

# PATENT SPECIFICATION

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(21) Application No. 43076/76 (22) Filed 16 Oct. 1976

(23) Complete Specification Filed 12 Oct. 1977

(44) Complete Specification Published 8 Jul. 1981

(51) INT. CL.<sup>3</sup> C08L 67/06 33/06 35/02

(52) Index at Acceptance

C3M 109 153 160 202 C

C3Y B262 B284 F620

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## (54) PREPARATION OF POLYESTER RESIN/FIBRE LAMINATES AND COMPOSITIONS FOR USE THEREIN

(71) We, BRITISH INDUSTRIAL PLASTICS LIMITED, a Company organised under the laws of Great Britain, of 20 St. Mary's Parsonage, Manchester M3 2NL (formerly of 77 Fountain Street, Manchester M2 2EA), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the preparation of polyester resin/fibre laminates and compositions for use therein.

In the well known method of preparing such laminates, fibrous material is impregnated with a liquid composition comprising a solution of an unsaturated polyester resin in a volatile monomer such as styrene. Such monomers as styrene being relatively volatile liquids, the emission of monomer vapour from the resin presents an environmental problem.

We have now found that by adding certain polymeric materials to the resin solution the level of monomer vapour emission can be substantially reduced.

According to the present invention, there is provided a method of preparing a resin/fibre laminate by impregnating fibrous material with a liquid composition comprising a solution of an unsaturated polyester resin in a volatile monomer and forming the desired laminate from said impregnated material, in which method the polyester resin solution employed is thixotropic and incorporates an addition polymer of an alkyl, aryl or aralkyl ester of an unsaturated mono- or di-basic carboxylic acid, which polymer is partially incompatible (as herein defined) with said polyester resin solution, so that monomer vapour emission from said solution is substantially reduced.

In this specification the expression "partially incompatible" with the polyester resin solution is used to indicate a polymer which can be dissolved in the polyester resin solution but which will not yield a clear solution, i.e. giving a hazy solution, and will not separate out of the solution on standing.

Preferably the "partially incompatible" polymer is a polymer of an ester of an  $\alpha\beta$  unsaturated acid. Examples of such polymers which have been found particularly effective are the polymers of dibutyl fumarate, 2-ethyl hexyl acrylate, didecyl itaconate, hexyl methacrylate and butyl acrylate. On the other hand the polymer of methyl methacrylate is compatible with unsaturated polyester resin solutions and has been found ineffective to suppress vapour emissions from them.

Preferably the content of said partially incompatible polymer in the composition is in the range 0.001% to 10% by weight, and more preferably 0.01% to 1.0% by weight.

The polyester is not critical and may be any unsaturated polyester which can be utilized as a solution in liquid monomer.

The preferred ester polymers are formed by addition polymerization using the carbon-carbon unsaturation e.g. by heating the ester with a free-radical initiator such as a peroxide. The preferred polymer is poly (dibutyl fumarate).

According to another aspect of the invention, a composition suitable for use in the method earlier defined comprises a solution of an unsaturated polyester resin in a volatile monomer, said solution being thixotropic and incorporating an addition polymer of an alkyl ester of an  $\alpha\beta$ -unsaturated dibasic carboxylic acid, said polymer being partially incompatible (as herein defined) with said polyester solution, so that monomer vapour emission from said solution is substantially reduced.

It will have been noted that the resin solutions provided in this invention are thixotropic.

We have found that neither the addition of thixotropic additives alone nor the addition of a partially incompatible polymer alone to the polyester solution provides any significant suppression of monomer vapour emission. When the partially incompatible polymer is added to a thixotropic polyester solution the monomer vapour suppression effect can be considerable. The effect initially increases rapidly with thixotropic index as the latter is increased from 1.0, and the rate of increase in effect falls away with increasing thixotropy until at a thixotropic index of 2.2 to 2.4 there is very little difference. Thus the thixotropic index of the polyester resin solution is preferably at least 1.3.

The amount of volatile monomer in the polyester solution is generally of the order of 35 to 45 per cent by weight in solutions of this kind but may be as low as 20 per cent or as high as 60 per cent if desired.

The invention will now be described in more detail by means of the following Examples:-

#### *Example 1*

##### *i Preparation of The Polyester Resin*

An unsaturated polyester resin was prepared by condensing the following materials together at 200°C until a resin with an acid value of 30-50 mgms of KOH/g of solid resin was obtained.

1.545 moles ethylene glycol	
1.545 " propylene glycol	
2.0 " phthalic anhydride	
1.0 " Maleic anhydride	

The resin was dissolved in styrene to form a solution containing 57.5% by weight of resin and 42.5% by weight of styrene to which were added 0.008% by wt. of hydrogenated castor oil as thixotropic additive, and 0.15% by wt. of a promotor consisting of Cobalt Siccato (Trade Mark) containing 10% by wt. cobalt metal.

##### *ii Preparation of Poly (dibutyl fumarate) (PDBF)*

A polymer was prepared by heating dibutyl fumarate at 73-77°C in the presence of benzoyl peroxide until the product had a viscosity of 12 poise at 25°C the determination of viscosity being carried out on an 80% solution of the polymer in n-butyl alcohol.

##### *iii Styrene Emission Tests*

1000 g of the polyester resin were catalysed by the addition of 1.5% methyl ethyl ketone peroxide (SD2 grade ex Laporte Industries). The resin was then used to prepare a flat laminate 2.5' x 2.5' with a resin: glass ratio of 2:1 using 2 layers of 1½ oz chopped strand mat. The upper surface of the laminate was left exposed to the atmosphere. Five, twenty and thirty five minutes after preparation of the laminate had been completed, samples of air taken at a distance of 3" above the centre of the laminate were collected and analysed for styrene content. The method, which is described in "The Determination of Toxic Substances In Air" (published by W. Heffer and Sons Ltd. Cambridge) pages 181 and 182 involves absorption of the styrene into ethyl alcohol, followed by measurement of optical density of the solution using U.V. spectrophotometer. An average figure for the styrene content of air above the laminate was then calculated from the three determinations. This procedure was repeated using samples of resin containing different amounts of poly (dibutyl fumarate).

Two series of such tests were carried out. The results were as follows:

Series 1. Conducted at an ambient temperature of 22°C.

a. Polyester resin without PDBF	64.8 ppm styrene
b. Polyester resin + 0.1% by wt. PDBF	41.0 " "

This clearly illustrated the reduced styrene emission of the resin containing PDBF.

Series 2. Conducted at an ambient temperature of 27°C.

d. Polyester resin + 0.01% PDBF	62.1 pp styrene
e. Polyester resin + 0.1% PDBF	65.9 " "
f. Polyester resin + 1.0% PDBF	69.0 " "
g. Polyester resin + 0.1% dibutyl fumarate (monomer)	136.4 " "

In the second series of tests a sample of resin containing dibutyl fumarate monomer was included for comparison and it will be seen that the monomer does not have the styrene emission reducing qualities of the polymer,

It is believed that the increased styrene emission with increased PDBF content was caused by the presence of increasing amounts of Butanol which was being used as Solvent for the PDBF.

#### Example 2

This example includes comparative tests using poly(dibutyl fumarate) in conjunction with various unsaturated monomers.

##### i Preparation of polyester resins

The resins used in the work consist of 59.5, 64.2 and 56.2% solutions in styrene, methyl methacrylate and vinyl toluene respectively of the following materials condensed together at 200°C until a resin with an acid value of 20-27 mg KOH/g of solid resin was obtained.

Propylene Glycol	2.08 moles
Maleic anhydride	1.0 moles
Phthalic anhydride	1.0 moles

The resins contained 0.008% hydroquinone as inhibitor, 0.15% hydrogenated castor oil as thixotropic additive, and 0.15% of a promotor consisting of cobalt Siccator containing 10% cobalt metal.

##### ii Emission Tests

A simple emission test was carried out for the purpose of this Example. The procedure for this was as follows:

26 ± 0.3g of resin were poured into a standard metal dish of diameter 7.2 cm and depth 1.3 cm. Monomer was allowed to evaporate freely from the resin, the dish being reweighed at 10 minute intervals over a period of 60 minutes. This procedure was carried out in the following experiments weight losses being quoted after periods of 20, 40 and 60 minutes.

##### iii Experimental

For each polymer solution an emission test was carried out on a sample containing no suppressant additive, as a control, and the same test was carried out on a sample to which had been added poly (dibutyl fumarate) in an amount of 0.1 parts by weight per 100 parts by weight of resin solution.

The results are tabulated below in Table I.

TABLE I

Monomer Poly (dibutyl fumarate) added	Styrene		methyl methacrylate		Vinyl Toluene	
	NO	YES	NO	YES	NO	YES
Ambient temperature (°C)	24.5	24.5	24.5	24.5	23	23
Weight Loss (g) by monomer evaporation after 20 mins.	0.19	0.18	0.63	0.17	0.07	0.07
40 mins.	0.36	0.30	1.24	0.26	0.14	0.13
60 mins.	0.53	0.38	1.78	0.32	0.19	0.18

It will be noticed from these results that the effect of the suppressant is most marked with the most volatile monomer (methyl methacrylate) and only slight with the least volatile monomer (vinyl toluene).

#### Example 3

This example includes comparative tests to show the effect of various polymers as emission suppressants. The Emission test used followed the same procedure as that used in Example 2, and the polyester solutions used were all the same as the styrene solution prepared in Example 2.

For each possible suppressant three samples were emission tested at the same time under exactly the same conditions; a control containing no suppressant, an samples containing 0.1 parts by weight per 100 parts by weight of solution of suppressant polymer and its monomer respectively.

The results for each control and polymeric additive are given below in Table II. In every case it was found that the monomer was not useful as a suppressant.

TABLE II

Suppressant	Poly (2 ethyl hexyl acrylate)		Poly (didecyl)		Poly (hexyl methacrylate)	
Ambient temperature (°C)	22	22	19	19	18	18
Weight loss (g) by Styrene evaporation in 20 mins.	0.16	0.16	0.18	0.15	0.20	0.17
40 mins.	0.31	0.27	0.34	0.27	0.38	0.30
60 mins.	0.45	0.35	0.51	0.36	0.55	0.38

TABLE II (contd.)

Suppressant	Poly (ethylene glycol)		Poly (methyl methacrylate)		Polycapro lactone		Poly (butyl acrylate)	
Ambient temperature (°C)	27.5	27.5	27.5		26	26	2 =	2 =
Weight Loss (g) after 20 mins.	0.21	0.25	0.23		0.21	0.18	0.18	0.16
40 mins.	0.41	0.47	0.41		0.38	0.35	0.35	0.25
60 mins.	0.59	0.67	0.58		0.57	0.53	0.52	0.32

From Table II it can be seen that the poly (ethylene glycol) and poly (methyl methacrylate) were detrimental to styrene vapour emission rather than suppressing it as the polycaprolactone had almost no effect. All the other polymers had a suppressant effect. It was noted that the two polymers which were detrimental were compatible with the polyester resin/styrene solution as was the polycaprolactone. The effective polymers all gave a hazy solution in the polyester resin/styrene solution and were considered to be partially incompatible. The molecular weights of all the above polymers were relatively low those of the poly(ethylene glycol) and the poly(caprolactone) being 600 and 4000 respectively. The other polymers were made by heating their monomers at a temperature of 80°C in the presence of 1% Benzoyl peroxide. It was necessary to carry out the preparations of poly (2 ethyl hexyl acrylate) and poly(hexyl methacrylate) in the presence of a chain stopper in order to achieve controllable reactions. A 1% (by wt.) addition of stearyl mercaptan was found suitable for this purpose. The final viscosities (at 25°C) of the polymers obtained were as follows: poly (dibutyl fumarate) 145 poise; poly (2 ethyl hexyl acrylate) 30 poise; poly (didecyl itaconate) 3 poise; poly (hexyl methacrylate) 28 poise.

#### Example 4

This example includes tests aimed at quantifying the "partial incompatibility" of the various polymers tested above.

Sample solutions of styrene emission suppressants were prepared using the polyester resin/styrene solution described in Example 2, and adding suppressant at a concentration of 0.1 parts by weight to 100 parts by weight of polyester solution.

The haze developed in these resin samples was measured using the 'Jackson Candle Turbidimeter' cited in the American Public Health Association Publication, 'Standard Methods for the Examination of Water and Wastewater including bottom sediments and sludges'.

Two "Unicam SP600" (Trade Mark) cells are required for the test. One cell is filled with the test resin and the other with resin which contains no suppressant. The latter represents a blank. The cells are positioned in a Sp600 Spectrophotometer and the optical density of the

test resin measured at a light wavelength of 530 nm. The haziness is given in APHA units by multiplying the optical density by 133.

The table below lists the suppressants which have been examined in this work, together with a measure of the haziness developed when dispersed in the polyester resin/styrene solution. The table also includes details of the effectiveness of the various additives as styrene emission suppressants.

TABLE III

Suppressant	Suppressant Effectiveness	Haziness (APHA units)
Poly (dibutyl fumarate)	Effective	164
Poly (2 ethyl hexyl acrylate)	Effective	181
Poly (didecyl itaconate)	Effective	150
Poly (hexyl methacrylate)	Effective	138
Poly (butyl acrylate)	Effective	138
Poly (ethylene glycol)	Non-effective	0
Poly (methyl methacrylate)	Non-effective	0

These results show that all the additives which were effective to suppress styrene emission developed a haze whilst the ineffective polymers did not.

We conclude therefore that in the haziness test the haziness developed by effective polymers should be at least 120 APHA units. Totally incompatible polymers which separate out of the polyester resin/styrene solution are, of course, unsuitable for use in this invention since they would create unacceptable storage and handling problems for the polyester resin solution even if they were effective.

#### Example 5

This example demonstrates the significance of thixotropy in the polyester resin solutions of this invention.

Two solutions of the polyester resin used in Example 2 were made up. One, designated as solution N was non-thixotropic and consisted of a 59.5% solution of the resin in styrene containing 0.008% hydroquinone as inhibitor and 0.15% of a promotor consisting of cobalt siccato containing 10% cobalt metal.

The other, designated as solution T corresponded to solution N except that it was rendered thixotropic by the addition of 0.5% by weight of "Aerosil" (Trade Mark) and 0.2% by weight of dipropylene glycol.

Mixed samples of the solutions N and T were made up in various proportions to vary the degree of thixotropy of the sample and to each sample was added poly (dibutyl fumarate) in an amount of 0.1 parts by weight per 100 parts by weight of solution.

The viscosity of each sample was measured with a Brookfield viscometer (Model RVT), using spindle No.2 at 25°C, at 5 rpm and 50 rpm and the thixotropic index of each sample calculated using the formula

$$\text{Thixotropic Index} = \frac{\text{Viscosity at 5 rpm}}{\text{Viscosity at 50 rpm}}$$

Emission tests were then carried out on all the samples using the same procedure as in Example 2.

The results are tabulated below in Table IV.

TABLE IV

	<i>Sample formulation</i>							
5	Solution T	100	80	60	40	20	0	5
	Solution N	0	20	40	60	80	100	
	Poly (dibutyl fumarate)	0.1	0.1	0.1	0.1	0.1	0.1	
10	<i>Thixotropic properties</i>							10
	Viscosity @ 5rpm (poise)	18.8	14.8	10.4	6.4	3.6	2.8	
	Viscosity @ 50 rpm (poise)	7.76	6.8	5.8	4.56	3.6	2.88	
15	Thixotropic Index	2.4	2.2	1.9	1.4	1.0	1.0	15
	Weight loss by styrene evap. after 20 mins. (g)							
20	40 mins. (g)	0.18	0.18	0.19	0.22	0.22	0.22	20
	60 mins. (g)	0.28	0.29	0.30	0.35	0.39	0.40	
		0.36	0.36	0.38	0.43	0.53	0.56	
	Ambient Temperature (°C)							
25		23	23	23	23	23	23	25
	These results show that the styrene emission suppression effect of the poly (dibutyl fumarate) is increased as the thixotropic index increases.							
	Direct comparison of thixotropic solutions with and without the suppressant was afforded by a further experiment.							
30	In this case emission tests were carried out on five samples as follows (A) as control, the non-thixotropic solution N containing no suppressant, (B) solution T containing no suppressant (thixotropic index 1.94), (C) a thixotropic resin solution corresponding to solution T except that the aerosil and dipropylene glycol were replaced by 0.15% by weight of "Armogel" - a thixotropic additive consisting of hydrogenated castor oil - (thixotropic index 2.10), (D) and (E) corresponding to (B) and (C) respectively but each with the addition of 0.1 p.b.w. of poly (dibutyl fumarate) per 100 p.b.w. of solution.							30
35	These results are given below in Table V.							35

TABLE V

40	SAMPLE	A	B	C	D	E	40
	Weight loss (g) by evap. of styrene						
45	after 20 mins	0.24	0.26	0.26	0.21	0.21	45
	40 mins	0.45	0.57	0.53	0.32	0.33	
	60 mins	0.63	0.79	0.76	0.41	0.41	
The ambient temperature in each case was 25°C.							
50	It will be observed that the styrene emission of the thixotropic samples B and C containing no PDBF was worse than that of the non thixotropic control. The presence of PDBP in samples D and E reduces the styrene emission to well below the level of the control A.						50
A further comparative test showed that addition to the control sample A of 0.1 pwb of PDBF per 100 parts of solution had no suppressant effect on styrene emissions.							
55	The result is given below as follows, the ambient temperature being 26°C.						55

TABLE VI

<i>PDBF added</i>		NO	YES	
60	weight loss (g) by styrene evap. after 20 mins	0.25	0.24	60
	40 mins	0.42	0.44	
	60 mins	0.58	0.58	

## WHAT WE CLAIM IS:-

1. A method of preparing a resin/fibre laminate by impregnating fibrous material with a liquid composition comprising a solution of an unsaturated polyester resin in a volatile monomer, and forming the desired laminate from said impregnated material, in which  
5 method the polyester resin solution employed is thixotropic and incorporates an addition  
polymer of an alkyl, aryl or aralkyl ester of an unsaturated mono- or di-basic carboxylic acid  
which polymer is partially incompatible (as herein defined) with said polyester resin solution,  
so that monomer vapour emission from said solution is substantially reduced.
2. A method according to claim 1 in which the partially incompatible polymer is a  
10 polymer of an ester of an  $\alpha\beta$ -unsaturated acid.
3. A method according to Claim 2 in which said ester is an alkyl ester of an  $\alpha\beta\delta$   
unsaturated acid.
4. A method according to Claim 3 in which said alkyl group contains from 4 to 12 carbon  
atoms.
5. A method according to Claim 4 in which said ester is an ester of fumaric, itaconic,  
15 methacrylic or acrylic acid.
6. A method according to any one of preceding claims in which the content of said  
partially incompatible polymer in the composition is in the range 0.001% to 10% by weight of  
the composition.
7. A method according to Claim 6 in which the content of said polymer is in the range of  
20 0.01 to 1.0% by weight of the composition.
8. A method according to any one of the preceding claims in which the volatile monomer  
is styrene.
9. A method according to any one of the preceding claims in which the composition has a  
25 thixotropic index of at least 1.3.
10. A method according to any one of the preceding claims in which the amount of  
volatile monomer in the composition is in the range 20% to 60% by weight.
11. A method according to any one of the preceding claims in which the partially  
incompatible polymer is selected from polymers of di-butyl fumarate 2-ethyl hexyl acrylate  
30 didecyl itaconate hexyl methacrylate and butyl acrylate.
12. A composition suitable for use in the method of Claim 1 comprising a solution of an  
unsaturated polyester resin in a volatile monomer, said solution being thixotropic and  
incorporating an addition polymer of an alkyl ester of an  $\alpha\beta$ -unsaturated di-basic carboxylic  
acid, said polymer being partially incompatible (as herein defined) with said polyester resin  
35 solution, so that monomer vapour emission from said solution is substantially reduced.
13. A composition according to Claim 12 in which said partially incompatible polymer is  
a polymer of dibutyl fumarate or didecyl itaconate.
14. A method according to Claim 1 in which there is employed a polyester resin composi-  
tion substantially as described herein in the foregoing Example 1.
- 40 15. A method according to Claim 1 in which there is employed a polyester resin composi-  
tion substantially as described herein in any one of Examples 2 to 5.

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