PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C08J 5/18, B29D 7/01, B32B 15/08

A1

(11) International Publication Number: WO 00/53665

(43) International Publication Date: 14 September 2000 (14.09.00)

(21) International Application Number: PCT/EP00/02211

(22) International Filing Date: 9 March 2000 (09.03.00)

(30) Priority Data:

1011518	10 March 1999 (10.03.99)	NL
1013101	21 September 1999 (21.09.99)	NL

(71) Applicant *(for all designated States except US)*: CORUS STAAL BV [NL/NL]; P.O. Box 10000, NL–1970 CA IJmuiden (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: BEENTJES, Petrus, Cornelis, Jozef [NL/NL]; Cieweg 43, NL–1902 AA Castricum (NL). DEN HARTOG, Huibert, Willem [NL/NL]; Troelstralaan 2, NL–2211 AC Noordwijkerhout (NL). VAN VEENEN, Willem, Jan [NL/NL]; Plesmanweg 67, NL–1945 WL Beverwijk (NL).

(74) Agent: KRUIT, Jan; Corus Technology BV, P.O. Box 10000, NL–1970 CA IJmuiden (NL).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR PRODUCING A PLASTIC WEB FOR COATING A METAL SUBSTRATE, LAMINATE COMPRISING THIS PLASTIC WEB, AND PRODUCT OR COMPONENT PRODUCED THEREWITH

(57) Abstract

The invention relates to a process for producing a plastic web for coating a metal substrate, in which the plastic used is polyester. According to the invention, the plastic web is produced by extruding a mixture of various polyesters. The invention also relates to a laminate comprising a metal substrate and a plastic layer, the plastic layer comprising an adhesive layer which substantially comprises a plastic web produced according to the method according to the invention. The invention also relates to products and components produced from this laminate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

PROCESS FOR PRODUCING A PLASTIC WEB FOR COATING A METAL SUBSTRATE, LAMINATE COMPRISING THIS PLASTIC WEB, AND PRODUCT OR COMPONENT PRODUCED THEREWITH

The invention relates to a process for producing a plastic web for coating a metal substrate, in which the plastic used is polyester. The invention also relates to a laminate containing a plastic web of this nature, and to a product or component which is produced using this laminate.

For various reasons, it is often desirable for metal to be provided with an additional layer in the form of a metallic or organic coating. This layer may serve to protect or decorate the metal, depending on its subsequent use. For packaging steel, a combination of a metallic and organic coating layer is generally used, so that the coated material, during its final use, protects the packaged foodstuff well, will not exhibit any corrosion, and the quality of the packaged foodstuff will be maintained.

The metallic covering layer used is often tin or chromium with chromium oxide on top, or a combination of these two layers. In the invention described below, good results have been obtained on packaging steel provided with a thin layer of chromium and chromium oxide (ECCS), but use of the invention is not limited to this type of packaging steel.

Lacquers are often used as the organic coating layer. Examples are epoxy and epoxyphenol lacquers, polyester lacquers and organosol lacquers, or combinations thereof. Sometimes, using these lacquers involves formability problems, with corrosion occurring or with undesirable substances being released from the lacquer to the packaged foodstuff, or with the undesirable emission of solvents.

In this respect, better results are obtained by packaging steel which is provided with a plastic web as a coating layer. Examples of plastics which can be used for this purpose are polypropylene, polyethylene, polyamide and polyester. The plastic web can be applied by producing it in a separate production process, rolling it up and unwinding it again at the location of the coating line, where it is stuck to the metal by the application of heat and pressure. It is also possible to produce a thin, molten web of plastic in the coating line by extrusion, which is applied to the metal in the molten or solidified state.

A drawback of using a polyester plastic web, such as a web made from PET (polyethyleneterephthalate), as a coating layer is that it is difficult to adhere this web to the packaging steel sufficiently well for it still to be possible to deform the coated metal without the coating layer becoming detached or ruptured when the coated material is subjected to a (wet) heat treatment.

CONFIRMATION COPY

Another drawback is that it is difficult to apply an additional layer to the coating layer which then adheres sufficiently firmly to the plastic coating layers which have previously been used. The additional layer is, for example, a PVC-containing sealing compound which is generally used to seal a screw cap on a glass jar in an airtight manner.

Another drawback is that most polyesters crystallize under the influence of heat. A heat treatment is often required in the production process, for example in order to cure a printing or a compound. During this process crystallisation takes place in many polyesters, which in the case of transparent coating layers results in undesirable discoloration, with the colour of the layer becoming opaque and whitish.

One object of the invention is to provide a process for producing a plastic web for coating a metal substrate in which the polyester used adheres securely to the metal even after deformation of the metal together with the coating layer and a (wet) heat treatment.

Another object is to provide a method of this nature in which the polyester provides good adhesion for a PVC-containing compound which is applied to it.

Yet another object is to provide a process of this nature which forms a plastic layer which remains highly transparent during a heat treatment.

Another object of the invention is to use this process to produce laminates, products and components which satisfy one or more of the abovementioned objects.

According to a first aspect of the invention, one or more of these objects are achieved by means of a process of the type described in the preamble in which the plastic web is produced by extruding a mixture of various polyesters.

It has been found that if the constituent components of the polyesters are selected appropriately and an appropriate preparation method is selected, the problems with adhesion to steel after deformation and use, of discoloration of the coating layer caused by a heat treatment, and of adhesion to PVC-containing compounds are solved.

Preferably, the process is such that the polyesters used are copolyesters. With the aid of these copolyesters, it is easy to manipulate the properties of the polyester layer.

Preferably, copolyesters based on terephthalic acid are used. This is a very standard type of copolyester. More preferably, copolyesters which are formed on the basis of PET are used. These are readily available.

According to an advantageous process, the mixture used is a mixture of a crystallisable polyester and a non-crystallisable polyester. By varying the ratio between the crystallisable polyester and the non-crystallisable polyester, it is possible to adapt the properties in such a manner that, for example, a good adhesion to packaging steel or to a PVC-containing compound or a good resistance to a heat treatment is obtained.

Preferably, the process is such that the non-crystallisable polyester used is a copolyester which contains CHDM (1,4-cyclohexanedimethanol). This polyester containing CHDM is very suitable for manipulation of the properties of the polyester layer.

Preferably, the CHDM-modified copolyester is obtained by reacting a mixture of terephthalic acid, ethylene glycol (ethanediol) and CHDM.

Alternatively, a process is used in which the non-crystallisable polyester used is a PET/PEN copolymer which is obtained by reacting a mixture of terephthalic acid, naphthalenedicarboxylic acid and ethylene glycol (ethanediol). Other non-crystallizable polyesters may also be suitable in order to obtain the effects described.

Preferably, the mixture used has a non-crystallisable weight fraction which is greater than 6%. If this percentage is lower, the adhesion is in many cases insufficient if the plastic web undergoes a subsequent heat treatment and/or substantial deformation.

Preferably, the mixture used has a non-crystallisable weight fraction which is less than 90%. An excessively high percentage of non-crystallisable polymer in some cases leads to undesirable deformation of the plastic web on a metal substrate, resulting in wrinkles, so that the laminate cannot be used as a substrate for, for example, screw caps which have been printed with heat-curing ink.

Advantageously, the mixture used has a non-crystallisable weight fraction which is approximately 25% or greater. In this way, reasonably good adhesion to PVC-containing compounds is obtained.

Advantageously, the mixture used has a non-crystallisable weight fraction which is approximately 33% or greater. This results in a plastic web which remains highly transparent during a heat treatment; a considerably higher percentage is required for a sterilisation treatment.

Good adhesion to PVC-containing compounds is obtained if the mixture used has a non-crystallisable weight fraction which is approximately 50% or greater, if the plastic-coated metal is at most pasteurised.

For sterilisation applications, it is preferable to use a mixture with a non-crystallisable weight fraction which is approximately 66% or greater.

Very good adhesion to compounds is obtained if the mixture used has a non-crystallisable weight fraction which is approximately 75% or greater.

With regard to the above, it should be borne in mind that it is always desirable for the amount of non-crystallisable polymer in the mixture to be kept as low as possible, since non-crystallisable polymer is much more expensive than crystallisable polymer.

According to a second aspect of the invention, a laminate is provided, comprising a metal substrate and a plastic layer, the plastic layer comprising an adhesive layer, this adhesive layer substantially comprising a plastic web produced according to the process

described above. The laminate thus exhibits good adhesion between the metal substrate and the plastic layer.

Preferably, the laminate is formed in such a manner that the plastic layer comprises a top layer, the top layer substantially comprising a plastic web produced according to the process described above. This gives the top layer good adhesion for a PVC-containing compound.

According to an advantageous embodiment, the plastic layer of the laminate has an adhesive layer and a top layer, an intermediate layer being present between the adhesive layer and the top layer, the intermediate layer substantially comprising a plastic web which is produced by extruding a polyester. Since the top layer and the adhesive layer primarily have an adhesive function and therefore may be thin, an intermediate layer is desirable in order to make the plastic layer sufficiently thick and strong. In order for it to be possible to extrude the plastic layer in a single operation, the intermediate layer also has to be extrudable.

It is possible to produce the intermediate layer using the process described above.

In this case, the intermediate layer is preferably produced from a mixture with a non-crystallisable weight fraction which is approximately 10% or greater. Preferably, this weight fraction is approximately 33% or greater. In this case too, the amount of non-crystallisable polymer must be kept as low as possible, for cost reasons. A higher percentage should be used for a sterilisation treatment.

The laminate can be used to produce, for example, screw caps, crown corks and easy open ends, as well as packagings and components thereof, such as the base, the lid or the body, a deep-drawn and/or wall-ironed can, a base, cap, wall or valve dish of an aerosol can, or a dish or tray, etc.

A third aspect of the invention provides a component produced from a laminate as described above, in which a PVC-containing compound is applied to the top layer of the plastic layer of the laminate.

In this case, the non-crystallisable weight fraction in the top layer is preferably approximately 25% or greater. This makes it possible to achieve good adhesion results between the top layer and the PVC-containing compound.

Preferably, the weight fraction is approximately 35% or greater. This improves the adhesion results.

In order for it to be possible to subject the component to pasteurisation or a similar heat treatment, however, the non-crystallisable weight fraction is preferably 50% or higher in order to be certain to obtain good adhesion.

For sterilisation applications, the said weight fraction is preferably approximately 66% or higher. The adhesion is then good for all PVC-containing compounds which have been investigated.

However, it has been found that the weight fraction of non-crystallisable polyester required in the top layer depends on the compound used, so that the minimum percentage required has to be determined on the basis of the compound employed.

The invention will be explained in more detail below.

Experiments have shown that a mixture of, for example, two types of polyester is particularly expedient for producing plastic-coated metal, for example packaging steel. This is, for example, a mixture of crystallisable PET, referred to below as PET A, and non-crystallisable PET, referred to below as PET B. An example of a suitable type of PET for PET A is Eastapak 9921w produced by Eastman Chemical Company. An example of a suitable type of PET for PET B is Eastar PETG 6763, also produced by Eastman Chemical Company.

A number of PET coatings were applied with adhesive, intermediate and top layers in which different quantities of PET B have been mixed with PET A.

Three types of polyester and mixtures thereof were tested. The following text will indicate the characteristics of the various types. The two types of polymer are PET A and PET B as defined above. Mixtures were made from these two types. These two types are copolymers of "normal" PET, in which, during the synthesis, a quantity of ethanediol was replaced with 1,4-cyclohexanedimethanol (referred to throughout the rest of this document as CHDM). PET A has a very low CHDM content, while a PET C, which is to be described below, has a higher CHDM content, and PET B has an even higher CHDM content. PET C is completely copolymerised and has a maximum achievable crystallinity which is lower than that of PET A. Eastar PETG 15086 is used for PET C. A copolymer of this nature has significantly different properties from a mixture of PET A and PET B. These PET grades and mixtures thereof are applied as a coating layer to the substrate.

The product codes of the plastic-coated products used and the associated composition of the plastic are given in the table below (all percentages are by weight).

Code	Adhesive layer	Intermediate layer	Top layer	Steel base
TP628A	PET A			0.21 mm ECCS, T61CA
TP628B	PET C			0.21 mm ECCS, T61CA
P 064	100% PET B	PET A	100% PET B	0.21 mm ECCS, T61CA
P 076	33% PET B	PET A	100% PET B	0.21 mm ECCS, T61CA
P 077	100% PET B	PET A	33% PET B	0.21 mm ECCS, T61CA
P 078	66% PET B	PET A	100% PET B	0.21 mm ECCS, T61CA
P 079	100% PET B	PET A	66% PET B	0.21 mm ECCS, T61CA
P080	100% PET B	PET A	100% PET B	0.21 mm ECCS, T61CA
P 086	100% PET B	PET A	100% PET B	0.155 mm ECCS, DR620CA
P 087	50% PET B	PET A	33% PET B	0.155 mm ECCS, DR620CA
P 088	50% PET B	PET A	50% PET B	0.155 mm ECCS, DR620CA
P 089	50% PET B	33% PET B	50% PET B	0.155 mm ECCS, DR620CA
P 090	75% PET B	PET A	66% PET B	0.155 mm ECCS, DR620CA

The percentage of PET A in the adhesive, intermediate and top layers is 100 minus the PET B percentage indicated. In variants TP628A and TP628B, a single-layer coating was applied.

Variants P076 – P080 and P086 – P090 were used for adhesion tests.

The reference material used in the compound tests was a lacquered can.

Specifications:

- steel base: 0.24 mm T57CA
- tin plating: 2.8/2.8 g/m^2
- passivation: 311 (approx. 5 mg/m^2 Cr)
- lacquer system (adhesive lacquer: approx. 5 g/m^2 and top lacquer: approx. 12 g/m^2, as is customarily used for screw caps).

To test the compound adhesion directly after application, a layer of compound is applied to the coating variant to be examined, and this layer is cured in a hot air furnace under suitable conditions. The specimen is cut into narrow strips, after which a blade is used to cut off a small piece of the compound applied. A 180° peel test was then carried out in a tensile strength tester, using the exposed substrate and the cut-out piece of compound as the point of engagement. The adhesion of the compound is excellent if the compound layer breaks during the peel test and sufficient if the peel strength is greater than 1 N/mm.

To establish the compound adhesion after sterilisation, after the compound has been applied and cured the entire specimen is placed in a high-pressure pan containing demineralised water. The pan is heated to a temperature of 121°C, after which the specimen is sterilised for 1 hour at this temperature. After cooling, the specimen is again cut into narrow strips and is kept moist through being immersed in demineralised water until, shortly afterwards, a peel test is carried out following the procedure described above.

In the first instance, it was attempted to carry out this test as an adhesion test for the compound. It was found that the adhesion of the compound to the PET was stronger than the adhesion of PET to ECCS. This method was therefore found to be suitable for determining the adhesion to ECCS.

In order to determine the adhesion after sterilisation, use is made of the (particular) phenomenon that it is possible to obtain excellent adhesion between cured PVC-containing compound and a top layer comprising 100% PET B. The procedure is as follows.

Slightly wider strips of P064 are laid onto the strips of material with cured compound already on them. This *sandwich* is placed between two stainless steel plates which are fixed at the four corners by means of a nut and bolt (manually tightened). This assembly is placed in a high-pressure pan containing demineralised water and is

heated. After 121°C (1 bar excess pressure) has been reached, sterilisation is carried out for a further hour. After cooling, the specimens which have been placed on top of one another are removed from the container and placed in a glass beaker containing water, in order to keep the specimens moist (drying generally allows the adhesion to improve). To carry out the peel test, an incision is then again made between the compound and the coated material to be tested. Then, the ends of the specimen plate to be tested and the support plate made of P064 are clamped in the test stand. Then, a 180° peel test is carried out in the same way as that described above.

The adhesion determined using this method represents a measure of adhesion in the wet state and thus provides an indication of the adhesion to, for example, the inside of a sterilised packaging.

There is a considerable difference in adhesion which can be achieved between compound and coating layer amongst the tested mixtures of the PET A and PET B variants, and PET C (copolymer).

PET A (TP628A) and PET C (TP628B) exhibit scarcely any adhesion to a PVC-containing compound. In both cases, the adhesion is very inadequate in the dry state. These variants are not suitable for use as a coating for the inside of screw caps (forces measured from approx. 0.1-0.2 N/mm; the peel strength should be above 1 N/mm).

In principle, very good adhesion can be obtained between PVC-containing compound and a top layer comprising a mixture of PET A and PET B. A number of PVC-containing compounds were tested. Some of the compounds are (according to the supplier) particularly suitable for pasteurisation, other types for sterilisation applications. Compounds from various suppliers were tested. As can be seen from the table containing the test results concerning the compound adhesion directly after application, the percentage of PET B which is required depends on the compound tested.

Adhesion of a number of compounds to the tested variants immediately after application

Variant code	Compound 1	Compound 2	Compound 3	Compound 4
P064	Breakage	Breakage	Not tested	Not tested
P077	Moderate adhesion	Breakage	Not tested	Not tested
P079	Breakage	Breakage	Not tested	Not tested
P086	Not tested	Not tested	Breakage	Breakage

P087	Breakage	Breakage	No adhesion	No adhesion
P088	Breakage	Breakage	Breakage	Strong adhesion
P089	Breakage	Breakage	Breakage	Breakage
P090	Breakage	Breakage	Breakage	Breakage

Compound 1: Compound from supplier A suitable for pasteurisation (fat-containing foodstuffs)

Compound 2: Compound from supplier A for sterilisation applications (fat-containing foodstuffs)

Compound 3: Compound from supplier B suitable for hot fill and pasteurisation applications

Compound 4: Compound from supplier B suitable for sterilisation applications

The compound adhesion is optimum if breakage occurs during the peel test. If good adhesion is obtained immediately after application (breakage in the compound during the peel test), in all cases it was found that, after sterilisation or pasteurisation, the adhesion of the compounds to the PET coating layer was greater than that of the coating layer to the ECCS. Good compound adhesion even after pasteurisation or sterilisation is essential for successful use of these materials, since a treatment of this nature is almost always used.

In all cases, it was found that the compounds tested exhibited highly insufficient adhesion to TP628A and TP628B. Of these variants, variant TP628B (PET C) exhibits slightly less poor adhesion, but still adheres insufficiently to PVC-containing compound.

For non-processable/pasteurisation applications, ≥ 50% PET B in the top layer is sufficient to obtain good adhesion to all the compounds tested. For sterilisation applications, a higher percentage is required: ≥ 66% PET B in the top layer. At these concentrations of PET B, all the compounds tested are suitable. However, for both cases it is possible that lower percentages may also give good results, depending on the compound used. Therefore, by making use of specific compounds for specific applications, it is possible to use lower percentages of PET B in the top layer.

By sealing the specimen to a reference specimen with a compound applied thereon, it is possible to determine the force which is required to pull the compound off. If the adhesion of the compound to the PET is sufficiently great, it is not the adhesion of the compound to the plastic, but rather the adhesion of the plastic layer to the steel which is measured. This is lower under wet conditions than the adhesion under dry conditions. A number of results are given in the table.

Variant code	F_{mean} Compound 1 N/mm	F_{mean} Compound 2 N/mm	Adhesive layer
P064	2.5; 2.6	1.7; 1.7	PET B
P076	1.2; 3.0	0.1*; 0.3*	33% PET B
P077	2.4; 2.4	1.6; 1.6	PET B
P078	2.8; 3.1	0.4*; 2.1, 0.6*, 0.7*	66% PET B
P079	2.6; 2.8	1.7; 1.7	PET B
P080	2.3; 2.5	0.9; 1.2	PET B
P088	n.d.	0.5*, 0.3*	50% PET B
P089	n.d.	0.3*, 0.2*	50% PET B
P090	n.d.	0.6, 1.0	75% PET B
Lac. Ref	2.2; 2.3	2.6; 1.4, 1.8, 1.3	
* : no adhesion or scarcely any adhesion, n.d.: not determined			

The impression of the coating with a 100% PET B adhesive layer is relatively consistent, although the two types of compound give a different effect to the adhesion. In the variants with an adhesive layer containing 33% PET B, there is a somewhat greater spread. It is clear that the adhesion to steel when using compound 2 is considerably lower (insufficient). This effect is also found when using compound 1, although in this case the effect is less intensive. With compound 1, the adhesion appears to remain sufficient in all cases.

The relationship between the quantity of PET B in the adhesive layer and the adhesion to the ECCS (under wet conditions) measured with compound 2 can be described according to the following formula:

$$Peel\ strength = 1.4 \cdot 10^{-4} * P^2$$

where P is the percentage of PET B in the adhesive layer and the peel strength is expressed in N/mm.

In the case of compound 1, the measured values are much higher. The difference between the two types is that compound 2 is a sterilisation compound, while compound 1 is more suitable for hot fill and pasteurisation. In this case, the relationship can be described by the following equation

$$Peel\ strength = \ln P - 1.96$$

A clear conclusion which can be drawn from these measurements is that different compounds lead to different adhesion. For certain applications, low PET B contents are possible.

The top layer of a PET coating (intended in particular for screw caps) must exhibit good adhesion to a PVC-containing compound. Adhesion of PET to a PVC is difficult to achieve. It is generally accepted that PET does not adhere to PVC. Known solutions for improving the adhesion to compound are relatively complex and, in some cases, use PVC-containing layers. With the above-described method of mixing a crystallisable PET and a non-crystallisable PET provides very good adhesion in a simple manner.

For the intermediate layer, it is important, in the case of transparent coating layers, that the appearance of the layer should not change visibly as a result of (dry) heat treatments. It has been found that with the crystallisable polyesters normally used, such as PET A, undesirable discoloration takes place as a result of a heat treatment. It has been found that if a polyester layer comprising a mixture of mainly crystallisable polyester (PET A) and some non-crystallisable polyester (PET B) is used, it is not possible to detect any change in appearance when used as transparent coating layer for metals which still have to undergo a heat treatment (for example for curing a compound or printing).

It has been found that in the case of sterilisation and pasteurisation, the adhesion of a PET A or PET C is insufficient to obtain a suitable material for use as base material for metal packaging.

The adhesion of PET to steel is considerably improved by using a mixture of PET B and PET A. An excessively high percentage of PET B leads to undesirable deformation of the coating (wrinkling), with the result that the laminate cannot be used as a material for, in particular, screw caps printed with heat-curing ink.

A comparison between PET C and a mixture of PET B and PET A indicates the importance of choosing a mixture. For example, compound adhesion to PET C is absolutely insufficient.

This means that other polyesters which have a non-crystallisable character will also give a similar effect, for example copolymerised PET in which approx. 15% of the terephthalic acid weight fraction is replaced by naphthalenedicarboxylic acid, preferably naphthalene-2,6-dicarboxylic acid. The pure polyester of naphthalenedicarboxylic acid and ethylene glycol (PEN) has the additional advantage of very good barrier properties.

It will be understood that the above mentioned examples do not limit the invention in any way. The scope of protection is defined by the claims which follow.

CLAIMS

1. Process for producing a plastic web for coating a metal substrate, in which the plastic used is polyester, characterised in that the plastic web is produced by extruding a mixture of various polyesters.

2. Process according to Claim 1, characterised in that the polyesters used are copolyesters.

3. Process according to Claim 2, characterised in that copolyesters based on terephthalic acid are used.

4. Process according to Claim 3, characterised in that polyesters which are formed on the basis of PET are used.

5. Process according to one of the preceding claims, characterised in that the mixture used is a mixture of a crystallisable polyester and a non-crystallisable polyester.

6. Process according to Claim 5, characterised in that the non-crystallisable polyester used is a copolyester containing CHDM (1,4-cyclohexanedimethanol).

7. Process according to Claim 6, characterised in that the CHDM-modified copolyester is obtained by reacting a mixture of terephthalic acid, ethylene glycol (ethanediol) and CHDM.

8. Process according to Claim 5, characterised in that the non-crystallisable polyester used is a PET/PEN copolymer which is obtained by reacting a mixture of terephthalic acid, naphthalenedicarboxylic acid and ethylene glycol (ethanediol).

9. Process according to one of Claims 5-8, characterised in that the mixture used has a non-crystallisable weight fraction which is greater than 6%.

10. Process according to Claim 9, characterised in that the mixture used has a non-crystallisable weight fraction which is less than 90%.

11. Process according to Claim 9 or 10, characterised in that the mixture used has a non-crystallisable weight fraction which is approximately 25% or greater.

12. Process according to one of Claims 9-11, characterised in that the mixture used has a non-crystallisable weight fraction which is approximately 33% or greater.

13. Process according to one of Claims 9-12, characterised in that the mixture used has a non-crystallisable weight fraction which is approximately 50% or greater.

14. Process according to one of Claims 9-13, characterised in that the mixture used has a non-crystallisable weight fraction which is approximately 66% or greater.

15. Process according to one of Claims 9-14, characterised in that the mixture used has a non-crystallisable weight fraction which is approximately 75% or greater.

16. Laminate comprising a metal substrate and a plastic layer, characterised in that the plastic layer comprises an adhesive layer, the adhesive layer substantially comprising a plastic web produced according to the process described in one of Claims 1-15.

17. Laminate comprising a metal substrate and a plastic layer, characterised in that the plastic layer comprises a top layer, the top layer substantially comprising a plastic web produced according to the process described in one of Claims 1-15.

18. Laminate according to Claims 16 and 17, characterised in that there is an intermediate layer between the adhesive layer and the top layer, the intermediate layer substantially comprising a plastic web which is produced by extruding a polyester.

19. Laminate according to Claim 18, characterised in that the intermediate layer is produced according to the process described in one of Claims 1-8.

20. Laminate according to Claim 19, characterised in that the intermediate layer is produced from a mixture with a non-crystallisable weight fraction which is approximately 10% or greater.

21. Laminate according to Claim 20, characterised in that the intermediate layer is produced from a mixture with a non-crystallisable fraction which is approximately 33% or greater.

22. Screw cap produced from a laminate according to one of Claims 16-21.

23. Crown cork produced from a laminate according to one of Claims 16-21.

24. Easy open end produced from a laminate according to one of Claims 16-21.

25. Component produced from a laminate according to one of Claims 17-21, in which a PVC-containing compound is applied to the top layer of the plastic layer of the laminate.

26. Component according to Claim 25, in which the non-crystallisable weight fraction in the top layer is approximately 25% or greater.

27. Component according to Claim 25, in which the weight fraction is approximately 35% or greater.

28. Component according to Claim 27, in which the said weight fraction is approximately 50% or greater.

29. Component according to Claim 28, in which the said weight fraction is approximately 66% or greater.

INTERNATIONAL SEARCH REPORT

Inte. .onal Application No
PCT/EP 00/02211

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J5/18 B29D7/01 B32B15/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J B29D B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 839 854 A (TORAY INDUSTRIES) 6 May 1998 (1998-05-06) page 3, line 1 - line 31 page 5, line 1 - line 10; claim 20; example 2 ---	1-7,9-21
X	EP 0 685 509 A (TEIJIN LTD) 6 December 1995 (1995-12-06) page 3, line 3 - line 36; example 1 ---	1-3,5-7, 9-14
X	DATABASE WPI Section Ch, Week 199908 Derwent Publications Ltd., London, GB; Class A23, AN 1999-090132 XP002129572 & JP 10 324754 A (TORAY IND INC), 8 December 1998 (1998-12-08) abstract --- -/--	1,5,8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
14 August 2000	21/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Attalla, G

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte. .onal Application No
PCT/EP 00/02211

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 437 942 A (ICI PLC) 24 July 1991 (1991-07-24) page 2, line 2-5 page 2, line 19 -page 3, line 2 page 3, line 44 - line 53	1
A	US 5 334 450 A (ZABROCKI VINCENT S ET AL) 2 August 1994 (1994-08-02) column 6, line 60 - line 61; claims 1,2	25

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/EP 00/02211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0839854 A	06-05-1998	JP 9302113 A	25-11-1997
		US 5948525 A	07-09-1999
		CA 2226933 A	20-11-1997
		CN 1197465 A	28-10-1998
		WO 9743332 A	20-11-1997
		JP 10120803 A	12-05-1998
		JP 10279708 A	20-10-1998
EP 0685509 A	06-12-1995	WO 9515993 A	15-06-1995
JP 10324754 A	08-12-1998	NONE	
EP 0437942 A	24-07-1991	AT 114326 T	15-12-1994
		AU 629078 B	24-09-1992
		AU 6812690 A	25-07-1991
		BR 9100225 A	22-10-1991
		CA 2032767 A	20-07-1991
		CN 1054081 A	28-08-1991
		DE 69014290 D	05-01-1995
		DE 69014290 T	27-04-1995
		JP 2991506 B	20-12-1999
		JP 4211432 A	03-08-1992
		KR 168674 B	20-03-1999
US 5334450 A	02-08-1994	NONE	