Title: PHENOLIC FOAMS AND PRODUCTION THEREOF

Abstract: A phenolic foam system comprises a resin blend of a resol type phenolic resin and a resorcinal modified Novolak-type resin, a blowing agent, an emulsifier/cell stabiliser and an acid catalyst. The resin blend typically comprises 60% of the resol type phenolic resin and 40% the resorcinal modified Novolak-type resin. The blowing agent is preferably a blend of perfluorinated triethylamine and cyclopentane.
BACKGROUND OF THE INVENTION

This invention relates to a phenolic foam system and method for its production.

Phenolic foams are used extensively as insulating material, for example, because of their excellent thermal stability, low toxicity and low smoke emission in a case of fire. The blowing agents traditionally used in these materials are chlorofluorocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs), however the use of these agents is unfavourable from an environmental standpoint, due to their ozone depleting potential (ODP). Although alternative blowing agents that are more environmentally friendly such as, for example, hydrocarbons and hydrofluorocarbons (HFCs) have been proposed, there is always a need for new blowing agents and phenolic foam systems to optimise production and quality of these insulants.
SUMMARY OF THE INVENTION

According to one aspect of the invention, a phenolic foam system comprises a resin blend of a resol type phenolic resin and a resorcinol modified Novolak-type resin, a blowing agent, an emulsifier/cell stabiliser and an acid catalyst. This is referred to as a two-component resin system.

The resin blend preferably consists of 40% to 70%, in particular 60% of the resol type phenolic resin and 30% to 60%, in particular 40% resorcinol modified Novolak-type resin.

The blowing agent preferably includes fluorinated aliphatic amines. It preferably consists of a blend of perfluorated aliphatic amines and a zero ODP rated blowing agent, such as n-pentane, isopentane, cyclopentane, hexane or Solkane 365 mfc, more preferably a blend of a perfluorated aliphatic amine and cyclopentane.

The perfluorated aliphatic amine is preferably perfluorated triethylamine.

According to a further aspect of the invention, a phenolic foam system comprises a conventional resol type resin suitable for foam production, a blowing agent as described for the two-component resin system, an emulsifier/cell stabiliser and an acid catalyst. This is referred to as a one-component resin system.

The blowing agent preferably consists of a blend of perfluorated triethylamine and a compound selected from the group consisting of n-pentane, isopentane, cyclopentane, hexane or Solkane 365 mfc, more preferably a blend of perfluorated triethylamine and cyclopentane.

The resol type phenolic resin may be a sulphonated resin, preferably sulfomethylated resol.
The resol type phenolic resin preferably has a phenol-formaldehyde ratio of from 1:1.7 to 1:2.75, most preferably of 1:2.5.

The resorcinol modified Novolak-type resin, when present, preferably has a 20% to 50% resorcinol content.

In the case of the resin blend, the acid catalyst is preferably based on phosphoric acid only and is employed at levels lower than in conventional one-resin foam processes.

According to another aspect of the invention, a method of producing a phenolic foam includes the step of curing a resin comprising a resol type phenolic resin and a resorcinol modified Novolak-type resin in the presence of an emulsifier/cell stabiliser, a blowing agent and an acid catalyst.

The blowing agent is preferably a blowing agent as defined for the two-component resin system.

The phenolic foam is preferably derivable from a phenolic foam system comprising about 60 parts resol type phenolic resin, about 40 parts resorcinol modified Novolak-type resin, about 3 parts emulsifier/cell stabiliser, about 6.5 parts blowing agent and about 4.5 parts acid catalyst.

According to yet another aspect of the invention, a method of producing a phenolic foam comprises curing a conventional resol type resin suitable for foam production in the presence of a blowing agent as defined above, preferably a blend of perfluorated triethylamine and cyclopentane, an emulsifier/cell stabiliser and an acid catalyst.
DETAILED DESCRIPTION OF THE INVENTION

In order to obtain a phenolic foam with a low thermal conductivity value, good mechanical properties and low corrosivity, a balanced system between resin, blowing agent, emulsifier/cell stabiliser and acid catalyst is essential.

It has been known that water compatible resol resins with relatively high viscosities (3000 to 10000 m Pa.s at ±80% non-volatile content) are particularly suitable for the production of phenolic foams. Most technologies use alkali or earth alkali hydroxide catalysed resols with a phenol/formaldehyde ratio between 1:1.4 and 1:2.5. The water content in the resin is usually between 10% and 20% as a portion of the water can be replaced by suitable solvents which can also act as plasticisers in the final product.

Conventional resol based phenolic foams are made from a single component resin. It has been found that when a resin blend comprising a resol type phenolic resin, with a high phenol/formaldehyde ratio, and a water compatible resorcinol modified Novolak is used, a highly reactive mixture is formed that results in the production of foams with a low corrosion potential. This is due to the high reactivity of resorcinol based resins with formaldehyde and methylol groups present in resols, which decreases the amount of acid catalyst required to obtain a satisfactory curing speed of the foam mixture. Another advantage of the two-component system over the single-component system is that the viscosity profile of the foam mixture can be better controlled during the initial phase of the foaming process. Maintaining high foam mixture viscosities during the initial phase increases the stability of cell structures thereby producing a better foam. Due to the high reactivity of the two-component system, catalysts based on phosphoric acid only are used, and the catalyst levels employed can be lower than in conventional single-component resin systems.
Resols used for the manufacture of conventional foams have to be produced to specified acid reactivity levels in order to allow for the production of good quality, uniform foam products. The change of acid reactivity that occurs with these resins on ageing is often problematic. In the two-component system of the invention, the acid reactivity of the resol component is not of great importance, as only the reactivity of the resorcinol modified Novolak needs to be taken into consideration and this reactivity is unaffected by ageing. This aspect obviously simplifies foam production as the changes in the resol component on ageing have very little effect on the quality of the resulting foams.

As has previously been mentioned, CFCs and HCFCs have been used traditionally as blowing agents, but these are being phased out for environmental reasons. These are being replaced by hydrocarbons and hydrofluorocarbons, for example. It has now been found that the quality of phenolic foams can be enhanced by using these newer zero ODP rated blowing agents in combination with fluorated aliphatic amines, in particular perfluorinated triethylamine, in a blowing agent blend.

In order to demonstrate the efficacy of the invention, phenolic foams were prepared by blending a resol type phenolic resin and a resorcinol modified, water compatible Novolak-type resin with an emulsifier/cell stabiliser, an acid-based catalyst and a blowing agent. The foam mixture was then placed into a mould in which the foaming and curing process occurred at elevated temperatures.

(A) RESIN PREPARATION

RESOL RESIN

Resols with a high phenol / formaldehyde ratio (1:1.7 to 1:2.75) are suitable for the dual resin foam process of the invention.
The following phenolic resol, with a phenol / formaldehyde ratio of 1:2.5, was prepared in the conventional way using triethylamine as a catalyst.

**Procedure:**

Phenol (1 mol) was reacted with (91% grade) paraformaldehyde (2.5 moles) using an aqueous 10% triethylamine solution as a catalyst (catalyst level – 18% on phenol charged). The reaction mixture was heated to 65°C and was kept at this temperature for 1 hour. The temperature was then raised to 85°C and the poly-condensation process was continued at this temperature until the specified viscosity was reached.

**Properties of Resol:**

- Solid Content - ± 80%
- Viscosity @ 25°C - ± 6000 m Pas

**RESORCINOL MODIFIED NOVOLAK-TYPE RESIN**

Water compatible, Novolak-type resins with a resorcinol content between 20 to 50% are suitable for the dual resin foam system of the invention.

The following resin with a phenol / resorcinol / formaldehyde ratio of 1:1:1.2 was selected.

**Procedure:**

Phenol (1 mol) was reacted with (91% grade) para-formaldehyde (1.2 moles) using triethylamine as catalyst (1.5% by weight on phenol charged). The reaction mixture was heated to 65°C and was kept at this temperature for 1 hour. The reaction temperature was then raised to reflux which was kept until the specified viscosity (± 2500 m Pa's) was reached. Water was then added (32% by weight on phenol charged) followed by resorcinol (1 mol). The resorcinol was dissolved at 65°C. Lactic acid (85% grade) was
added once the resorcinol was dissolved (5.8% by weight on phenol charged) and the reaction temperature was slowly raised to reflux. The resin was kept at reflux until the specified viscosity was reached.

Properties of Resin:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Content</td>
<td>± 80%</td>
</tr>
<tr>
<td>Viscosity @ 25°C</td>
<td>± 6000 m Pa's</td>
</tr>
<tr>
<td>Water Tolerance at 25°C</td>
<td>± 70%</td>
</tr>
</tbody>
</table>

The two resins described above were used for all the foams produced for these evaluations.

(B) BLOWING AGENTS

The following products are examples of zero ODP rated blowing agents which could be used in combination with aliphatic fluorated amines, specifically perfluorated triethylamine, for the manufacture of phenolic foam insulants:

- n-pentane, iso-pentane, cyclo-pentane
- Hexane
- Solkane 365 mfc
- (1.1.1.3.3 Pentafluorobutane).

(C) EMULSIFIERS/CELL STABILISER

Non-ionic tensides are the products of choice for phenolic foam processes. These surfactants aid the formation of a stable blowing agent emulsion in the resin / acid blend. They also stabilise the cells which form when the blowing agent droplets present in the foaming blend start to evaporate and form minute gas bubbles.

The following products were found to be the most effective:
Dow Corning 193 Surfactant
This product is described as a silicone – polyoxyalkylene copolymer.

Tween-60 ex ICI
P O E (20) Sorbitan mono stearate

Eumulgin HRE-60 ex Henkel (Cognis)
(PEG 60 hydrogenated castor oil)

Eumulgin HRE-60 was selected for manufacturing the foam samples that have been evaluated.

LAB FOAM PRODUCTION

The two resins described were blended with the surfactant and blowing agent followed by the acid catalyst. The well-mixed foaming blend was then transferred into a heatable steel mould lined with polyethylene foil.

The initial mould temperature was set to 45°C. This temperature was slowly raised to 90°C at which the curing of the foam occurred within approximately 1.5 hours. The foam blocks were removed immediately after cooling. The size of the foam blocks produced was 230 x 230 x 215 mm.

Approximately 550 g of the following foam mixture was used per block for the four foam samples evaluated. The samples were identical but for the addition of increasing amounts of perfluorated triethylamine in the samples 2, 3 and 4, respectively.

Standard Composition of Foam Blend:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resol Resin</td>
<td>60</td>
</tr>
<tr>
<td>Novolak-Type Resin</td>
<td>40</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>3</td>
</tr>
</tbody>
</table>
Blowing Agent 6.5 parts
Catalyst (Phosphoric Acid 80%) 4.5 parts

Composition of Blowing Agents Used For the Four Foam Samples:

Sample 1  cyclo-pentane only
Sample 2  +0.5% PFTEA* on total foam mix
Sample 3  +1.0% PFTEA* on total foam mix
Sample 4  +1.5% PFTEA* on total foam mix

* perfluorated triethylamine

EVALUATION RESULTS

<table>
<thead>
<tr>
<th>Foam Ref. No.</th>
<th>Sample No. 1</th>
<th>Sample No. 2</th>
<th>Sample No. 3</th>
<th>Sample No. 4</th>
</tr>
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<tbody>
<tr>
<td>Density kg/m³ of Dry Foam</td>
<td>39.6</td>
<td>39.5</td>
<td>38.7</td>
<td>39.9</td>
</tr>
<tr>
<td>Compressive Strength kN/m²</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• parallel to rise</td>
<td>±170</td>
<td>±240</td>
<td>±255</td>
<td>±240</td>
</tr>
<tr>
<td>• perpendicular to rise</td>
<td>±170</td>
<td>±225</td>
<td>±215</td>
<td>±225</td>
</tr>
<tr>
<td>* Thermal Conductivity K-Value (W/mk)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 days after manufacture stored at 25°C</td>
<td>0.0282</td>
<td>0.0271</td>
<td>0.0187</td>
<td>0.0158</td>
</tr>
<tr>
<td>20 days after manufacture stored at 25°C</td>
<td>0.0291</td>
<td>0.0279</td>
<td>0.0192</td>
<td>0.0160</td>
</tr>
<tr>
<td>After 10 days stored at 70°C</td>
<td>0.0287</td>
<td>0.0275</td>
<td>0.0230</td>
<td>0.0167</td>
</tr>
</tbody>
</table>

* An Anacon TCA Point 2 thermal conductivity analyser was used to measure the above K-values.
From the tabulated evaluation results it can be seen that the quality of the cell structure of the foam samples is directly proportional to the levels of PFTEA present in the foam mixtures. It can be seen that samples 2, 3 and 4 all significantly outperformed sample 1 in terms of compressive strength. In addition, with increasing amounts of perfluorated triethylamine added, thermal conductivities also improved. Sample 1 provided unacceptable thermal conductivity values, and the material appeared coarse and crumbly. Whilst sample 2 had a much better compressive strength than sample 1, its K-values were not much better than those for sample 1. Samples 3 and 4 both showed improved K-values, although the K-value stability of sample 3 was not as good as that for sample 4. Sample 4 provided the best overall results. The slight decrease in the compressive strength (parallel to rise) in sample 4 as compared to sample 3 can be seen as a result of the greater flexibility of the foam, due to a further improvement of its cell structure. It has been established that foam properties can be further improved if higher proportions of cyclo pentane are replaced by PFTEA, particularly the fire ratings of these foams are upgraded significantly.

Whilst the above results relate to a two-component resin foam system, it is believed that the foam properties derived from one-component resol resin foam systems will also be upgraded by using perfluorated triethylamine modified blowing agents. Likewise, it is believed that the advantages of the two-component system could also be employed using a different type of blowing agent, although the blowing agent blend of the invention is preferred.
CLAIMS

1. A phenolic foam system comprising a resin blend of a resol type phenolic resin and a resorcinol modified Novolak-type resin, a blowing agent, an emulsifier/cell stabiliser and an acid catalyst.

2. A phenolic foam system according to claim 1, wherein the resin blend comprises 40% to 70% of the resol type phenolic resin and 30% to 60% of the resorcinol modified Novolak-type resin.

3. A phenolic foam system according to claim 2, wherein the resin blend comprises 60% of the resol type phenolic resin and 40% of the resorcinol modified Novolak-type resin.

4. A phenolic foam system according to any one of the preceding claims, wherein the blowing agent includes a fluorinated aliphatic amine.

5. A phenolic foam system according to claim 4, wherein the blowing agent comprises a blend of a perfluorated aliphatic amine and a zero ODP rated blowing agent.

6. A phenolic foam system according to claim 5, wherein the zero ODP rated blowing agent is selected from the group comprising n-pentane, isopentane, cyclopentane, hexane and Solkane 365 mfc.

7. A phenolic foam system according to claim 6, wherein the blowing agent comprises a blend of a perfluorated aliphatic amine and cyclopentane.

8. A phenolic foam system according to claim 7, wherein the perfluorated aliphatic amine is perfluorated triethylamine.

9. A phenolic foam system according to any one of the preceding claims, wherein the resol type phenolic resin is a sulphonated resin.
10. A phenolic foam system according to claim 9, wherein the resol type phenolic resin is sulfomethylated resol.

11. A phenolic foam system according to any one of the preceding claims, wherein the resol type phenolic resin has a phenol-formaldehyde ratio of from 1:1.7 to 1:2.75.

12. A phenolic foam system according to claim 11, wherein the resol type phenolic resin has a phenol-formaldehyde ratio of from 1:2.5.

13. A phenolic foam system according to any one of the preceding claims, wherein the resorcinol modified Novolak-type resin has a 20% to 50% resorcinol content.

14. A method of producing a phenolic foam including the step of curing a resin comprising a resol type phenolic resin and a resorcinol modified Novolak-type resin in the presence of an emulsifier/cell stabiliser, a blowing agent and an acid catalyst.

15. A method according to claim 14, wherein the phenolic foam is derived from a phenolic foam system comprising about 60 parts resol type phenolic resin, about 40 parts resorcinol modified Novolak-type resin, about 3 parts emulsifier/cell stabiliser, about 6.5 parts blowing agent and about 4.5 parts acid catalyst.

16. A method according to claim 14 or claim 15, wherein the blowing agent comprises a blend of perfluorated triethylamine and cyclopentane.

17. A method of producing a phenolic foam including the step of curing a resol type resin suitable for foam production in the presence of a blowing agent comprising a blend of perfluorated triethylamine and cyclopentane, an emulsifier/cell stabiliser and an acid catalyst.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C08J9/14 C08L61/06

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J C08L

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)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<th>Category</th>
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<tr>
<td>X</td>
<td>DE 25 49 441 A (CIBA GEIGY AG) 13 May 1976 (1976-05-13) page 3, paragraph 2 page 6, paragraph 1-3 page 7, line 11 - line 12 page 12, table 1 claims 1,13,16</td>
<td>1-3, 4-10,16,17</td>
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<td>Y</td>
<td>US 5 187 206 A (MAURER WALTER ET AL) 16 February 1993 (1993-02-16) claims 1,6 column 10, line 25 - line 43 column 11, line 3 - line 40</td>
<td>4-10,16</td>
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**X** Further documents are listed in the continuation of box C.

**X** Patient family members are listed in annex.

* Special categories of cited documents:

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

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  *L* document which may throw doubt 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

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**Date of the actual completion of the international search**

13 January 2005

**Date of mailing of the international search report**

21/01/2005

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentiarum 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-0040, Te: 31 651 epo nl, Fac: (+31-70) 340-3016

**Authorized officer**

Milli, S
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Form PCT/SA210 (continuation of second sheet) [January 2004]
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