

**Claims**

1. A phenolic foam comprising a phenolic resin comprising a plurality of cells, said cells comprising a blowing agent comprising:  
 at least one hydrofluoroolefin and at least one chlorinated hydrofluoroolefin;  
 5 and said blowing agent further comprising at least one C<sub>3</sub>-C<sub>6</sub> hydrocarbon;  
 wherein said phenolic foam has a density of from 10 kg/m<sup>3</sup> to 100 kg/m<sup>3</sup>, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA<sub>0.2MJ</sub> of 150 W/s or less, when measured according to EN13823.
- 10 2. The phenolic foam according to claim 1, wherein said foam has a FIGRA<sub>0.2MJ</sub> of 125 W/s or less, such as 120 W/s or less, or 110 W/s or less, or 100 W/s or less, or 95 W/s or less, or 90 W/s or less, or 85 W/s or less, when measured according to EN13823.
- 15 3. A phenolic foam comprising a phenolic resin comprising a plurality of cells, said cells comprising a blowing agent comprising at least one chlorinated hydrofluoroolefin and at least one hydrofluoroolefin, and at least one C<sub>3</sub>-C<sub>6</sub> hydrocarbon, wherein said phenolic foam has a density of from 10 kg/m<sup>3</sup> to 100 kg/m<sup>3</sup>, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA<sub>0.4MJ</sub> of 80 W/s or less, when measured according to EN13823.
- 20 4. The phenolic foam according to any preceding claim, wherein said foam has a FIGRA<sub>0.4MJ</sub> of 80 W/s or less, such as 75 W/s or less, or 65 W/s or less, or 60 W/s or less, or 55 W/s or less, when measured according to EN13823.
- 25 5. The phenolic foam according to any preceding claim, wherein said foam has a total heat release of 7.5 MJ or less, such as 7.0 MJ or less, or 6.5 MJ or less, or 6.25 MJ or less, or 6.0 MJ or less, or 5.75 MJ or less, or 5.5 MJ or less, or 5.25 MJ or less, or 5.15 MJ or less, or 5.0 MJ or less, or 4.8 MJ or less, or 4.6 MJ or less, or 4.4 MJ or less, when measured according to EN13823.

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6. The phenolic foam according to any preceding claim, wherein said foam has a closed cell content of 90% or more, such as 95% or more, preferably 98% or more, as determined in accordance with ASTM D6226.
- 5 7. The phenolic foam according to any preceding claim, wherein the cells of the foam have an average cell diameter in the range of from 50 to 250  $\mu\text{m}$ , preferably in the range of from 80 to 180  $\mu\text{m}$ .
8. The phenolic foam according to any preceding claim, wherein said foam has a  
10 thermal conductivity of 0.020 W/m·K or less, suitably of 0.018 W/m·K or less, preferably 0.0175 W/m·K or less, or 0.0170 W/m·K or less, or 0.0165 W/m·K or less, 0.0162 W/m·K or less when measured at a mean temperature of 10°C, in accordance with EN 13166:2012.
- 15 9. The phenolic foam according to any preceding claim, said foam having a limiting oxygen index of 34% or more, preferably 35% or more, suitable 36% or more, such as 37% or more as determined in accordance with ISO 4589-2.
10. The phenolic foam according to any preceding claim, wherein said foam has a  
20 stable moisture content of from 3% to 5% by weight when determined at  $(23 \pm 2)^\circ\text{C}$  and a relative humidity of  $(50 \pm 5)\%$  in accordance with EN1249:1998.
11. The phenolic foam according to any preceding claim, wherein the at least one chlorinated hydrofluoroolefin is selected from 1-chloro-3,3,3-trifluoropropene(HCFO-  
25 1233zd) and 1-chloro-2,3,3,3-tetrafluoropropene (HCFO-1224yd).
12. The phenolic foam according to any preceding claim, wherein the at least one hydrofluoroolefin comprises 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz).
- 30 13. The phenolic foam according to any preceding claim, wherein the hydrocarbon comprises at least one butane, preferably isobutane, and/or at least one pentane, preferably isopentane.

14. A phenolic foam formed by foaming and curing a phenolic resin foamable composition comprising a phenolic resin, a surfactant, an acid catalyst, and a blowing agent, said blowing agent comprising:
- 5 at least one hydrofluoroolefin and at least one chlorinated hydrofluoroolefin,  
and said blowing agent further comprising at least one C<sub>3</sub>-C<sub>6</sub> hydrocarbon;
- wherein said phenolic foam has a density of from 10 kg/m<sup>3</sup> to 100 kg/m<sup>3</sup>, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA<sub>0.2MJ</sub> of 150 W/s or less (preferably 125 W/s or less, 120 W/s or less, or 110 W/s or less, or 100 W/s or less, or 95 W/s or less, or 90 W/s or less, or 85 W/s or less) when measured according to EN13823.
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15. The phenolic foam according to claim 14, wherein the at least one chlorinated hydrofluoroolefin is selected from 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) and 1-chloro-2,3,3,3-tetrafluoropropene (HCFO-1224yd).
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16. The phenolic foam according to any preceding claim, wherein the at least one hydrofluoroolefin comprises 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz).
17. The phenolic foam according to any preceding claim, wherein the at least one C<sub>3</sub>-C<sub>6</sub> hydrocarbon comprises at least one butane, preferably isobutane, and/or at least one pentane, preferably isopentane.
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18. The phenolic foam according to any preceding claim, wherein the blowing agent comprises 1-chloro-3,3,3-trifluoropropene and/or 1-chloro-2,3,3,3-tetrafluoropropene and 1,1,1,4,4,4-hexafluoro-2-butene.
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19. The phenolic foam according to any one of claims 14 to 18, wherein the phenolic resin has a weight average molecular weight of from about 700 to about 2000, and/or wherein the phenolic resin has a number average molecular weight of from about 330 to about 800, such as from about 350 to about 700.
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20. The phenolic foam according to any one of claims 14 to 19, wherein the phenolic resin has a molar ratio of phenol groups to aldehyde groups in the range of from about 1:1 to about 1:3, suitably from about 1:1.5 to about 1:2.3.

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21. The phenolic foam according to any one of claims 14 to 20, wherein the water content of the phenolic resin foamable composition is in the range of from about 5 wt% to 12 wt%, such as from 6 wt% to 10 wt%, based on the total weight of the phenolic resin foamable composition.

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22. The phenolic foam according to any one of claims 14 to 21, wherein the phenolic resin has a water content in the range of from about 10 wt% to about 14 wt%.

23. The phenolic foam according to any one of claims 14 to 22, wherein the phenolic resin has a viscosity of from about 2,500 mPa·s to about 18,000 mPa·s when measured at 25°C, such as from about 2500 mPa·s to about 16,000 mPa·s when measured at 25°C for example from about 4,000 mPa·s to about 8,000 mPa·s when measured at 25°C.

24. The phenolic foam according to any one of claim 14 to 23, wherein the blowing agent is present in an amount of from about 1 to about 20 parts by weight per 100 parts by weight of the phenolic resin.

25. The phenolic foam according to any preceding claim having a compressive strength in the range of from about 95 kPa to about 200 kPa as determined in accordance with EN826.

26. The phenolic foam according to any preceding claim having a density of from about 15 kg/m<sup>3</sup> to about 60 kg/m<sup>3</sup>, such as from about 20 kg/m<sup>3</sup> to about 50 kg/m<sup>3</sup>, suitably of from about 24 kg/m<sup>3</sup> to about 48 kg/m<sup>3</sup>.

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27. A method for manufacturing a phenolic resin foam comprising foaming and curing a foamable composition comprising a phenolic resin, a surfactant, an acid catalyst, and a blowing agent, said blowing agent comprising at least two hydrofluoroolefins each of said two hydrofluoroolefins having a thermal conductivity of 0.0125 W/m·K or less, and  
5 at least one C<sub>3</sub>-C<sub>6</sub> hydrocarbon, to form a phenolic resin foam having a density in the range of from 10 kg/m<sup>3</sup> to 100 kg/m<sup>3</sup>, a closed cell content of at least 85% as determined in accordance with ASTM D6226, and a FIGRA<sub>0.2MJ</sub> of 150 W/s or less, when measured according to EN13823.

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28. A composition comprising:  
at least one chlorinated hydrofluoroolefin selected from HCFO-1233zd and HCFO-1224yd,  
a hydrofluoroolefin, wherein the hydrofluoroolefin is HFO-1336mzz; and  
15 a hydrocarbon, wherein the hydrocarbon is isopentane;  
wherein said at least one chlorinated hydrofluoroolefin is present in an amount of about 72 wt% to about 92 wt%,  
the HFO-1336mzz is present in an amount of from about 5 wt% to about 15 wt%; and  
the isopentane is present in an amount of from about 4 wt% to about 25% such as about  
20 20 wt% based on the total weight of the composition.

29. The composition of claim 28, wherein the chlorinated hydrofluoroolefin is present in an amount of from 72 wt% to 82 wt%, the HFO-1336mzz is present in an amount of from 8 wt% to 14 wt% and the isopentane is present in an amount of from 8 wt% to 18  
25 wt%.

30. A foamable composition comprising a polymeric resin or prepolymer and the composition of claim 28 or 29.

30 31. A thermoset foam formed by foaming and curing the foamable composition according to claim 30.