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(54) Title: LOW VAPORIZABLE ETHYLENICALLY UNSATURATED MONOMER EMISSION VINYL ESTER AND POLYESTER RESIN COMPOSITIONS

(57) Abstract

Vinyl ester or polyester resins containing polymerizable, vaporizable, ethylenically unsaturated monomers and an emission suppressing amount of ceresin wax is improved with the addition of a drying oil such as corn oil and an epoxidized drying oil such as epoxidized soybean oil. The improvement is in secondary adhesion.

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LOW VAPORIZABLE ETHYLENICALLY UNSATURATED MONOMER EMISSION VINYL ESTER AND POLYESTER RESIN COMPOSITIONS

The present invention concerns low styrene emission vinyl ester and polyester formulations containing ceresin wax as a styrene emission depressant and drying oil and epoxidized drying oil as secondary adhesion promoters.

Most vinyl ester resins and unsaturated polyester resins contain polymerizable, vaporizable, ethylenically unsaturated monomers such as styrene as a reactive diluent. Since styrene or other polymerizable, vaporizable, ethylenically unsaturated monomer is a volatile component which tends to be released to the atmosphere during storage and/or curing of the thermosettable vinyl ester and unsaturated polyester resins, it is becoming more and more desirable to reduce the level of styrene or other polymerizable, vaporizable monomer which is released to the atmosphere during storage and/or cure. One method for reducing the release of styrene or other polymerizable, vaporizable monomer into the atmosphere is to include ceresin wax in the formulation. While this does indeed reduce the amount of styrene released into the atmosphere, the composition suffers from a loss in secondary adhesion. It would therefore be highly desirable and beneficial to incorporate into the formulation components which will eliminate or decrease the loss in secondary adhesion.

It has now been discovered that the loss in secondary adhesion from polymerizable, vaporizable, ethylenically unsaturated monomer such as styrene containing vinyl ester and unsaturated polyester formulations containing ceresin wax as a polymerizable, vaporizable, ethylenically unsaturated monomer emission suppressant can be accomplished by incorporating into the formulation a combination of corn oil and epoxidized soybean oil.

The present invention concerns an improvement in vinyl ester and unsaturated polyester resin compositions containing a polymerizable, vaporizable, ethylenically unsaturated monomer and a polymerizable, ethylenically unsaturated monomer emission suppression amount of ceresin wax; which improvement comprises employing in said compositions a secondary adhesion promoting amount of at least one drying oil and at least one epoxidized drying oil.

Another aspect of the present invention pertains to a polymerizable, vaporizable, ethylenically unsaturated vinyl monomer suppressant/secondary adhesion promoter additive composition comprising (1) at least one vaporizable ethylenically unsaturated monomer, (2) ceresin wax, (3) at least one drying oil, and (4) at least one epoxidized drying oil.

Another aspect of the present invention pertains to a curable composition comprising (A) at least one vinyl ester resin or at least one unsaturated polyester resin or a combination thereof; (B) at least one polymerizable, vaporizable, ethylenically unsaturated monomer; (C) a polymerizable, ethylenically unsaturated monomer emission suppression amount of ceresin wax; (D) a secondary adhesion promotion amount of at least one drying oil; (E) a secondary adhesion promotion amount of at least one epoxidized drying oil; and (F) a curing amount of a suitable curing agent.

A further aspect of the present invention pertains to a substrate material saturated or impregnated with the aforementioned curable composition.

A further aspect of the present invention pertains to the product or article resulting from shaping one or more plies of the aforementioned saturated or impregnated substrate material into a desired configuration and curing.

The present invention may suitably comprise, consist of, or consist essentially of, the aforementioned components.

The invention illustratively disclosed herein may suitably be practiced in the absence of any component which is not specifically disclosed or enumerated herein.

Additive Composition

The vaporizable ethylenically unsaturated vinyl monomer suppressant/secondary adhesion promoter additive composition of the present invention usually comprises (1) from 20 percent to 40 percent, preferably from 20 percent to 35 percent, more preferably from 25 percent to 35 percent percent by weight of at least one vaporizable ethylenically unsaturated monomer, (2) from 10 percent to 25 percent, preferably from 10 percent to 20 percent, more preferably from 13 percent to 17 percent percent by weight ceresin wax, (3) from 10 percent to 30 percent, preferably from 18 percent to 28 percent, more preferably from 20 percent to 26 percent percent by weight of at least one drying oil, and (4) from 20 percent to 40 percent, preferably from 20 percent to 35 percent, more preferably from 25 percent to 35 percent by weight of at least one epoxidized drying oil.

Vinyl Ester Resins

Suitable vinyl ester resins which can be employed herein include any such resin prepared by the reaction of an epoxy resin having an average of more than one vicinal epoxy group per molecule with an unsaturated carboxylic acid. The reactants are usually employed in amounts which provide a ratio of acid groups per epoxy group of from 0.95:1 to 1.05:1, preferably from 1:1.

Suitable epoxy resins include those which contain an average of more than one glycidyl group per molecule such as for example glycidyl derivatives of aliphatic, cycloaliphatic or aromatic compounds containing an average of more than one hydroxyl, carboxyl or amine group per molecule or any combination thereof. Particularly suitable such epoxy resins include, for example, the glycidyl ethers of resorcinol, catechol, hydroquinone, bisphenol A, bisphenol F, bisphenol K, fluorene, phenol- or cresol-aldehyde resins, halogenated, particularly bromine substituted derivatives thereof, or any combination thereof.

Suitable unsaturated carboxylic acids which can be employed in the preparation of the vinyl ester resins include, for example, acrylic acid, methacrylic acid, glacial methacrylic acid, or any combination thereof.

The reaction between the epoxy resin and the unsaturated acid is usually conducted at temperatures of from 90°C to 130°C, preferably from 100°C to 120°C, more preferably from 105°C to 115°C for a time sufficient to complete the reaction. The reaction is usually considered complete when the percent acid has reached a value of 1. The reaction time is usually from 3 to 6 hours.

If desired, a catalyst for promoting the reaction between the epoxy resin and the unsaturated acid can be employed. Suitable such catalysts include, tris(dimethylaminomethyl)phenol, tetraethyl ammonium bromide, or any combination thereof. Particularly suitable such catalysts include, for example, or any combination thereof. Particularly suitable such catalysts include, for example tris(dimethylaminomethyl)phenol, or any combination thereof. The catalysts are usually employed in amounts of from 0.05 to 0.08, preferably from 0.055 to 0.075, more preferably from 0.065 parts of catalyst per 100 parts of resultant mixture of the carboxylic acid and epoxy resin.

Unsaturated Polyester Resins

Suitable unsaturated polyester resins which can be employed herein include, for example, those prepared by reacting a compound having an average of more than one, preferably two, aliphatic, cycloaliphatic or aromatic hydroxyl groups per molecule with a compound having an average of more than one aliphatic, cycloaliphatic or aromatic carboxyl groups per molecule, with the proviso that there be present at least one reactant which contains polymerizable unsaturated groups. The reactants are usually employed in amounts which provide a ratio of acid groups per hydroxyl group.

Particularly suitable compounds containing an average of more than one hydroxyl group per molecule from which unsaturated polyester resins can be prepared include, for example, those compounds having aliphatic, cycloaliphatic or aromatic hydroxyl groups. Particularly suitable such compounds include, for example propylene glycol, ethylene glycol, bisphenol A, or any combination thereof.

Suitable compounds containing an average of more than one carboxylic acid group per molecule from which unsaturated polyester resins can be prepared include, for example, fumaric acid, maleic anhydride, succinic anhydride, chlorendic anhydride, orthophthalic acid or anhydride isophthalic acid or anhydride, terephthalic acid or anhydride, or any combination thereof.

The reaction between the hydroxyl containing compound and the acid is usually conducted at temperatures of from 150°C to 190°C, preferably from 170°C to 190°C, more preferably from 175°C to 185°C for a time sufficient to complete the reaction. The reaction is usually considered complete when the acid number has reached a value of 50 or below. The reaction time is 6 to 16 hours.

If desired, a catalyst for promoting the reaction between the hydroxyl-containing compound and the catalyst can be employed. Suitable such catalysts include, butyl stannoic acid, para-toluene sulfonic acid, or any combination thereof. Particularly suitable such catalysts include, for example butyl stannoic acid, or any combination thereof. The catalysts are usually employed in amounts of from 0.05 to 1.0, preferably from 0.05 to 0.1, more preferably from 0.075 parts of catalyst per 100 parts resultant mixture of carboxylic acid and hydroxyl containing compound.

Polymerizable, vaporizable ethylenically unsaturated monomers

Suitable polymerizable, vaporizable, ethylenically unsaturated monomers which can be employed herein include, for example, styrene, alpha-methyl styrene, chlorostyrene, vinyl benzene, vinyl toluene, p-methylstyrene, divinylbenzene, or any combination thereof. Also suitable are the C_1-C_8 alkyl esters of acrylic and methacrylic acid. Styrene is the preferred polymerizable, vaporizable, ethylenically unsaturated vinyl monomer.

The polymerizable, vaporizable, ethylenically unsaturated monomers are usually employed in amounts of from 20 to 60, preferably from 35 to 55, more preferably from 40 to 50 percent by weight based upon the combined weight of the resin and the polymerizable, vaporizable, ethylenically unsaturated monomer.

Ceresin Wax

Ceresin wax employed herein is a mixture of hydrocarbons of complex composition purified by treatment with concentrated sulfuric acid and filtered through boneblack having a melting point of 61°C to 78°C. Other names for ceresin wax are: ozokerite wax 170-D, ozokerite wax 170 M.B., white ozokerite wax, yellow ozokerite wax, yellow ozokerite wax S special, S&P ozokerite wax yellow, etc. Strahl & Pitsch Inc., a producer of ceresin wax, defines ozokerite as a hydrocarbon wax derived from mineral or petroleum sources.

The ceresin wax is employed in any amount which will suppress emission of styrene or other volatile polymerizable ethylenically unsaturated monomers contained in the formulation during storage and curing. Particularly suitable amounts of ceresin wax include, for example, from 0.15 percent to 0.4 percent, preferably from 0.15 percent to 0.3 percent, more preferably from 0.18 percent to 0.25 percent by weight based upon the combined weight of the styrene (polymerizable ethylenically unsaturated monomer), any other reactive diluent (polymerizable ethylenically unsaturated monomer) which may be present, and resin.

Drying Oil

The term "drying oil" as employed herein means any naturally occurring oil which contains glycerides of linoleic and/or linolenic acids. Suitable drying oils will have an Iodine value of from 100 to 210, preferably from 115 to 150, more preferably from 115 to 140. Particularly suitable such drying oils include, for example, corn oil, linseed oil, safflower oil, soybean oil, sunflower oil, cottonseed oil, rapeseed oil, perilla oil, hempseed oil, or any combination thereof. Corn oil and soybean oil are preferred.

The drying oil is employed in any amount which in combination with the epoxidized drying oil will enhance the secondary adhesion of the formulation. Particularly suitable amounts of drying oil include, for example, from 0.1 percent to 0.7, preferably from 0.2 percent to 0.5 percent, more preferably from 0.25 percent to 0.4 percent percent by weight based upon the combined weight of the styrene (polymerizable ethylenically unsaturated monomer), any other reactive diluent (polymerizable ethylenically unsaturated monomer) which may be present, and resin.

Epoxidized Drying Oil

The term "epoxidized drying oil" includes any naturally occurring oils which contains glycerides of linoleic and or linolenic acids and which have been epoxidized. Suitable such epoxidized drying oils include, for example, epoxidized soybean oil, epoxidized corn oil, epoxidized linseed oil, epoxidized safflower oil, epoxidized sunflower oil, epoxidized cottonseed oil, epoxidized rapeseed oil, epoxidized perilla oil, epoxidized hempseed oil, or any combination thereof. Epoxidized soybean oil and epoxidized corn oil are preferred.

The epoxidized drying oils can be prepared by reacting an epihalohydrin with the desired drying oil and then dehydrohalogenating the resultant halohydrin intermediate with a suitable basic-acting compound such as, for example, an alkali metal halide, alkali metal carbonate. Sodium hydroxide is preferred. Several epoxidized drying oils are available commercially such as, for example epoxidized soybean oil is available from Atochem North America as VIKOFLEX 7170, epoxidized Linseed Oil is available from Atochem North America as VIKOFLEX 7190.

The epoxidized drying oil is employed in any amount which in combination with the drying oil will enhance the secondary adhesion of the formulation and retard styrene volatilization some. Particularly suitable amounts of epoxidized drying oil include, for example, from .2 to .7, preferably from .3 to .6, more preferably from 0.35 to 0.55 percent by weight based upon the combined weight of the styrene (polymerizable ethylenically unsaturated monomer), any other reactive diluent (polymerizable ethylenically unsaturated monomer) which may be present, and resin.

Curing Agents and Accelerators or Promoters

The compositions of the present invention can be cured by any means suitable for curing vinyl ester resins and unsaturated polyester resins. They can be suitably cured by means of azo compounds, peroxides, or any combination thereof. Particularly suitable curing agents include, for example, methyl ethyl ketone peroxide, cumene hydroperoxide, benzoyl peroxide, or any combination thereof.

The curing catalysts are usually employed in amounts of from 1 to 2.5, preferably from 1 to 1.5, more preferably from 1 to 1.25 percent by weight based upon the weight of the resin.

Also, if desired, curing accelerators or promoters can be employed. Suitable such curing accelerators or promoters include, for example, cobalt naphthenate, cobalt octoate, N,N-dimethylaniline, N,N-dimethylacetoacetamide, or any combination thereof.

The curing accelerators or promoters are usually employed in amounts of from 0.05 to 0.6, preferably from 0.1 to 0.4, more preferably from 0.1 to 0.3 percent by weight based upon the weight of the resin.

Substrate Materials

Suitable substrate materials which can be saturated or impregnated with the curable compositions of the present invention include natural or synthetic fibers in woven, mat or multifilament strand form. Suitable such materials can be nylon, rayon, cotton, glass, graphite, carbon, aramid, polyester, or any combination thereof.

Other additives can be added to the compositions of the present invention such as, for example, pigments, dyes, fillers, or any combination thereof.

The curable compositions are useful in the preparation of laminates, coatings, polymer concrete.

The following components were employed in the examples and comparative experiments.

Vinyl Ester Resin (VER) A was a vinyl ester resin prepared from a diglycidyl ether of bisphenol A having an epoxide equivalent weight of 380 to 420 and methacrylic acid in an equivalent ratio of acid per epoxy group of 1:1. The resin contained 45 percent styrene by weight.

Polyester Resin (PER) A was a rigid, low reactivity, low viscosity, thixotropic, orthophthalic laminating resin commercially available from Reichhold as POLYLITE™ Polyester Resin 33-087. The resin was prepromoted for room temperature curing with the addition of methyl ethyl ketone peroxide. The resin contained 43-47 percent styrene by weight.

The following tests were performed on the vinyl ester and/or unsaturated polyester compositions.

ETHYLENICALLY UNSATURATED MONOMER EMISSIONS

The test was based on a completely catalyzed, curable, system since it was under curing conditions that most of the volatile ethylenically unsaturated monomer was lost.

The temperature and relative humidity conditions at which the test was conducted was recorded. 100 +/-.5 grams of catalyzed resin was poured into a tared one gallon (3.78 l) paint can lid having an opened paper clip and the ethylenically unsaturated monomer emissions measured by the weight loss as the resin formulation gels and up to one hour after the gel time. The gel time was determined by raising the paper clip from the resin periodically until the resin tears or sticks to the paper clip. The ethylenically unsaturated monomer loss was reported in g/m^2 and was determined by multiplying the gram weight loss by the factor 60.56. The factor was given in the procedure from the California South Coast Air Quality Board.

SECONDARY ADHESION

The secondary adhesion promotion test was a cycle flexing test conducted on cured laminates at 70% of the flexural strength determined by ASTM D 790-86. The secondary adhesion test was determined by ASTM D 3479-76(82).

The primary laminate was prepared by saturating 6" x 12" glass layers in the following sequence, CSM/WR/CSM/WR/CSM. All layers were thoroughly wet with resin, but the surface of the last layer of chopped strand mat was not excessively resin rich. The last chopped strand mat layer was allowed to wet out almost entirely from the addition of resin on the preceding mat layer. (If the layer of chopped strand mat in the initial lay-up was excessively resin rich, satisfactory secondary adhesion may not be achieved. Too high of an amount of ceresin wax per surface werea may develop, which the secondary adhesion promoter may not overcome. A resin rich surface was not as structurally sound as one that contained the appropriate amount of glass near the surface.) The five-ply laminate was then cured at a temperature of approximately 25°C for 20-24 hours.

The secondary laminate was then prepared on top of the primary laminate by saturating 6" X 12" glass layer in the following sequence, CSM/WR/CSM.

CSM = 1.5 oz. chopped strand mat

WR = 24 oz. woven roving.

The secondary laminate was then cured at a temperature of approximately 25°C for at least 20-24 hours. The resultant cured laminate was then subjected to the aforementioned ASTM tests.

EXAMPLE 1

Several formulations were tested for styrene emission and secondary adhesion. The composition and test results are given in Table I.

Table I

	Formulation							
	A*	B*	C*	D*	E*	F*	G*	H*
Resin Type	VER A	VER A	VER A	VER A	VER A	VER A	VER A	VER A
Styrene content, %^{a}	45	45	45	45	45	45	45	45
MEK peroxide, %^{b}	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Co Nap^{d}, percent^{b}	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Ceresin Wax, %^{b}	0	0	0.2	0.2	0.2	0.2	0.2	0.2
Corn oil, %^{b}	0	0	0	0	0.7	0.7	0	0
ESO^{c}, %^{b}	0	0	0	0	0	0	0.7	0.7
Temp., °F , °C	78 25.6	70-74 21.1-23.3	74 23.3	70-71 21.1-21.7	74-76 23.3-24.4	76-78 24.4-25.6	80-81 26.7-27.2	78-79 25.6-26.1
Relative Humidity, %	56	60-63	86	56-61	60-62	68-76	62-66	70-76
Styrene loss, g/m^{2}	157	213	35	51.5	98.42	98.69	61.1	79.9
Secondary Adhesion, Cycles^{e}	21,680	----	8,460	---	11,540	---	11,680	----

Table I (contd.)

	Formulation							
	I	J	K*	L*	M*	N*	O*	P*
Resin Type	VER A	VER A	PER A	PER A	PER A	PER A	PER A	PER A
Styrene content, %[a]	45	45	43-47	43-47	43-47	43-47	43-47	43-47
MEK peroxide, %[b]	1.25	1.25	1.5	1.5	1.5	1.5	1.5	1.5
Co Nap[d], percent[b]	0.3	0.3	---	---	---	---	---	---
Ceresin Wax, %[b]	0.2	0.2	0	0	0.2	0.2	0.2	0.2
Corn oil, %[b]	0.3	0.3	0	0	0	0	0.7	0.7
ESO[c], %[b]	0.4	0.4	0	0	0	0	0	0
Temp., °F , °C	73-74 22.8-23.3	74-75 23.3-23.9	73 22.8	74-76 23.3-24.4	71-72 21.7-22.2	71-72 21.7-22.2	72 22.2	72 22.2
Relative Humidity, %	60-62	62-64	66-75	74-76	52-56	54-57	58-62	58-62
Styrene loss, g/m^2	46	76	163.5	156.2	54.5	55.1	89	92.6

* Not an example of the present invention.

a Percent by weight based on the weight of the resin.

b Percent by weight based on the weight of resin plus styrene.

c Epoxidized soybean oil.

d Cobalt naphthenate (6% Co).

e Cycles to failure.

Table I (contd.)

	Formulation							
	I	J	K*	L*	M*	N*	O*	P*
Secondary Adhesion, Cyclese	24,580	---	5,100	---	10,100	---	11,540	---

* Not an example of the present invention.

a Percent by weight based on the weight of the resin.

b Percent by weight based on the weight of resin plus styrene.

c Epoxidized soybean oil.

d Cobalt naphthenate (6% Co).

e Cycles to failure.

Table I (contd.)

	Formulation			
	Q*	R*	S	T
Resin Type	PER A	PER A	PER A	PER A
Styrene content, %[a]	43-47	43-47	43-47	43-47
MEK peroxide, %[b]	1.5	1.5	1.5	1.5
Co Nap[d], percent[b]	---	---	---	---
Ceresin Wax, %[b]	0.2	0.2	0.2	0.2
Corn oil, %[b]	0	0	0.3	0.3
ESO[c], %[b]	0.7	0.7	0.4	0.4
Temp., °F ,°C	71-72 21.7-22.2	71-72 21.7-22.2	72 22.2	72 22.2
Relative Humidity, %	53-55	52-55	59-63	59-63
Styrene loss, g/m2	43.6	41.8	26	38.1
Secondary Adhesion, Cycles[e]	11,680	---	8,540	---

EXAMPLE 2

A paste concentrate for addition to vinyl ester and unsaturated polyester resins was prepared by blending the following:

styrene	30.8 percent
ceresin wax	15.3 percent
corn oil	23.1 percent
epoxidized soybean oil	30.8 percent
	100.0 percent

The blending operation was conducted in a 7-gallon (26.5 L) glass vessel using an air driven stirrer at a temperature of 75°C. When mixture was clear, all wax dissolved, the mixture was allowed to cool to 65°C to 70°C. Gallon (3.8 L) quantities of the mixture were drained into one gallon (3.8 L) cans, which were sealed and shaken until the cans were at room temperature.

This paste concentrate was employed as an additive to vinyl ester resin A and polyester resin A and tested for styrene loss. The formulations and results are given in Table II.

Table II

	Formulation			
	A	B	C	D
Resin-Styrene preblend, gms	100	100	100	100
Resin, Type	VER A	VER A	PER A	PER A
, gms	55	55	53-57	53-57
Styrene, gms	45	45	43-47	43-47
, percent[a]	45	45	43-47	43-47
Paste Additive, gms	1.3	1.3	1.3	1.3
percent[b]	1.3	1.3	1.3	1.3
Ceresin Wax, gms	0.2	0.2	0.2	0.2
percent[c]	0.2	0.2	0.2	0.2
Corn oil, gms	0.3	0.3	0.3	0.3
percent[c]	0.3	0.3	0.3	0.3
ESO[d], gms	0.4	0.4	0.4	0.4
percent[c]	0.4	0.4	0.4	0.4
Styrene, gms	0.4	0.4	0.4	0.4
percent[e]	0.7	0.7	0.7-0.8	0.7-0.8
Temp., °F	74-76	75	77	76-77
,°C	23.3-24.4	23.9	25	24.4-25
Relative Humidity, percent	62-70	66	60-63	60-64
Styrene loss g/m^2	96	86	40	56

[a] Percent by weight based on the weight of the resin.

[b] Percent by weight based on the weight of resin plus styrene excluding the styrene included in the paste additive.

[c] Percent by weight based on the weight of resin plus styrene including the styrene added via the paste additive.

[d] Epoxidized soybean oil.

[e] Percent by weight based on the weight of the resin.

WHAT IS CLAIMED IS:

1. A composition comprising at least one vinyl ester resin or at least one unsaturated polyester resin or a combination of such resins, at least one polymerizable, vaporizable, ethylenically unsaturated monomer and a polymerizable, vaporizable, ethylenically unsaturated monomer emission suppression amount of ceresin wax; CHARACTERIZED BY employing in said composition a secondary adhesion promoting amount of a drying oil and a secondary adhesion promoting amount of an epoxidized drying oil.

2. A composition of Claim 1 wherein said ceresin wax is employed in an amount of from 0.15 to 0.4 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer, said drying oil is employed in an amount of from 0.1 to 0.7 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer, and said epoxidized drying oil is employed in an amount of from 0.2 to 0.7 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer.

3. A vaporizable ethylenically unsaturated vinyl monomer suppressant/secondary adhesion promoter

additive composition comprising (1) at least one polymerizable, vaporizable, ethylenically unsaturated monomer, (2) ceresin wax, (3) drying oil, and (4) epoxidized drying oil.

4. A composition of Claim 5 wherein said polymerizable, vaporizable, ethylenically unsaturated monomer is employed in an amount of from 20 percent to 40 percent percent by weight based upon the combined weight of polymerizable, vaporizable, ethylenically unsaturated monomer, ceresin wax, drying oil, and epoxidized drying oil, said ceresin wax is employed in an amount of from 10 to 25 percent by weight based upon the combined weight of polymerizable, vaporizable, ethylenically unsaturated monomer, ceresin wax, drying oil, and epoxidized drying oil; said drying oil is employed in an amount of from 10 to 30 percent by weight based upon the combined weight of polymerizable, vaporizable, ethylenically unsaturated monomer, ceresin wax, drying oil, and epoxidized drying oil; and said epoxidized drying oil is employed in an amount of from 20 to 40 percent by weight based upon the combined weight of polymerizable, vaporizable, ethylenically unsaturated monomer, ceresin wax, drying oil, and epoxidized drying oil.

5. A curable composition comprising (A) at least one vinyl ester resin or at least one unsaturated polyester resin or a combination thereof; (B) at least one polymerizable, vaporizable, ethylenically unsaturated monomer; (C) a polymerizable, vaporizable, ethylenically unsaturated monomer emission suppression amount of ceresin wax;

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additionally employing (D) a secondary adhesion promotion amount of drying oil; (E) a secondary adhesion promotion amount of epoxidized drying oil; and (F) a curing amount of a suitable curing agent.

6. A curable composition of Claim 9 wherein said polymerizable, vaporizable, ethylenically unsaturated monomer is employed in an amount of from 20 to 60 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer, said ceresin wax is employed in an amount of from 0.15 to 0.40 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer, said drying oil is employed in an amount of from 0.1 to 0.70 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer, and said epoxidized drying oil is employed in an amount of from 0.2 to 0.7 percent by weight based upon the combined weight of resin and polymerizable, vaporizable, ethylenically unsaturated monomer.

7. A substrate material saturated or impregnated with the curable composition of any one of Claims 5 or 6.

8. The product or article resulting from shaping one or more plies of the saturated or impregnated substrate material of Claim 7 into a desired configuration and curing.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/09076

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 C08L67/06; C08L63/10; //(C08L67/06,91:06,91:00)
(C08L63/10,91:06,91:00)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08L ; C08F ; C08K

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]
A	GB,A,2 011 918 (AB SYNTES) 18 July 1979 see claims 1-4,10-16 ---	1-8
A	EP,A,0 000 941 (BASF AG) 7 March 1979 see page 8, line 11 - line 16; claim 1 ---	1
A	EP,A,0 031 434 (UNION CARBIDE CORPORATION) 8 July 1981 see page 13, line 20 - page 14, line 12; claims 1,3-8 ---	1-8
A	US,A,4 918 120 (VANDERLAAN ET AL) 17 April 1990 see claims 1-14 --- -/--	1-8

° Special categories of cited documents : [10]

- "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
- "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 29 JANUARY 1993	Date of Mailing of this International Search Report -4. 02. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer DECOCKER L.

PCT/US 92/09076

International Application No

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 269 745 (NEUMANN) 26 May 1981 see abstract -----	1

Form PCT/ISA/210 (extra sheet) (January 1985)

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

US 9209076
SA 66088

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 29/01/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		SE-A- 7812970	06-07-79
		US-A- 4201826	06-05-80
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		JP-A- 56155218	01-12-81

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82