(54) Title: LAMINATED METAL SHEET
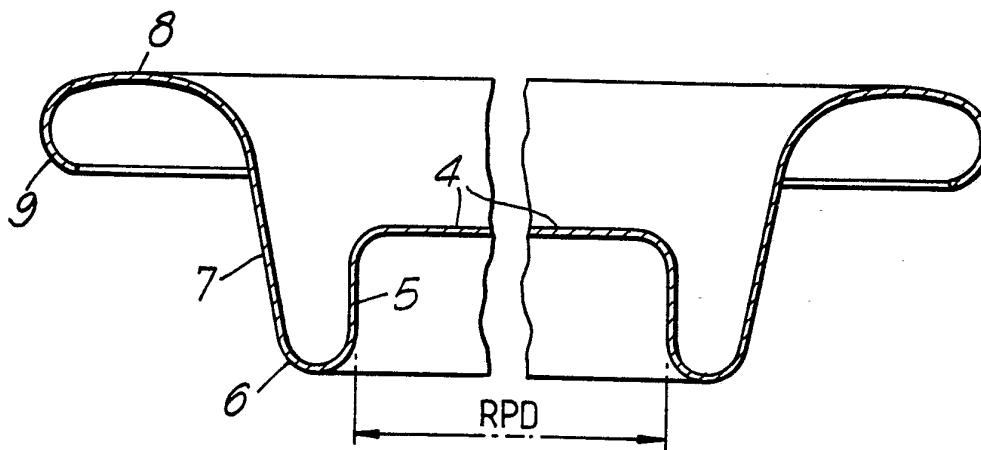
(57) Abstract

A can end is formed from a metal sheet having adhered thereto a coating of a semi-crystalline thermoplastic polyester film. The can end comprises a central panel (4), a panel wall (5) dependent from the periphery of the centre panel, an annular counter-sink bead (6) extending outwardly from the panel wall (5), a chuck wall (7) extending upwardly from the periphery of the counter-sink bead and an annular seaming panel (8) extending radially from the chuck wall (7). The metal sheet comprises an aluminium alloy having a magnesium content between 0.8 % and 2.0 % by weight and manganese content between 0.6 % and 1.5 % by weight; the polyester coating has a crystallinity factor in the range 0.05 to 0.5 measured by X-ray diffraction; and the distance between the chuck wall and panel wall is between 0.85 mm and 1.0 mm as measured at a height of 0.45 mm above the lowest part of the upper surface of the countersink bead

- 1 -

LAMINATED METAL SHEET

FIELD OF THE INVENTION

The present invention relates to a process for producing
polymer film coated metal sheet and to can ends of polymer
film coated metal sheet.

BACKGROUND TO THE INVENTION

Metal materials coated with thermoplastic polymer film are
well known. The use of such materials for rigid metal
packaging has been widely described.

Simultaneous lamination of polyester and polyolefin films
to metal sheet is disclosed in EP-A-0312302. This
specification is primarily concerned with lamination to
steel sheet of a composite polyester film on one major
surface and a polyolefin containing film on the other
major surface. The polymer film coated steel sheet was
found to be useful in the production of can ends.

Simultaneous lamination of a polyester/metal/polyester
laminate is also disclosed in EP-A-0312303 in which a
composite coextruded polyester film is adhered to steel
sheet. Good corrosion resistance was imparted by the use
of an outer polyester layer having a crystallinity greater
than 30% as measured by density.

EP-A-0312304 describes a polymer film coated metal sheet
to which is adhered an amorphous polyester. The polymer
film coated metal sheet was found to be particularly
useful in the formation of drawn and wall ironed cans
made from aluminium 3004 alloy.

- 2 -

JP 58-25591 describes a process for the production
of a metal substrate coated with a thermoplastic
polyester resin using low crystallinity starting film
material. It was found that a crystallinity range of
5 to 50% for the polyester in the laminate was useful
because the forming and processing properties of
coated metals and the corrosion resistance of the formed,
processed products were dramatically increased by
maintaining the degree of crystallisation of the resin
layer to within the specified limits.

GB-A-2123746 discloses a method of producing a metal sheet
laminated with a polyester resin film by coating the metal
with a crystalline and oriented polyester resin film.
Laminates of steel or aluminium were produced by a
controlled single step, metal heating process, film
application and then without reheating, quenching.

Techniques for the manufacture of beverage can ends are
well established.

EP-A-0153115 discloses a method of making a can end.
According to this method, a disc is blanked and a shallow
drawn cup is formed from the disc. The shallow drawn cup
is reformed into a shell by forming a centre panel,
allowing the wall of the cup to fold and producing a
countersink or reinforcing channel. The presence of the
countersink is acknowledged to be important in rendering
the can end resistant to internal carbonation pressure. In
a typical can end, the profile of the countersink and the
size of the countersink radius limit the geometric
strength. In general, the smaller the countersink radius,
the stronger the can end in resistance to outward movement
when pressurised as part of a filled can.

- 3 -

Conventionally, a material which has hitherto been
extensively used commercially for easy open beverage can
ends is lacquer coated aluminium alloy AA5182. This alloy
has a high magnesium content of around 4 to 5% and the high
magnesium content of the 5182 alloy gives it high
strength. Because of its strength and good formability,
this alloy confers excellent pressure resistance, typically
100psi to can ends for a 5182 gauge of 0.28mm. A problem
with the 5182 alloy is that, because of its high strength,
the cost to produce material for can ends is relatively
large. In particular, the high magnesium content adds to
the material cost and increases the mill power, mill energy
consumption and time required to roll 5182 to can endstock
gauges compared to a lower magnesium content alloy such as
AA3004. Both factors, combined with a poorer metal yield
for 5182, result in a higher manufacturing cost for 5182
than 3004.

In order to reduce the cost of producing the can ends,
lacquered 5182 alloy can be made to thinner gauge.
However, thinner gauge 5182 alloy is less resistant to
pressure. The pressure resistance of can end shells
produced from thinner gauge 5182 can be increased to
acceptable values (90psi) by deepening the countersink
depth. For 0.245mm 5182 the countersink depth must be
increased from the standard 0.250 inches to 0.270 inches,
however the end is no longer seamable to cans without a
change in the seamer operation. Ends not interchangeable
on seaming with standard ends used in the beverage industry
are not desirable.

- 4 -

Attempts to increase the pressure resistance of thinner gauge 5182 by tightening the countersink radius of the can ends are comparatively ineffective (see Figure 8) and may result in a new problem. Cracks appear in the reformed lacquered 5182 material which in production could result in an unacceptable level of end metal failures and, if used commercially, would result in corrosion of the can end with consequential damage to the contents of the can.

In order to overcome the problems of cost and interchangeability, it has been surprisingly found that thermoplastic polymer film coated aluminium alloys of lower magnesium content than 5182 and lower strength than 5182 can be used to form can ends having a countersink radius of sufficient tightness to confer upon the can ends commercially useful pressure resistances.

SUMMARY OF THE INVENTION

The present invention provides a can end formed from a metal sheet having adhered thereto a coating of a semi-crystalline thermoplastic polyester film comprising a central panel, a panel wall dependent from the periphery of the centre panel, an annular countersink bead extending outwardly from the panel wall, a chuck wall extending upwardly from the periphery of the countersink bead and an annular seaming panel extending radially from the chuck wall, characterised in that the metal sheet comprises an aluminium alloy having a magnesium content between 0.8% and 2.0% by weight and a manganese content between 0.6% and 1.5% by weight; the polyester coating has a crystallinity factor in the range 0.05 to 0.5 measured by X-ray diffraction; and the distance between the chuck wall and panel wall is between 0.85mm and 1.0mm as measured at a height of 0.45mm above the lowest part of the upper surface

- 5 -

of the countersink bead. Preferably the polyester coating
has no substantial regions of oriented crystalline material
having a crystallinity factor above 0.5.

That distance is hereinafter defined as the "countersink
parameter". Preferably the countersink parameter is in the
range 0.87 to 0.95mm.

The crystallinity factor is determined by the method as
defined herein. Preferably the crystallinity factor is in
the range 0.08 to 0.45.

The aluminium alloy optionally includes: up to 0.4%
silicon; up to 0.35% copper, typically 0.2 to 0.35% such as
up to 0.25 % to 0.3%; up to 0.8% iron, typically to 0.7%;
and up to 0.25% zinc. Aluminium alloys falling within this
composition range are hereinafter referred to as 3XXX.
Thus, 3XXX includes aluminium 3004 but not the entire range
of 5017 (on alloy produced from recycled beverage cans).

Preferably the magnesium is present in the alloy up to
1.8%, more preferably above 1%. Preferably the manganese
is present in the alloy up to 1.2%, more preferably above
0.7%.

Preferably the entire polyester film reaches during coating
to the metal sheet a temperature equivalent to at least the
onset melting temperature of the polyester less 16°C.

The present invention also provides a process for producing
a coated metal sheet in which at least one surface is
coated with a semi-crystalline thermoplastic polyester.

- 6 -

The metal sheet comprises an aluminium alloy of the 3XXX type. The polyester may be laminated as a monolayer film, a coextruded film or a composite film.

The thickness of the metal will be in a range compatible with the double seaming operation for sealing the can end to a can, typically 0.26mm to 0.30mm for 206 diameter ends with a 0.250 inch countersink depth.

Aluminium alloys useful as the metal sheet of the present invention typically have, after coating, a proof stress at 0.2% elongation in the range 265 to 300 MPa.

Among preferred aluminium alloys containing manganese and magnesium are those from the aluminium AA3000 series of alloys and new alloys produced from recycled used beverage cans such as 5017. A particularly preferred aluminium alloy is aluminium AA3004. This alloy has relatively low manufacturing costs, is widely commercially available and can be readily laminated with polyester films in such processes as described in EP-A-312303 or EP-A-312304. The laminates produced may have a proof stress in the range 265 - 300 MPa depending on the in-going 3004 strength and lamination temperature.

Such polymer coatings can provide deep formability and excellent corrosion protection even after very severe forming, such as in DWI can forming. However, the formability is reduced if the polyester coating is not amorphous and typically a semi-crystalline coated 3004 can be wall ironed by only about 20% compared to about 70% for amorphous coatings. The thermoplastic plastic polymer in

the laminate must be a semi-crystalline thermoplastic
polymer. If an amorphous polyester is used,
recrystallisation occurs during pasteurisation of the
filled can. The result of the recrystallisation is that
the polyester coating has a cloudy or blushed appearance.
The degree of blushing may be variable depending on the
contact area with the water used in the pasteurisation
process. This is undesirable because poor end appearance
of the cans is commercially unacceptable.

Use of amorphous polyester is also undesirable because easy
open ends must open without excess feathering of the
internal coating around the opened scored region.
Amorphous polyester coatings are too elastic and do not
break cleanly but instead stretch to give a ragged edge
upon opening. Polyesters in a semi-crystalline form are
less elastic and break cleanly at the score.

Semi-crystalline thermoplastic polyesters usable in the
invention include polyethylene terephthalate and closely
related copolyesters. Typically such copolyesters will be
derived from at least 60 mole% terephthalic acid, 60 mole%
ethylene glycol and up to 40 mole % of a second
dicarboxylic acid and 40 mole % of a second dihydric
alcohol. Typical acids include: isophthalic acid, azeleic
acid, sebacic acid, adipic acid. Typical alcohols include:
diethylene glycol, triethylene glycol, and cyclohexane
dimethanol (CHDM). The polymer may be adhered to the metal
sheet as a monolayer film, or as a coextruded film or as a
composite film. Where a monolayer polyester film is used,
copolyesters are preferred such as copolyesters of
terephthalic acid, ethylene glycol and diethylene glycol or

- 8 -

copolyesters of terephthalic acid, azelaic acid, ethylene glycol and diethylene glycol or copolyesters of terephthalic acid, isophthalic acid and ethylene glycol. Advantageously, the proportions of the components of the copolyester are such that the resin onset melting point lies in the range $195^{\circ}C$ to $230^{\circ}C$. Onset melting points above $230^{\circ}C$ demand excessively high metal temperatures in lamination and those below $195^{\circ}C$ have the disadvantage of being difficult to control in the process of biaxial orientation. Film onset melting temperatures are measured by differential scanning calorimetry (DSC).

Where the semi-crystalline thermoplastic polymer comprises a coextruded film, the coextruded film comprises an inner layer and an outer layer. Typically, the inner layer has a lower melting temperature than the outer layer so that the coextruded film may be adhered to the metal sheet without melting the outer layer.

The inner layer of the coextruded film typically comprises a copolyester. The copolyester may be formed from two dicarboxylic acids and one or more dihydric alcohols, preferably from isophthalic acid, terephthalic acid, and a dihydric alcohol such as ethylene glycol. Advantageously, the proportions of the components of the copolyester are such that the onset melting point lies in the range $160^{\circ}C$ to $220^{\circ}C$. Melting points below $160^{\circ}C$ lead to difficulties in film processing particularly in the coextrusion process owing to problems of mis-matching of the temperature-viscosity characteristics of the polymer layers in the coextrudate. Melting points above about $220^{\circ}C$ lead to reduced adhesion to the metal. The outer

- 9 -

layer of the coextruded film is typically a polyester such as polyethylene terephthalate or a copolyester with an onset melting point typically in the range 230°C to 250°C.

Where the semi-crystalline thermoplastic polyester comprises a composite film, the composite film comprises an inner layer and an outer layer. Typically the outer layer is a biaxially oriented polyethylene terephthalate (PET) film with an onset melting point in the range 230°C to 260°C and a crystallinity factor in the range 0.05 to 0.5.

The inner layer is applied as a coating to the PET film either during or after the PET film manufacturing process. The inner layer thickness is typically 0.5 microns to 5 microns, preferably 1 microns to 2 microns, typically applied by extrusion coating or roller coating techniques.

The inner layer typically comprises a copolyester or a maleic anhydride graft modified polyolefin such as polypropylene. Such materials may be applied from solution or dispersion in solvents by roller coating or by extrusion coating.

Copolyesters may be formed from two dihydric alcohols and two dicarboxylic acids as described above and should melt in the range 150°C to 210°C giving the laminate stability if ends are printed and adhesion performed at low Tl values.

The extent of maleic anhydride graft modification of the polyolefin should be sufficient to give adhesion to both PET and aluminium and will typically be 0.2 to 0.5%.

- 10 -

In another aspect of the invention, there is provided a process which comprises thermally laminating a monolayer polyester film to the metal sheet by heating the metal sheet to a temperature T1, applying the film to a major surface of the metal sheet to form an initial laminate and reheating the initial laminate to a temperature T2, wherein, for a melting temperature Tm of the monolayer polyester film Tm <= T1 <= Tm + 40°C and Tm - 5°C >= T2 >= Tm - 20°C, so that the crystallinity factor of the polyester in the laminate is in the range 0.05 to 0.5. For the avoidance of any doubt, expressions of the form Tm <= T1 <= Tm + 40°C (and Tm - 5°C >= T2 >= Tm - 20°C, etc) appearing in this specification mean that T1 is in the range Tm to Tm + 40°C (and T2 is in the range Tm - 20°C to Tm - 5°C, etc).

In a further aspect the process comprises thermally laminating a two layer polyester film to the metal sheet by heating the metal sheet to a temperature T1, applying the film to a major surface of of the metal sheet to form an initial laminate and reheating the initial laminate to a temperature T2, the polyester film comprising an inner layer and an outer layer, wherein, for melting temperatures Tm(i) and Tm(o) of the inner and outer layers respectively, Tm(i) <= T1 <= Tm(o) + 15°C and Tm(o) - 3°C >= T2 >= Tm(o) - 16°C, so that the crystallinity factor of the polyester in the laminate is in the range 0.05 to 0.5.

Where the two layer polyester film is a composite polyester film in which the inner layer is a non-crystallisable polyester, T1 needs only to be high enough to ensure the formation of an intimate and complete contact between film and metal surfaces so that bonding takes place.

- 11 -

In the process of the present invention where a monolayer
film is used, this may be a polyester or copolyester single
layer film with a gauge in the range 6 to 35 microns,
typically 12 microns. Preferably, a biaxially oriented
film is used. The onset melting point of the polymer in
the film is advantageously in the range 195 to 230°C,
preferably about 200-220°C.

Monolayer films of various crystallinities can be used.
The film crystallinity is controlled largely by the heat
setting temperature following orientation. The starting
crystallinity of the film can affect the lamination
conditions and hence the crystallinity of the polyester in
the final product. Advantageously, the crystallinity
factor of the monolayer film applied to the metal sheet
exceeds 0.05. Films with starting crystallinities in the
range 10% to 45% as measured by density may be used.

A film of a starting crystallinity greater than around 10%
as measured by density is desirable. In the production of
biaxially oriented polyester film, the temperature to which
the film is heated after stretching dictates the heat
stability or shrinkage properties. If the crystallinity of
the film is too low, excessive shrinkage occurs during
lamination which is undesirable. The practical lower limit
for the heat set temperature is the temperature necessary
to stretch the film. The film must be stretched above the
glass transition temperature. (Stretching the film alone
can introduce around 8% crystallinity as measured by
density).

In the process of the present invention a coextruded film,
may be used, for example, a 12 micron polyester film
comprising a 10 micron outer layer and a 2 micron inner

- 12 -

layer.   Preferably   the   polyester   film   is   biaxially
oriented.   The   outer   layer   may   comprise   polyethylene
terephthalate with an onset melting point in the range
$230^{\circ}C$ to $250^{\circ}C$, preferably about $240^{\circ}C$.   The inner
layer may comprise a copolyester of onset melting point in
the   range $160^{\circ}C$ to $220^{\circ}C$,   preferably $180^{\circ}C$ to
$190^{\circ}C$.   The film heat setting temperature will be. chosen
to control film crystallinity and ensure that the inner
layer is amorphous.

Following the heating of the metal sheet to temperature T1,
the film to be laminated is typically applied to the metal
sheet under pressure.   This step is conveniently performed
with the use of pinch rolls to achieve intimate and
complete contact of the polyester with the hot metal
surface.   Reheating the laminate to temperature T2 is
preferably achieved by indirect means such as induction
heating.   Advantageously,   the   laminate   is   held   at
temperature T2 for a period (typically two seconds)
preferably followed by a rapid quenching.   A rapid
quenching step is conveniently performed in water, for
example through a curtain of water.

Typical apparatus and conditions for these process steps
are to be found in EP-A-0312302 and EP-A-0312303, both of
the present applicant.

BRIEF DESCRIPTION OF THE DRAWINGS
Figure 1 shows a schematic representation of a cross
section through a can end;

Figures 2 and 2A show schematic representations of composite or coextruded film laminated to one or both sides of a metal sheet with the same (2) or different (2A) films;

Figures 3 and 3A show schematic respresentations of a laminate of monolayer film laminated to one or both sides of a metal sheet with the same (3) or different (3A) polyester films;

Figure 3B shows a combination of coextruded and monolayer films on a metal sheet;

Figure 4 shows in greater detail a cross section of the countersink portion of a can end;

Figure 5 shows in partial section a tooling for can end manufacture;

Figure 6 shows a graph of crystallinity dependence of coextruded film on lamination temperature T2;

Figure 7 shows a graph of crystallinity dependence of monolayer film on lamination temperature T2;

Figure 8 shows a graph to illustrate the relationship between end peaking performance and reform pad diameter for 5182 and 3004 alloys;

Figures 9 and 9A show schematic representations of a metal sheet coated with a composite or coextruded polyester film (9) or a monolayer film (9A) on one side and a coextruded polypropylene film on the other;

- 14 -

Figures 10 and 10A show a diffraction pattern as measured by XRD between 4 and 20 degrees theta showing the peak resulting from the 100 diffraction planes of Example 35(iii) and a control Example respectively; and

Figure 11 shows a differential scanning calorimetry trace made between 40°C and 300°C giving the onset and peak melting temperatures of film B, as described in Table 6.

DESCRIPTION OF THE PREFERRED EMBODIMENTS
Lamination of Monolayer Film

Where Tm is the onset melting temperature of the monolayer film, $Tl >= Tm$. If Tl reduces below Tm, when the film contacts the metal, melting of the layer in contact with the metal does not occur. In such circumstances there is poor intimacy of film and metal and a sufficiently good even bond is not achieved. Scanning electron microscopy examination of a coated metal surface following lamination with a Tl below Tm shows blisters in the coating. Such blisters can result in pack test failure with beverage products.

The condition $Tl <= Tm + 40$, must be met. As Tl increases, so does the depth of film that melts on contact with the hot metal. If Tl is too high, the film becomes difficult to laminate because it creases and sticks to the lamination rolls. The crystallinity of the polymer in the laminated product is not sufficient to prevent blushing. The limit for Tl is lower for lower crystallinity films. Typically a monolayer film having an onset melting point of about 215°C with crystallinity as measured by density of

$$10\% \text{ requires a } T1 \text{ of } >= 210^{\circ}C$$
$$21\% \quad " \quad >= 230^{\circ}C$$
$$28\% \quad " \quad >= 240^{\circ}C$$
$$36\% \quad " \quad > =250^{\circ}C$$

Additionally, if T1 exceeds Tm + 50°C, the metal strength is reduced, thicker metal gauges are needed for adequate end performance and can end costs are increased.

The relationships of crystallinity and T2 for different T1 temperatures for a monolayer biaxially oriented polyester film are shown in Figure 7. The resin onset melting point is about 215°C as measured by differential scanning calorimetry (DSC).

A further condition to be fulfilled is that the reheating temperature T2 <= Tm - 5°C. Preferably, T2 <= Tm - 20°C. As T2 increases so does the amorphous fraction of the polymer. For the reasons discussed, high amorphous content is undesirable.

The lower limit to the reheating temperature is T2 = Tm - 20°C. There is no practical advantage in reducing T2 too greatly. No further significant gains can be made on selecting T2 values below Tm - 20°C because T1 then predominantly affects the crystallinity of the polymer and so T2 would no longer influence the crystallinity. No significant adhesion improvements occur below Tm - 20°C.

Lamination of Coextruded Film

In this embodiment, the melting temperature of the inner layer polymer is designated Tm(i) and the onset melting

- 16 -

point of the outer layer polymer is designated Tm(o). In
this process T1 >= Tm(i). If T1 is below Tm(i) the inner
layer polyester does not flow into the metal surface and a
continuous bond is not achieved. The temperature of the
first heating step, T1 <= Tm(o) + 15°C. If T1 is above
Tm(o) + 15°C, the polymer film becomes difficult to
laminate. The film creases badly and sticks to lamination
rolls. Additionally, the metal strength is significantly
reduced and the outer layer starts to melt in the first
stage heating by contact with the metal. The result is
that crystallinity of the polymer is undesirably reduced.

Reheating temperature is defined to be T2 <= Tm(o) -
3°C. As T2 increases above Tm(o), the film becomes
amorphous. At Tm(o) - 3°C the crystallinity of the
polymer is very sensitive to even small temperature changes
and so it is preferred that T2 <= Tm(o) - 16°C. This is
illustrated in Figure 6 for a polyethylene terephthalate
outer layer film in which the resin (PET) onset melting
point is about 240°C and the film a biaxially oriented 12
micron coextruded film.

Reheating temperature T2 is preferably greater than Tm(o) -
40°C, preferably Tm(o) - 30°C. If T2 is maintained too
low, the crystallinity of the film outer layer may not be
significantly reduced, which can lead to cracking of the
film when the score is produced. Additionally, preferably
T2 >= Tm(i). There is also no practical advantage in using
T2 below the melting point of the inner layer because
little improvment in adhesion is achieved.

Coated Metal Configurations

Referring to Figure 2 and 2A, a laminate of metal sheet and coextruded film is shown in one of two embodiments. A coextruded film comprising inner layer Ai and outer layer Ao is either adhered directly to one major surface of the metal only or a first coextruded film is adhered to one major surface of the metal sheet and a further coextruded film comprising inner layer Ai' and outer layer Ao' (which may be the same or different from the first coextruded film) is applied to the other major surface of the metal sheet.

Figure 2 also describes a laminate of metal sheet and a composite film in which Ao is PET and Ai is the inner layer of coating material.

Referring to Figure 3, 3A and 3B a monolayer film A is applied to one major surface of the metal sheet. Alternatively, the monolayer film A is applied to one major surface of the metal sheet and a further monolayer film A' (which may be the same or different from monolayer film A) or a coextruded film is applied to the other major surface of the metal sheet.

Figures 9 and 9A show schematic representations of a metal sheet coated with a polyester film Ao/Ai (9) or A (9A) on one side and a coextruded polypropylene film Bo/Bi on the other side, in which Bl is a poly(propylene-ethylene) copolymer containing a maleic anhydride graft modified polypropylene.

- 18 -

Can End Dimensions

The countersink parameter may be measured by the following
method. Referring to Figure 4, a countersink is shown
formed by a panel wall 5 extending from panel 4 to chuck
wall 7. Panel wall 5 and chuck wall 7 are joined by
countersink bead 6 defining the lowest point of the
countersink. Seaming panel 8 runs from chuck wall 7 to
curl 9. Countersink depth H runs from the highest point of
the seaming panel 8 to the lowest point of the countersink
bead 6.

The end or shell to be measured is embedded in a cold
curing transparent epoxy resin, such as Epofix, and allowed
to cure. A line is marked at 90° to the rolling
direction of the metal diametrically across the end and the
end is cut in half along this line. The exposed surface is
ground and polished to a 6 microns finish.

The countersink area is then examined using a microscope
and the following measurements are made.

Distance d is the countersink parameter and is measured
between chuck wall 7 and panel wall 5. Line 1 is drawn
parallel to and in continuation of panel 4 to meet the
chuck wall 7. Line 2 is drawn perpendicular to line 1 to
pass through the maximum depth of the countersink bead 6.
A distance of 450 ± 10 microns is measured from the
countersink bead 6 along line 2 towards line 1 and a point
at this distance is defined (distance denoted "h" on Figure
4). Line 3 is drawn perpendicular to line 2 to intersect
line 2 at the point defined and to meet the chuck wall 7
and panel wall 5. The length of line 3 is denoted the
countersink parameter "d".

- 19 -

Referring to Figure 5, tooling for can end manufacturing
is shown. Shell 13 is punched by punch centre 12 onto
reform pad 14. Knockout ring 15 is provided above die
centre ring 11 and contained within punch 16. The
operation gives punch centre radius 17 and draw radius 18.

EXAMPLES

Coils of AA3004, 3XXX, 5017 and AA5182 aluminium were
converted into thermoplastic polyester coated material by
the following process.

1.   Cleaning and Pretreatment

        The surface of coils of aluminium from the rolling
        mill (as rolled) are covered in rolling lubricant
        and aluminium fines. This does not produce an
        effective surface for bonding to polymer.

        Suitable pretreatments used to remove rolling oil
        and aluminium fines and to create a uniform
        surface layer with good adhesion to coatings
        include sulphuric acid anodising (SAA) phosphoric
        acid anodising (PAA), chromium phosphate
        pretreatment and zirconium phosphate
        pretreatment. These treatments incorporate three
        stages. Firstly the strip is cleaned. In the
        case of anodising, the anodising acid is used; in
        the case of chromium or zirconium phosphate
        treatments an alkaline preclean may be used. The
        cleaned strip is treated by hot immersion
        anodising (SAA or PAA) or by a spray or roller
        applied treatment for chromium or zirconium

- 20 -

phosphates. The strip is either rinsed to remove
any residual acid and dried or the roller applied
treatments dried in-place.

2.   Lamination

The cleaned and treated coil was laminated by the
following process.

The metal was heated to a temperature T1, the two
polymer films were each brought in contact with
one of the major surfaces of the metal using
pressurised nip rolls. The three layer laminate
was heated to a temperature T2 and the laminate
retained at an elevated temperature for around two
seconds before being rapidly quenched by uniform
weirs of water. The temperature ranges for both
T1 and T2 are described in detail in the text.

3.   Waxing

The surface of the polymer coated aluminium was
lubricated with a thin layer of a paraffin wax
typically 200 ± 100 mg per m^2.

Using apparatus of type described briefly with reference
to Figure 5, it is possible to vary the profile of the
countersink and the size of the countersink parameter.
Further details of such apparatus may be found in
EP-A-0153115 of the present applicant.

The dimensions of the countersink parameter are determined
by the die centre ring-reform pad gap or, for a fixed die

- 21 -

centre ring (DCR), the reform pad diameter. When the reform pad diameter (RPD) is varied and the cross section of lacquered aluminium 5182 end shells examined, it is observed that, as the countersink parameter is reduced by increasing RPD, there is a critical value at which the end is no longer interchangeable in double seaming or disruption appears in the 5182 material caused by forming/folding operations.

Interchangeability

Can ends are described as interchangeable when the double seam specifications are achieved without altering the operational settings of the double seaming machine from those appropriate to standard commercial can ends.

Certain critical dimensions are defined in Industry Specifications such as the Metal Packaging Manufacturer's Association Recommended Industry Specifications for Beer and Carbonated Soft Drink Cans. Section 6 of this document deals with Double Seam Standards. Provided the specified parameters are met, the double seam integrity is assured and seams will not leak. For 206 diameter beverage can ends, the critical dimensions are as follows:

Bodyhook butting	- 70% minimum
Actual overlap of	- 0.76mm minimum
Bodyhook and Endhook	-
Tightness Rating for Endhook	- 90% minimum

The following end seam dimensions are used to achieve acceptable seams:

- 22 -

Bodyhook Length   - 1.65 ± 0.13mm
Countersink Depth   - 6.35 ± 0.13mm
Seam Length   - 2.80mm maximum
Endhook Length   - 1.5 ± 0.13mm
Seam Gap   - 0.13mm maximum
Seam Thickness   - (3xEnd Thickness
                                + 2xBody Thickness
                                + 0.15mm)

The geometry, gauge and dimensions of a can end all influence the double seaming process and ability to achieve the required seam dimensions.

In particular:

(1)   The countersink parameter will influence the fit of the end to the seaming chuck and hence the bodyhook formation. If the countersink parameter is too small, the bodyhook length is inadequate.

        Seam dimensions effectively limit the extent to which the countersink may be tightened.

(2)   The endstock gauge cannot vary from the industry average by more than ± 0.02mm.

In the following Examples an X-ray diffraction method is used for calculating a measure of the crystallinity and orientation of the polymer coatings, which is called the "Crystallinity Factor", the measurement of which is defined below.

- 23 -

Crystallinity Factor Measurement

This X-ray diffraction (XRD) method may be summarised as follows.

Test Sample

A sample of laminate is cut from the strip and mounted on a flat aluminium plate (44 x 44 mm) using double sided adhesive tape so that the sample overlaps the plate by between 3 and 7mm. The final trim of the sample is from the front to avoid raised edges. The sample is inserted with the bottom resting on the sample holder support and fixed in a central position with a backing screw. An X-ray tube is fitted with a copper target and is set at 40 KV and 25mA. The XRD pattern is recorded from 4 to 20 degrees theta in steps of 0.02 degrees theta and with a count time of 1 second per point.

Control Sample

A control sample of ICI Melinex 800 polyester film of 12um thickness is mounted on a similar backing plate using double sided adhesive tape and its diffraction pattern is recorded under identical conditions as the test materials. The specification of this grade of film is described in ICI technical data sheet MX TD312 fourth edition 1985.

The scattering pattern from the control sample is recorded during the same working day as the test samples are measured.

- 24 -

Analysis

The diffraction patterns of the test samples are analysed
by measuring the height of the (100) peak at approximately
13 degrees theta. The peak and its surrounding area are
smoothed visually to remove the random noise. The
baseline is constructed by drawing a straight line
connecting the smoothed intensities at 12 and 14.5 degrees
theta. An example of a typical diffraction pattern is
shown in Figure 10. The peak heights measured to the
nearest millimetre are then coverted to counts. The
control sample is analysed using an identical procedure.

A diffraction pattern of ICI Melinex 800 film is shown in
Figure 10A. The baseline construction is shown. The
broad peak centred at approximately 8.5 degrees theta is
due to the scattering from the amorphous adhesive tape.

A ratio is calculated by dividing the counts of the test
sample by the counts of the control sample. This is
called the CRYSTALLINITY FACTOR (CF). It provides a
composite measure of the orientation and crystallinity of
the PET film in comparison to Melinex 800 film which is
known to have a high degree of orientation and
crystallinity.

$$(CF) = \frac{I(100)T}{I(100)C}$$

where I(100)T-Intensity of (100) peak for test sample
      I(100)C=Intensity of (100) peak for control sample

- 25 -

Reproducibility of Control Samples

Three samples were taken from a reel of Melinex 800 12um
film as specified above and the results were as follows,
    Sample A   7332 cts
    Sample B   7332 cts
    Sample C.   7264 cts
    Mean=7309 cts   Sample standard deviation (SD)=39 cts

Based on a normal distribution it would be expected that
>99% of the control samples should be within +/- 3 SD of
the mean, that is between 7417 and 7201 cts. Any value
outside of these limits is an indication that something
has changed unexpectedly, for example either the film has
aged or the output intensity of the X-ray tube has
decreased.

Measurement of Aluminium Strip Temperature

1.   Uncoated Aluminium

The measurement of moving, uncoated aluminium strip
temperature presents significant difficulties. Contact
measurements using thermocouples, for example, risk
damaging the metal surface, are often inaccurate for
rapidly moving strip and are not considered acceptable.
Of the non-contact techniques, infra-red pyrometers are
the most promising particularly for strip temperatures
above 150°. The significant limitation of this
infra-red radiation detection system lies in the very low
and variable emissivity of uncoated aluminium surfaces.
These properties give rise to inaccuracy and variability
in recorded temperatures.

Of the systems available commercially, the Williamson 12300 pyrometer is considered one of the more successful devices for the temperature range of 200°C to 300°C.

The temperature of the aluminium as it enters the lamination rolls is defined as T1.

2. Polymer Film Coated Aluminium

The coated aluminium surface temperature cannot be measured satisfactorily by contact techniques without unacceptable coating damage.

The presence of a polymer film on the metal surface after lamination increases the thermal emissivity substantially and effectively eliminates the variability in emissivity. For both polypropylene and polyester film coatings, commercial pyrometers exist that operate with a wavelength matching a strong absorption band in the polymer, permitting the accurate measurement of temperature for polymer coated aluminium

Polypropylene - 3.43 microns
Polyester   - 7.9 microns.

3.   Measurement (Estimation) of Temperature T1

The lamination equipment was configured initially as follows:
(1)   Unwind system for uncoated coil.
(2)   Triple induction-heated roll strip heater with fixed, constant roll temperatures adjusted to give accurately known metal temperatures for the strip leaving the roll heater system (TIS).

- 27 -

(3)   Downward strip path at 45° to the vertical.

(4)   Williamson 12300 pyrometer (measures T1 Williamson).

(5)   Lamination rolls 0.5m from the roll heater exit.

(6)   Agema TPT300 (7.9um) Pyrometer (measures T2E - the laminate temperature just prior to entering the transverse flux induction heater).

(7)   A transverse flux induction heater 0.5m from the nip rolls.

(8)   Agema TPT 300 (7.9 um) pyrometer (measures T2).

(9)   A quench 0.7m from the induction heater.

(10)   A turn roll in the quench.

(11)   Strip drying, bridle and rewinder.

The strip temperature (TIS) was set using the roll heater and temperatures (T1 Williamson, T2E and T2) measured. (Table 1), for a line speed of 20M/minute, laminating 12um polyester films to the AA 3004 aluminium (gauge 0.3mm).

The loss of temperature between the roll heater and the lamination rolls is conveniently calculated using a mathematical model of the convective and radiative heat losses from the surface of the hot sheet to the surrounding environment at ambient temperature. The model takes into consideration plate orientation, natural convective losses, forced convection due to sheet motion and radiation from the plate which is assumed to have an emissivity of 0.1. The surrounding environment is assumed to have grey body characteristics with an emissivity of 0.9.

- 28 -

Table 1

Temperature ($^\circ$C)

T1S	T1 Williamson	T2E	T Loss	T1	(T1-T2E)
220	213	170	9.0	211	41
240	228	189	9.4	230.6	41.6
260	248	207	10.5	249.5	42.5
280	270	222	11.7	268.3	46.3

The temperature of aluminium entering the lamination rolls
(T1) was estimated and (T1-T2E) calculated. (Table 1).

The value of T1 is the critical temperature for thermal
lamination of polymer film to metal. The relationship
between T1 and the mean melting point of the polyester
film contacting the hot metal governs the tacking of film
to the metal, the critical intimacy of contact that
eliminates voids at the polymer-metal interface, and the
adhesion of polymer to metal.

T1 is difficult to measure, particularly if the aluminium
strip is heated by techniques such as transverse flux
induction heating or if the strip speed changes. T1 is
estimated by taking an accurately known temperature, T2E
and correcting the value for the calculated losses in the
pre-lamination and lamination processes. The calculation
in Table 1 illustrates the calculation of:

- 29 -

(1)   Tl where TIS was accurately known.
(2)   (Tl-T2) for 12 micron PET film.

The lamination loss   is used with the measured T2E to
estimate Tl where no TIS value is known, as for example
where a transverse flux induction heater or an air
floatation oven (with high air over-temperature) is used
to heat the aluminium.

In Table 3 (T2E +   ) has been used to calculate Tl.

Film Resin Melting Point

Polymer materials, unlike metals, have no single
temperature melting point but exhibit melting behaviour
over a range of temperatures. The spread in molecular
weight thermoplastic polymers like polyesters and
polypropylenes and the variation in crystal sizes
underlies the melting behaviour.

Differential Scanning Calorimetry (DSC) can be used to
illustrate the melting behaviour and define an onset
melting temperature T_m. It is the relationship between
T_m of the polyester contacting the metal and Tl that
governs the effectiveness of lamination.

<u>Method for measuring the onset melting point of PET
film by DSC</u>

The measurement is conveniently made on the Perkin Elmer
DSC7. Calibration is performed at two positions, with
Indium using a melting point onset of $156.60^{\circ}C$ and with
Tin using a melting point onsert of $231.88^{\circ}C$.

- 30 -

Sample preparation

The sample of PET is tested in the "as received" condition. If there is any indication that the sample has inadvertantly been heated above 50°C it should be disgarded and another sample obtained. Discs of about 5mm are punched from the film and a sample of 5 to 10 mg weighed to an accuracy of 0.01mg. The sample is encapsulated in an aluminium pan with the lid crimped to seal the pan.

Testing conditions

The sample is heated at a range of 20°C per minute from 40°C to 300°C. The sample chamber is purged with dry nitrogen during the heating run.

Calculation of Onset Temperature

The melting peak around 230°C is identified and the baseline is constructed by connecting the two stable lines on either side of the peak. Another construction line is made by extrapolating to the baseline a line from a tangent at the point or part of the curve prior to the Tm-peak where the line subtends the maximum angle with the baseline. Where this line meets the baseline is defined as the onsert temperature. This is illustrated in Figure 11, which shows the onset and peak melting temperatures of film B, as described in Table 6. According to the Figure an onset temperature of approximately 216.5°C is measured, with a peak melting temperature of 230.4°C.

- 31 -

Precision

Repeatability: Duplicate determinations on two specimens
by the same analyst should not differ by more than 1.5°C.

Reproducibility: Duplicate determinations on specimens of
the same sample analysed in different laboratories should
not differ by more than 2°C.

Copper Sulphate Test

In the following Examples the copper sulphating test to
which the can ends are subjected requires a solution of
acidified copper sulphate. This solution is prepared with
the following composition:

        1750 mls water
        500 g hydrated copper sulphate
        215 mls hydrochloric acid (35%).

Copper sulphate is placed in a can to a depth of 2.5cm (1
inch) and the end to be tested is seamed on the can. The
can is then stored upsidedown for 24 hours so that the end
to be tested is covered in copper sulphate. The ends are
then removed and examined.

Coating Integrity

In order to assess the integrity of the internal coating,
ends were tested using a 1% sodium chloride solution as a
conducting electrolyte. Ends were attached by a vacuum
device to a cylindrical container holding the electrolyte
and a voltage of 6.3 volts was applied across an electrode
and the end. The current passing between the electrode

- 32 -

and the end is a measure of the aluminium exposure through
the coating on the end and is called the Enamel Rating
Value (ERV).

Blushing and Adhesion

Ends are pasteurised at 70°C for 45 minutes in water and
inspected visually for change in appearance (blushing).

Adhesion is assessed by applying 3M 610 tape to an area of
cross hatched scores cut into the polyester coating prior
to pasteurisation, score spacing 1mm in a 10x10 array of
scores.   Adhesion   is   assessed   by   the   percentage   of
delaminated squares after vigorous removal of the tape.

Rapid Pack Test (RPT)

A solution is prepared containing citric acid, phosphoric
acid and sodium chloride dissolved in deionized water.
This solution is placed in the can and the can is covered
with a plastic wrap and placed in an oven at 150°F until
the can fails by perforation.   20 cans are tested per
variable and the mean time to failure is calculated and
recorded.

Assessment of cracking of the polymer in the score and
rivet region

The preferred method is to examine the internal polymer
coating using a steromicroscope.   A brightfield episcope
ring illumination was used at magnifications ranging from x
10 to x 40 to give the preferred conditions.   Cracking
around the rivet and along the score potentially leading to
metal exposure could be easily observed, if present.

Assessment of crazing after seaming

The end should be seamed onto a can under the standard seamer settings for beverage ends. The can should then be carefully cut away to expose the product side of the countersink wall region. This region should be examined using an optical microscope for the crazing of the polymer film.

Description of the Examples

The Examples are described in six tables:

TABLE 2   Table 2 demonstrates the relationships between metal composition, film type, end forming and end performance.

TABLE 3   Table 3 illustrates the relationships between film type and lamination conditions on coating properties and performance.

TABLE 4   Table 4 demonstrates the importance in selecting some shell forming tooling on shell performance.

TABLE 5   Table 5 defines the metal compositions.

TABLE 6   Table 6 defines the films used.

TABLE 7   Table 7 describes the metal surface treatment.

Unless otherwise stated all the Examples are examples of the invention.

- 34 -

TABLE 2

Table 2 demonstrates relationships in metal composition, film type and end performance.

Examples 1 to 4

Examples 1 to 4 demonstrate the effect of varying the RPD on a coextruded polyester film coated 0.30mm 3004 material. As the RPD is increased from 2.044" to 2.056", the countersink parameter falls from 0.97 to 0.93mm, peaking pressure rises by 15psi and no metal deterioration occurred in the critical reformed region. Over the RPD range, chuck fit was maintained and shells remained interchangeable.

Comparison of Examples 1 to 4 with 11 to 13 and 16 (Figure 8) demonstrates that the behaviour of polymer film coated 3004 is unexpected and unusual, when compared to coated 5182.

Examples 8 to 10

Example 10 illustrates a comparison with Example 4 but with a 0.28mm 3004 material. The peaking pressure is lower as expected from the relationship between metal gauge and shell strength.

- 35 -

Peaking Pressure   = $kT.t^{1.1}$

k   =   constant dependent on end design
T   =   tensile strength
t   =   metal gauge

Examples 5 to 7

In Examples 5 to 7, a similar pattern of behaviour
is observed as for Examples 2 to 4 but with a
coextruded polyester film coated aluminium (3XXX)
lying outside the 3004 specification, having a
1.42% magnesium content. The peaking pressure
rises by 10psi and the countersink parameter falls
from 1.0 to 0.92mm as the RPD is increased from
2.048" to 2.056".

Examples 11 to 14

Comparative Examples 11 to 14 are not examples of
the invention. The material J lacquer coated 5182
has a magnesium content of 4.67% and manganese
content of 0.34% both outside the range of the
invention.

Internal lacquer   -   PVC organosol
External lacquer   -   epoxy based.

The peaking pressure rises by only 2psi as the RPD
is increased from 2.044" to 2.056" and countersink
parameter falls from 1.05 to 0.93mm. Some
disturbance of the reformed area occured at 2.056"
and 2.060" RPD values.

Examples 11 to 14 represent the known behaviour of commercial end stock materials in end forming.

Examples 16 and 17

Comparative Examples 16 and 17 are not examples of the invention.

In Examples 16 and 17, polyester film coated 5182 was used instead of the lacquer coated 5182 of Examples 13 and 14. The performance and material disturbance characteristics of Examples 13 and 14 and 16 and 17 are similar, demonstrating that the type of coating or coating process are not important to the physical strength or cracking behaviour of 5182 end shells.

Examples 30 and 31

Comparative Example 30 is not an example of the invention having manganese and magnesium contents outside the range of the invention.

Comparison of Examples 11 and 30 illustrate that thinner gauge 5182 materials (Example 30) can give acceptable peaking performance but with a countersink depth of 0.270 inches that
renders it not interchangeable with standard 0.250 inch countersink ends in commercial double seaming operations.

Similarly thin gauge products of the invention
also give acceptable physical performance with a
0.270 inch countersink depth as illustrated by
Example 31.

Examples 10, 18 and 19

The importance of countersink depth on peaking
performance is further illustrated in Examples 18
and 19.

An increase in countersink depth from 0.250" to
0.255" increases the peaking pressure by 4psi
without loss of interchangeability. The limit for
interchangeability in double seaming is 0.255".

Comparison of Examples 10 and 18 illustrates the
variation experienced with similar tooling on
different presses. Both utilise the same material
but Example 18 was produced on a single-out press
operated at low speed and Example 10 a double die
press operating at 300 strokes per minute.

Examples 1, 20 to 24

Examples 1 and 20 to 23 demonstrate a range of
biaxially oriented film types that can be combined
with aluminium alloys of the invention, in these
particular examples 3004.

Example 1 used coextruded polyester films on both
metal surfaces and is illustrated in Figure 2A in
which both Ao and Ao' are the same PET and Ai and
Ai' are both the same copolyester.

For Examples 20 and 23 monolayer copolyester films
were used as illustrated in Figure 3A in which A
and A' are the same film. The films B and E were
identical in composition but were heat set at
different temperatures to give different
crystallinities.

Example 21 is equivalent to Example 1 but used a
coextruded film with different copolyester layer
Ai, different PET layer Ao and different resin
fillers.

In Example 22 a monolayer copolyester film was
used but of a different composition to Examples 20
and 23.

Example 24 combines two different films as
illustrated in Figure 9. The coextruded polyester
film is the film used in Example 1 and forms the
external coating. The coextruded polypropylene
film Bo/Bi is a co extrusion of:-

Bi - Maleic anhydride graft modified polypropylene
Bo - Polypropylene.

These examples illustrate that different types of polyester film can be used successfully and combined with other film types for the internal film.

Examples 25 to 29 and 32

Examples 25 to 29 demonstrate that a range of manganese and magnesium contents may be used (with advantages in reduced metal production costs) and that there is no simple relationship between magnesium or manganese content and the physical performance (compare Examples 7 and 26). There is some evidence that end performance falls as magnesium and manganese contents rise.

Based on the general trend between end physical performance and magnesium and manganese contents of these low magnesium alloys, the upper limits for the contents of these elements can be judged. The upper limit for manganese is set at 1.5% and for magnesium at 2%. Thus, Examples 25 and 28 are considered to be comparative examples.

Examples 33 and 34

Examples 33 and 34 illustrate the use of coloured and white films as external coatings for can ends.

Example 34 also describes the use of a composite film.

TABLE 3

Table 3 illustrates the relationships between film type and lamination conditions on coating properties and performance. All the polymer film coated examples are based on metal compositions conforming to the invention.

Examples 4(i) to 4(iv)

Example 4(i) is not an example of the invention.

Examples 4(i) to 4(iv) and Figure 6 demonstrate the effect of lamination temperature T2 on film crystallinity and coating "blushing" on pasteurisation of ends for coextruded PET film.

As T2 increases from $220^{\circ}C$ towards the PET melting point, film crystallinity falls as the lower molecular weight or smaller crystals melt. At a T2 of $250^{\circ}C$ the entire film is melted. Low crystallinity factor values, particularly below 0.05 allow visible recrystallisation to occur in pasteurisation giving an unsightly effect (Example 4(i)).

Table 3 also shows that amorphous (crystallinity factor = 0) Example 4(i)) coatings perform badly in the copper sulphate accelerated corrosion test that simulates shelf life testing with aggressive real beverage products. Semi-crystalline coatings 4(ii) to 4(iv) perform well.

- 41 -

In Example 4(v) examination of the coated metal
showed the presence of very small blisters at the
polymer/metal interface and visible whitening of
the coating on the end shell countersink region.
The voiding effect occurs when the Tl value is
below the melting point of the polymer contacting
the metal surface and there is inadequate melting
of the polymer into the metal surface. The
melting point for the coextruded copolyester
contacting the metal of film A lies in the range
180 - 190°C and in Examples 4(i) to 4(v),
voiding only occurs in 4(v) where Tl is below the
resin onset melting point.

Example 4(v) lies outside the preferred range in
Tl.

When the lamination temperature T2 lies close to
the melting point inevitable temperature variation
across the metal strip will give variability in
coating crystallinity across the coated metal. It
is advisable to maintain T2 at a value where there
is little variation in crystallinity with
temperature (see Figure 6), typically below
235°C for PET based film.

Examples 4, 7 and 10

Examples 4, 7 and 10 demonstrate that a range
(210°C to 250°C) of Tl values can be used
successfully with a common T2 (230°C) for
coextruded polyester film A. In each case the Tl
value lies above the coextruded inner resin layer
melting point which is in the range 180-190°C.

- 42 -

Examples 4, 20 to 24 and 15

Examples 20 to 24 illustrate the use of different
film types from those in Example 4. In each case
Tl is chosen to lie above the film or inner layer
onset melting point (to prevent interfacial
voiding) and T2 selected to prevent significant
loss of film crystallinity.

None of the polymer film coated examples suffered
from blushing or adhesion failure.

Comparison of the RPT shelf life (an accelerated
test) results for polymer coated examples (4,
20-24) and the lacquer coated 5182 Example 15
shows that polymer coatings enhance shelf life
even where the countersink radius is tighter than
for lacquered ends.

Example 15 is not an example of the invention but
illustrates the deficiencies of lacquer coatings.

Example 25 demonstrates the use of a film with the
onset melting point near the bottom end of the
suggest range. Correspondingly lower T1 and T2
temperatures have been used to ensure the right
combination of properties.

Examples 20(i) to (v) and 23(i) to (iv)

In Examples 20 and 23 the polymer films B and E
are monofilm polyesters with the same chemical
composition and melting point (212-216°C) but

- 43 -

with different crystallinities arising from
different heat-setting temperatures in the
post-biaxial orientation phase of film making.

Comparative Examples 20(i), (iv) and (v), are not
examples of the invention. Examples 20(i) and
(iv) illustrate that T1 values below the onset
melting point (Tm) give metal/polymer interface
voids or blisters. Examples 20(i) and 20(iv) have
T2 values close to Tm and the consequential loss
of crystallinity that leads to "blushing" on
pasteurisation. For Example 20(iv) the absence of
second stage heating and relatively low T1 leads
to poor adhesion of coating to metal. Only in
Example 20(ii) and 20(iii) is there a satisfactory
combination of properties.

Comparative Examples 23(i), (ii) and (iii) are not
examples of the invention.

Examples 23(i) and (ii) illustrate the problems of
poor adhesion if no second stage heating is used.
In comparative Example 23(iii) a very high T1 has
ensured good adhesion but caused loss of
crystallinity that leads to "blushing" on
pasteurisation (recrystallisation). This is not
an example of the invention as the crystallinity
factor is below 0.05. Therefore Examples 23(i),
(ii) and (iii) lie outside the invention.

Example 23(iv) defines the preferred lower limit
to polyester film crystallinity factor at about

- 44 -

0.05 by demonstrating the slight tendency to
recrystallise with a crystallinity at about 0.05.
Example 23(iv) therefore lies just inside the
invention.

Examples 23(i), (ii) and (iii) follow the teaching
of GB2123746 and demonstrate the deficiencies in
this prior art.

Examples 35(i) to 35(vi)

Examples 35(i), 35(ii), 35(v) and 35(vi) are not
examples of the invention.

Examples 35(i) to 35(iv) demonstrate the possible
failure modes that can occur because the
crystallinity factor is not maintained in the
claimed range.

In examples 35(i) and 35(ii) the second stage
heating temperature is too low and hence the
crystallinity factor for the film is outside the
upper limit of 0.5. In these examples severe
cracking of the internal coating occurred around
the rivet and score. The effect of this is in
part demonstrated by the increased metal exposure
found on enamel rating the ends.

In examples 35(v) and 35(vi) the second stage
temperature is too high, and hence the
crystallinity factor for the polymer coating is
below the limit of 0.05. No cracking occurred on
these ends, however after the ends were seamed

onto cans, crazing could be seen around the countersink wall. This can lead to aluminium from the end dissolving into the product over the storage period.

Only in examples 35(iii) to 35(iv) do the right combination of properties ensure no cracking around the score of rivet or crazing on the countersink wall occurs.

Examples 36(i) to 36(vii)

Examples 36(i) 36(ii), 36(v), 36(vi) and 36(vii) are not examples of the invention.

In examples 36(i) and 36(ii) the second stage heating temperature is too low, outside the range specified in the formula $(Tm(o) - 3^{o}C >= T2 >= Tm(o) - 16^{o}C)$, which for this film $(Tm(o) = 241^{o}C)$ would give a range of $225-238^{o}C$. In this case, the elevated metal temperature used reduces the crystallinity of the layer contacting the metal but does not affect the crystallinity of the outer region of the film. The crystallinity of the outer region then exceeds the required crystallinity factor, leading to severe cracking of this region of internal coating around the rivet and score. The effect of this is in part demonstrated by the increased metal exposure found on enamel rating the ends.

In examples 36(v), 36(vi) and 36(vii) the second

- 46 -

stage temperature is too high, and hence the
crystallinity factor for the polymer coating is
below the limit of 0.05. No cracking occurred on
these ends. However after the ends were seamed
onto cans crazing could be seen around the
countersink wall. This can lead to aluminium from
the end dissolving into the product over the
storage period.

Only in examples 36(iii) and 36(iv) do the right
combination of properties ensure no cracking
around the score of rivet or crazing on the
countersink wall occurs. In these examples the
entire polyester coating reaches a temperature of
at least the onset temperature of the polyester
less 16°C. This temperature results in an
absence of any regions having a high degree of
oriented crystalline material.

TABLE 4

Selection of tooling geometries is important in the end
making and reforming processes and those skilled in the
art will understand which parameters to control. Table 4
illustrates the importance of several factors.

Examples 1 to 2(a) show that the punch centre radius has a
significant effect on material disturbance in the reformed
region. A PCR of 0.040" is preferred to 0.080".

Examples 3 to 6(a) show that Draw Radius influences the
countersink parameter and peaking performance.

- 47 -

TABLE 5

Table 5 defines the metal compositions in Tables 1 to 3.

TABLE 6

Table 6 describes the films used in Tables 1 and 2. All
the films were biaxially oriented by the following
process:-

(1)   Extrude resin onto chill roll.
(2)   Draw in the forward direction on heated rollers.
(3)   Draw in the transverse direction.
(4)   Heat set in an oven.
(5)   Cool.
(6)   Rewind.

The polyester films had a draw ratio of about 3x3 to 4x4
and the biaxially oriented polypropylene a draw ratio of
about 5x8 to 5x9.

TABLE 7

Table 7 describes the range of metal surface treatments
used in the Examples of Table 1, 2 and 3.

Table 2 - Page 1

Example Code	Metal Code	Metal Comp Mn	Metal Comp Mg	Metal Gauge (mm)	Proof Stress Laminated MPa	Film	RPD (Inches)	Peaking Pressure (psi)	Cracking or Roughening (sl = slight)	d (mm)	Punch Centre Radius Inchx1000	Chuck fit	Inter Changeability	Counter sink depth (Inches)
1	A	1.02	1.22	0.30	274	A	2.044	86	None	0.97	40	Yes	Yes	0.250
2	A	1.02	1.22	0.30	274	A	2.048	93	None	0.96	40	Yes	Yes	0.250
3	A	1.02	1.22	0.30	274	A	2.052	98	None	0.94	40	Yes	Yes	0.250
4	A	1.02	1.22	0.30	274	A	2.056	101	None	0.93	40	Yes	Yes	0.250
5	C	1.04	1.42	0.29	285	A	2.048	88	None	1.01	40	Yes	Yes	0.250
6	C	1.04	1.42	0.29	285	A	2.052	96	None	0.95	50	Yes	Yes	0.250
7	C	1.04	1.42	0.29	285	A	2.056	98	None	0.92	40	Yes	Yes	0.250
8	H	0.07	1.20	0.28	260	A	2.048	-	None	-	40	Yes	Yes	0.250
9	H	0.07	1.20	0.28	260	A	2.052	-	None	-	40	Yes	Yes	0.250
10	H	0.07	1.20	0.28	260	A	2.056	92	None	0.92	40	Yes	Yes	0.250
11	J	0.34	4.67	0.28	322	L	2.044	101	None	1.04	40	Yes	Yes	0.250
12	J	0.34	4.67	0.28	322	L	2.048	102	No cracking but sl roughening	0.96	40	Yes	Yes	0.250
13	J	0.34	4.67	0.28	322	L	2.056	103	No cracking but sl roughening	0.93	40	Yes	Yes	0.250
14	J	0.34	4.67	0.28	322	L	2.060	104	No cracking but roughened	0.89	40	Marginal	No	0.250
15	J	0.34	4.67	0.28	-	L	2.044	103	None	1.07	50	Yes	Yes	0.250
16	J	0.34	4.67	0.28	316	A	2.056	104	Incipient crack	0.93	40	Yes	Yes	0.250
17	J	0.34	4.67	0.28	316	A	2.060	104	Roughened	0.93	40	Marginal	No	0.250
18	H	0.07	1.20	0.28	260	A	2.056	87	None	-	40	Yes	Yes	0.250
19	H	0.07	1.20	0.28	260	A	2.056	91	None	-	40	Yes	Yes	0.255

Table 2   Page 2

Example Code	Metal Code	Metal Comp Mn	Metal Comp Mg	Metal Gauge (mm)	Proof Stress Laminated MPa	Film	RPD (inches)	Peaking Pressure (psi)	Cracking or Roughening	d (mm)	Punch Centre Radius (Inch x1000)	Chuck fit	Inter Changeability	Counter sink depth (inches)
20	F	0.88	1.18	0.29		B	2.056	93	None	0.88	40	Yes	Yes	0.255
21	A	1.02	1.22	0.30	274	C	2.044	-	-	-	50	Yes	Yes	0.250
22	A	1.02	1.22	0.30	274	D	2.044	-	-	-	50	Yes	Yes	0.250
23	F	0.88	1.18	0.29		E	2.056	96	None	0.88	40	Yes	Yes	0.255
24	F	0.88	1.18	0.29		A out F in	2.056	95	None	-	40	Yes	Yes	0.255
25	I	1.09	2.02	0.28	270	K	2.056	84	None	0.88	40	Yes	Yes	0.250
26	D	0.90	1.44	0.28	290	B	2.056	89	Sl busting	-	40	Yes	Yes	0.255
27	F	0.88	1.18	0.28	270	A	2.056	92	None	1.02	40	Yes	Yes	0.251
28	I	1.09	2.02	0.28	270	A	2.044	84	None	0.88	40	Yes	Yes	0.255
29	E	0.95	1.55	0.295	300	A	2.056	103	Sl roughening	0.88	40	Yes	Yes	0.255
30	J	0.34	4.67	0.245	322	L	2.044	92	None	-	-	-	No	0.270
31	F	0.88	1.18	0.26	270	A	2.044	103	None	-	-	-	No	0.270
32	D	1.06	1.04	0.295	296	A	2.052	103	-	-	40	Yes	Yes	0.250
33	A	1.02	1.22	0.30	-	G out A in	2.044	-	-	-	40	Yes	Yes	0.250
34	A	1.02	1.22	0.30	-	J out H in	2.044	-	-	-	40	Yes	Yes	0.250
35	K	1.05	1.25	0.27	-	A	2.052	97	None	0.92	40	Yes	Yes	0.253
36	K	1.05	1.25	0.27	-	C	2.056	91	None	0.92	40	Yes	Yes	0.253

Table 3 (part 1)

Example Code	Metal Code	Film Code	T1 (°C)	T2 (°C)	Crystal- linity factor	"Blush"	ERV's (mA)	Corrosion by CuSO4	Adhesion Failure	RPT Days	Blisters in Coating	Cracking around score and mnt	Crazing on countersink wall after seaming
4	A	A	211	230	0.465	None	0.6	None	None	-	No		
7	C	A	195	230		None	0.005	None	None	29	No		
10	II	A	224	230	0.315	None	0.05	None	None	34	No		
20	F	B	222	210	0.15	None	0.2	None	None	20			
21	A	C	230	230	-	None	-	None	None	-			
22	A	D	230	210	-	None	-	None	None	28			
23	F	E	250	220	-	None	0.0	None	None	22			
24	F	A outside F inside	210	230	0.48 (A)	None	0.0	None	None	25			
15	J	L	-	-	-	None	0.39	None	None	19*	No		
25 (i)	I	K	206	190	0.160	None	0.	None	None	-			
cf 4 (i)	G	A	210	250	0.	Severe		Severe	None	-	No		
4 (ii)	G	A	213	240	0.06	None		None	"	-	No		
4 (iii)	G	A	213	230	0.465	None		None	"	-	No		
4 (iv)	G	A	220	220	0.575	None		None	"	-	No		
4 (v)	G	A	160	230	0.479	None		None	"	-	Yes		
cf 20 (i)	A	B	211	230	0.15	Severe		Severe	None	-	Yes		
20 (ii)	A	B	222	210	0.17	None		None	None	-	No		
20 (iii)	A	B	222	200	0.40	None		None	None	-	No		
20 (iv)	A	B	213	-	0.40	None		None	Fail	-	Yes		
20 (v)	A	B	230	230	0.	Severe		Severe	None	-	No		
cf 23 (i)	A	E	230	-	0.33	None		None	Fail	-	Yes		
23 (ii)	A	E	250	-	0.25	None		None	Marginal	-	No		
23 (iii)	A	E	269	-	0.03	Moderate		None	None	-	No		
23 (iv)	A	E	250	210	0.05	Very slight		None	None	-	Yes		

Table 3 (part 2)

Example Code	Metal Code	Film Code	T1 (°C)	T2 (°C)	Crystal-linity factor	"Blush"	ERV's (mA)	Corrosion by CuSO4	Adhesion Failure	RPT Days	Blisters in Coating	Cracking around score and mmt	Crazing on countersink wall after seaming
31	F	A	250	230		None	0.05	-	None	-	No		
35 (i)	K	A	228	215	0.576	None	1.14		None	-	No	Severe	None
35 (ii)	K	A	228	220	0.555	None	1.53		None	-	No	Severe	None
35 (iii)	K	A	228	225	0.433	None	1.80		None	-	No	v.slight	None
35 (iv)	K	A	228	230	0.093	None	0.34		None	-	No	None	None
35 (v)	K	A	228	235	0.010		0.23		None	-	No	None	Severe
35 (vi)	K	A	228	240	0.000		0.40		None	-	No	None	Severe
36 (i)	K	C	248	215	0.422	None	6.89		None	-	No	Severe	None
36 (ii)	K	C	248	220	0.308	None	22.2		None	-	No	Severe	None
36 (iii)	K	C	248	225	0.292	None	2.45		None	-	No	Slight	None
36 (iv)	K	C	248	230	0.236	None	1.0		None	-	No	None	None
36 (v)	K	C	248	235	0.037		1.4		None	-	No	None	Moderate
36 (vi)	K	C	248	240	0.004		0.6		None	-	No	None	Severe
36 (vii)	K	C	248	245	0.000		0.8		None	-	No	None	Severe

Note

* The RPT failure mode was by corrosion on the countersink radii.

Table 4 – The Effect of Tooling Configurations on Performance

Example Code	Metal Code	Film Code	RPD (Inches)	Shell Performance (psi)	Cracking	PCR (Inches x 1000)	Draw Radius (Inches x 1000)	Countersink parameter 'd' (mm)
1	A	A	2.044	86	No	40	40	0.97
1 (a)	A	A	2.044	-	Yes	80	40	1.05
2	A	A	2.048	93	No	40	40	0.91
2 (a)	A	A	2.048	92	Yes	80	40	0.96
3	A	A	2.052	90	No	40	40	0.94
3 (a)	A	A	2.052	99	No	40	70	0.91
4	A	A	2.056	101	No	40	40	0.93
4 (a)	A	A	2.056	102	No	40	70	0.87
6	O	A	2.052	95	No	40	40	0.99
6 (a)	C	A	2.052	96	No	40	70	0.91

Table 5 - Metal Composition

Metal Code	Cu	Si	Fe	Mn	Mg	Zn	Cr	Ti	Notes (1)
A	0.21	0.10	0.38	1.02	1.22	0.03	0.01	0.03	3004
B	0.135	0.18	0.47	1.06	1.04	0.019	0.02	0.02	3004
C	0.22	0.14	0.27	1.04	1.42	0.04	0.01	-	3XXX
D	0.19	0.15	0.34	0.98	1.44	0.01	0.03	0.008	3XXX Not Homogenised
E	0.14	0.17	0.5	0.95	1.55	0.015	0.01	0.025	3XXX
F	0.14	0.23	0.38	0.88	1.18	0.01	-	0.01	3004
G	0.22	0.20	0.40	0.67	1.40	-	-	-	3XXX
H	0.22	0.20	0.40	0.87	1.20	-	-	-	3004
I	0.21	0.23	0.34	1.09	2.02	0.03	0.01	-	Cast and rolled 5017
J	0.15	0.20	0.35	0.34	4.67	0.25	0.1	0.1	5182
K	0.30	0.17	0.8	1.05	1.25	0.25	-	0.1	3XXX

Note

(1) 3XXX is a material closely related to 3004 but with a magnesium content above 1.3% and below the 1.9% for 5017.

Table 6 - Film Types

Film Code	Construction	Bonding layer mp (°C) ONSET	Bonding layer mp (°C) PEAK	Bulk layer mp (°C) ONSET	Bulk layer mp (°C) PEAK	Composition bonding layer	Composition bulk layer	Gauge (microns)	Heat set (°C) (1)
A	Coextruded	185	205 ± 5	237	248	2 acids 1 glycol	"PET"	12	220
B	Monolayer		-	217	235	-	2 acid 2 glycols	12	165
C	Coextruded	220	235	241	255	Blend of two copolyesters	"PET"	12	220
D	Monolayer		-	213	230	-	1 acid 2 glycols	12	100
E	Monolayer		-	215	232	-	2 acids 2 glycols	12	190
L	Monolayer		-	215	232	-	2 acids 2 glycols	12	185
F	Coextruded	135	150	150	168	Maleic anhydricle graft modified polypropylene	Polypropylene	20	155
L	Lacquered		-			-	Internal-organosol External-epoxy	8 / 3	- / -
G	Coextruded	185	205 ± 5	235	250	2 acids 1 glycol	Titanium dioxide in "PET"	25	210
H	Composite		105 (2)	-	250	Amorphous polyester	PET	12	220
J	Coextruded	185	205 ± 5	235	250	2 acids 1 glycol	PET containing Red Dye	15	220
K	Monolayer		-	200	215		1 acid 2 glycols	12	190

Notes   1) Approximate values from DSC
           2) Softening point (amorphous polyester)

- 55 -

Table 7

Metal Surface Composition

Example	Metal Code	Surface Treatment
1 to 4	A	SAA
5 to 7	C	SAA
8 to 10	H	SAA
11 to 15,30	J	Chromium phosphate
16	J	PAA
17	J	Zirconium phosphate
18 to 19	H	SAA
2,23,24	F	Chromium phosphate
21 to 22	A	PAA
25,28	I	None
26	D	SAA
27	F	SAA
31	F	Chromium phosphate
32	B	Chromium phosphate
33	A	SAA
34	A	SAA
35	K	CHromium phosphate

Note

1.   SAA is sulphuric acid anodised.
2.   PAA is phosphoric acid anodised.

- 56 -

CLAIMS:

1.   A can end formed from a metal sheet having adhered
thereto a coating of a semi-crystalline thermoplastic
polyester film comprising a central panel, a panel wall
dependent from the periphery of the centre panel, an
annular countersink bead extending outwardly from the panel
wall, a chuck wall extending upwardly from the periphery of
the countersink bead and an annular seaming panel extending
radially from the chuck wall, characterised in that the
metal sheet comprises an aluminium alloy having a
magnesium content between 0.8% and 2.0% by weight and a
manganese content between 0.6% and 1.5% by weight; the
polyester coating has a crystallinity factor in the range
0.05 to 0.5 as measured by X-ray diffraction and has no
substantial oriented crystalline regions having a
crystallinity factor above 0.5; and the distance between
the chuck wall and panel wall is between 0.85mm and 1.0mm
as measured at a height of 0.45mm above the lowest part of
the upper surface of the countersink bead.

2.   A can end according to claim 1, wherein the entire
polyester film has reached during coating to the metal
sheet a temperature equivalent to at least the onset
melting temperature of the polyester less 16°C.

3.   A can end according to claim 1 or claim 2, wherein the
aluminium alloy is aluminium 3004.

- 57 -

4. A can end according to any one of claims 1 to 3, wherein the semi-crystalline thermoplastic polyester film comprises a monolayer film.

5. A can end according to any one of the preceding claims, wherein the semi-crystalline thermoplastic polyester comprises a copolyester of terephthalic acid, azelaic acid, ethylene glycol and diethylene glycol.

6. A can end according to any one of claims 1 to 4, wherein the semi-crystalline thermoplastic polyester comprises a copolyester of terephthalic acid, ethylene glycol and diethylene glycol.

7. A can end according to any one of claims 4 to 6, wherein the monolayer film has been adhered to a major surface of the metal sheet by thermal lamination comprising heating the metal sheet to a temperature T1, applying the film to form an initial laminate and reheating the initial laminate to a temperature T2 to form the laminate of metal sheet and semi-crystalline thermoplastic polymer, wherein, for an onset melting temperature Tm of the monolayer film, $Tm <= T1 <= Tm + 40^{\circ}C$ and $Tm - 5^{\circ}C >= T2 >= Tm - 20^{\circ}C$.

8. A can end according to any one of claims 1 to 3, wherein the semi-crystalline thermoplastic polyester comprises a coextruded film comprising an inner layer and an outer layer.

- 58 -

9. A can end according to claim 8, wherein the inner
layer of the coextruded film comprises a copolyester of
isophthalic acid, terephthalic acid and ethylene glycol.

10. A can end according to claim 8, wherein the inner
layer of the coextruded film comprises a copolyester of
terephthalic acid, ethylene glycol and diethylene glycol.

11. A can end according to any one of claims 8 to 10,
wherein the outer layer of the coextruded film comprises
polyethylene terephthalate.

12. A can end according to any one of claims 8 to 11,
wherein the coextruded film has been adhered to a major
surface of the metal sheet by thermal lamination comprising
heating the metal sheet to a temperature T1, applying the
film to form an initial laminate and reheating the initial
laminate to a temperature T2 to form the laminate of metal
sheet and semi-crystalline thermoplastic polymer, wherein,
for onset melting temperatures Tm(i) and Tm(o) of the inner
and outer layers respectively, Tm(i) <= T1<= Tm(o) + 15°C
and Tm(o) - 3°C >= T2 >= Tm(o) - 16°C.

13. A can end according to any one of claims 1 to 3,
wherein the semi-crystalline thermoplastic polyester film
comprises a composite film comprising an inner layer and an
outer layer.

14. A can end according to claim 13, wherein the outer
layer is biaxially oriented polyethylene terephthalate.

- 59 -

15. A can end according to claim 13 or claim 14, wherein the inner layer comprises an amorphous polyester.

16. A can end according to any one of the preceding claims, wherein the other major surface of the metal sheet is coated with a coextruded polyolefin film comprising an inner layer of maleic anhydride graft modified polyolefin and an outer layer of polyolefin.

17. A can end according to claim 16, wherein the polyolefin is polypropylene.

18. A can end according to claim 16, wherein the polyolefin is an ethylene-propylene copolymer.

19. A can end according to claim 16, wherein the coextruded polyolefin film is biaxially oriented.

20. A can end according to any one of the preceding claims, wherein the polyester film is pigmented with titanium dioxide.

21. A can end according to any one of claims 1 to 19, wherein the polyester is coloured with a coloured dyestuff.

22. A can end according to any one of the preceding claims, wherein the surface of the metal sheet is pretreated after cold rolling by chromium phosphate, zirconium phosphate or anodising processes.

- 60 -

23. A process for producing a laminate of metal sheet and polyester, the metal sheet comprising an aluminium alloy having a magnesium content of 0.8 to 2.0%, and manganese content 0.6 to 1.5%, which process comprises thermally laminating a monolayer polyester film to a major surface of the metal sheet heated to a temperature T1 to form an initial laminate and reheating the initial laminate to a temperature T2, characterised in that, for a melting temperature Tm of the monolayer polyester film Tm <=T1 <= Tm + 40°C and Tm - 5°C >= T2 >= Tm - 20°C, so that the crystallinity factor of the polyester in the laminate is in the range 0.05 to 0.5 as measured by X-ray diffraction.

24. A process according to claim 23, wherein the crystallinity factor of the monolayer polyester film applied to the metal sheet is in the range 0.08 to 0.45 as measured by X-ray diffraction.

25. A process according to claim 23 or claim 24, wherein the polyester comprises a copolyester of terephthalic acid, azelaic acid, ethylene glycol and diethylene glycol.

26. A process according to claim 23 or claim 24, wherein the polyester comprises a copolyester of terephthalic acid, ethylene glycol and diethylene glycol.

27. A process for producing a laminate of metal sheet and polyester, the metal sheet comprising an aluminium alloy having a magnesium content of 0.8 to 2%, and manganese content 0.6 to 1.5%, which process comprises thermally laminating a coextruded polyester film to a major surface of the metal sheet heated to a temperature T1 to form an

- 61 -

initial laminate and reheating the initial laminate to a temperature T2, the composite polyester film comprising an inner layer and an outer layer, characterised in that, for melting temperatures Tm(i) and Tm(o) of the inner and outer layers respectively, Tm(i) <= T1 <= Tm(o) + 15°C and Tm(o) - 3°C >=T2 >= Tm(o) - 15°C, so that the crystallinity·factor of the polyester in the laminate is in the range of 0.05 to 0.5 as measured by X-ray diffraction.

28. A process according to claim 27, wherein the inner layer comprises a copolyester of isophthalic acid, terephthalic acid and ethylene glycol.

29. A process according to claim 27, wherein the inner layer comprises a copolyester of terephthalic acid, ethylene glycol and diethylene glycol.

30. A process according to any one of claims 27 to 29, wherein the outer layer comprises polyethylene terephthalate.

31. A process for producing a laminate of metal sheet and polyester, the metal sheet comprising an aluminium alloy having a magnesium content of 0.8 to 2%, and manganese content 0.6 to 1.5%, which process comprises thermally laminating a composite polyester film to a major surface of the metal sheet heated to a temperature T1 to form an initial laminate and reheating the initial laminate to a temperature T2, the composite polyester film comprising an inner layer and an outer layer, characterised in that, for melting temperatures Tm(i) and Tm(o) of the inner and outer layers

- 62 -

respectively, Tm(i) <= Tl <= Tm(o) + 15°C and Tm(o) -
3°C >=T2 >= Tm(o) - 15°C, so that the crystallinity of
the polyester in the laminate is in the range 0.05 to 0.5
as measured by X-ray diffraction.

32. A process according to claim 31, wherein the outer
layer is biaxially oriented polyethylene terephthalate.

33. A process according to claim 31 or claim 32, wherein
the inner layer comprises an amorphous polyester.

34. A process according to any one of claims 23 to 33,
wherein the aluminium alloy is aluminium 3004.

35. A process according to any one of claims 23 to 34,
wherein the other major surface of the metal is coated with
a coextruded polypropylene film having an inner layer of
maleic anhydride graft modified polypropylene and an outer
layer of polypropylene or poly (propylene-ethylene)
copolymer.

36. A process according to claim 35, wherein both major
surfaces of the metal sheet are coated simultaneously.

37. A process according to any one of claims 23 to 36,
which further comprises the step of forming the laminate of
metal sheet and polyester into a can end.

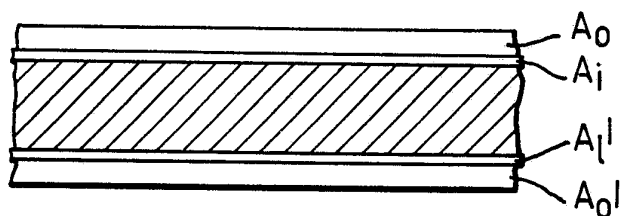38. A process according to claim 37, wherein the can end
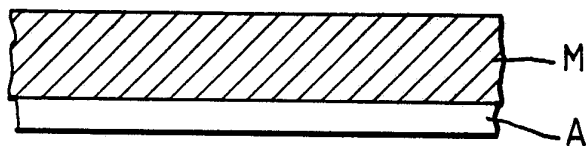is as defined in claim 1.

Fig.1.
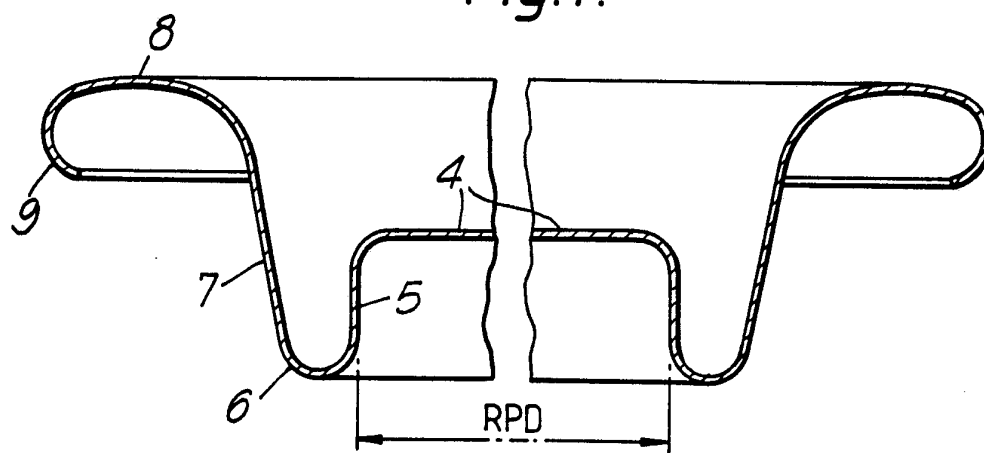
Fig.2.
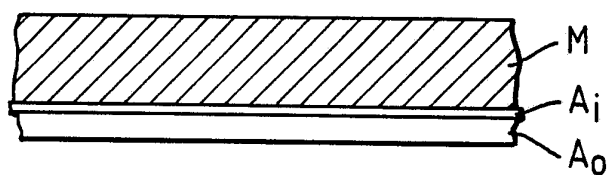
Fig.2A.

Fig.3.

Fig.3A.

Fig.3B.

A_o
A_i
M
A

Fig.9.

A_o
A_i
M
B_i
B_o
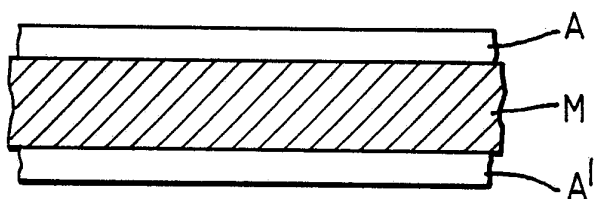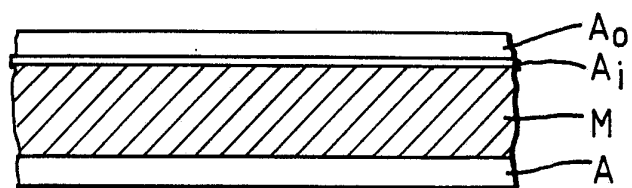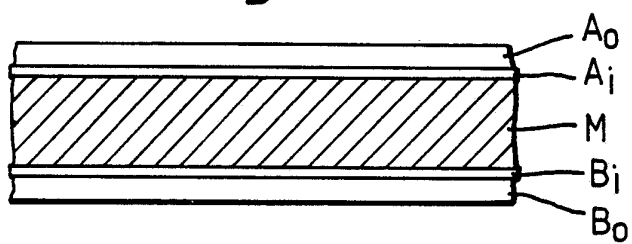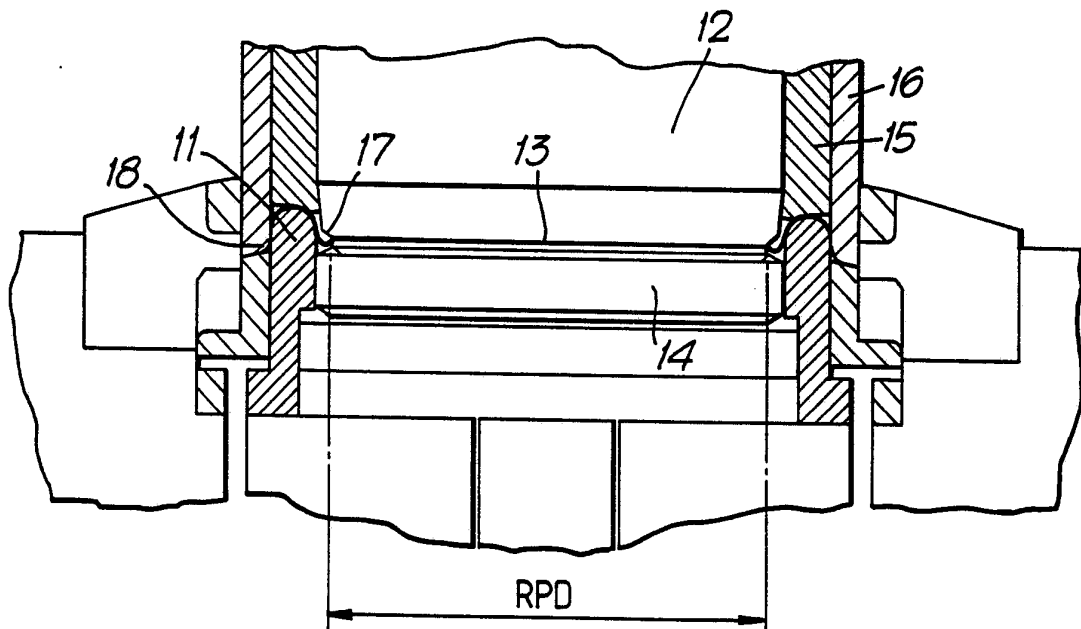
Fig.9A.
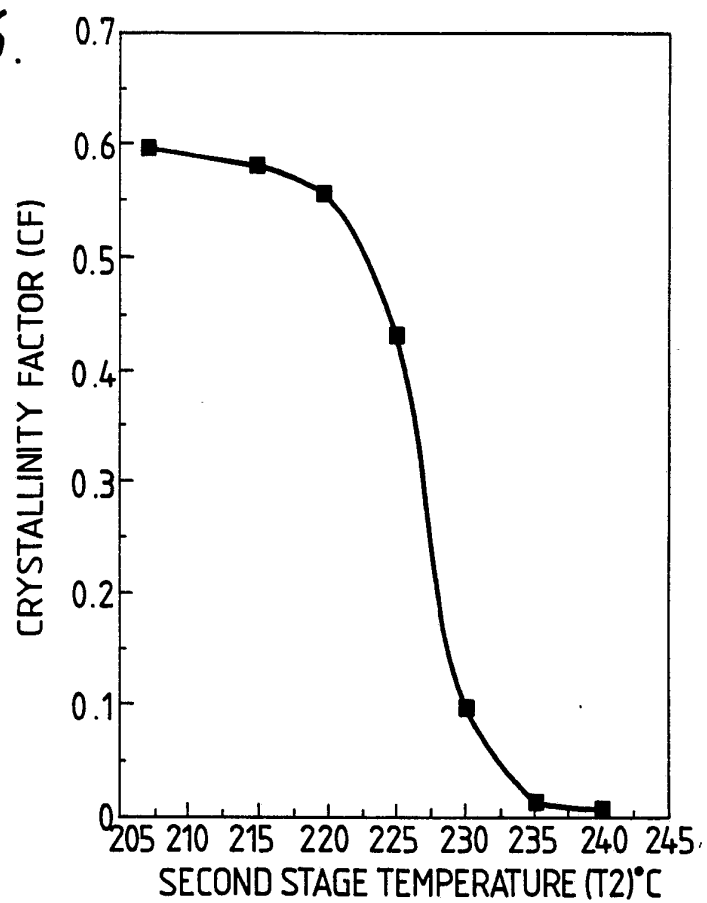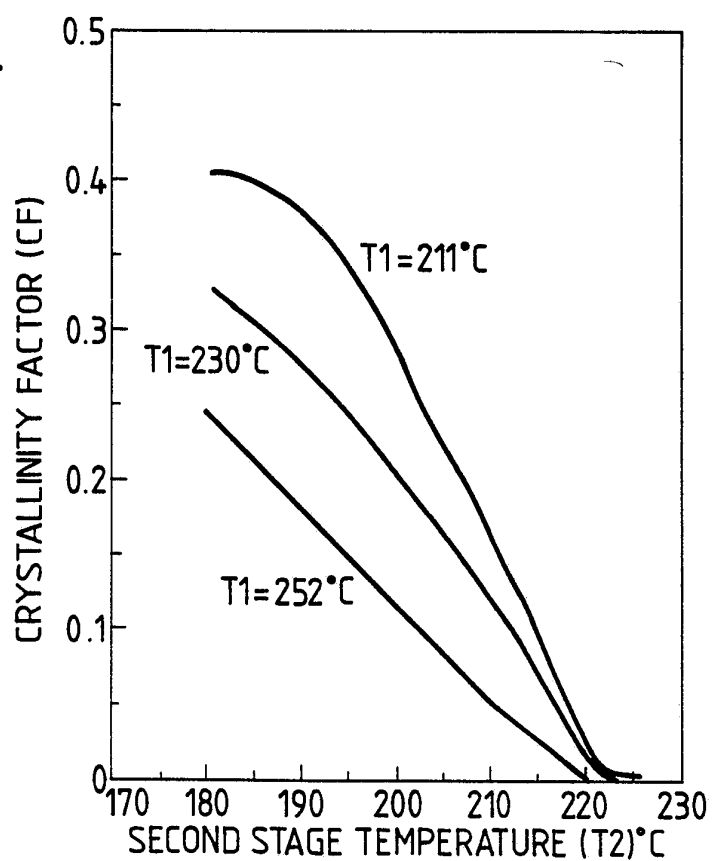

B_o
B_i
M
A
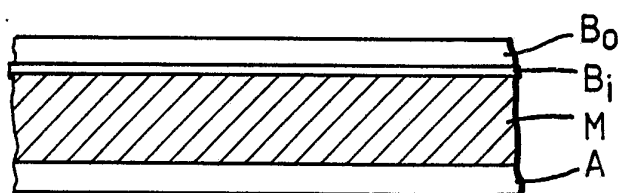
Fig.4.
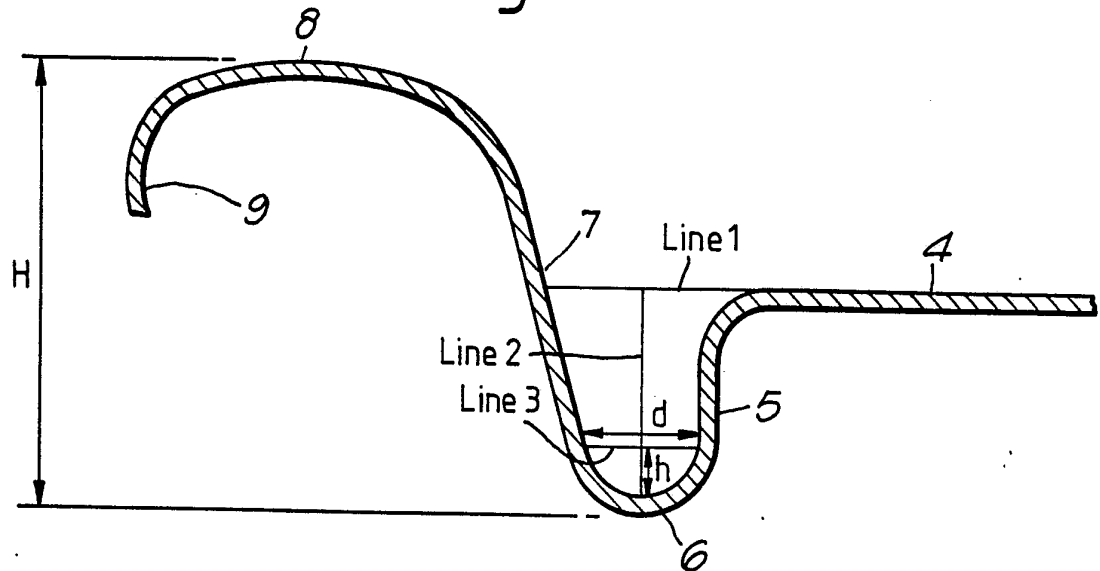
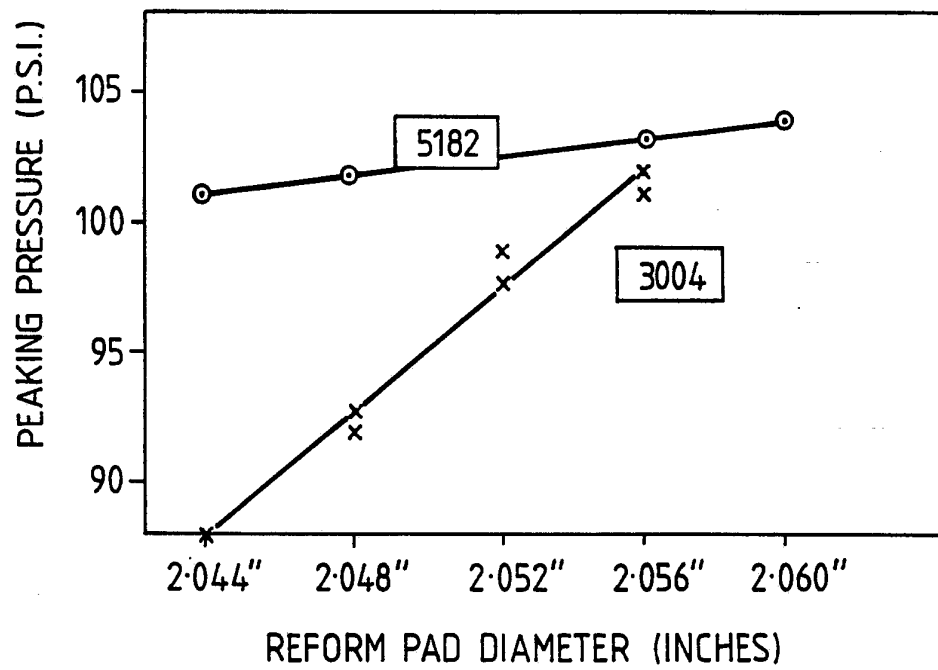## Fig.5.

Fig.6.

Fig.7.

Fig.8.
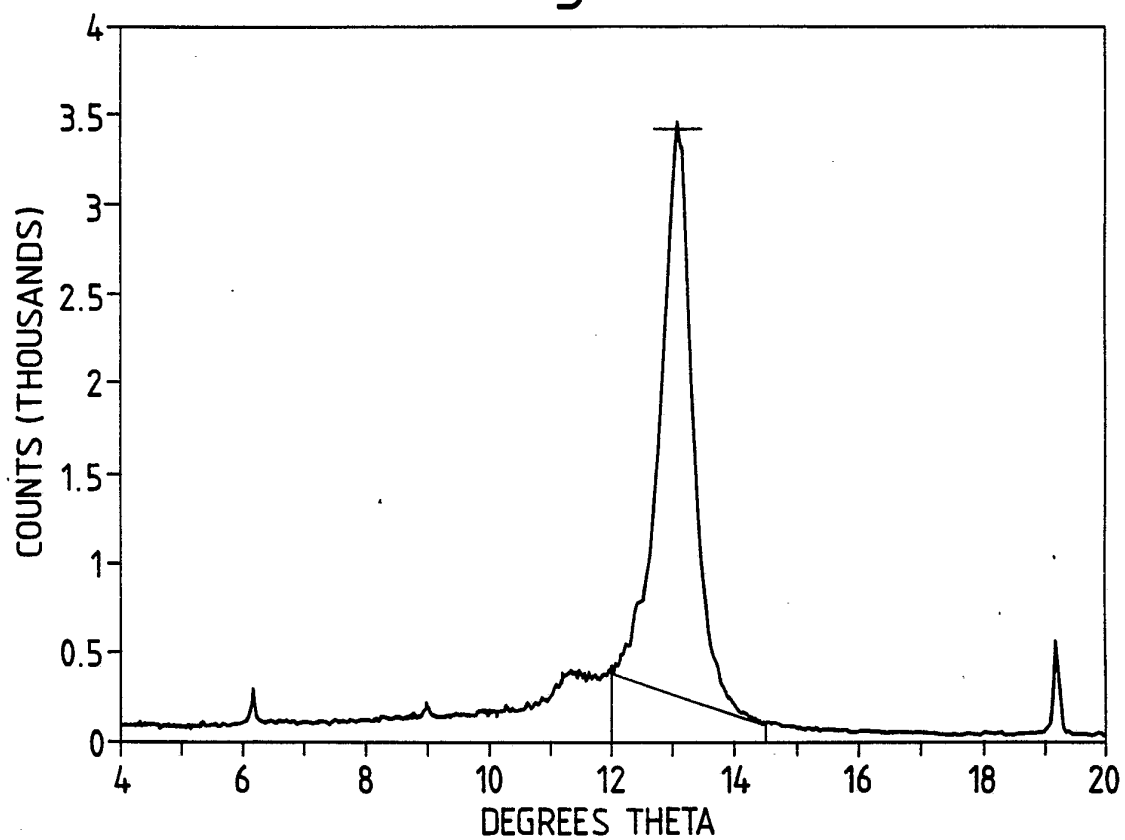

x   3004 — EXAMPLE 1 TO 4

⊙ 5182 — EXAMPLE 11 TO 14

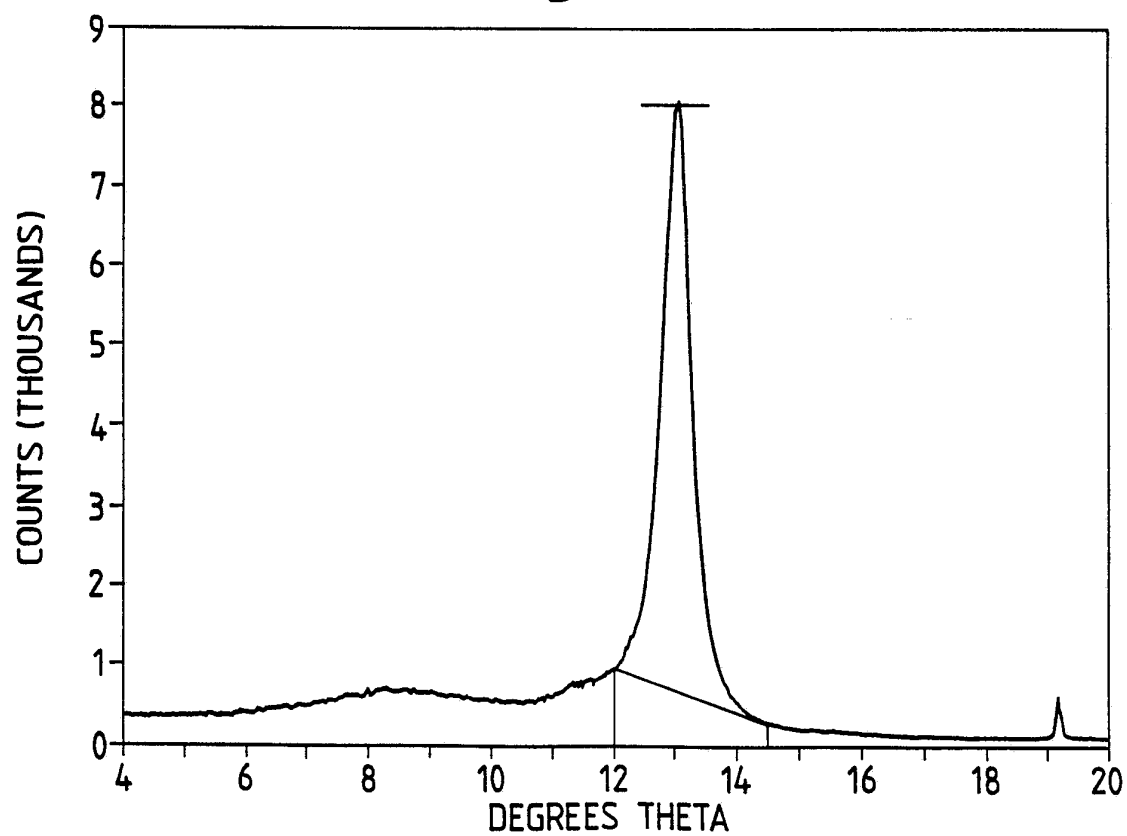## Fig.10.

Fig.10A.

Fig.11.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER   (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B32B15/08;   B65D1/28;   B32B31/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷	
Classification System	Classification Symbols
Int.Cl. 5	B32B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category°	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No.¹³
Y	GB,A,1 566 422 (TORAY INDUSTRIES INC.) 30 April 1980 see page 6, line 10 - line 45; claims 2,6,10-17	1-38
Y	EP,A,0 402 004 (CMB FOODCAN PLC) 12 December 1990 see the whole document	1-38
A	EP,A,0 384 606 (CMB FOODCAN PLC) 29 August 1990 see figure 2	1
A	EP,A,0 312 302 (MB GROUP PLC) 19 April 1989 cited in the application see the whole document	1-38

-/--

° Special categories of cited documents : ¹⁰

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
04 MAY 1993	25. 05. 93
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	DE JONGE S.J.P.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 312 303 (MB GROUP PLC) 19 April 1989 cited in the application see the whole document ---	1-38
A	EP,A,0 312 304 (MB GROUP PLC) 19 April 1989 cited in the application see the whole document -----	1-38
Category°		Relevant to Claim No.

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.   GB   9300446
  SA   70726

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.   04/05/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-1566422	30-04-80	JP-C-	1327577	30-07-86
		JP-A-	52065588	31-05-77
		JP-B-	57023584	19-05-82
		AU-B-	504152	04-10-79
		AU-A-	1994276	01-06-78
		CA-A-	1088820	04-11-80
		US-A-	4143790	13-03-79
EP-A-0402004	12-12-90	GB-A-	2233277	09-01-91
		AU-B-	631885	10-12-92
		AU-A-	5728690	07-01-91
		CN-A-	1047828	19-12-90
		WO-A-	9014948	13-12-90
		GB-A-	2232922	02-01-91
		JP-T-	4500185	16-01-92
EP-A-0384606	29-08-90	AU-A-	5084090	05-09-90
		WO-A-	9009280	23-08-90
		GB-A,B	2229393	26-09-90
		JP-T-	3504703	17-10-91
EP-A-0312302	19-04-89	AU-B-	599522	19-07-90
		AU-A-	2604388	02-05-89
		CA-A-	1296607	03-03-92
		DE-A-	3871707	09-07-92
		WO-A-	8903302	20-04-89
		GB-A,B	2211134	28-06-89
		JP-T-	2501644	07-06-90
		US-A-	4957820	18-09-90
EP-A-0312303	19-04-89	AU-B-	599520	19-07-90
		AU-A-	2554688	02-05-89
		DE-A-	3871708	09-07-92
		WO-A-	8903304	20-04-89
		GB-A,B	2211135	28-06-89
		JP-T-	2501640	07-06-90
		US-A-	5059460	22-10-91
EP-A-0312304	19-04-89	AU-B-	616442	31-10-91
		AU-A-	2547788	02-05-89

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.   04/05/93

Page   2

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0312304		WO-A-	8903303	20-04-89
		GB-A,B	2211465	05-07-89
		JP-T-	2501638	07-06-90
		US-A-	5149389	22-09-92
		US-A-	5093208	03-03-92

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82