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(54) Title: FOAMED ARTICLES WITH UNSATURATED POLYESTER RESIN COATING AND PROCESS FOR THEIR MANUFACTURE

(57) Abstract

An article comprising a core or layer of a foamed material and at least one layer of an unsaturated polyester resin characterized in that the layer polyester is obtained from a polyester resin composition comprising an unsaturated polyester and a monomeric solvent reactive with said polyester, wherein the monomeric solvent comprises styrene and hydroxyalkyl acrylate or methacrylate wherein alkyl is C^{1}–?4? and wherein the amounts of styrene, hydroxyalkyl (meth)acrylate and unsaturated polyester in said composition comply with the following equation (I) in parts by weight: styrene (parts by weight)/polyester (parts by weight) + hydroxyalkyl(meth)acrylate (parts by weight) = 0.12 to 0.18. A process for preparing such article is also disclosed.

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FOAMED ARTICLES WITH UNSATURATED POLYESTER RESIN COATING AND PROCESS FOR THEIR MANUFACTURE

The present invention relates to an unsaturated polyester resin composition, to its use for applications with foamed plastics materials, and to articles comprising a core or layer of a foamed plastic material and a layer or coating obtained from said resin composition.

More particularly, the invention relates to a polyester resin composition comprising an unsaturated polyester and a monomeric solvent which is cross-reactive with said polyester.

Conventional unsaturated polyester resin compositions include relatively high amounts of ethylenically unsaturated monomeric solvents, particularly styrene-based monomeric solvents. The relatively high amount of styrene makes such compositions unsuitable for coating polystyrene foamed plastics materials or generally foamed polymers including styrene as a co-monomer, since the styrene-based solvent attacks and dissolves the polymer containing styrene.

Polystyrene foam is a widely used rigid plastic material; in many cases it is used as an insulation material, in other cases it is used for its structural properties combined with its chemical and water resistance. In many applications, the foam core needs to be covered by a protective layer; reasons therefore might be the need for high impact resistance, fire regulations, improving the long-term weathering properties and/or aesthetic reasons. This is the case, for example, in insulated trailers, insulated containers and buoyancy applications.

There are applications where foamed materials such as polyurethane are coated with unsaturated polyester resin or are bonded using unsaturated polyester to a sheet. In this type of application, there are basically two problems, one relating to the polyurethane (i) and one relating to the unsaturated polyester resin (ii).

(i) Polyurethane is not always the most appropriate material for many of these applications. In applications such as refrigerated transport, the insulation is subject to high moisture loads. However, polyurethane is known to be highly moisture sensitive.

In the past, tests have been carried out on insulated truck bodies or trailers which had been in use for several years. These tests showed that the polyurethane foam cores were soaked with water while the extruded polystyrene cores still were practically dry.

It is obvious that the insulation value of the wet polyurethane cores was reduced substantially and, thus, did not meet the requirements anymore.

(ii) The unsaturated polyester resins typically employed have a high styrene monomer content (35 to 45 weight percent); this causes high styrene monomer contents in the manufacturing halls creating an unhealthy working environment. The high styrene monomer contents in the working environment cannot be reduced unless manufacturing process is changed or unless the manufacturing units are restructured including the necessary evacuation units. The use of such evacuation units is not economically feasible in most cases.

There are currently applications where extruded polystyrene foam is used as a core for articles wherein the bonding is carried out by using a polyurethane-based adhesive. However, using a polyester resin as an adhesive instead of polyurethane-based adhesive results in several advantages, one being the fact that polyester resin bonds are less rigid bonds which results in a good mechanical performance vibrations and dynamic loads. Especially in insulated transport applications this improves the long-term performance of the articles.

Another advantage of using polyurethane polyester resin as adhesive is being that polyurethane polyester adhesives cannot be employed for reparations, since it would not provide joint-less repairs. Polyester resin polyurethane adhesives, however, would not readily enable such joint-less technique.

Furthermore, previous attempts to provide articles including a core of polystyrene foam and a structural surface coating made from conventional unsaturated polyester resin compositions or bonded articles comprising a layer of polystyrene foam and an unsaturated polyester resin sheet reinforced with glass fibers (GRP) bonded to said layer by means of an unsaturated polyester-based glue were unsuccessful, due to the attack of the polystyrene surface by the relatively high amounts of styrene monomer.

DE-A-1236187 describes protecting coatings for foamed polystyrene articles which are obtained by coating the polystyrene foam with a composition containing 25 to 75 percent by weight (weight percent) of a polymerizable ethylenically unsaturated polyester and 25 to 75 weight percent of a polymerizable ethylenically unsaturated monomer of which 50 to 100 weight percent is an allyl-ether of N-methylolurea or a derivative thereof.

JP 01319547-A describes molded articles of polystyrene foam onto which an unsaturated polyester resin is applied; the process comprises coating and/or laminating together with a reinforcing material on a polystyrene foam a resin composition containing 100 parts by weight of unsaturated polyester resin and 5 to 200 parts by weight of a compound such as dicyclopentenyl oxy ethyl acrylate or dicyclopentenyl oxy ethyl methacrylate.

JP 63260936-A describes a composite material comprising a core foam material, such as polystyrene foam and a radical polymerized composition impregnated in the core foam; the composition comprises an unsaturated polyester resin, a cross-linking agent, a curing promoting agent and a curing agent; the cross-linking agent is a monofunctional acryl monomer or a multifunctional acryl monomer.

JP49-021428-A describes a coating composition for thermoplastic moldings, particularly of polystyrene foam comprising an unsaturated polyester and a monoester from (mesh) acrylic acid and a C_2-C_8 polyol or a C_4-C_{18} ether linkage-containing polyol, or the reaction product of a C_2-C_{18} alkylene oxide and (mesh) acrylic acid, such as particularly 2-hydroxyethyl acrylate. Whereas styrene monomer can be used as a co-solvent for the unsaturated polyester together with the above-mentioned compounds, as shown by the working examples, even relatively low amounts of styrene in combination with 2-hydroxyethyl acrylate caused at least partial erosion of the polystyrene foam.

According to the examples, a partial erosion of the polystyrene foam takes place with the use of a composition comprising about 60 weight percent of polyester resin and about 32 weight percent of hydroxyethyl acrylate (HEA) and as little as about 8 weight percent of styrene monomer.

It is reported that when HEA is used as the only monomeric solvent, the surface of polystyrene foam does not appear to be substantially eroded; it has been found however that the use of HEA as the only monomeric solvent causes substantial increase of the curing time necessary to achieve the desired mechanical properties of the unsaturated polyester coating, and a post-curing treatment appears to be required which is undesirable. An increase of the curing temperature in order to reduce the curing time is not advisable, since higher curing temperatures such as 70°C to 80°C would be detrimental to foamed plastics materials, in particular polystyrene foams.

Therefore, it would be highly desirable to provide an improved polyester resin composition which contains lower amounts of monomeric styrene without impairing the mechanical properties thereof and which does not dissolve polystyrene foam or styrene-based copolymer foams. It would also be desirable to have coated and/or bonded articles including a foam core or layer wherein the foam does not undergo surface degradation or chemical attack when in contact with a polyester resin.

Thus, a first object of the present invention is to provide an improved polyester resin composition which does not dissolve polystyrene foam or styrene-based copolymer foams or in general polymers obtained from the polymerization of ethylenically unsaturated monomers.

Another object of the invention is to provide a polyester resin composition having a reduced amount of styrene monomer, without impairing the mechanical properties of the cured polyester resin.

Still another object of the invention is to provide coated and/or bonded articles including a core or layer of a styrene polymer or copolymer foam or in general polymers obtained from the polymerization of ethylenically unsaturated monomers and a coating of an unsaturated polyester resin, wherein the foam does not undergo surface degradation or chemical attack and/or delamination as a result of a contact with the polyester resin.

A further object of the invention is to provide a process for coating foams of styrene polymers or copolymers or in general polymers obtained from the polymerization of ethylenically unsaturated monomers with a layer of polyester resin having structural properties or for bonding a polyester sheets, such as GPR sheets or plywood sheets, to said polymers by means of a polyester-based adhesive.

Still another object is to provide a polyester resin composition which allows application on foamed materials without causing such high unacceptable styrene-monomer emissions in the working environment.

The present invention offers new perspectives to all of the above-described problems.

Being able to use polystyrene-based foam for making articles by bonding sheets, by way of an unsaturated polyester resin composition results in better workability as there is no dust creation during cutting operations of polystyrene-based foams. Further, polystyrene foam is mechanically recyclable while polyurethane is not; this improves the end product and the manufacturing process from the environmental point of view.

Secondly, the present invention offers even more opportunities to improve the properties of the manufactured articles, because the mechanical properties of extruded polystyrene are superior than those of polyurethane of equal density. This means that articles that have a constructive aspect/role have either an improved performance, or can be optimized.

Another aspect of the present invention is that extruded polystyrene foam hardly takes up any water moisture, is to a very high degree resistant to moisture and has a very high resistance to a broad range of chemicals. This results in a superior long term performance of the articles made thereof (e.g. a refrigerated truck body, an insulated container, a pontoon).

According to the invention, it has been found that such objects are achieved when the polyester resin composition comprises, as the monomeric solvent, styrene and an hydroxy alkyl acrylate or methacrylate in a defined ratio with respect to the amount of unsaturated polyester.

Accordingly, the invention provides an unsaturated polyester resin composition comprising an unsaturated polyester, and a monomeric solvent reactive with said polyester, characterized in that the monomeric solvent comprises styrene and a hydroxy alkyl methacrylate or acrylate, wherein alkyl is C_1 to C_4 and wherein the amount of styrene, hydroxyalkyl (meth)-acrylate and unsaturated polyester in said composition comply with the following equation in parts by weight:

(I)

$$\frac{\textit{styrene (parts by weight)}}{\textit{Polyester (parts by weight)+ hydroxy alkyl (meth)acrylate (parts by weight)}} = 0.12 \text{ to } 0.18$$

It has been found that values of the above-mentioned ratio lower than 0.12 do not provide a suitable chemical bonding of the polyester resin onto the styrene polymer or copolymer foam, whereas values higher than 0.18 cause an at least partial surface degradation and/or dissolution of the foam; preferred values for the above ratio are between 0.16 to 0.18.

The teaching of the invention provides for polyester resin compositions varying in a wide range, preferably from 65 weight percent to 80 weight percent and more preferably between 65 weight percent to 75 weight percent .based upon the total amount of unsaturated polyester and monomeric solvent. Correspondingly, the amount of monomeric solvent in the composition is preferably from 35 weight percent to 20 weight percent and more preferably from 35 weight percent to 25 weight percent. The amount of styrene monomer in the monomeric solvent is preferably from 10 to 16 weight percent based upon the amount of polyester and monomeric solvent. According to the teaching of the invention, if the amount of styrene in said polyester resin composition, is increased, for example by 1 weight percent. correspondingly, the amount of hydroxy alkyl (mesh) acrylate is to be increased in the amount of 5.55 weight percent to 8.33 weight percent. in order to provide a polyester resin composition which does not detrimentally affect the surface of the styrene polymer or copolymer foam or in general polymers obtained from the polymerization of ethylenically unsaturated monomers.

The unsaturated polyester in the composition is preferably the product of esterification of a glycol, an unsaturated dicarboxylic acid or anhydride and optionally a saturated dicarboxylic acid or anhydride, preferably in the presence of a chain termination agent which is preferably an allyl ether of a C_3-C_{10} polyol, most preferably a diallyl ether of C_3-C_{10} aliphatic or cycloaliphatic polyol such as glycerol, trimethylol propane or ethane.

Suitable glycols comprise ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 2,2-dimethylpropane diol, 1,3-butane diol, 1,2-butylene glycol, and 2,3-butylene glycol.

The unsaturated acid or anhydride is preferably maleic or fumaric acid or anhydride; however also itaconic acid and chloromaleic acid or anhydride may conveniently be used. Mixtures of different unsaturates acid or anhydrides may also be used.

The saturated acid or anhydride, when used, is preferably selected from phthalic acid, tetrahydrophthalic acid, cyclohexane dicarboxylic acid, adipic acid, sebacic acid, succinic acid, azelaic acid, isophthalic acid, terephthalic acid and the corresponding anhydrides, HET acid and chlorendic anhydride and mixtures thereof.

Usually, a slight molar excess of glycol is used with respect to the overall amount of the acid, such as preferably a 5 percent to 20 percent molar excess.

The chain termination agent, is preferably trimethylol propane diallyl ether.

The unsaturated polyester of the present invention typically has an acid unsaturation index, expressed as the ratio between the number of equivalents of unsaturated acid in the polyester and the total number of equivalents of acid in said polyester, higher than 0.50, more preferably not lower than 0.70, and most preferably not lower than 0.85.

The average numerical molecular weight (Mn) of the polyester is preferably from 800 to 1400; and the average weight molecular weight (Mw) is preferably from 1800 to 2300.

The polyester resin composition preferably has an overall percentage of unsaturations, expressed as the ratio between the total number of unsaturated moles in the composition (polymer plus solvent) and the total number of moles from which the polyester resin composition is obtained, from 0.55 to 0.75.

The polyester resin composition preferably has an acid number of from 30 to 50 mg KOH/mL, and an hydroxyl number of from 50 to 105 me KOH/mL.

The polyester resin composition of the present invention may further comprise additives which are usually present in conventional unsaturated polyester resin compositions, such as inhibitors, storage stabilizers, curing promoters and inorganic fillers. Preferred inhibitors are hydroquinone and toluene hydroquinone. Preferred promoters are the so-called metal soaps such as cobalt, copper or vanadium octoate, naphthenate and acetonate.

The resin composition of the present invention is cured by means of the already known unsaturated polyester resin curing methods, preferably by means of peroxide initiators particularly such as, methyl ethyl ketone (MEK) peroxide and methyl isobutyl ketone peroxide. The curing system consisted of 0.2 weight percent cobalt octoate (6 weight percent Co) and 2 weight percent of a MEK-MEK peroxide solution (50 percent by weight for each component in the solution), per 100 grams of the polyester resin composition. The resin composition preferably has a curing time of from 8 to 15 minutes, a gel time of from 10 to 90 minutes and an exothermic peak of 150°C to 170°C.

The preferred use of the resin composition of the present invention is for coating the surface of foamed articles. The foamed materials on which the resin composition can be applied include polystyrene foam (extruded and expanded), syndiotactic polystyrene foam, styrene copolymer foams such as ABS, polyurethane foam, polyethylene terephthalate (PET) foam, polypropylene foam, polyethylene foam, polyphenyl ether foam and polyvinyl chloride (PVC) foam. The application is carried out by means of conventional methods, such as brushing, rolling, spraying or dipping and other existing known methods. The coating layer may have a thickness higher than 1 mm, preferably in the range of from 2 to 5 mm. After application the coating layer is cured according to conventional methods. The curing temperature is typically within the range of 15°C (room temperature) to 50°C.

Additionally, the polyester resin composition according to the invention may be used as an adhesive in order to bond sheets of conventional unsaturated polyester resin to the surface of said foamed articles. The temperature of the press plates between which the resin composition is cured may vary between 30°C and 60°C. The preferred press temperature is between 30°C and 40°C.

Furthermore, the polyester resin composition of the present invention can be used as a primer coating of foamed articles which can then be either coated or bonded with any conventional unsaturated polyester resin.

Accordingly, the invention comprises within its scope articles comprising a core or layer made of a foamed material and at least one layer (either as a coating or as an adhesive) obtained from the polyester resin composition of the present invention.

Also comprised within the scope of the invention are articles, as defined above, having an additional primer coating layer consisting of the polyester resin composition of the present invention which is applied between the surface of said foamed core and any conventional unsaturated polyester resin (either used as a coating or an adhesive).

The resin composition may also be used to manufacture composite materials wherein the polyester resin composition according to the invention is reinforced by fabric, mats and/or fibers.

Preferred applications of the polyester resin composition of the present invention are for manufacturing sandwich panels having a core of polystyrene foam, such as panels for thermally insulated trailers or containers. The polyester resin composition of the present invention is also suitable for manufacturing coated parts for marine applications, such as for pontoons.

<u>Example 1</u> Preparation of Polyester Resin Composition

12.55 parts by weight of propylene glycol, 24.25 parts by weight dipropylene glycol, 7.04 parts by weight phthalic anhydride, 8.9 parts by weight trimethylol propane diallyl ether, 31.99 parts by weight fumaric acid, 0.01 parts by weight hydroquinone, were charged into a reactor equipped with a mixer, a partial condenser and a shielding gas system. The esterification reaction was carried out under nitrogen gas flow by the conventional fusion method at a temperature of from 175°C to 180°C by periodically checking the viscosity in the reactor, and until the acid value of the polyester resin reached value from 36 to 47 mg KOH/mL.

The reaction product was then cooled to 150°C and discharged into a dilutor vessel containing 15 parts by weight styrene and 12 parts by weight hydroxyethyl methacrylate and 0.001 part by weight copper naphthenate (6 percent), while keeping the internal temperature in the dilutor vessel no higher than 80°C.

The obtained polyester resin composition had a polyester polymer content of about 74 weight percent. The polyester had an acid unsaturation index of 85 percent.

Tests were carried out in order to confirm that the polyester resin composition of the present invention could be applied onto a polystyrene foam and to check the compatibility, that is, chemical attack (Example 2) and the tensile bond strength (Example 3) of polystyrene sandwich panels.

In all the tests, the polyester resin composition was cured with a curing system consisting of 0.2 weight percent cobalt octoate (6% wt Co) and 2 weight percent of a MEK-MEK peroxide solution (50 percent by weight for each component in the solution), per 100 grams of polyester resin composition.

<u>Example 2</u> Compatibility

In a first series of laboratory tests, the compatibility of the polyester resin of this invention with the polystyrene foam was evaluated as follows: a first set of samples (Combination 2A) was prepared wherein the polyester resin composition of Example 1, to which the curing system had been added, was poured on the surface of a STYROFOAM* RTM polystyrene board (Trademark of The Dow Chemical Company) and distributed uniformly by means of a brush, in order to obtain a layer having a thickness of 24 mm. After curing of the polyester resin at ambient temperature (about 25°C), a hardened layer of polyester bonded to the polystyrene surface was obtained.

According to the same procedure, another two sets of samples were made, one combining the STYROFOAM* RTM polystyrene with the commercially available polyester resins (EXTER 102S available from COIM spa) (Combination 2B) and one combining the polyester resin of the invention (Example 1) with polyurethane having a density of 40 kg/m (Combination 2C).

Visual comparison between the 3 combinations showed that on the set of samples of the Combinations 2A and 2C there was no chemical attack or dissolution and the surface coating was smooth.

In addition, the coating layer was removed from the foam of each of the above-described three combinations. Visual inspection and comparison showed again that the surface had not been chemically attacked in the Combinations 2A and 2C, and had not degraded, which was the case in the Combination 2B.

Example 3 Bonding Properties

Another series of tests was carried out in order to measure the bonding properties and to prove the technical feasibility of the coating process. These tests were carried out by bonding a 2 mm GRP sheet (manufactured by General Plast, Italy) to a foam core by using the unsaturated polyester resin of the present invention. Approximately 1 kg of resin was used per square meter resulting in a 1 mm thick coating layer.

The tensile bonding strength and the tensile modulus were measured according to ASTM D-1623. The shear bonding strength and the shear modulus were measured according to ASTM C-273.

A set of samples was prepared for each foam type, that is,. polystyrene foam and polyurethane foam. The polystyrene foam used was an extruded polystyrene foam STYROFOAM* RTM, (*Trademark of The Dow Chemical Company), having a density of 40 kg/m3 (set 3A) and was coated with the unsaturated polyester resin of Example 1. For comparison purposes, a polyurethane foam was coated with a commercially available unsaturated polyester resin (EXTER 102S from COIN spa) (set 3B). The polyurethane used was a 40 kg/m density polyurethane commercially available.

In all samples, the foam cores were 50 mm thick. Curing was done under a pressure of 0.5 kg/cm^2 and at a temperature of 50°C.

Average tensile bonding strength values measured on samples according to the present invention (set 3A) were: 424 kPa; and the shear bonding strength tests gave shear strengths of 354 kPa.

The measurements on the polyurethane foam samples (set 3B) gave: tensile bonding strength of 337 kPa and the shear strength of 210 kPa.

Example 4 Bonding vs. Coating

Further mechanical tests were carried out to confirm the above tests and to compare the bonding technique to the coating technique.

For this purpose, one set of samples comprising extruded polystyrene foam STYROFOAM* RTM were bonded to a 2 mm GRP sheet (commercially available from General Plastic, Italy) using the polyester resin of the invention (set 4A) and another set of samples comprising said polystyrene foam were coated with a 3 mm thick layer of the polyester resin of the present invention (set 4B). The bonded samples were cured under pressure (0.5 kg/cm^2) and at a temperature of 50°C. The coated samples were cured at room temperature under pressure (0.5 kg/cm^2).

For the bonded samples (set 4A), the average tensile bonding strength was 650 kPa, and the average shear strength was 493 kPa and the average shear modulus was 5,836 kPa.

For the coated samples (set 4B), the average tensile bonding strength was 600 kPa (standard deviation of 110 kPa), the average shear strength was 513 kPa and the average shear modulus was 6,219 kPa.

The tests also showed that the invention applied on extruded polystyrene foam having a density of 40 kg/m^3 provided results typically 30 to 50 percent better than the results obtained by the existing techniques applied on polyurethane foam also having a density of 40 kg/m^3.

CLAIMS:

1. An article comprising a core or layer of a foamed material and at least one layer of an unsaturated polyester resin characterized in that the layer of unsaturated polyester is obtained from a polyester resin composition comprising an unsaturated polyester and a monomeric solvent reactive with said polyester, wherein the monomeric solvent comprises styrene and hydroxy alkyl acrylate or methacrylate wherein alkyl is C_1-C_4 and wherein the amounts of styrene, hydroxy alkyl (mesh) acrylate and unsaturated polyester in said composition comply with the following equation in parts by weight:

$$\frac{\textit{styrene (parts by weight)}}{\textit{polyester (parts by weight)+ hydroxyalkyl (meth) acrylate (parts by weight)}} = 0.12 \text{ to } 0.18 \qquad \text{(I)}$$

2. An article according to Claim 1, wherein the unsaturated polyester is the product of esterification of a glycol, at least an unsaturated dicarboxylic acid or anhydride, optionally a saturated dicarboxylic acid or anhydride and a chain termination agent consisting of an allyl ether of a C_3-C_{10} polyol.

3. An article according to Claim 2, wherein said unsaturated dicarboxylic acid or anhydride is selected from maleic acid or anhydride, fumaric acid or anhydride, itaconic acid and chloromaleic acid or anhydride and mixtures thereof.

4. An article according to Claim 2, wherein said saturated acid or anhydride is selected from phthalic acid or anhydride, tetrahydrophthalic acid or anhydride, cyclohexane dicarboxylic acid or anhydride, adipic acid, sebacic acid, succinic acid, azelaic acid, isophthalic acid, terephthalic acid or anhydrides, NET acid, chlorendic anhydride and mixtures thereof.

5. An article according to Claim 2, wherein said chain termination agent is trimethylol propane diallyl ether.

6. An article according to Claim 2, wherein said glycol is selected from ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 2,2-dimethylpropane diol, 1,3-butane diol, 1,2-butylene glycol, 2,3-butylene glycol and mixtures thereof.

7. An article according to any one of Claims 1 to 6, wherein the unsaturated polyester has an acid unsaturation index, expressed as the ratio between the number of equivalents of unsaturated acid in the polyester and the total number of equivalents of acid in said polyester higher than 0.50.

8. An article according to any one of Claims 1 to 7 wherein the polyester has an acid unsaturation index not lower than 0.85.

9. An article according to any one of Claims 1 to 8, wherein the polyester resin composition has an overall percentage of unsaturations, expressed as the ratio between the total number of unsaturated moles in the composition (polymer plus solvent) and the total number of moles from which the resin composition is obtained, from 0.55 to 0.75.

10. An article according to any one of the preceding Claims wherein the resin composition has an acid number of from 30 to 50 mg KOH/mL, and a hydroxyl number of from 50 to 105 mg KOH/mL.

11. An article according to any one of the preceding claims wherein the applied polyester resin composition comprises from 65 weight percent to 80 weight percent of unsaturated polyester and from 35 weight percent to 20 weight percent of monomeric solvent.

12. An article according to any one of the preceding claims wherein the applied polyester resin composition comprises from 10 weight percent to 16 weight percent styrene referred to the overall composition.

13. An article according to any one of the preceding caims wherein said resin composition comprises curing promoters and/or fillers.

14. An article according to any one of the preceding claims further comprising a surface coating or sheet of cured conventional unsaturated polyester resin bonded to the surface of the foamed material by means of said unsaturated polyester resin composition.

15. An article according to any one of the preceding claims wherein the layer or core of foamed material is selected polystyrene foam (extruded or expanded), syndiotactic polystyrene foam, styrene copolymer foams, polyurethane foam, polyethylene terephthalate

(PET) foam, polypropylene foam, polyethylene foam, polyphenyl ether foam and polyvinyl chloride (PVC) foam.

16. An article according to Claim 15 wherein the layer core of foamed material is extruded polystyrene foam.

17. An article according to Claim 15 wherein the layer of said unsaturated polyester resin is bonded to the layer or core of foamed material.

18. An article according to Claim 15 wherein the layer of said unsaturated polyester resin is coated to the layer or core of foamed material.

19. An article according to any of the preceding claims wherein the ratio according to equation (I) of the polyester resin composition is of from 0.16 to 0.18.

20. An article according to any one of the preceding claims consisting of a sandwich panel having a core of foamed material coated on its upper and lower side by a layer of said unsaturated polyester resin composition.

21. A process for preparing an article according to any one of Claims 1 to 20 comprising applying to a core or layer of a foamed material a layer of an unsaturated polyester resin composition comprising an unsaturated polyester and a monomeric solvent, wherein in said resin composition the monomeric solvent comprises styrene and hydroxy alkyl acrylate or methacrylate wherein alkyl is C_1-C_4 and wherein the amounts of styrene, hydroxyalkyl(mesh)acrylate and unsaturated polyester in said composition comply with the following equation in parts by weight:

(I)

$$\frac{\textit{styrene (parts by weight)}}{\textit{polyester (parts by weight)} + \textit{hydroxyalkyl (meth)acrylate (parts by weight)}} = 0.12 \text{ to } 0.18$$

and curing the applied layer.

22. A process according to Claim 21 wherein the unsaturated polyester is the product of esterification of a glycol, at least an unsaturated dicarboxylic acid or anhydride, optionally a saturated dicarboxylic acid or anhydride and a chain termination agent consisting of an allyl ether of a C_3-C_{10} polyol.

23. A process according to Claim 22, wherein said unsaturated dicarboxylic acid or anhydride is selected from maleic acid or anhydride, fumaric acid or anhydride, itaconic acid and chloromaleic acid or anhydride and mixtures thereof.

24. A process according to Claim 22, wherein said saturated acid or anhydride is selected from phthalic acid or anhydride, tetrahydrophthalic acid or anhydride, cyclohexane dicarboxylic acid or anhydride, adipic acid, sebacic acid, succinic acid, azelaic acid, isophthalic acid, terephthalic acid or anhydrides, HET acid, chlorendic anhydride and mixtures thereof.

25. A process according to Claim 22, wherein said chain termination agent is trimethylolpropane diallyl ether.

26. A process according to Claim 22, wherein said glycol is selected from ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 2,2-dimethylpropane diol, 1,3-butane diol, 1,2-butylene glycol, 2,3-butylene glycol and mixtures thereof.

27. A process according to any one of Claims 21 to 26, wherein the unsaturated polyester has an acid unsaturation index, expressed as the ratio between the number of equivalents of unsaturated acid in the polyester and the total number of equivalents of acid in said polyester higher than 0.50.

28. A process according to any one of Claims 21 to 27, wherein the unsaturated polyester has an acid unsaturation index not lower than 0.70.

29. A process according to any one of Claims 21 to 28 wherein the polyester has an acid unsaturation index not lower than 0.85.

30. A process according to any one of Claims 21 to 29, wherein the polyester resin composition has an overall ratio of 0.55 to 0.75 percent of unsaturations, between the total number of unsaturated moles in the composition (polymer plus solvent) and the total number of moles from which the resin composition is obtained, from.

31. A process according to any one of Claims 21 to 30 wherein the resin composition has an acid number of from 30 to 50 mg KOH/mL, and a hydroxyl number of from 50 to 105 mg KOH/mL.

32. A process according to any one of Claims 21 to 31 wherein the polyester resin composition comprises from 65 weight percent to 80 weight percent of unsaturated polyester and from 35 weight percent to 20 weight percent of monomeric solvent.

33. A process according to any one of Claims 21 to 32 wherein the polyester resin composition comprises from 10 weight percent to 16 weight percent styrene based upon the overall composition.

34. A process according to Claims 21 to 33 wherein the polyester resin composition comprises inhibitors selected from hydroquinone and toluene hydroquinone.

35. A process according to any of Claims 21 to 34 wherein the polyester resin composition further comprises curing promoters and/or fillers.

36. A process according to any one of Claims 21 to 35 wherein the ratio according to equation (I) of the polyester resin composition is of from 0.16 to 0.18.

37. A process according to any one of Claims 21 to 36 wherein the polyester resin composition is cured by means of a peroxide curing system.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/06767

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J9/36 B32B27/36 //C08L67/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C09D C09J C08L B32B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 583 884 A (BAUM MELVIN E) 8 June 1971 see claims 2,4 see column 3, line 21 - line 32 see column 2, line 47 - line 62 see column 4, line 31 - line 36 see examples V,,VI ---	1,11-18, 21,32, 33,35,37
A	DATABASE WPI Section Ch, Week 7444 Derwent Publications Ltd., London, GB; Class A14, AN 74-76354V XP002068335 & JP 49 021 428 A (JAPAN CATALYTIC CHEM IND CO) cited in the application see abstract --- -/--	1

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 June 1998	26/06/1998

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 98/06767

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8739 Derwent Publications Ltd., London, GB; Class A17, AN 87-273839 XP002068336 & JP 62 190 236 A (NIPPON STYRENE PAPER KK) see abstract -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .tional Application No
PCT/US 98/06767

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3583884 A	08-06-1971	NONE	