THERMOPLASTIC IMPERMEABLE HOLLOW BODY

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ABSTRACT

Impermeable hollow body suitable as a fuel tank, made of thermoplastic material comprising at least one polyolefin and coated with a polyvinyl alcohol film impermeable to and insoluble in water owing to its crosslinking by a chemical agent and/or owing to the presence of an epoxy protective layer.

Two-step process for impermeabilizing a hollow body made of thermoplastic material comprising at least one polyolefin. In the first step, the surface of the hollow body is firstly coated with a polyvinyl alcohol film and, in the second step, the polyvinyl alcohol film is made insoluble and impermeable by crosslinking the polyvinyl alcohol molecules by means of a chemical agent and/or by depositing an epoxy coating on the film.
THERMOPLASTIC IMPERMEABLE HOLLOW BODY

[0001] The present invention relates to an impermeable hollow body made of thermoplastic material.

[0002] Impermeable hollow bodies made of thermoplastic materials have been known for a long time. In particular, fuel tanks made of thermoplastic material with a very low permeability to gaseous and liquid hydrocarbons are known. These known tanks can be essentially divided into two separate categories, namely tanks whose internal surface has been treated by means of a reactive gas (for example F₂ or SO₂) which modifies the properties of the plastic and makes the surface of the treated tank impermeable, and tanks formed from a multilayer structure containing an internal layer made of a barrier material, which is generally thin and not very strong from the mechanical standpoint, the barrier material preventing the permeation of the hydrocarbons.

[0003] Also known is Patent GB-1 006 622 which describes a method for improving the adhesion properties of thin polypropylene films intended for packaging, by coating these films with a polyvinyl alcohol layer protected by an epoxy coating (“Treatment 4”, page 9, line 18).

[0004] However, it is observed that with this known method the adhesion of the polyvinyl alcohol layer itself to the polypropylene substrate is not good. In particular, when the wall thickness is substantially greater than that of a thin packaging film, such as the walls encountered in the hollow bodies that can for example be used as a fuel tank, the adhesion is insufficient to guarantee long term the mechanical integrity of the polyvinyl alcohol layer.

[0005] It is an object of the invention to provide a hollow body made of thermoplastic material that is impermeable to hydrocarbons and does not require treatment by means of highly reactive gases, such as fluorine or sulphur trioxide, nor the necessary complex use of multilayer structures containing a barrier layer within the structure.

[0006] For this purpose, the invention relates to a hollow body made of thermoplastic material, comprising at least one polyolefin and coated on at least one of its faces and at least part of its surface with a polyvinyl alcohol film, in which the film has a water permeability and a water solubility that are greatly reduced owing to the crosslinked state of its molecules caused by means of a chemical agent chosen from esterification and acetalization agents and/or by the presence of a protective layer that covers it at its interface with the atmosphere.

[0007] The term “hollow body” denotes any structure whose surface has at least one empty or concave part. Preferably, the hollow body is understood here to mean a closed structure intended to contain a liquid and/or a gas. Particularly preferred are containers and tanks. The hollow bodies according to the invention are particularly well suited to their use as fuel tank, especially those present on—or intended to be fitted into—motor vehicles. By extension, they also mean the various accessories that may be associated with these hollow bodies, and also interfaces for connecting these accessories to the hollow bodies. Such accessories are, for example, fluid-drawing modules and pumps, canisters, valves and pipework associated with the hollow body, which are fixed to this hollow body or are simply connected thereto.

[0008] The hollow body according to the invention is a hollow body of very low permeability to liquid or gaseous fuels, particularly to hydrocarbons and to alcohols containing less than 10 carbon atoms, and also to mixtures thereof. The hollow bodies according to the invention make it possible to limit accumulative transmission over a total of 24 hours to less than 2 g of hydrocarbons and/or alcohols.

[0009] The term “thermoplastic material” is understood to mean any material comprising at least one polymer that may be temporarily formed by at least one heat treatment. The term “polymer” is understood to mean both homo-polymers and copolymers (especially binary or ternary copolymers). Examples of such copolymers are, non-limitingly, random copolymers, linear block copolymers, other block copolymers and graft copolymers.

[0010] Thermoplastic polymers also comprise thermoplastic elastomers, and blends thereof.

[0011] Any type of thermoplastic polymer or copolymer whose melting point is below the decomposition temperature is suitable. Synthetic thermoplastic materials having a melting range spread over at least 10 degrees Celsius are particularly suitable. Examples of such materials are those exhibiting polydispersity in their molecular mass.

[0012] In particular, polyolefins, grafted polyolefins, thermoplastic polyesters, polyketones, polyamides and copolymers thereof may be found in the hollow body.

[0013] A copolymer often used is the copolymer ethylene-vinyl alcohol (EVOH). A blend of polymers or copolymers may also be used, as may a blend of polymeric materials with inorganic, organic and/or natural fillers such as, for example, but not limiting, carbon, salts and other inorganic derivatives, and natural or polymeric fibres.

[0014] The thermoplastic material of the hollow body according to the invention comprises at least one polyolefin. Preferably, this polyolefin is polyethylene. High-density polyethylene (HDPE) has given excellent results.

[0015] According to the invention, the thermoplastic material is coated on at least one of its faces and at least part of its surface with a polyvinyl alcohol film. The coating may be produced over all of one face or of both faces of a hollow body. It may also be only located on part of its surface, at the places requiring a higher degree of impermeabilization.

[0016] Polyvinyl alcohol is usually manufactured by hydrolysing polyvinyl acetate. However, polyvinyl alcohol may also contain a certain proportion of acetate groups that have not been hydrolysed during its manufacture. The amount of polyvinyl alcohol present in the thermoplastic material of the hollow bodies according to the invention may vary within a certain range depending on its degree of hydrolysis. Degrees of hydrolysis corresponding to at least 80%, and preferably at least 95%, of the total number of acetate groups being hydrolysed are, for example, very suitable for the films covering the thermoplastic material of the hollow bodies according to the invention.

[0017] The polyvinyl alcohol film covering the thermoplastic material of the hollow body according to the invention has the advantage of having a permeability to water and a solubility in water that are greatly reduced. These particular properties stem directly from a particular state of the polyvinyl alcohol film that is crosslinked by a chemical
agent or, alternatively, is covered at its interface with the external atmosphere by a protective layer that insulates the polyvinyl alcohol film from the water vapour in the atmosphere, and also from water that may be contained inside the hollow body. It is also possible at the same time to combine the crosslinked state, caused by a chemical agent, and the protective layer covering the polyvinyl alcohol film.

[0018] An interesting variant of the hollow body according to the invention is that in which the thermoplastic material includes an adhesion promoter. This promoter may be distributed within the thickness of the wall of the hollow body or, on the contrary, it may be present only in its surface part in the vicinity of the polyvinyl alcohol film.

[0019] Any composition capable of enhancing the adhesion properties of the polyvinyl alcohol film to the substrate comprising a polyolefin is suitable as adhesion promoter. One adhesion promoter that has given good results is an acid peroxide or a polyolefin grafted by at least one polar group. Particularly suitable polar groups are carboxylic groups. Polyethylene grafted by an anhydride, in particular maleic anhydride, has given excellent results.

[0020] Another beneficial variant for promoting adhesion is the presence of acid sites at the interface with the thermoplastic material. These acid sites are particularly advantageous when the polyvinyl alcohol film is crosslinked by an ester.

[0021] In the case in which the polyvinyl alcohol film is covered with a protective layer, this may be a layer that comprises a flexible epoxy, a polyurethane varnish or an acrylic paint.

[0022] When the polyvinyl alcohol film is crosslinked by a chemical agent, the latter is chosen from esterification and acetalization agents, or from a mixture of two or more of these agents. It is also possible to choose the chemical agent from a mixture of several agents belonging to at least one of the two aforementioned categories. The expression “esterification and acetalization agents” is understood to mean any composition that comprises at least one chemical compound capable of reacting with at least the surface molecules of the polyvinyl alcohol film in order to produce, respectively, either ester groups or acetal groups with the hydroxyl groups present on the carbon chains of these molecules.

[0023] Preferably, the chemical crosslinking agent is an esterification agent. Particularly suitable esterification agents that may be chosen include acetic acid, ethylhexyl glycidyl ether, long-chain organic acids or diacids and acid chlorides thereof, isocyanates and urea.

[0024] The expression “long-chain organic acids or diacids” is understood to mean aliphatic and/or aromatic carboxylic acids containing at least one carbon chain with at least 8 carbon atoms.

[0025] The term “isocyanates” is understood to mean compounds that contain at least one isocyanate (—NCO) radical. Monoisocyanates and diisocyanates are particularly suitable. Monoisocyanates are preferred.

[0026] One esterification agent that has given excellent results is acetic acid.

[0027] The invention also relates to a process for impermeabilizing a hollow body made of thermoplastic material comprising at least one polyolefin, in which, in a first step, the surface of the hollow body is firstly coated with a polyvinyl alcohol film and, in a second step, the polyvinyl alcohol film is made insoluble and impermeable by crosslinking the polyvinyl alcohol molecules by means of a chemical agent and/or by depositing an epoxy coating on the film.

[0028] In this process, the common terms have the same meaning as that given above in the description of the hollow body.

[0029] One particularly advantageous method of implementing the process according to the invention consists in activating the adhesion of the polyvinyl alcohol film. One method of activation that is very suitable is the localized generation of heat. Any means capable of generating heat at the interface between the polyvinyl alcohol film and the thermoplastic substrate present in the hollow body may be used. Localized heat generation may take place, for example, by a stream of hot air directed onto the polyvinyl alcohol film or by scanning the surface of the polyvinyl alcohol film covering the thermoplastic substrate with electromagnetic radiation of suitable wavelength in order to generate heat by absorption in the polymers.

[0030] Preferably, the localized heat generation takes place by scanning the surface of the polyvinyl alcohol film covering the thermoplastic substrate with infrared radiation or laser radiation of wavelength at most equal to 15 000 nm. It is also usually suitable for the infrared radiation or the laser radiation used for scanning the surface to have a wavelength of at least 500 nm.

[0031] Another preferred method of localized heat generation is the use of a plasma in the gaseous atmosphere directly in contact with the polyvinyl alcohol film. All types of plasma and the methods for generating them that are compatible with the operating conditions of coating the surface of the hollow body with the polyvinyl alcohol film are suitable.

[0032] When it is the internal face of a closed hollow body (i.e. the concave side) that is coated, a vacuum plasma is preferred, for example an argon plasma, a nitrogen plasma or a plasma consisting of an argon/nitrogen mixture.

[0033] When it is the outer face of a hollow body (i.e. the convex side) that is coated, it is preferred to use an atmospheric nitrogen plasma torch.

[0034] In both cases, it is advantageous to enhance the plasma generation with a microwave generator.

[0035] The use of a plasma as localized heat generator may also be combined with prior generation of acid sites as explained above. This generation of acid sites may advantageously be carried out also by means of a plasma. Preferably, a CO2 plasma is used in this case. Here again, it is possible to work in a vacuum or at atmospheric pressure (plasma torch) depending on whether it is the internal face of a closed hollow body or its outer face that is coated. After acid sites have been generated, it is then possible to promote adhesion of the polyvinyl alcohol film by localized heat generation using an argon or nitrogen vacuum plasma or a nitrogen atmospheric plasma torch.

[0036] The step of coating the surface of the hollow body with polyvinyl alcohol may be carried out by any method or
technique capable of producing a polyvinyl alcohol film coating of uniform thickness. One technique that has given good results is that consisting in spraying the surface to be coated with an aqueous polyvinyl alcohol solution and then in drying the coated hollow body for the purpose of evaporating the water of the solvent. It is very suitable to dry by means of hot air.

1. Hollow body made of thermoplastic material, comprising at least one polyolefin and coated on at least one of its faces and at least part of its surface with a polyvinyl alcohol film, characterized in that the film has a water permeability and a water solubility that are greatly reduced owing to the crosslinked state of its molecules caused by means of a chemical agent chosen from esterification and acetalization agents and/or by the presence of a protective layer that covers it at its interface with the atmosphere.

2. Hollow body according to the preceding claim, characterized in that the protective layer is chosen from those comprising a flexible epoxy, a polyurethane varnish and an acrylic paint.

3. Hollow body according to claim 1, characterized in that the chemical crosslinking agent is an esterification agent chosen from at least one of the following compounds: acetic acid, ethylhexyl glycidyl ether, long-chain organic acids or diacids and acid chlorides thereof, isocyanates and urea.

4. Hollow body according to the preceding claim, characterized in that the esterification agent is acetic acid.

5. Process for impermeabilizing a hollow body made of thermoplastic material comprising at least one polyolefin, characterized in that, in a first step, at least part of the surface of at least one of the faces of the hollow body is firstly coated with a polyvinyl alcohol film and, in a second step, the solubility in water of the film is reduced by crosslinking its molecules by means of a chemical agent and/or by depositing an epoxy coating on the film.

6. Process according to the preceding claim, characterized in that the thermoplastic material also contains an adhesion promoter for the polyvinyl alcohol film and in that the adhesion reaction is activated by localized heat generation.

7. Process according to the preceding claim, characterized in that the localized heat generation takes place by scanning the surface with electromagnetic radiation of wavelength from 500 to 15 000 nm chosen from infrared radiation and laser radiation.

8. Process according to claim 6, characterized in that the localized heat generation takes place by using an argon or nitrogen plasma.

9. Process according to any one of claims 6 to 8, characterized in that the adhesion promoter is selected from polyolefins grafted by an anhydride, acid peroxides and acid sites produced by a CO₂ plasma.

10. Process according to any one of claims 5 to 9, characterized in that the step of coating the surface of the hollow body with polyvinyl alcohol is carried out by spraying the surface with an aqueous polyvinyl alcohol solution followed by drying for the purpose of evaporating the water of the solvent.

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