

PATENT SPECIFICATION

1,180,925

NO DRAWINGS.

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COMPLETE SPECIFICATION.

A Method of Bonding Polyethylene to a Metal Surface.

We, VAN LEER (U.K.) LIMITED, formerly Metal Containers Limited, a British Company of Passfield Research Laboratories, Passfield, Liphook, Hampshire, formerly of Seymour House, 17 Waterloo Place, Pall Mall, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a method of coating ferrous metal articles with polyethylene.

It is difficult, and sometimes impossible, to obtain good adherence between commercially available polyethylene, whether in powder or film form, and ferrous metal surfaces by sintering alone (the term sintering being used in this specification to mean a heat treatment resulting in fusion of the polyethylene, whether in powder or film form, on the substrate to form a pore-free continuous layer).

A number of procedures have been proposed for bonding polyethylene to ferrous metal surfaces with a view to obtaining good adherence. Thus in British Specification No. 859,728 it is proposed that polyethylene should be adhered to steel by means of an adhesive composition comprising a polyisobutylene, a tertiary amine, a polyethylene glycol and a condensation product derived from a hydroxy group containing polyester and an organic polyisocyanate.

British Specification No. 887,875 describes a method of bonding pre-formed polyolefin film to a metal by coating the metal and the polyolefin film with a curable

polymer mixture comprising a peroxide and an oily polymer or copolymer of a C_4 to C_6 conjugated diolefin.

Canadian Patent No. 575,652 describes a method of bonding polyethylene to a metal surface by forming a thin coating of polyethylene on the metal surface, oxidising the thin polyethylene coating by baking it above its melting point, and then bonding the main body of the polyethylene to the thin coating of oxidised polyethylene by heating.

We have now found that firmly adherent polyethylene coatings can be formed using a single polyethylene application stage, if the metal surface to be coated is first coated with an oxidation-promoting substance so that during sintering partial oxidation of the polyethylene in a superficial zone adjacent the metal surface occurs.

According to the present invention, therefore, we provide a method of making polyethylene-coated ferrous metal articles, which comprises applying to the surface to be coated an oxidation-promoting substance and then sufficient polyethylene to give the desired final coating thickness and heating the assembly to effect partial oxidation of the polyethylene only in a superficial zone adjacent the ferrous metal surface and to cause fusion of the polyethylene.

The polyethylene is preferably substantially free from anti-oxidants.

Any substance which will promote the partial oxidation of the polyethylene can be used as the oxidation-promoting substance. Suitable substances include peroxides, such as dicumyl peroxide and di(ter. butylperoxy)hexane, and oxidation-

[Price 5s. 0d.]

promoting metallic compounds, such as organo-metallic paint driers, for example iron naphthenate, iron octoate and cobalt octoate. When a peroxide is used as the oxidation-promoting substance, it may be applied to the ferrous metal surface as a powder and then melted on the surface.

The wet bond strength of the polyethylene coating can be considerably increased by interposing a layer of thermosetting resin lacquer between the ferrous metal surface and the polyethylene. The lacquer layer should not be more than 100 microns thick. The lacquer may contain the oxidation-promoting substance or it may be applied without the oxidation-promoting substance and the latter then applied to the lacquer layer. Suitable thermosetting resins for such lacquers are, for example, epoxy-phenolic, phenolic and polyurethane resins. Any of the above-mentioned oxidation-promoting substances can be used in association with such a lacquer, but it is preferred to use the organo-metallic paint driers.

Where the oxidation-promoting substance is incorporated in the lacquer, it appears that during the heating stage it migrates to the surface of the lacquer layer remote from the ferrous metal surface so as to be in direct contact with the polyethylene. The oxidation-promoting substance may be incorporated in the lacquer as a solution or otherwise and the lacquer may be applied to the metal surface in any suitable manner, such as by spraying, pouring or dipping. A preferred oxidation-promoting substance-containing lacquer is an epoxy-phenolic lacquer containing cobalt octoate, the lacquer being applied to the ferrous metal surface to form a layer having a thickness of from 10 to 25 microns.

When the lacquer is applied by itself, that is without an oxidation-promoting substance being contained therein, the oxidation-promoting substance may be applied to the lacquer layer by any suitable method, for example by applying a solution of the oxidation-promoting substance, such as a 1% solution of iron naphthenate in acetone, to the lacquer layer.

When an intermediate lacquer layer is present, the polyethylene is partially oxidised only in a superficial zone adjacent the lacquer layer.

As stated above, the use of an intermediate lacquer considerably improves the wet bond strength of the polyethylene coating. If the polyethylene-coated metal surface is not intended to come into contact with water during use, the intermediate lacquer layer is not necessary.

In order that the invention may be more fully understood, the following examples, in which all percentages and proportions are

by weight, are given by way of illustration only. In these examples, Examples 1, 2, 5, 7, 9 and 10 illustrate processes according to the invention, Example 3 illustrates, for the purpose of comparison, a process according to Canadian Patent No. 575,652, and Examples 4, 6 and 8 are also given for the sake of comparison.

Example 1.

Polyethylene as obtained from suppliers, was dissolved in hot tetralin and subsequently precipitated by adding butanol and ethanol, in order to remove antioxidant.

A panel of ordinary 20 BG mild steel was degreased in trichloroethylene vapour, dipped into 5N hydrochloric acid for 30 seconds and then rinsed in demineralised water while swabbing with cotton wool to remove loose smut. The panel was then washed in methyl alcohol and dried in a stream of warm air.

The steel panel was heated to 200°C for 10 minutes. 0.25 g of dicumyl peroxide per 150 cm² of steel surface was applied to the hot surface. The dicumyl peroxide melted very quickly and spread over the surface. Although it took only a few seconds for the molten peroxide to spread over the panel, a soft brush can be used to accelerate spreading. The panel was then held horizontally and the polyethylene powder was applied to its surface to a depth of 1 cm. After 1 minute excess powder is tapped off and the panel heated at 200°C for 10 minutes. After cooling, the panel was immersed in water at 90°C for 1 hour, allowed to cool to room temperature and then tested for adhesion by peeling. The peel strength was entirely satisfactory.

Example 2.

Polyethylene and an 18 BG mild steel panel were pretreated as in Example 1.

The degreased steel panel was coated with an epoxy phenolic lacquer containing 2% by weight of iron octoate. The coating was stoved at 230°C for 10 minutes and then coated with the powdered polyethylene (which had a melt flow index of 2 at 190°C). After sintering for a further 15 minutes at 230°C, cooling, immersion in water at 90°C for 1 hour and cooling to room temperature, the adhesion was tested by peeling. The adhesion was so good that the polyethylene broke on peeling (A.S.T.M. D 903-49).

Example 3.

A 6 in. × 4 in. 18 BG steel panel was degreased in trichloroethylene vapour and dried. The panel was then dipped in a hot solution of 1.5 g of polyethylene (having a melt viscosity of 3000 poises at 190°C) in 80 g of xylene, held in air for 3 minutes

(but not completely dried), and baked in an oven at 250°C for 15 minutes. The panel was then taken out of the oven and covered with powdered polyethylene (having a melt flow index of 20). After allowing to stand for 3 minutes, the excess of powder was removed and the polyethylene coated panel inserted in the oven again for 10 minutes at 230°C. After cooling, the panel was immersed in water of 90°C for 1 hour, allowed to cool to room temperature and then tested for adhesion by peeling. The peel strength was 1.3 kg/cm width.

Example 4.

A panel of 20 BG mild steel was degreased and heated to 180°C. Powdered "Alkathene" WJG47 (trade mark; polyethylene having a melt flow index of 2), was applied and after three minutes excess powder was removed. The coating was then fused in an oven at 180°C for a further 20 minutes. After cooling, adhesion of the polyethylene to the steel was examined by the peel test. The panel was immersed in water at 90°C for one hour and after cooling the adhesion was again examined. In both cases the adhesion was poor.

Example 5.

A panel of 20 gauge mild steel was degreased and sprayed with a coating of polyurethane lacquer F 663-2007 (marketed by I.C.I. Ltd.) containing 2% of iron octoate. The coating was stoved at 210°C for 20 minutes. Powdered "Alathon" 20 (trade mark) was applied. After removal of excess powder, the coating was stoved at 210°C for 20 minutes. After cooling it was found that the adhesion of the polyethylene to the lacquer was excellent, exceeding the cohesive strength of the polyethylene.

Example 6.

A panel of 20 BG mild steel was degreased and trichloroethylene vapour and heated to 180°C. A powdered polyethylene (having a melt flow index of 2) containing 150 ppm of "Santonox" R antioxidant (trade mark) was applied and after 3 minutes excess powder was removed. The coating was then fused in an oven at 180°C for a further 12 minutes. After cooling, the adhesion of the polyethylene to the steel was examined using a peel test. Adhesion was found to be very low, less than 0.5 kg/cm width.

Example 7.

Polyethylene having a melt flow index of 2, a density of 0.918 and containing 150 ppm of "Santonox" as described in Ex-

ample 6 was sintered onto a mild steel sheet which had been sprayed with a 5% solution of dicumyl peroxide in toluene. The adhesion of the polyethylene to the steel was measured by peel strength and was found to be 3.5 kg/cm width. However, the adhesion after immersion in water at 90°C and then cooling was found to be only 0.4 kg/cm width.

Example 8.

A mild steel panel was degreased in trichloroethylene vapour and then sprayed with a 0.5 mil coating of an epoxy-phenolic lacquer of the type that is commonly used for the internal coating of steel shipping containers. This was heated to 230°C for 10 minutes. Polyethylene containing 15 ppm of antioxidant was then applied. The panel was further heated at 230°C for 8 minutes. On cooling, the adhesion of the polyethylene to the lacquer surface was found to be so low as not to be measurable.

Example 9.

Example 8 was repeated with the addition of 5% of iron "SiccatoI" to the epoxy-phenolic lacquer. The adhesion both dry and after immersion in water at 90°C followed by cooling was greater than the cohesive strength of the polyethylene.

Example 10.

A mild steel panel was degreased in trichloroethylene vapour and sprayed with a heat-curable polyurethane lacquer to form a 1.0 mil coating. The coating was heated to 210°C for 20 minutes and then allowed to cool. The lacquer coating was then sprayed with 10% solution of iron naphthenate in toluene and reheated to 210°C. Polyethylene having a melt flow index of 7 and containing 30 ppm of "Santonox" antioxidant was then applied. The adhesion of the polyethylene to the polyurethane lacquer was found to be greater than 3.5 kg/cm width, both dry and after immersion in water at 90°C followed by cooling.

WHAT WE CLAIM IS:—

1. A method of making polyethylene-coated ferrous metal articles, which comprises applying to the surface to be coated an oxidation-promoting substance and then sufficient polyethylene to give the desired final coating thickness and heating the assembly to effect partial oxidation of the polyethylene only in a superficial zone adjacent the ferrous metal surface and to cause fusion of the polyethylene.
2. A method according to claim 1, in which the oxidation-promoting substance is a peroxide.
3. A modification of the method according to claim 1, in which the oxidation-



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(but not completely dried), and baked in an oven at 250°C for 15 minutes. The panel was then taken out of the oven and covered with powdered polyethylene (having a melt flow index of 20). After allowing to stand for 3 minutes, the excess of powder was removed and the polyethylene coated panel inserted in the oven again for 10 minutes at 230°C. After cooling, the panel was immersed in water of 90°C for 1 hour, allowed to cool to room temperature and then tested for adhesion by peeling. The peel strength was 1.3 kg/cm width.

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A panel of 20 BG mild steel was degreased and heated to 180°C. Powdered "Alkathene" WJG47 (trade mark; polyethylene having a melt flow index of 2), was applied and after three minutes excess powder was removed. The coating was then fused in an oven at 180°C for a further 20 minutes. After cooling, adhesion of the polyethylene to the steel was examined by the peel test. The panel was immersed in water at 90°C for one hour and after cooling the adhesion was again examined. In both cases the adhesion was poor.

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A panel of 20 gauge mild steel was degreased and sprayed with a coating of polyurethane lacquer F 663-2007 (marketed by I.C.I. Ltd.) containing 2% of iron octoate. The coating was stoved at 210°C for 20 minutes. Powdered "Alathon" 20 (trade mark) was applied. After removal of excess powder, the coating was stoved at 210°C for 20 minutes. After cooling it was found that the adhesion of the polyethylene to the lacquer was excellent, exceeding the cohesive strength of the polyethylene.

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55 *Example 7.*

Polyethylene having a melt flow index of 2, a density of 0.918 and containing 150 ppm of "Santonox" as described in Ex-

ample 6 was sintered onto a mild steel sheet which had been sprayed with a 5% solution of dicumyl peroxide in toluene. The adhesion of the polyethylene to the steel was measured by peel strength and was found to be 3.5 kg/cm width. However, the adhesion after immersion in water at 90°C and then cooling was found to be only 0.4 kg/cm width.

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A mild steel panel was degreased in trichloroethylene vapour and then sprayed with a 0.5 mil coating of an epoxy-phenolic lacquer of the type that is commonly used for the internal coating of steel shipping containers. This was heated to 230°C for 10 minutes. Polyethylene containing 15 ppm of antioxidant was then applied. The panel was further heated at 230°C for 8 minutes. On cooling, the adhesion of the polyethylene to the lacquer surface was found to be so low as not to be measurable.

Example 9.

Example 8 was repeated with the addition of 5% of iron "Siccatol" to the epoxy-phenolic lacquer. The adhesion both dry and after immersion in water at 90°C followed by cooling was greater than the cohesive strength of the polyethylene.

Example 10.

A mild steel panel was degreased in trichloroethylene vapour and sprayed with a heat-curable polyurethane lacquer to form a 1.0 mil coating. The coating was heated to 210°C for 20 minutes and then allowed to cool. The lacquer coating was then sprayed with 10% solution of iron naphtenate in toluene and reheated to 210°C. Polyethylene having a melt flow index of 7 and containing 30 ppm of "Santonox" antioxidant was then applied. The adhesion of the polyethylene to the polyurethane lacquer was found to be greater than 3.5 kg/cm width, both dry and after immersion in water at 90°C followed by cooling.

WHAT WE CLAIM IS:—

1. A method of making polyethylene-coated ferrous metal articles, which comprises applying to the surface to be coated an oxidation-promoting substance and then sufficient polyethylene to give the desired final coating thickness and heating the assembly to effect partial oxidation of the polyethylene only in a superficial zone adjacent the ferrous metal surface and to cause fusion of the polyethylene.

2. A method according to claim 1, in which the oxidation-promoting substance is a peroxide.

3. A modification of the method according to claim 1, in which the oxidation-

- promoting substance is applied to the ferrous metal surface in admixture with a thermosetting resin lacquer to form a layer having a thickness not exceeding 100 microns, the polyethylene is applied to said layer, and the assembly is heated to effect partial oxidation of the polyethylene only in a superficial zone adjacent the resin lacquer layer.
4. A method according to claim 3, in which the thermosetting resin present in the lacquer is an epoxy-phenolic, a phenolic or a polyurethane resin.
5. A method according to any of claims 1, 3 and 4, in which the oxidation-promoting substance is an organo-metallic compound capable of acting as a paint drier.
6. A method according to claim 5, in which the organo-metallic compound is iron naphthenate, iron octoate or cobalt octoate.
7. A method according to claim 3, in which a mixture of epoxy-phenolic lacquer and cobalt octoate is applied to the ferrous metal surface to form a layer having a thickness of from 10 to 25 microns.
8. A modification of the method according to any of claims 3 to 6, in which a layer of the thermosetting resin lacquer (not containing the oxidation-promoting substance) is first formed on the ferrous metal surface, the oxidation-promoting substance is then applied to the lacquer layer and the polyethylene is finally applied over the oxidation-promoting substance, and the assembly is heated to effect partial oxidation of the polyethylene only in a superficial zone adjacent the lacquer layer.
9. A method according to any of claims 1 to 8, in which the polyethylene is substantially free from anti-oxidants.
10. A method according to claim 1, 3 or 8 substantially as herein described in any of Examples 1, 2, 5, 7, 9 or 10.
11. Ferrous metal articles having a polyethylene coating thereon when produced by the method claimed in any of claims 1 to 10.

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