



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 283/01, C08J 7/04 // (C08F 283/01, 220:20)		A1	(11) International Publication Number: WO 98/45343
			(43) International Publication Date: 15 October 1998 (15.10.98)
(21) International Application Number: PCT/EP98/01883 (22) International Filing Date: 1 April 1998 (01.04.98) (30) Priority Data: TO97A000286 4 April 1997 (04.04.97) IT (71) Applicant (for all designated States except US): C.O.I.M. S.P.A. - CHIMICA ORGANICA INDUSTRIALE MILANESE [IT/IT]; Via Manzoni, 28/32, I-20019 Settimo Milanese (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): LIGUTTI, Marzio [IT/IT]; Via Bissolati, 69, I-26100 Cremona (IT). MONTECCHI, Massimo [IT/FR]; Bâtiment E, escalier C-3 ter, 3 ter, avenue J.B. Clément, F-92100 Boulogne Billancourt (FR). (74) Agents: RAMBELLI, Paolo et al.; Jacobacci & Perani S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: AN UNSATURATED POLYESTER RESIN COMPOSITION $\frac{\text{Styrene (parts wt)}}{\text{Polyester (parts wt)} + \text{hydroxy alkyl (meth) - acrylate (parts wt)}} = 0.12 - 0.18$			
(57) Abstract An unsaturated polyester resin composition is disclosed, comprising an unsaturated polyester and a monomeric solvent reactive with said polyester, characterised in that the monomeric solvent comprises styrene and hydroxy alkyl acrylate or methacrylate, wherein alkyl is C ₁ to C ₄ and wherein the amounts of styrene, hydroxy alkyl (meth)acrylate and unsaturated polyester in said composition comply with the equation (I) in parts by weight. The composition is particularly useful for coating or bonding foamed articles, particularly foamed polystyrene.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

An unsaturated polyester resin composition

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 therefor might be the need for high impact resistance, fire regulations, improving the long term weathering properties and/or æsthetic reasons. This is the case, for example, in insulated trailers, insulated containers and buoyancy applications.

There are applications where foamed plastics materials, such as polyurethane, are coated with unsaturated polyester

resin or are bonded using unsaturated polyester to a plastics or wood material. In this type of application, there are basically two problems, one relating to the polyurethane (i) and one related 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% wt); 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. How-

ever, using a polyester resin as 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 to vibrations and dynamic loads. Especially in insulated transport applications this improves the long term performance of the articles.

Another advantage of using polyester resin as adhesive is that polyester adhesives can be employed for reparations, since it provides joint-less repairs. 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 fibres (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-12 36 187 describes protecting coatings for foamed polystyrene articles which are obtained by coating the polystyrene foam with a composition containing 25-75 percent by weight (% wt) of a polymerisable ethylenically unsaturated polyester and 25-75% wt of a polymerisable ethylenically unsaturated monomer of which 50 to 100% wt is an allyl-ether of N-methylol-urea or a derivative thereof.

JP-01319547-A describes moulded 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 5-200 parts by weight of a compound, such as di-cyclo-pentenyl oxy ethyl acrylate or di-cyclo-pentenyl oxy ethyl meth-acrylate.

JP-63260936-A describes a composite material comprising a core foam material, such as polystyrene foam and a radical polymerised 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.

JP-49021428-A describes a coating composition for thermoplastic mouldings, particularly of polystyrene foam comprising an unsaturated resin and a monoester from (meth) acrylic acid and a C₂-C₈ polyol or a C₄-C₁₈ ether linkage-containing polyol, or the reaction product of a C₂-C₁₈ alkylene oxide and (meth) 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-hydroxy ethyl 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% wt of polyester resin and about 32% wt of hydroxy ethyl acrylate (HEA) and as little as about 8% wt 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 desirable mechanical properties of the 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 70-80°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 polymerisation 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 ob-

tained from the polymerisation 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 polymerisation of ethylenically unsaturated monomers with a layer of polyester resin having structural properties or for bonding sheets, such as GRP sheet 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 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 den-

sity. This means that articles that have a constructive aspect/role have either an improved performance, or can be optimised.

Another aspect of the present invention is that extruded polystyrene foam hardly takes up any water, 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, characterised in that the monomeric solvent comprises styrene and a hydroxy alkyl methacrylate or acrylate, wherein alkyl is C₁ to C₄ 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)

$$\frac{\text{Styrene (parts wt)}}{\text{Polyester (parts wt) + hydroxy alkyl (meth) - acrylate (parts wt)}} = 0.12 - 0.18$$

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 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 allows to provide polyester resin compositions including an amount of polyester varying in a wide range, preferably from 65% wt to 80% wt and more preferably between 65% and 75% wt, referred to the total amount of unsaturated polyester and monomeric solvent. Correspondingly, the amount of monomeric solvent in the composition is preferably from 35 to 20% wt and more preferably from 35 to 25% wt. The amount of styrene monomer in the monomeric solvent is preferably from 10 to 16% wt referred to 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% wt, correspondingly, the amount of hydroxy alkyl (meth)-acrylate is to be increased in the amount of 5.55% wt to 8.33% wt, 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 polymerisation 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 C₃-C₁₀ polyol, most preferably a diallyl ether of C₃-C₁₀ aliphatic or cycloaliphatic polyol, such as glycerol, trimethylol propane or ethane.

Suitable glycols comprise ethylene glycol, diethylene glycol, tri-ethylene glycol, polyethylene glycol, propylene

glycol, di-propylene glycol, tri-propylene glycol, polypropylene glycol, 2,2-di-methylpropane diol, 1,3-butane diol, 1,2-butylene glycol, 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 unsaturated acid or anhydrides may also be used.

The saturated acid or anhydride, when used, is preferably selected from the group consisting of 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 to 20% 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 (M_n) of the polyester is preferably from 800 to 1400; and the average weight molecular weight (M_w) is preferably from 1800 to 2300.

The polyester resin composition has preferably 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 has preferably an acid number of from 30 to 50 mg KOH/ml, an hydroxyl number of from 50 to 105 mg 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 stabilisers, 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 acetate.

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, such as particularly methyl-ethyl-ketone (MEK) peroxide and methyl isobutyl ketone peroxide. A typical curing system consists of 0.2% wt cobalt octoate (6% wt Co), 2% wt of a MEK-MEK peroxide solution (50% by weight for each component in the solution), referred to 100 grams polyester resin composition. The resin composition has preferably a curing time of from 8 to 15 minutes, a gel time of from 10 to 90 minutes and an exothermic peak of about 150-170°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, 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 and 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 with the range of from 15°C (ambient 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, within which the resin composition is cured, may range between 30°C and 60°C. The preferred temperature of the press plates 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 above defined 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 fibres.

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 to manufacture coated parts for marine applications, such as pontoons.

Example 1 - 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 are charged into a reactor equipped with a mixer, a partial condenser and a shielding gas system. The esterification reaction is carried out under nitrogen gas flow by the conventional fusion method at a temperature of from 175 to 180°C by periodically checking the viscosity into the reactor, until the acid value of the polyester resin has 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 hydroxy-ethyl-methacrylate and 0.002 part by weight copper naftenate (6%), while taking care that the internal temperature in the dilutor vessel is not higher

than 80°C.

The obtained polyester resin composition has a polyester polymer content of about 74% wt. The polyester has an acid unsaturation index of 85%.

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, i.e., 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% wt of cobalt octoate (6% wt Co) and 2% wt of a MEK-MEK peroxide solution (50% by weight for each component in the solution), referred to 100 grams polyester resin.

Example 2 - 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 has been added, was poured on top 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 2-4 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 S.p.A.) (Combination 2B) and one combining the polyester resin of the invention (Example 1) with polyurethane having a density of 40 kg/m^3 (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, i.e. 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 COIM S.p.A.) (set 3B). The polyurethane used was a 40 kg/m³ density rigid polyurethane foam commercially available.

In all samples, the foam cores were 50 mm thick. Curing was done under a pressure of 0.5 kg/cm² and at 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 bonding 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 Plast, 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/cm²) and at 50°C. The coated samples were cured at room temperature under pressure (0.5 kg/cm²).

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

For the coated samples (set 4B), the average tensile bonding strength = 600 kPa, the average shear strength = 513 kPa and average shear modulus = 6,219 kPa.

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

CLAIMS

1. An unsaturated polyester resin composition comprising an unsaturated polyester and a monomeric solvent reactive with said polyester, characterised in that the monomeric solvent comprises styrene and hydroxy alkyl acrylate or methacrylate, wherein alkyl is C₁ to C₄ and wherein the amounts of styrene, hydroxy alkyl (meth) acrylate and unsaturated polyester in said composition comply with the following equation in parts by weight:

(I)

$$\frac{\text{Styrene (parts wt)}}{\text{Polyester (parts wt)} + \text{hydroxy alkyl (meth) - acrylate (parts wt)}} = 0.12 - 0.18$$

2. A composition 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 C₃-C₁₀ polyol.

3. A composition according to Claim 2, wherein said unsaturated dicarboxylic acid or anhydride is selected from the group consisting of maleic acid or anhydride, fumaric acid or anhydride, itaconic acid and chloromaleic acid or anhydride and mixtures thereof.

4. A composition according to Claim 2, wherein said unsaturated acid or anhydride is selected from the group consisting of phthalic acid or anhydride, tetra-hydrophthalic 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.

5. A composition according to Claim 2, wherein said chain termination agent is trimethylol propane diallyl ether.
6. A composition according to Claim 1, wherein said glycol is selected from the group consisting of ethylene glycol, diethylene glycol, tri-ethylene glycol, polyethylene glycol, propylene glycol, di-propylene glycol, tri-propylene glycol, polypropylene glycol, 2,2-di-methylpropane diol, 1,3-butane diol, 1,2-butylene glycol, 2,3-butylene glycol and mixtures thereof.
7. A composition according to any of Claims 1-6, 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. A composition according to any of Claims 1-7, wherein the unsaturated polyester has an acid unsaturation index not lower than 0.70.
9. A composition according to any of Claims 1 to 8, wherein the polyester has an acid unsaturation index not lower than 0.85.
10. A composition according to any of Claims 1 to 9, 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.
11. A composition according to any 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.

12. A composition according to any of the preceding Claims, comprising from 65 to 80% wt of unsaturated polyester and from 35 to 20% wt of monomeric solvent.

13. A composition according to any of the preceding Claims, comprising from 10 to 16% wt styrene referred to the overall composition.

14. A composition according to any of the preceding Claims, comprising inhibitors selected from hydroquinone and toluene hydroquinone.

15. A composition according to any of the preceding Claims, further comprising curing promoters and/or fillers.

16. An unsaturated polyester resin composition according to the preceding Claims, wherein the ratio according to equation (I) is of from 0.16 to 0.18.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/01883

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F283/01 C08J7/04 //(C08F283/01,220:20)

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 C08F C08J

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 ³	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 366 330 A (HOECHST AG) 28 April 1978	1,12,13, 16
X	see table 3	
X	see table 1	2-6
X	see page 8, line 15 -----	15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

³ Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"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 when the document is taken alone

"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

Date of the actual completion of the international search

28 August 1998

Date of mailing of the international search report

11/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Friederich, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/01883

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2366330 A	28-04-1978	DE 2644691 A	06-04-1978
		BE 855129 A	16-09-1977
		GB 1583171 A	21-01-1981
		JP 53043741 A	20-04-1978
		NL 7705846 A	04-04-1978
		SE 7706237 A	03-04-1978
		US 4259224 A	31-03-1981
