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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number:
B32B 27/36, F25D 23/06	A1	WO 91/15366
		(43) International Publication Date: 17 October 1991 (17.10.91)

(21) International Application Number: PCT/US91/01507

(22) International Filing Date: 5 March 1991 (05.03.91)

(30) Priority data:
504,369 4 April 1990 (04.04.90) US

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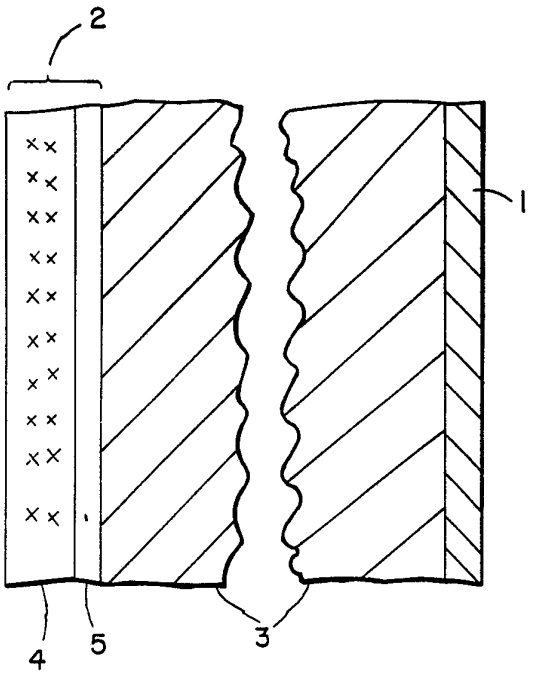
(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: BARRIER FILMS FOR PREVENTING SOLVENT ATTACK ON PLASTIC RESINS

(57) Abstract

This invention relates to the use of a barrier film consisting essentially of thermoplastic copolymer polyester resin to protect a styrenic resin sheet which constitutes the inner liner wall of an insulative cabinet wall of, for example, a refrigeration appliance unit from attack by the halogen-containing blowing agents present in the insulative polyurethane foam found within the cabinet wall.



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BARRIER FILMS FOR PREVENTING SOLVENT ATTACK ON PLASTIC RESINS

This invention pertains to an insulative cabinet wall comprising a barrier film or layer used to protect plastic resins employed in the construction of the wall from attack by solvents. More specifically this invention relates to the use of barrier films consisting essentially of a polyester polymer to protect styrenic resins such as, for example, high impact polystyrene (HIPS) or acrylonitrile-butadiene-styrene (ABS) copolymers.

Styrenic material such as HIPS and ABS resins is frequently susceptible to solvent attack by compounds, especially the halocarbon compounds used as blowing agents in the preparation of the insulative material contained within for example, an appliance, refrigeration or boiler unit.

The styrenic resin may be attacked by the halocarbon compounds becoming weakened and susceptible to failure and fracture. Material susceptible to attack

in such manner is not desirable in an appliance unit as it can lead to loss in the overall thermal insulating efficiency of the unit and in some instances give rise to structural strength problems and eventual deformation of the unit.

It is known that the composition of the styrenic liner material may be modified to increase its resistance to attack from solvents. Greater resistance to some solvents, especially halogenated solvents, can be obtained by increasing the acrylonitrile content of an ABS copolymer or introducing a greater rubber content, see for example, U.S.Patent 4,144,206. However, such a solution is not always feasible as other physical properties of the material such as impact strength or more critically moldability may change making them unsuitable for the intended application

An alternative to modifying the composition of the styrenic liner material is to protect such material by the use of a barrier film or layer, wherein the insulative material is prevented from contacting the styrenic resin liner wall, see for example U.S. Patent 3,960,631. In this document the use of a coextruded film comprising a low density polyethylene and an ethylene acrylic acid copolymer is disclosed. The film provides a physical barrier preventing adhesion of the insulative polyurethane foam to the styrenic liner. Preventing such adhesion greatly reduces environmental stress crack failure thereby significantly reducing the formation of fracture sites in the styrenic liner. Such fracture sites are the principal points where solvent attack can subsequently take place weakening and eventually allowing the polymer matrix to break.

Similar barrier films serving the purpose to restrict adhesion and minimize stress crack failure are also disclosed in U.S. Patents 4,707,401 and U.S. Patents 4,196,950. In U.S. Patent 4,005,919 use of barrier films in conjunction with ABS liner material is disclosed wherein the barrier film is a rubber-modified high nitrile polymer.

Such barrier films as described above are capable of offering some protection indirectly by minimizing occurrence of stress failure sites of the liner from attack by the halogenated compounds such as, for example, trichlorofluoromethane (Refrigerant-11) frequently employed in the manufacture of polyurethane foam. However, the continued use of certain fully halogenated compounds and especially trichloro-fluoromethane is undesirable in view of the current opinion that their presence in earth's upper atmosphere may be a contributory factor in the recently observed reduction of ozone concentrations.

Recent developments in polyurethane technology has led to the identification of certain hydrogen--containing halogenated carbon compounds as being suitable physical blowing agent replacements for the traditionally employed fully halogenated chlorofluorocarbon compounds. Such recently identified alternative blowing agents are the "soft" chlorofluorocarbon compounds (HCFCs) and include dichlorotrifluoroethane (Refrigerant-123) and dichlorofluoroethane (Refrigerant-141b). These compounds are described as "soft" compounds due to the presence of hydrogen on the carbon backbone and are characterized by having very low or negligible ozone

depletion potentials in contrast to the "hard", fully halogenated compounds.

However, in recent evaluation studies of the "soft" chlorofluorocarbon compounds a severe problem of attack on the styrenic resins used as liner material in the preparation of insulative cabinet walls has been observed. The attack of the liner is observed even in the presence of the barrier film commonly employed to prevent adhesion of the polyurethane foam to the styrenic liner, thus indicating that the material currently used as a physical adhesion barrier does not have sufficient chemical barrier properties to prevent attack by the halogenated blowing agent.

It is also apparent from evaluation studies that the aggressivity of some of the HCFC compounds, particularly Refrigerant-123, towards styrenic resins typically used in the construction of insulative cabinet walls is too great to be conveniently overcome by chemical modification of the composition of the styrenic resin without, for example, a significant loss in the moldability of the resin.

It is therefore desirable to consider the possibility of modifying or using an alternative barrier film. Desirably such an alternative barrier film should allow for efficient preparation of the shaped liner employed in the appliance unit and more importantly minimize or prevent attack of the styrenic resin by blowing agents, especially the newly identified HCFCs, used in manufacturing the polyurethane foam.

It has now been discovered that thermoplastic polyester material can adequately function as such a barrier film in insulative cabinet walls containing polyurethane foam.

In one aspect, this invention is an insulative cabinet wall structure for use in a thermally insulated apparatus which comprises:

a. an outer wall element;
b. an inner wall element comprising a thermoplastic styrenic resin;
c. a foamed-in-situ polyurethane foam prepared in the presence of a halogen-containing physical blowing agent wherein said foam is contiguous to said outer wall element and positioned between said outer wall element and said inner wall element; and
d. a barrier film interposed between said foamed-in-situ polyurethane foam and said inner wall element,

characterized in that the barrier film consists essentially of an amorphous thermoplastic polyester resin which is copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material.

In a second aspect, this invention is a composite material which comprises:

- a thermoplastic styrenic resin sheet; and
- a barrier film in contact with said resin sheet,

characterized in that the barrier film constitutes at least 4 percent of the combined thickness of the resin sheet and barrier film and consists essentially of an amorphous thermoplastic polyester resin which is a copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material.

In yet a third aspect, this invention is a process for preparing an insulative cabinet wall structure comprising foamed-in-situ polyurethane foam by mixing intimately under reaction conditions an organic polyisocyanate with an isocyanate reactive compound in the presence of a halogen-containing physical blowing agent and introducing the foam-forming mixture into a space defined by an inner and outer wall element held in a spaced relationship characterized in that the inner wall is a composite material comprising a thermoplastic styrenic resin sheet and contiguous to said styrenic resin a barrier film that consists essentially of an amorphous thermoplastic polyester resin which is copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material, and wherein the foam-forming mixture is contacted with the said barrier film.

Our investigations have surprisingly shown that the use of such polyester barrier film adequately protects the styrenic resin material employed in the construction of insulative cabinet walls from attack by the halogenated blowing agent present in the polyurethane foam. The protection afforded by the barrier film to the styrenic resin is surprising as normally the polyester material itself is considered susceptible to swelling and dissolution in halogenated

compounds similar to the blowing agents as used in the preparation of polyurethane foams.

The insulative cabinet wall of this invention can be that of, for example, a refrigeration appliance unit or a boiler housing. Such a unit generally comprises an outer cabinet wall (1), which may be, for example, a metal sheet or foil, wood, synthetic resin or the like; an inner liner wall (2); and a body of foamed-in-place insulation (3) therebetween.

The inner liner wall (2) is characterized in that it is a composite material comprising a thermoplastic styrenic resin sheet (4) defining a first surface portion and having applied to said surface a barrier film (5) which consists essentially of a thermoplastic polyester resin. The barrier film is applied to the surface of the styrenic resin sheet that would normally come into contact with the insulation material. Additionally, barrier film may be also applied to other remaining surfaces of the styrenic resin sheet when it is desirable to benefit from other properties offered by the presence of the film such as, for example, surface gloss.

The inner liner wall is molded thermally and/or by pressure into the desired liner configuration and inserted into the outer cabinet wall with the insulation being foamed-in-place. The two walls are held in a spaced relationship whilst the insulating material is introduced by a foam-in-place operation. The method of construction a refrigeration appliance unit in such a manner is disclosed in, for example, U.S. Patents 3,960,631: 4,196,950; 4,505,919 and 4,707,401.

The barrier film is present in a quantity and thickness sufficient to protect the styrenic resin sheet from attack by the physical blowing agent used in preparing the foamed-in-situ insulation. The quantity of barrier film present on the surface of the styrenic resin is conveniently expressed as a percentage thickness of the combined thickness of the styrenic resin sheet and barrier film. Prior to molding, the barrier film constitutes at least 4, preferably at least 5 and more preferably at least 6 percent of said total thickness. Advantageously and for commercial reasons, the amount of barrier film present need not be greater than 20, preferably not greater than 15, and more preferably not greater than 12 percent of the combined resin sheet and barrier film thickness.

The thickness of barrier film present in the different regions of the shaped liner may vary depending on the degree of drawing or extension in the molding procedure. When preparing shaped or molded liners the draw ratio, or degree of extension of resin sheet to shaped liner, may be from 1:2 to 1:10 and preferably from 1:2 to 1:6. When the liner material has been molded to a given shape and configuration, the thickness of the resulting barrier film advantageously is at least 30, preferably at least 40 and more preferably at least 50, microns. Where the barrier film is present in quantities less than this, then sufficient protection to the styrenic resin may not be afforded. The upper limit is defined by the quantity of film present on the non-shaped composite material and the draw ratio employed when shaping the liner. Typically, after shaping of the liner the amount of barrier film present will not exceed

200, preferably not exceed 150, and more preferably not exceed 120 microns.

The barrier film used in this present invention consists essentially of an amorphous copolymer adduct of an aromatic dicarboxylic acid reacted with an active hydrogen-containing compound, such adducts are commonly referred to as polyester polymers or resins.

Copolyester polymers are derived from the reaction of at least two active hydrogen-containing compounds with one acid compound or inversely two acid compounds with one active hydrogen-containing compound. Such copolyester polymer resins are frequently described as "glycol-modified" or "acid-modified" copolyesters, respectively.

The acid compound is an aromatic dicarboxylic acid such as, for example, isophthalic acid, terephthalic acid, chloroterephthalic acid, methylterephthalic acid, or 4,4'-biphenyldicarboxylic acid. Preferred for this present invention are polyester polymers prepared from mono-aromatic dicarboxylic acids including isophthalic acid and especially terephthalic acid, or mixtures thereof.

The active hydrogen-containing adduct generally employed in the preparation of polyester resins is a polyhydroxyl compound. Advantageously, to confer the thermoplastic properties of the resin such a hydroxyl compound contains a molar average of two hydroxyl groups. Exemplary of such hydroxyl compounds are the glycols including, for example, ethylene glycol, tetramethylene glycol, 1,4-cyclohexanedimethanol, dipropylene

glycol, tripropylene glycol and aromatic dihydroxyl compounds such as, for example, bishydroxylphenyl compounds including 2,2-bis(4 hydroxyphenyl)propane. Preferred thermoplastic polyester resins for use in this present invention are those copolymers which are obtained by reaction of glycols, especially ethylene glycol or tetramethylene glycol, and cyclo-hexanedimethanol or mixtures thereof with the preferred aromatic dicarboxylic acids. Available commercially, and especially preferred for use in this present invention are the copolyester polyester resins, especially the glycol-modified polyethylene terephthalate resins such as, for example, KODAR™ PETG-6763 sold by Eastman Chemical Products Inc. Such copolyester resins have a greater tendency to be amorphous polymers, thereby having wider molding and extrusion process latitudes of value when preparing thin films.

Suitable thermoplastic polyester resins can be obtained by conventional preparation procedures such as disclosed in U.S. Patents 2,597,643; 3,740,371; 4,018,738 and 4,034,016 and especially U.S. 4,474,918; U.S. 4,552,948; U.S. 4,565,851 and U.S. 4,578,437.

As already described, the liner wall is a composite material comprising a thermoplastic styrenic resin sheet to which has been applied an above described polyester resin.

For the purpose of this present invention preferred styrenic resins are acrylonitrile-butadiene-styrene (ABS) copolymers and high impact polystyrene (HIPS) polymers. Such resins are preferred because they

offer some inherent environmental stress crack resistance and primarily have good moldability.

The ABS copolymer resins sheets that can be used in this present invention are well known to those skilled in the art, the preparation of such material is disclosed in, for example, U.S. Patents 3,563,845; 3,565,746; and 3,509,237.

Exemplary of the preferred styrenic polymers are those commercially available from The Dow Chemical Company and include the ABS resins such as MAGNUM™ 3404 and MAGNUM™ 3153, MAGNUM™ 9043 and the high impact polystyrene resins such as STYRON™ 469 and STYRON™ 464.

The composite liner wall may be prepared by any of the conventionally known procedures. The barrier film may be laminated to the styrenic resin sheet by utilizing the inherent heat of extrusion of the styrenic resin sheet and a pressure application therebetween such as by suitable pressure rolls. Alternatively, the surface of the barrier film or the styrenic resin may be treated, preferably electrostatically, to promote adhesion of the film to the sheet.

Optionally, the composite material used to prepare the inner wall of the insulative cabinet wall of this present invention may contain a tie layer to promote the adhesion of the barrier film to the styrenic resin. However, in a preferred embodiment of this invention such a tie layer is absent. The patent publication WO 8908556 is illustrative of general tie layer technology where tie layers consisting of olefinic copolymers and dicarboxylic acids are disclosed.

In certain applications where rigidity is desired, a tie layer is necessary. When a thermoplastic polyester film (e.g. PETG) sheet is laminated to an acrylonitrile-butadiene-styrene (ABS) copolymer sheet, the interfacial bond is typically very strong. However, when PETG sheet is laminated to a high impact polystyrene (HIPS) sheet, the interfacial bond is typically weak, resulting in a peelable film. In order to strengthen the interfacial bond between the PETG sheet and the HIPS sheet and make the film non-peelable, a tie layer can be incorporated between the HIPS sheet and the PETG sheet. For scrap recovery, this tie layer material can also serve to compatibilize the PETG from the recycled sheet with the HIPS resin.

Examples of suitable materials for the tie layer includes ABS copolymer containing from 5 to 20 weight percent of acrylonitrile. Also suitable as a tie layer are ethylene vinyl acetate adducts.

Techniques involving coextrusion of the styrenic resin and barrier film may also be employed to prepare the composite liner material.

Techniques of applying a film by lamination to, or coextrusion with a styrenic resin sheet are well known to those skilled in the art of producing composite materials. Such techniques for the application of film are disclosed in, for example U.S. Patents 3,960,631; 4,005,919; 4,707,401 and 4,196,950.

A preferred technique of preparing the composite material employed as liner material in this present invention is by coextrusion.

For the purpose of practicing recovery and recycling of waste composite material, it is advantageous for the barrier layer to be peelable from the styrenic resin sheet, or compatible with the styrenic resin such that a significant loss in impact resistance does not occur when reground composite sheet is blended and reprocessed with the virgin styrenic resin.

The insulation used in the insulative cabinet wall of this invention is a closed-celled foamed material. Such material is light weight and advantageously, has a high thermal resistance and a high compressive strength sufficient to contribute to the benefit of overall structural strength of the wall. As the configuration and geometry of the outer and inner walls may vary, construction of the cabinet wall is facilitated if the insulation can be prepared by a foam-in-place procedure.

In the present invention, the preferred foamed-in-situ insulation is polyurethane foam. Polyurethane foam can be prepared by mixing intimately under reaction conditions an organic polyisocyanate with an isocyanate reactive, active hydrogen-containing compound such as, for example, a polyol in the presence of a blowing agent and introducing the foam-forming mixture into the space between the inner and outer liner walls of the cabinet.

Blowing agents employed in the preparation of the polyurethane are generally organic compounds having an atmospheric boiling point of from -50°C to +100°C. Generally, such compounds selected for this purpose are halogenated organic compounds especially those

containing fluorine and or chlorine as this additionally helps confers good thermal insulation properties to the foam.

In the present invention, the preferred blowing agent for use in preparing the polyurethane foam are those comprising a hydrohalocarbon. Hydrohalocarbons are preferred over perhalogenated carbon compounds due to their generally lower ozone depleting potentials, though the use of perhalogenated carbon compounds such as trichlorofluoromethane and dichlorodifluoromethane in small amounts is not precluded from the present invention.

Suitable hydrohalocarbon compounds include hydrochlorofluorocarbons, hydrofluorocarbons and hydrochlorocarbons, particularly those which are C_{1-3} compounds due to their suitable boiling points. In the following description suitable hydrohalocarbon compounds, for convenience, are identified by their Refrigerant number according to the standard ASHRAE 34-78, (American Society of Heating, Refrigerating and Air Conditioning Engineers).

Exemplary of suitable hydrochlorofluorocarbons are Refrigerant 21 (b.p.8.9°C), Refrigerant-123 (b.p. 27.1°C), Refrigerant-123a (b.p. 28.2C), Refrigerant-124 (b.p. -12°C), Refrigerant-124a (b.p. -10.2°C), Refrigerant-133 (all isomers, b.p. 6.1 to 17°C), Refrigerant-141b (b.p. 32°C), Refrigerant-142 (all isomers b.p. -9.2 to 35.1°C), Refrigerant-131 (b.p. 101°C) and Refrigerant-151a (b.p.16.1°C).

Exemplary of suitable hydrochlorocarbon compounds are 1,1,1-trichloroethane (b.p. 74.1°C), 1,2-dichloroethane (b.p. 93.5°C), 2-chloropentane (b.p. 96.9°C) and 1,3-dichloropentane (b.p. 80.4°C).

Exemplary of suitable hydrofluorocarbon compounds are Refrigerant-134 (b.p. -19.7°C), Refrigerant-134a (b.p. -26.5°C), and Refrigerant-143 (b.p. 5°C).

Exemplary of non-halogen-containing organic compounds suitable as blowing agents halogen include cyclohexane (b.p. 80.7°C), n-hexane (b.p. 69°C) and pentane (b.p. 35°C). Mixtures of two or more such blowing agents are also suitable.

Preferred blowing agents for preparing the insulative polyurethane foam used in the present invention include Refrigerant-123, Refrigerant-141b, Refrigerant-142b, Refrigerant-134 and -134a and 1,1,1-trichloroethane due to availability, ease of handling and due to the desirable physical properties of polyurethane foams prepared therewith.

The blowing agent is employed in quantities sufficient to provide for a foam advantageously having an overall bulk density of from 10 to 200, preferably 15 to 100, and more preferably 18 to 60 kg/m^3.

Active hydrogen-containing compounds which are useful in the preparation of the polyurethane foam include those materials having two or more groups which contain an active hydrogen atoms that can react with an isocyanate, such as are described in U.S. Patent

4,394,491. Collectively, such compounds are referred to as polyahls. Preferred among such polyahl compounds are those having at least two hydroxyl, primary or secondary amine, carboxylic acid, or thiol groups per molecule. Polyols, i.e., compounds having at least two hydroxyl groups per molecule, are especially preferred due to their desirable reactivity with polyisocyanates.

Suitable isocyanate reactive materials for preparing rigid polyurethanes include those having an equivalent weight of from 50 to 700, preferably from 70 to 300 and more preferably from 70 to 150. Such isocyanate-reactive materials also advantageously have a functionality of at least 2, preferably from 3, and up to 16, preferably up to 8, active hydrogen atoms per molecule.

Representative of isocyanate-reactive materials include polyether polyols, polyester polyols, polyhydroxyl-terminated acetal resins, hydroxyl-terminated amines and polyamines. Examples of these and other suitable isocyanate-reactive materials are described more fully in U.S. Patent 4,394,491, particularly in columns 3-5 thereof. Most preferred for preparing rigid foams, on the basis of performance, availability and cost, is a polyether polyol prepared by adding an alkylene oxide to an initiator having from 2 to 8, preferably from 3 to 8 active hydrogen atoms. Exemplary of such polyether polyols include those commercially available under the trademark "VORANOL" such as VORANOL 202, VORANOL 360, VORANOL 370, VORANOL 446, VORANOL 490, VORANOL 575, VORANOL 800 all sold by The Dow Chemical Company, and PLURACOL™ 824, sold by BASF Wyandotte.

Other most preferred polyols include alkylene oxide derivatives of Mannich condensates, as taught, for example, in U.S. Patents 3,297,597; 4,137,265 and 4,383,102; and aminoalkylpiperazine-initiated polyether polyols as described in U.S. Patents 4,704,410 and 4,704,411.

Polyisocyanates useful in making polyurethanes include aromatic, aliphatic and cycloaliphatic polyisocyanates and combinations thereof. Representative of these types are diisocyanates such as m- or p-phenylene diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate (and isomers), naphthylene-1,5-diisocyanate, 1-methylphenyl-2,4-phenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 4,4'-biphenylenediisocyanate, 3,3'-dimethoxy-4,4'-biphenylene-diisocyanate and 3,3'-dimethyldiphenylpropane-4,4'-diisocyanate; triisocyanates such as toluene-2,4,6-triisocyanate and polyisocyanates such as 4,4'-dimethyldiphenylmethane-2,2',5',5'-tetraisocyanate and the diverse polymethylenepolyphenylpolyisocyanates.

A crude polyisocyanate may also be used in the practice of this invention, such as the crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamines or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude diphenylmethanediamine. The preferred undistilled or crude polyisocyanates are disclosed in U.S. Patent 3,215,652.

Especially preferred are methylene-bridged polyphenylpolyisocyanates, due to their ability to crosslink the polyurethane. The isocyanate index (ratio of equivalents of isocyanate to equivalents of active hydrogen-containing groups) is advantageously from 0.9 to 5.0, preferably from 0.9 to 3.0, more preferably from 1.0 to 1.5.

In addition to the foregoing critical components, it is often desirable to employ certain other ingredients in preparing cellular polyurethane. Among these additional ingredients are water, catalyst, surfactant, flame retardant, preservative, colorant, antioxidants, reinforcing agent, and filler.

Water is often employed in the role as a blowing agent precursor and processing aid. Water can react with isocyanate leading to the generation of carbon dioxide gas which then functions as a blowing agent in the foam-forming reaction. When present, the water is preferably used in amounts not exceeding 7, preferably not exceeding 6, more preferably not exceeding 5 parts by weight per 100 parts by total weight active hydrogen-containing compound(s) present. Beneficial effects are seen when at least 0.5 and preferably at least 1 part of water per 100 parts total weight active hydrogen-containing compound(s), is present. Using amounts of water which exceeds these ranges is possible but the resulting foam may have undesirable physical properties such as poor dimensional stability and poor thermal insulation.

In making polyurethane foam, it is generally highly preferred to employ a minor amount of a

surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants advantageously comprise a liquid or solid organosilicone surfactant. Other, less preferred surfactants include polyethylene glycol ethers of long chain alcohols, tertiary amine or alkanolamine salts of long chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the formation of large, uneven cells. Typically, from 0.2 to 5 parts of the surfactant per 100 parts by total weight active hydrogen-containing compound(s) present is generally sufficient for this purpose.

One or more catalysts for the reaction of the active hydrogen-containing compound(s) with the polyisocyanate are advantageously used. Any suitable urethane catalyst may be used, including tertiary amine compounds and organometallic compounds. Exemplary tertiary amine compounds include triethylenediamine, N-methyl morpholine, pentamethyldiethylenetriamine, tetramethylethylenediamine, 1-methyl-4-dimethylamino-ethylpiperazine, 3-methoxy-N-diethylpropylamine, N-ethyl morpholine, diethylethanolamine, N-coco morpholine, N,N-dimethyl-N',N'-dimethyl isopropylpropylenediamine, N,N-diethyl-3-diethylaminopropylamine, and dimethyl-benzylamine. Exemplary organometallic catalysts include organomercury, organolead, organoferric and organotin catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids such as dibutyltin di-2-ethyl hexanoate, as well as other organometallic compounds such as are disclosed in U.S.

Patent 2,846,408. A catalyst for the trimerization of polyisocyanates, such as an alkali metal alkoxide, may also optionally be employed herein. Such catalysts are used in an amount which measurably increases the rate of reaction of the polyisocyanate. Typical amounts are from 0.001 to 1 parts of catalyst per 100 parts by total weight of active hydrogen-containing compound(s) present.

In making a polyurethane foam, the active hydrogen-containing compound(s), polyisocyanate and other components are contacted, thoroughly mixed and permitted to react and to expand and cure into a cellular polymer. The particular mixing apparatus is not critical, and various types of mixing head and spray apparatus are conveniently used. It is often convenient, but not necessary, to pre-blend certain of the raw materials prior to reacting the polyisocyanate and active hydrogen-containing components. For example, it is often useful to blend the active hydrogen-containing compound(s), blowing agent, surfactants, catalysts and other components except for polyisocyanates, and then contact this mixture with the polyisocyanate. Alternatively, all components can be introduced individually to the mixing zone where the polyisocyanate and polyol(s) are contacted. It is also possible to pre-react all or a portion of the active hydrogen-containing compound(s) with the polyisocyanate to form a prepolymer, although such is not preferred.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

Example 1

A shaped inner liner suitable for preparing a refrigeration appliance unit is prepared by thermal molding of a composite material. The composite material is characterized in that a high impact polystyrene resin, STYRON™ 469, has applied to it a polyester film, KODAR™-PETG-6373. The amount of polyester film present in the composite material prior to thermal molding, expressed as a percent thickness based on the total thickness of the composite material is given in Table I. The thermal molding, or draw rates of the composite material to the shaped inner liner is 1:5.

The shaped inner liner is placed in a suitable mold and polyurethane foam poured-in-place against the polyester film of the shaped liner. On curing the complete unit comprising molded polyurethane foam having an average molded density of 30 Kg/m^3 and an inner liner with barrier film is subjected to thermocycling.

Thermocycling serves the purpose of accelerating the observation of solvent attack, if any on the inner line.

The thermocycle study comprises holding the foam and inner liner material at -20°C for 8 hours, proceeding by a period of 8 hours at +20°C and then a second period of 8 hours at -20°C and so forth for a given period of time. It is found that conducting thermocycle studies for periods up to 10 weeks is

sufficient to provide for a realistic estimation of performance of the unit.

When the thermocycling is complete, the degree of attack upon the styrenic resin by the blowing agent used in preparing the polyurethane foam can be assessed through counting the number of "surface" blisters observable on the opposite face of the inner liner to that in contact with the barrier film and polyurethane foam.

Table I indicates the results of the thermocycling study for a different thickness of PETG barrier film (indicated percent thickness is for composite material prior to drawing and shaping to give the inner liner) against different polyurethane foam.

Foam A is an appliance-designed rigid polyurethane foam prepared from the commercially available polyol formulation VORANOL™ RST 461 sold by The Dow Chemical Company reacted with a crude polymeric polyisocyanate average functionality 2.7. The physical blowing agent is dichlorotrifluoroethane (R-123) used in an amount to provide a foam having a free rise density of 22 Kg/M3.

Foam B is polyurethane foam prepared from similar components as Foam A only in this instance the polyol formulation VORANOL™ RST 461 has been modified by addition of water allowing for a 50 percent weight reduction in the amount of Refrigerant-123 required to provide foam of free-rise density about 22 Kg/M3. An additional amount of isocyanate is used to compensate for the greater amount of water present.

The shape of the molded inner liner is such to provide regions particularly susceptible to attack. These regions are identified as the edge or door frame; the lip or glider support/runner for a shelf; and the partition finger separating the colder freezer box of the refrigeration appliance unit from the slightly warmer main storage area.

TABLE I

Sample No.	Foam type	PETG thickness %	Thermocycling (weeks)	Blister Count/Region		
				Edge	Glider	Partition
1	A	5	0	1(i)	0	0
2	A	5	4	3	0	0
3	A	5	10	2	10	10
4	B	5	4	2	2	1
5	B	10	4	0	0	0
A*	A	0	4	>100	20	>100
B*(ii)	A	0	4	>100	14	>100

* not an example of this invention

Footnotes:

i Blister count after storage of freshly prepared foam 24 hours at room temperature.

ii In comparative example B, the high impact polystyrene resin STYRON™ 469 is replaced by the ABS resin, MAGNUM™ 3403.

The data presented in Table I indicates the significant reduction in the number of blisters to be observed in the styrenic resin when protected by the polyester barrier film.

As an alternative to polyester film and representative of the art such as U.S. Pat 3,960,631, a coextruded film comprising a low density polyethylene, ethylene vinyl alcohol, and polyvinylidene chloride polymers sold under the trademark SARANEX™ by The Dow Chemical Company is applied to the high impact polystyrene resin, STYRON™ 469 and contacted with Foam A. The thickness of the SARANEX™ film on the surface of the polystyrene resin is about 50 microns and the blister counts observed after 4 weeks thermocycling for the above-identified regions, respectively, are >100; 18; and >100.

Claims :

1. An insulative cabinet wall structure for use in a thermally insulated apparatus which comprises:

a. an outer wall element;
b. an inner wall element comprising a thermoplastic styrenic resin;
c. a foamed-in-situ polyurethane foam prepared in the presence of a physical blowing agent wherein said foam is contiguous to said outer wall element and positioned between said outer wall element and said inner wall element; and
d. a barrier film interposed between said foamed-in-situ polyurethane foam and said inner wall element,

characterized in that the barrier film consists essentially of an amorphous thermoplastic polyester resin which is copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material.

2. A structure as claimed in Claim 1 wherein the physical blowing agent is a hydrochlorocarbon or a hydrochlorofluorocarbon comprising Refrigerant-123, Refrigerant-141b Refrigerant-142b, or a hydrofluorocarbon comprising Refrigerant-134a.

3. A structure as claimed in Claim 1 wherein the the barrier film has a thickness of at least 30 microns.

4. A structure as claimed in Claim 3 wherein the barrier film is a glycol-modified polyethyleneterephthalate resin.

5. A structure as claimed in Claim 1 wherein the thermoplastic styrenic resin is a high impact polystyrene resin or an acrylonitrile-butadiene-styrene copolymer resin.

6. A structure as claimed in Claim 1 further having a tie layer between the thermoplastic styrenic resin and the barrier film wherein the tie layer comprises an acrylonitrile-butadiene-styrene copolymer resin or an ethylene vinyl acetate adduct.

7. A composite material which comprises:

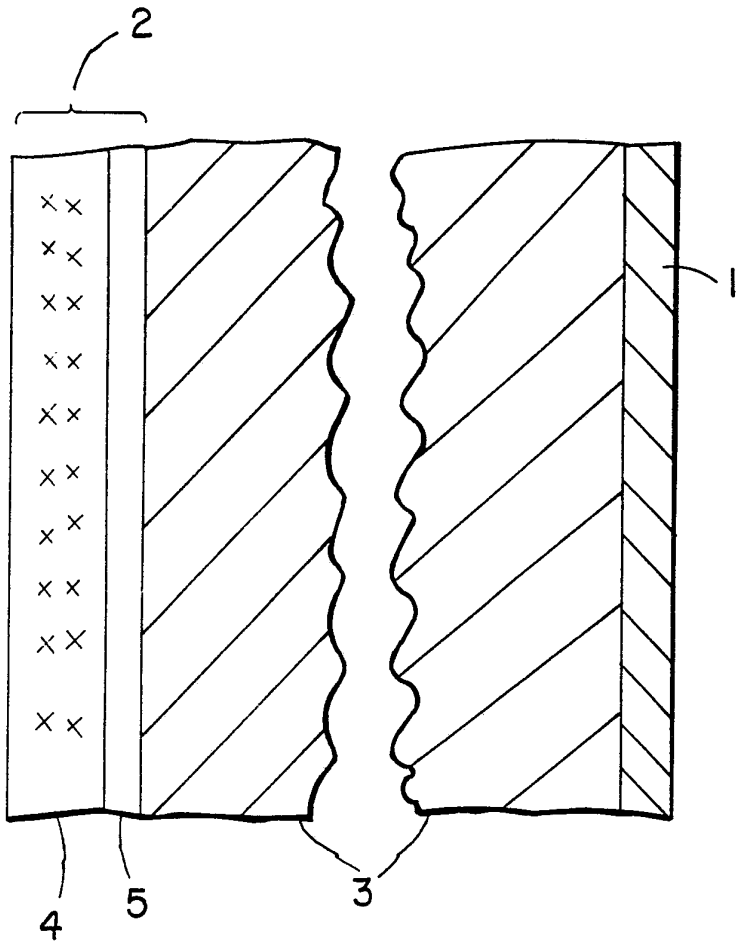
- a thermoplastic styrenic resin sheet; and
- a barrier film in contact with said resin sheet,

characterized in that the barrier film constitutes at least 4 percent of the combined thickness of the resin sheet and barrier film and consists essentially of an

amorphous thermoplastic polyester resin which is a copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material.

8. A process for preparing an insulative cabinet wall structure comprising foamed-in-situ polyurethane foam by mixing intimately under reaction conditions an organic polyisocyanate with an isocyanate reactive compound in the presence of a physical blowing agent and introducing the foam-forming mixture into a space defined by an inner and outer wall element held in a spaced relationship characterized in that the inner wall is a composite material comprising a thermoplastic styrenic resin sheet and contiguous to said styrenic resin a barrier film that consists essentially of an amorphous thermoplastic polyester resin which is copolymer adduct of an aromatic dicarboxylic acid and an active hydrogen-containing material, and wherein the foam-forming mixture is contacted with the said barrier film.

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/01507

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

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

Int.Cl. 5 B32B27/36 ; F25D23/06 .

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B32B ; F25D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US,A,4196950 (CHURCHILL ET AL.) 08 April 1980 see column 1, lines 10 - 63 see column 3, lines 44 - 52 see column 5, lines 28 - 29; figures 1, 2 (cited in the application)	1-5, 7, 8
X	DE,B,1242250 (GENERAL MOTORS CORPORATION) 15 June 1967 see column 1, line 45 - column 2, line 38	1, 2, 5
A	see column 5, line 4 - column 6, line 5; claim 1 ; lists A, E	3, 4, 7, 8
A	US,A,4048274 (HOGE ET AL.) 13 September 1977 see column 1, lines 45 - 62; claims 1, 2; figure V	1, 2, 5
A	US,A,4707401 (BENFORD) 17 November 1987 see column 2, line 44 - column 3, line 17; claims 1, 3, 8, 9; figure 3	1, 5, 6

° Special categories of cited documents :[10]

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

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"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)

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

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

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

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12 JULY 1991	22. 07. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DERZ T.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9101507
SA 46074

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 12/07/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4196950	08-04-80	None	
DE-B-1242250		None	
US-A-4048274	13-09-77	None	
US-A-4707401	17-11-87	None	