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NEW ECOLOGICAL POLYESTER RESINS WITH STYRENE EVAPORATION SUPPRESSANT

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Introduction

Unsaturated polyester resins /UPR/ are solutions of unsaturated polyesters in styrene, which serves as crosslinking monomer. During the processing of UPR's in the manufacture of glass fibre reinforced polyesters / GRP/, considerable amount of styrene evaporates from the surface of glass mat or fabric, which is impregnated with UPR. Styrene evaporation takes place, in particular, in course of the manufacture of large-dimensional GRP products, e.g. boat hulls, by the hand-lay-up method.

Styrene concentration in the atmosphere of production rooms is limited by competent authorities.For example I present you this limits for a few countries. That concentration can be decreased by installing more intense ventilation. This leads, however, to higher air stream velocity above the surface of not yet gelled GRP, thus increasing the amount of evaporating styrene. In that way the amount of styrene, which is thrown out to the environment, increases considerably.

Another way of decreasing of styrene concentration in the production rooms and of the amount of styrene exhausted to the environment through ventilation ducts is the introduction of wax-like additives into the UPR. These additives are called Styrene Evaporation Suppressants /SES/.

General Remarks

The Styrene Evaporation form a very thin film on the surface of liquid UPR . The film is impermeable for styrene vapours. Paraffin and numerous waxes could be used as SES, if they would not deteriorate inter laminar adhesion in GRP products.

We developed a series of additives, which are used as SES. They have a very high styrene emission decreasing efficiency and still do not cause a decrease in inter laminar adhesion. The developed products are being used in Poland and abroad. One of most effective evaporation suppressant is polyhydroxyester on base aromatic epoxy resins and monocarboxylic acid (trade name STOPVOL).

On the picture I would like to present you general chemical formula of polymer that is a component of STOPVOL.

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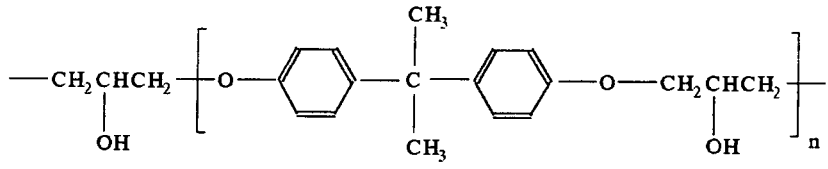
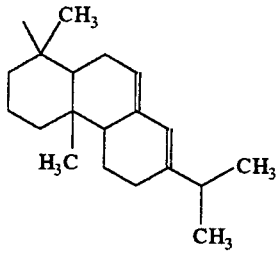
General formula:
BOOC-A-COOB'
where:

A:



n= 3 - 5

B:



B: CH_3-[-CH_2-]$_x$ x=16

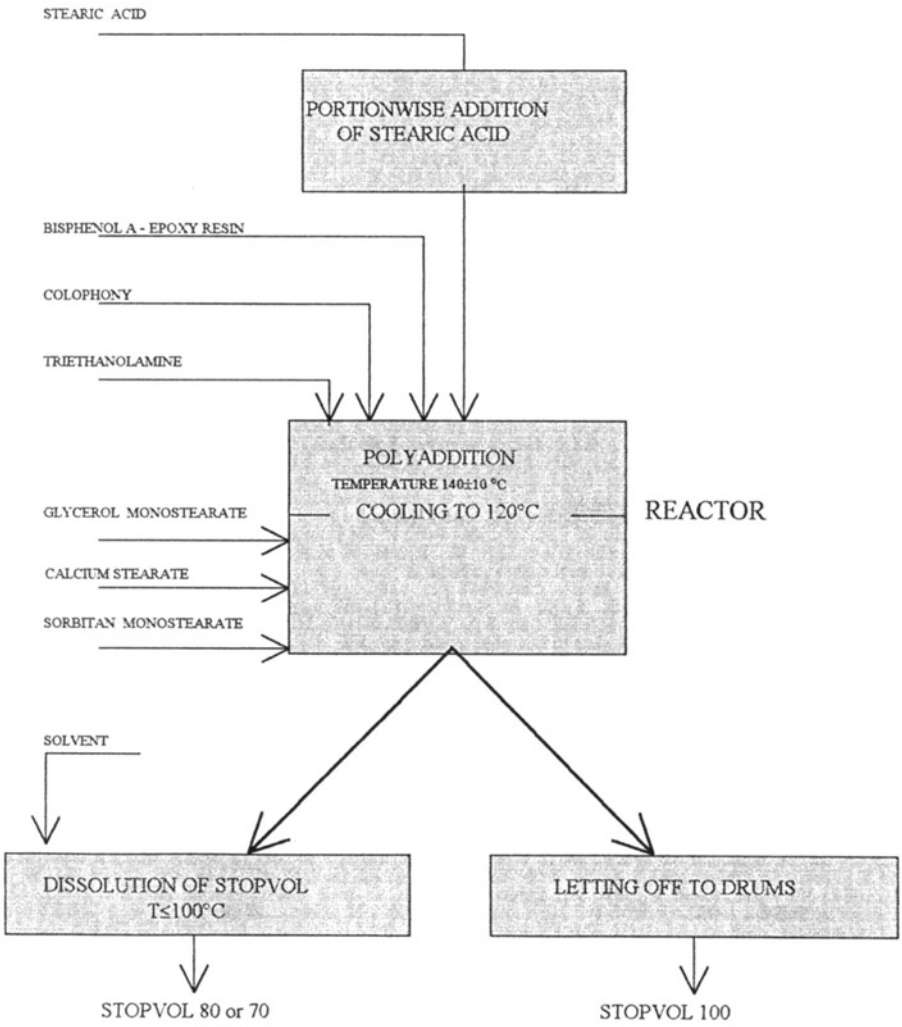
The weight fraction of this polymer is:

with n=3 30-45%
n=4 30-45%
n=5 20-45%

That SES is dissolved in UPR in the amount of 0,6-1,0% . It decreases styrene losses from an UPR at ambient temperature in lab tests by 95-99%. This means that the amount of evaporated styrene is about 2-10% of that from the same UPR without additive.

Manufacturing Process

Next picture describe scheme of manufacturing process of STOPVOL.



Specifications of raw materials

- Higher fatty acid
- Balmy colophony
- Bisphenol A - epoxy resin
- Catalyst
- Esters of higher fatty acids

Bisphenol A - epoxy resin, colophony and catalyst are

added in suitable proportions to a reactor equipped with a stirrer, thermometer and a reflux cooler.

The reactants in the reactor are heated progressively and nitrogen gas is flushed above the surface of the reaction mixture. After the reactans are melted and the temperature attains 90-100°C, the stirrer is switched on and stearic acid is added portionwise (3-5 portions).

The temperature of the reaction mixture within the limits of 140 ± 10^0 C. The reaction is run at this temperature with optional cooling applied during the exothermic process which occurs at the initial stage of the reaction.

In one hour from the completion of addition of stearic acid, the reaction mixture is sampled and acid number is determined. The determination is repeated every one hour. When the acid number falls below 10 , the process is considered to be completed.

Then the reactor contents is allowed to cool to 120±10°C and the following feeds are added in succession: esters of higher fatty acids.. At this temperature the process is continued for 2 hours with constant stirring and then the product is let off into drums.

When STOPVOL is used, a selected organic solvent (toluene, xylene, mineral spirit) is added to the reactor or the mixer in excess and dissolution is carried out at a temperature 100^0 C for 1 hour with constant stirring.

When the stirring period is nearing to an end, samples are withdrawn at the lower and the upper section of the mixer and viscosities of the samples are measured. The dissolution process is considered to have been completed after the product has been found to be homogeneous.

Next picture present you general chemical properties of STOPVOL with specification in conformity with adequate test methods.

Acid number
Melting point
Epoxy value
Average molecular weight

CHEMICAL PROPERTIES:

Property	Specification	Test Method
Acid number, mg KOH/g	max. 10	ISO 2114-74
Melting point (Boetius instrument), °C	53±5	ISO 3146-85
Epoxy value, val/100g	max. 0.01	ISO/DIS 3001
Average molecular weight, g/mol	800±100	VPO

Description of STOPVOL application

STOPVOL 1, i.e., a Styrene Evaporation Suppressant (S.E.S.) , is dissolved in Unsaturated Polyester Resin in amounts of 0,6 to 1,0% (wt).

Determination of styrene emission

Laboratory Test Method

Weigh at least three Petri dishes, Pour 50± 1g of S.E.S. free resin onto one dish and 50±1g of resin with S.E.S. addition into each of the remaining dishes and place the dishes into a laboratory ventilating hood.

Switch on the ventilator and allow air to flow above the surfaces of the resins in the dishes at a rate about 0,4 m/sec. at a temperature of 22± 3^0 C. In 60 min. reweigh the dishes.. Calculate the suppressing efficiency (E,%) of the S.E.S. agent as follows:

$$\text{Efficiency, \%} = \frac{L_1 - L}{L_1} \times 100$$

where: L_1 = weight loss of the resin sample without S.E.S. addition
L = weight loss of the resin sample with S.E.S. addition.

Table 1 show the results of STOPVOL efficiency studies in selected polyester resins after 1 hour. According this results we obtain a very high styrene emission decreasing efficiency - relative efficiency 97-98%.

Table 1. Results of STOPVOL efficiency studies in selected polyester resins after 1 hour.

Bench-scale studies carried out by methods described in the Chapter „Laboratory Test Method"

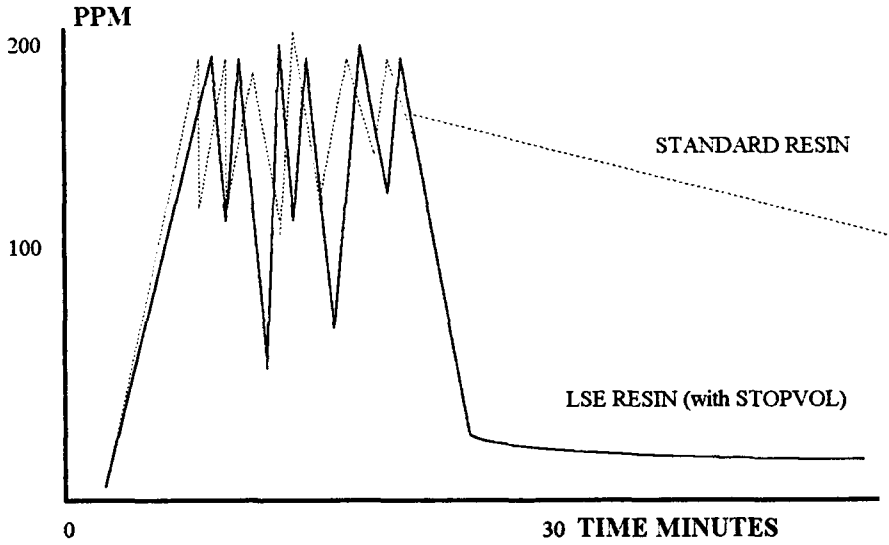
Resin	Additive	Additive, wt. parts / p.h.r.		Weight loss		Relative efficiency, %
		0.6	1.0	g/h	g/m^2h	
Maleic-isophthalic-propylenic	----	----	----	2.32	244.2	----
Maleic-isophthalic-propylenic	Stopvol 100		----	0.06	6.3	97.4
Maleic-isophthalic-propylenic	Stopvol 100	----		0.03	3.1	98.7
Maleic-isophthalic-propylenic	Stopvol 80	----		0.06	6.3	97.4
Maleic-orthophthalic-propylenic	----	----	----	2.49	262.0	----
Maleic-orthophthalic-propylenic	Stopvol 100		----	0.05	5.2	98.0
Maleic-orthophthalic-propylenic	Stopvol 100	----		0.04	4.2	98.4
Maleic-orthophthalic-propylenic	Stopvol 80	----		0.06	6.3	97.6

Air- borne Styrene Concentration at Industrial Workplace

To determine the concentration of styrene in the industrial workplace atmosphere, use any standard method approved in a given country.

For the determination, sample the air in a working room approximately at the height of the head of the operator performing impregnation by the manual lay-up method.

Next picture present you styrene emission during lamination GRP with ecological our resin in comparison the same GRP on base standard resin.



Typical styrene emission during lamination

Determination of interlaminar adhesion

The dynamic test methods used for the determination of interlaminar adhesion generally involve impact tests which are performed in different ways. The ICRI experience speaks in favour of the peel strenght qualitative test.

Test Method for Peeling Strength

Prepare the laminate to be tested by the manual lay-up method. Apply polyester resin which contains a hardener and an accelerator, but no glass fibre, with a brush onto a neutral polyester-glass laminate. For comparison, use the polyester resin with S.E.S. addition and the other one without the S.E.S. addition.

To prepare the layer, use 12% (wt) of the resin amount usually applied for preparation of a standard three - layer polyester-glass laminate. Allow 1 to 7 days to pass and then lay up thee layers of polyester-glass laminate, using the tested resin, i.e. one resin with S.E.S. addition and the other resin without S.E.S. addition. Laminate a polyethylene terephtalate (PET) film in between the glass fibre-free layer and the polyester glass laminate for 24 hrs at room temperature and then cure it up for 4 hrs at 60°C.

Peel the laminate manually by pulling the special film or use a suitable tool to separate easily the layers. Assess the separation surface visually (qualitatively) by referring to a five-degree scale.

On the table 2 I would like to present you the results of tests interlaminar adhesion GRP without additives, with our STOPVOL and for comparison - the same GRP with parafin. In conclusion - STOPVOL still do not cause a decrease in interlaminar adhesion.

Table 2. Test conditions: laminate layers examined at 24-hour intervals. Curing system: Ketonox, 2%; cobalt naphthenate (1%Co), 0.4%.

Composition used to prepare laminate	Split test
Maleic-phthalic-propylene (M-F-P) resin	1
M-F-P resin + paraffin, 0.1% by wt.	5
M-F-P resin + STOPVOL-100, 0.6% by wt.	1
M-F-P resin + STOPVOL-100, 1.0% by wt.	2

The five-degree scale was used above, where:

5 - complete delamination of layers
1 - very good adhesion of layers
2 - good adhesion of layers

Main direction of application of this ecological UPR and GPP are:
a/ shipbuilding (parts of boats),
b/ transportation means (benches for railway carriages),
c/ building industry and construction, electronics industry.

I would like to present you conclusions from our research and practical industrial wark.

1. The process of manufactured STOPVOL by addition aromatic epoxy resin and monocarboxylic acid reduced waste.

2. STOPVOL have a very high styrene emission decreasing efficiency.

3. STOPVOL do not cause a decrease in interlaminar adhesion of GRP.

4. We recommend our STOPVOL for orthophtalic, isophthalic and vinyl unsaturated polyester resins.

STOPVOL is the effective Styrene Evaporation Suppressant additive for this resins.

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