthalate) copolymers and melting point and percent crystallinity for biaxially-oriented and heat-set films.

|    | <u>Mole Percent<br/>DEG</u> | <u>T<sub>m</sub></u> | <u>Crystallinity<br/>(%)</u> |
|----|-----------------------------|----------------------|------------------------------|
| 25 | 1.5                         | 258.5                |                              |
| 30 | 3.9                         | 256.5                |                              |
|    | 10                          | 230.1                | 36.8                         |
| 35 | 18                          | 226.2                | 30.3                         |
|    | 26                          | 202.8                | 23.0                         |
| 40 | 32                          | 183.7                | 15.1                         |

Example 17

45 The following table shows examples of the relationship between mole percent DEG in poly(ethylene-co-diethylene terephthalate) copolymers and water vapor

transmission rates in biaxially oriented films. Film thicknesses are approximately 100 microns. This example shows how the copolyester films become more permeable to water as the amount of DEG in the polymer is increased.

|    |                     |                                          |
|----|---------------------|------------------------------------------|
| 5  |                     |                                          |
|    | Mole Percent<br>DEG | WVTR*<br>g/mm/100 cm <sup>2</sup> /24 Hr |
| 10 | 10                  | 19.9                                     |
|    | 18                  | 23.7                                     |
|    | 26                  | 33.8                                     |
| 15 | 32                  | 40.0                                     |

\*Water vapor transmission rate

Example 18

20        These biaxially oriented copolyester films were laminated to aluminum. Approximately 1-inch square sections of film (18 microns thick) were placed between two 1 X 4 inch 300 microns thick sheets of No. 3104 aluminum and pressed together with a Sentinel heat

25        sealer press for 20 seconds at 0.41 mPa. The laminates were bonded at various temperatures. The following table shows examples of the relationship between mole percent DEG in poly(ethylene-co-diethylene terephthalate) copolymer films and T-peel strength.

30        This table shows the drastic increase in bond strength when the level of DEG in the copolymer is 10 percent and above, especially at bonding temperatures of 230°C.

Peel Strength vs. Copolyester Composition:  
Aluminum Bonded at 215 and 230°C

|    | Mole Percent<br>DEG | Peel Strength<br>(g/mm) at 215°C | Peel Strength<br>(g/mm) at 230°C |
|----|---------------------|----------------------------------|----------------------------------|
| 5  | 2                   | no bond                          | no bond                          |
|    | 10                  | no bond                          | 31.7                             |
| 10 | 18                  | 25.0                             | 80.1                             |
|    | 26                  | 72.9                             | 104.0                            |
| 15 | 32                  | 83.3                             | 107.0                            |

Example 19

These biaxially oriented copolyester films were laminated to steel plates. Approximately 1-inch square sections of film (18 microns thick) were placed between two 1 X 4 inch 380 microns thick sheets of steel and pressed together with a Sentinel heat sealer press for 20 seconds at 0.41 mPa. The laminates were bonded at various temperatures. The following table shows examples of the relationship between mole percent DEG in poly(ethylene-co-diethylene terephthalate) copolymer films and T-peel strength. This table shows the drastic increase in bond strength when the level of DEG in the copolymer is 10 percent and above, especially at bonding temperatures of 250°C.

Peel Strength vs. Copolyester Composition:  
Steel Bonded at 230 and 250°C

|    | Mole Percent<br>DEG | Peel Strength<br>(g/mm) at 230°C | Peel Strength<br>(g/mm) at 250°C |
|----|---------------------|----------------------------------|----------------------------------|
| 35 | 2                   | no bond                          | no bond                          |
|    | 10                  | no bond                          | 98.9                             |
| 40 | 18                  | 22.6                             | 64.2                             |
|    | 26                  | 111.8                            | 98.7                             |
| 45 | 32                  | 114.5                            | 123.7                            |



This Sheet Has Been Replaced



- 19 -

### CLAIMS

We claim:

- 5        1.    Oriented film material having a thickness of from 5  
         to 50 microns, said film material comprising a  
         copolyester having an inherent viscosity of from  
         0.3 to 1.5 dL/g, and having repeat units from at  
10       least 85 mol % terephthalic acid, 70-90 mol %  
         ethylene glycol and 30-10 mol % diethylene glycol,  
         wherein the total of repeat units from ethylene  
         glycol and diethylene glycol are at least 90 mol %.
2.    Film material according to Claim 1 wherein the  
15       repeat units from terephthalic acid are at least  
         95 mol % and the total repeat units from ethylene  
         glycol and diethylene glycol are at least 95 mol %.
3.    Film material according to Claim 1 wherein the  
20       repeat units from diethylene glycol are at from 15  
         to 25 mol %.
4.    Film material according to Claim 1 which is  
         biaxially oriented.
- 25       5.    Film material according to Claim 1 which has a  
         thickness of 9 to 25 microns.
6.    A laminate comprising a substrate and the film  
30       material according to Claim 1.
7.    A laminate comprising a metal substrate and the  
         film material according to Claim 1.



8. A laminate according to Claim 7 wherein said metal is selected from steel and aluminum.
- 5 9. A container wherein at least a portion thereof comprises the laminate according to Claim 6.
- 10 10. A container wherein at least a portion thereof comprises the laminate according to Claim 8.
- 10 11. The method of making a laminate having improved water vapor barrier properties comprising  
15 (1) laminating a metal layer to an oriented copolyester layer at a temperature of 180°C-260°C, said copolyester layer having a thickness of from 5 to 50 microns, said copolyester having an inherent viscosity of from 0.3 to 1.5 dL/g and having repeat units from at least 85 mol % terephthalic acid, 70-90 mol % ethylene glycol and 30-10 mol % diethylene glycol [again, at least 90 mol % =  
20 (DEG + EG)], and optionally quenching said laminate to a temperature below the glass transition temperature of said copolyester.
- 25 12. The method of making a laminate in accordance with Claim 11, wherein the unquenched laminate is heated to a temperature of 225°C-280°C, and quenching said laminate to a temperature below the glass transition temperature of said copolyester whereby said copolyester layer becomes substantially  
30 amorphous.



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- 21 -

13. The method of making an article of manufacture comprising making a laminate in accordance with the method of Claim 11 or 12, followed by stretching said laminate whereby the film material is oriented.

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