

HIGH-RESISTANCE LAMINATED STEEL AND MANUFACTURING METHOD THEREFOR

Technical Field

The present disclosure relates to a composite material and a manufacturing method thereof, and in particular to a laminated steel and a manufacturing method thereof.

Background Art

Laminated steel typically refers to a composite material obtained by directly laminating a polyester film to a steel substrate through a heating and melting process. It can be used for both can bodies and can lids, and is applicable to food cans, beverage cans, standard lids, easy-open lids, etc. The application of food canning is one of the important development directions for laminated steel. Among them, when the contents of the can food are primarily meat or differentiated foods like marinated garlic or crabs, there are higher resistance requirements for the can body. The resistance of laminated steel is closely related to the type and structure of the surface film, as well as the interfacial performance between the film and the substrate.

The Chinese patent publication No. CN101646712A, published on February 10, 2010, with a title of "Polyester Resin for Sheet Metal Coating and Method for Producing the Same" provides a polyester resin for sheet metal coating, which is formed from an acid component comprising terephthalic acid as the main component and 1-15 mol% isophthalic acid and 2-10 mol% dicarboxylic acid, and an alcohol component comprising ethylene glycol as the main component. It is characterized by excellent impact resistance and processing fitness; however, its corrosion resistance is evaluated with a simulation liquid of distilled water at 125°C for 30 minutes, which does not reflect its resistance to simulated liquids containing salts or sulfur.

In addition, the current focus on the performance of laminated steel is primarily on its adhesion properties, while its corrosion resistance is typically enhanced by designing modified polymer films. However, with respect to a composite material, existing

technology has not paid attention to the impact of the surface state of the substrate and the interface state between the film and the substrate on the resistance of the product.

Therefore, it is desirable to provide a laminated steel and a manufacturing method thereof that can meet the requirement for high resistance.

Summary

One of the objects of the present disclosure is to provide a laminated steel with high resistance, which is formed by using a substrate with low roughness and then thermally laminating a polyester film having a multi-layer structure onto the substrate, resulting in a laminated steel product that has high resistance to high-temperature sterilization after deformation during canning, particularly high resistance to salts and sulfur.

In order to achieve the above object, the present disclosure proposes a laminated steel with high resistance, which comprises a substrate and a polyester film laminated on a surface of the substrate, wherein:

the substrate has a surface roughness of $0.15\text{-}0.35\mu\text{m}$, and the surface of the substrate is treated with an oil;

the polyester film comprises, in order from top to bottom in the thickness direction, a thermal-laminating layer, an intermediate layer, and a barrier layer, where the thermal-laminating layer is made of a modified copolyester, the intermediate layer is a mixture of a modified copolyester and a homopolyester, and the barrier layer is made of a non-modified homopolyester.

In the laminated steel with high resistance, the thermal-laminating layer of the polyester film is in contact with the substrate.

The present disclosure utilizes a substrate with low surface roughness, and further employs a polyester film having a three-layer structure, which is laminated onto the substrate through a thermal lamination method, providing high interfacial adhesion performance, while greatly enhancing its resistance through high-temperature sterilization after it is subjected to can forming, so as to allow it suitable for the field of metal packaging for food products that requires high resistance to the filled contents.

In particular, the low surface roughness of 0.15 to 0.35 μm is an important surface quality indicator of the substrate, which is closely related to the surface performance of the laminated steel, affecting the adhesion and corrosion resistance of the laminated steel of the present disclosure.

In some embodiments, the substrate in the laminated steel with high resistance of the present disclosure has a surface roughness of 0.25-0.30 μm .

With respect to the polyester film having a three-layer structure, the upper layer (thermal laminating layer) can effectively meet the thermal lamination between the substrate and the film, exhibiting excellent adhesion performance suitable for processing and forming. The lower layer (barrier layer) provides good barrier properties, meeting high resistance requirements. The intermediate layer acts as a transition layer, preventing structural damage to the non-laminated layer due to heat and preventing delamination during the film deformation process.

Further, in the laminated steel with high resistance of the present disclosure, the substrate is a chrome-plated sheet.

Of course, in other embodiments, the substrate may be other types of sheets, such as tin-plated sheets.

Further, in the laminated steel with high resistance of the present disclosure, the surface of the substrate is coated with an oil, with an oil coating amount of 1.5 to 3.5 mg/m^2 .

In general, the main purpose of coating the substrate with an oil is to prevent rust and lubricate to reduce friction. However, the inventors of the present disclosure found that excessive coating with an oil can negatively affect the adhesion performance of the laminated interface. During normal use, the deformation of the laminated steel during canning leads to a decrease in interface adhesion, thereby affecting the corrosion resistance. Therefore, in the present disclosure, the amount of oil coated on the substrate surface is reduced to 1.5-3.5 mg/m^2 to ensure better interface adhesion performance.

Further, in the laminated steel with high resistance of the present disclosure, the oil is at least one selected from the group consisting of dioctyl sebacate (DOS), cottonseed oil

(CSO) and acetyl tri-*n*-butyl citrate (ATBC).

Further, in the laminated steel with high resistance of the present disclosure, the melting point of the modified copolyester is 220-232°C.

Further, in the laminated steel with high resistance of the present disclosure, the modified copolyester is obtained by copolymerizing polyesters with isophthalic acid or an aliphatic diol. In some embodiments, the modified copolyester is obtained by copolymerizing polyethylene terephthalate with isophthalic acid or an aliphatic diol.

Further, in the laminated steel with high resistance of the present disclosure, the aliphatic diol is at least one selected from the group consisting of propanediol, butanediol, pentanediol, hexanediol, neopentyl glycol, and 1,4-cyclohexanedimethanol.

Further, in the laminated steel with high resistance of the present disclosure, the aliphatic diol is selected from neopentyl glycol and/or 1,4-cyclohexanedimethanol.

Further, in the laminated steel with high resistance of the present disclosure, the non-modified homopolyester is polyethylene terephthalate.

Further, in the laminated steel with high resistance of the present disclosure, the non-modified homopolyester has a melting point of 250-260°C.

Further, in the laminated steel with high resistance of the present disclosure, the mass percentage of the modified copolyester in the intermediate layer is 20%-80%.

Further, in the laminated steel with high resistance of the present disclosure, the homopolyester in the intermediate layer is a non-modified homopolyester, such as polyethylene terephthalate.

Further, in the laminated steel with high resistance of the present disclosure, the modified copolyester in the intermediate layer is the same as the modified copolyester in the thermal-laminating layer, and the homopolyester in the intermediate layer is the same as the non-modified homopolyester in the barrier layer.

Still further, the mass percentage of the modified copolyester in the intermediate layer is 30%-70%, such as 30%-50%.

Further, in the laminated steel with high resistance of the present disclosure, the thickness of the polyester film is 20-35 μm .

Further, the thickness of the polyester film is 25-30 μm .

Still further, in the polyester film, the thickness of the thermal-laminating layer is 5-10 μm , the thickness of the intermediate layer is 10-15 μm , and the thickness of the barrier layer is 5-10 μm .

Another object of the present disclosure is to provide a method for manufacturing the laminated steel with high resistance. A laminated steel product with high resistance can be prepared by this method.

Based on the above object, the present disclosure also provides a method for manufacturing the laminated steel with high resistance, which comprises the following steps:

- (1) pretreating a substrate with heating;
- (2) laminating with a film;
- (3) cooling and squeeze-drying.

Further, in the step of pretreating with heating of the manufacturing method according to the present disclosure, the substrate with oil coated on the surface is heated to 150-180 $^{\circ}\text{C}$.

Heating the substrate to a temperature of 150~180 $^{\circ}\text{C}$ is beneficial for the volatilization of the oil coated on the substrate surface, further reducing the amount of oil coated on the substrate surface. After the oil has volatilized, the substrate temperature can be brought to the target value for film laminating and maintained stable by induction heating rollers.

Further, in the manufacturing method according to the present disclosure, in the step of laminating with a film, the laminating speed is controlled at 60-120m/min.

Further, in the step of cooling and squeeze-drying of the manufacturing method according to the present disclosure, the laminated steel is firstly cooled to 80 $^{\circ}\text{C}$ or lower by water spray, quenched in a water quenching tank, and then squeeze-dried with squeeze-drying rollers.

The laminated steel with high-resistance according to the present disclosure has the following advantages and beneficial effects:

The present disclosure adopts a substrate with low roughness and low oil coating, which is pre-treated with surface heating to remove oil. Then, a polyester film having a three-layer structure is laminated onto the substrate via thermal lamination, creating a laminated steel product that meets high resistance requirements, particularly against salts and sulfur.

The polyester film having a three-layer structure used in the present disclosure has an upper layer that can effectively satisfy the thermal lamination between the substrate and the film, a lower layer that provides good barrier properties to meet high resistance requirements, and an intermediate layer that serves as a transition layer to prevent delamination during the deformation process of the film.

In some preferred embodiments of the present disclosure, the present disclosure adopts a substrate having a roughness Ra value in the range of from 0.15 to 0.35 μm and an amount of oil coated on the surface of 1.5 to 3.5 mg/m^2 , which can effectively improve the interfacial adhesion performance of the laminated steel and meet the requirements for high resistance after canning deformation.

The laminated steel according to the present disclosure undergoes high-temperature sterilization at 121°C for 60 minutes using a 3wt% NaCl solution and a cysteine simulation liquid after canning forming. It shows no abnormal phenomena such as whitening, white bubbles, or sulfide spots on the inner wall, thus meeting the high resistance requirements of the contents such as fish and meat.

Detailed Description

The laminated steel with high resistance and the method for manufacturing the same according to the present disclosure will be further explained and illustrated below with reference to the specific Examples. However, such explanation and illustration do not constitute any improper limitation on the technical solution of the present disclosure.

Examples 1-6 and Comparative Examples 1-2

In the present disclosure, the laminated steels of Examples 1-6 were prepared according to the following steps:

(1) a chrome-plated or tin-plated substrate was pretreated by heating with an induction heater: wherein the surface roughness Ra of the substrate was 0.15 to 0.35 μm , and the amount of oil coated on the substrate surface was 1.5 to 3.5 mg/m^2 , and the substrate was heated to a temperature of 150 to 180°C.

(2) Thermal Laminating with a Film: A polyester film having a three-layer structure was thermally laminated onto the substrate at a laminating speed of 60~120 m/min using laminating rollers. The polyester film comprised, in order from top to bottom in thickness direction, a thermal laminating layer, an intermediate layer, and a barrier layer. The thermal laminating layer was made of a modified copolyester, the intermediate layer was a mixture of a modified copolyester and a homopolyester, and the barrier layer was made of a non-modified homopolyester, wherein the non-modified homopolyester was polyethylene terephthalate, the modified copolyester was obtained by copolymerization of polyethylene terephthalate with isophthalic acid or an aliphatic diol. The modified copolyester in the intermediate layer was the same as that in the thermal laminating layer, and the homopolyester in the intermediate layer was the same as the non-modified homopolyester in the barrier layer. The thermal laminating layer of the polyester film was in contact with the substrate.

In some embodiments, the modified copolyester is obtained by copolymerization of the polyester with isophthalic acid or an aliphatic diol, wherein the aliphatic diol may be selected from neopentyl glycol and/or 1,4-cyclohexanedimethanol.

It should be noted that although it is not listed the following examples, the aliphatic diol may also be at least one selected from the following group consisting of propanediol, butanediol, pentanediol and hexanediol.

In some embodiments, the melting point of the modified copolyester may be from 220 to 232°C. The melting point of the non-modified homopolyester is from 250 to 260°C. The mass percentage of the modified copolyester in the intermediate layer is 20%-80%.

In some embodiments, the thickness of the polyester film is 20-35 μm , wherein the thickness of the thermal laminating layer is 5-10 μm , the thickness of the intermediate layer is 10-15 μm , and the thickness of the barrier layer is 5-10 μm .

(3) Cooling and squeeze-drying: the laminated steel was firstly cooled to $\leq 80^{\circ}\text{C}$ by water spray, then quenched in a water quenching tank, and finally squeeze-dried with squeeze-drying rollers.

Table 1, Table 2-1 and Table 2-2 list the specific process parameters of Examples 1-6 and Comparative Examples 1-2.

In the present disclosure, the testing standard for the surface roughness Ra of the substrate is: GB/T 1031-2016 Geometrical Product Specification (GPS)- Surface texture: Profile method-surface roughness parameters and their values.

Table 1.

	Type of the substrate	Substrate Ra(μm)	Amount of oil coated on substrate (mg/m^2)	Type of oils	Preheating temperature ($^{\circ}\text{C}$)
Ex. 1	chrome-plated substrate	0.35	3.5	DOS	180
Ex. 2	chrome-plated substrate	0.35	1.5	DOS	180
Ex. 3	chrome-plated substrate	0.30	3.5	DOS	170
Ex. 4	chrome-plated substrate	0.25	1.5	DOS	170
Ex. 5	chrome-plated substrate	0.20	2.0	ATBC	170
Ex. 6	chrome-plated substrate	0.15	1.5	CSO	150
CEx. 1	chrome-plated substrate	<u>0.40</u>	1.5	DOS	180
CEx. 2	chrome-plated substrate	<u>0.40</u>	<u>5</u>	DOS	180

Table 2-1.

	Polyester film thickness (μm)	Melting point of modified copolyester ($^{\circ}\text{C}$)	Components for copolymerization modification of polyester	Melting point of homopolyester ($^{\circ}\text{C}$)	Mass percentage of modified copolyester in the intermediate layer (%)	Laminating speed (m/min)	Final cooling temperature of water spray cooling ($^{\circ}\text{C}$)
Ex. 1	20	220	isophthalic acid	250	20	120	80
Ex. 2	20	224	Neopentyl glycol	250	20	100	80
Ex. 3	28	228	isophthalic acid	255	30	100	80
Ex. 4	28	228	1,4-cyclohexanedimethanol	250	50	80	70
Ex. 5	35	232	1,4-cyclohexanedimethanol	260	80	80	70
Ex. 6	35	232	isophthalic acid	260	70	60	70
CEx. 1	15	228	isophthalic acid	250	10	120	80
CEx. 2	15	224	isophthalic acid	250	90	100	70

Table 2-2.

	Thermal-laminating layer thickness (μm)	Intermediate layer thickness (μm)	Barrier layer thickness (μm)
Ex. 1	5	10	5
Ex. 2	5	10	5
Ex. 3	8	12	8
Ex. 4	8	12	8
Ex. 5	10	15	10
Ex. 6	10	15	10
CEx. 1	4	7	4
CEx. 2	4	7	4

The laminated steels of Examples 1-6 prepared according to the process of the present disclosure and comparative laminated steels of Comparative Examples 1-2 were sampled. The sample of each Example and Comparative Example was tested for the interfacial adhesion performance, salt resistance, and sulfur resistance, and the test results were listed in Table 3 below. The test methods for the interfacial adhesion performance, salt resistance, and sulfur resistance were as follows:

Interface adhesion performance: The adhesion after deformation was measured using the cross-cut cupping-peeling test method. A 10cm $\times$ 10cm size laminated steel was taken, and "#-shaped grids" were drawn on the flat surface with 5mm spacing, cutting through the film (be careful not to cut the substrate). Then the cupping deformation method was applied, keeping the highest point of the cupping deformation in the middle area of the "#-shaped grids". Next, the sample was placed into a pressure steam sterilizer and treated with high-temperature sterilization at 121°C for 60 minutes. After removing the sample, the cross-cut area was observed, especially whether there was any film peeling at the intersections of the "#-shaped grids" to evaluate the adhesion performance of the film.

Salt resistance performance: After the laminated steel was formed into a can (can

type 538), the laminated steel can was filled with 3wt% NaCl solution. After it was sealed with a lid, it was boiled at a high temperature of 121°C for 30 minutes. After cooling, the sample was taken out to observe whether there were any abnormal phenomena such as whitening, bubbling, or film peeling on the surface, so as to evaluate the salt resistance of the laminated metal sheet.

Sulfur resistance performance: After the laminated steel was formed into a can (can type 538), the laminated steel can was filled with a cysteine simulation liquid (the reagent for sulfur resistance test was prepared by dissolving 0.56 g of L-cysteine, 3.6 g of potassium dihydrogen phosphate, and 7.2 g of disodium hydrogen phosphate to a total volume of 1000 mL). After it was sealed with a lid, it was boiled at a high temperature of 121°C for 60 minutes. After cooling, the sample was taken out to observe whether there were any abnormal phenomena such as whitening, sulfide spots, or film peeling on the surface, so as to evaluate the sulfur resistance of the laminated metal sheet.

Table 3 lists the test results of the relevant performances of the laminated steels in Examples 1-6 and Comparative Examples 1-2.

Table 3.

No.	Adhesion	Sulfur-resistance	Salt-resistance
Ex. 1	◎	○	○
Ex. 2	◎	○	○
Ex. 3	◎	◎	◎
Ex. 4	◎	◎	◎
Ex. 5	○	◎	◎
Ex. 6	○	◎	◎
CEx. 1	○	△	△
CEx. 2	△	×	×

Note: in the above Table 3, "×" indicates that the corresponding performance is unqualified; "△" indicates that the corresponding performance is qualified; "○" indicates that the corresponding performance is good; "◎" indicates that the corresponding

performance is excellent. The evaluation standards are shown in Table 4 below.

Table 4.

Rating level	Adhesion	Sulfur-resistance	Salt-resistance
excellent	No peeling	No whitening	No white bubbles, no discoloration
good	Peeling length $\leq 0.5\text{mm}$	Slight whitening at the bottom of the can.	No white bubbles, slight discoloration at the bottom and body of the can.
qualified	$0.5\text{mm} < \text{Peeling length} \leq 1.0\text{mm}$	Slight whitening at the bottom and body of the can.	1-2 white bubbles at the body of the can
unqualified	Peeling length $> 1.0\text{mm}$	Bubbles and delamination at the bottom and body of the can	> 2 white bubbles at the body of the can

As can be seen from Table 3, the laminated steels in Examples 1-6 of the present disclosure have excellent surface adhesion properties, while also exhibiting excellent resistance to salts and sulfur.

The laminated steel according to the present disclosure undergoes high-temperature sterilization at 121°C for 60 minutes using a 3wt% NaCl solution and a cysteine simulation liquid after canning forming. It shows no abnormal phenomena such as whitening, white bubbles, or sulfide spots on the inner wall, thus meeting the high resistance requirements of the contents such as fish and meat.

It should be noted that combinations of the various technical features in this case are not limited to the combinations described in the claims of this case or the combinations described in the specific Examples. All technical features recorded in this case can be combined freely or associated in any way unless a contradiction occurs.

It should also be noted that the Examples listed above are only specific embodiments

of the present disclosure. Obviously, the present disclosure is not limited to the above Examples, and changes or modifications made thereto can be directly derived from the present disclosure or easily conceived of by those skilled in the art, all of which fall within the protection scope of the present disclosure.

What is claimed is:

1. A laminated steel with high resistance, which comprises a substrate and a polyester film laminated on a surface of the substrate, wherein:

the substrate has a surface roughness of 0.15-0.35 μm ;

the polyester film comprises, in order from top to bottom in the thickness direction, a thermal-laminating layer, an intermediate layer, and a barrier layer, where the thermal-laminating layer is made of a modified copolyester, the intermediate layer is a mixture of a modified copolyester and a homopolyester, and the barrier layer is made of a non-modified homopolyester.

2. The laminated steel with high resistance according to claim 1, wherein the substrate is a chrome-plated sheet.

3. The laminated steel with high resistance according to claim 1, wherein the surface of the substrate is coated with an oil, and the amount of the oil coated on the surface of the substrate is 1.5-3.5mg/m².

4. The laminated steel with high resistance according to claim 3, wherein the oil is at least one selected from the group consisting of dioctyl sebacate, cottonseed oil and acetyl tributyl citrate.

5. The laminated steel with high resistance according to claim 1, wherein the modified copolyester has a melting point of 220-232°C.

6. The laminated steel with high resistance according to claim 1, wherein the modified copolyester is obtained by copolymerizing polyesters with isophthalic acid or an aliphatic diol.

7. The laminated steel with high resistance according to claim 6, wherein the aliphatic diol is at least one selected from the group consisting of propanediol, butanediol, pentanediol, hexanediol neopentyl glycol, and 1,4-cyclohexanedimethanol.

8. The laminated steel with high resistance according to claim 7, wherein the aliphatic diol is selected from neopentyl glycol and/or 1,4-cyclohexanedimethanol.

9. The laminated steel with high resistance according to claim 1, wherein the non-modified homopolyester is polyethylene terephthalate.

10. The laminated steel with high resistance according to claim 1, wherein the

non-modified homopolyester has a melting point of 250-260°C.

11. The laminated steel with high resistance according to claim 1, wherein the modified copolyester in the intermediate layer has a mass percentage of 20%-80%.

12. The laminated steel with high resistance according to claim 1, wherein the polyester film has a thickness of 20-35 μm .

13. A method for manufacturing the laminated steel with high resistance according to any one of claims 1-12, which comprises the following steps:

- (1) pretreating a substrate with heating;
- (2) laminating with a film;
- (3) cooling and squeeze-drying.

14. The method according to claim 13, wherein in the step of pretreating with heating, the substrate with oil coated on the surface is heated to 150-180 °C; and/or, in the step of laminating with a film, the laminating speed is controlled at 60-120m/min.

15. The method according to claim 13, wherein in the step of cooling and squeeze-drying, the laminated steel is firstly cooled to $\leq 80^{\circ}\text{C}$ by water spray, quenched in a water quenching tank, and then squeeze-dried with squeeze-drying rollers.