

Phenolic foam and method of manufacture thereof

Field

- 5 **[0001]** The present invention relates to phenolic foams and methods of manufacture thereof. The phenolic foams of the present invention have excellent reaction and resistance to fire performance in combination with excellent thermal insulation performance.

Background

- 10 **[0002]** The Paris Agreement aims to keep the increase in global average temperatures to below 2°C above pre-industrial levels. Reducing energy consumption is vital to achieve this goal. The construction of energy efficient buildings, and retrofitting existing buildings to make them energy efficient is necessary to decrease the energy required to maintain such buildings. Thermal insulation materials are key to reducing the energy
15 consumption requirements of buildings.

- [0003]** A wide variety of thermal insulation materials are commercially available for a myriad of applications including roofing systems, building panels, building facades, flooring systems and cold storage applications. The selection of the most appropriate type of insulation product for a given application involves assessment of a number of
20 criteria, for example, insulation properties (i.e. thermal conductivity), compressive strength, dimensional stability, water resistance, fire performance, thickness of the insulation product, and expected lifetime of the insulation product. For example, vacuum insulation panels have excellent thermal insulation performance and a lifetime of up to about 20 years, however, generally speaking they are not very robust, and if the outer
25 envelope is perforated, their insulation ability is significantly reduced. Accordingly, they are used in cold storage applications such as refrigerators, where they are protected from perforation by a refrigeration unit liner. The use of vacuum insulation panels in other applications where the risk of perforation is greater - during installation and/or in use - such as in cavity walls is less common.

- 30 **[0004]** Wrapping a building in a building envelope, or facade is an efficient way to protect the building from the elements, to insulate the building, and such building methodology affords significant scope for design expression.

[0005] Accordingly, using insulation materials having excellent fire performance is highly advisable in building façades. Desirably, the insulation products in building facades should combine excellent thermal insulation performance with excellent fire performance.

- 5 [0006] Aerogels are materials that combine good fire performance with excellent insulating properties. However, the cost of these products is currently relatively high and therefore the widespread use of aerogels, particularly in building applications, is not currently commercially viable.

- 10 [0007] Man-made mineral wool (MMMW) insulation materials have excellent fire performance, however, closed cell polymeric foams have superior thermal insulation performance. Consequently in order to achieve a given U-value, the thickness of a MMMW insulation product, will usually be significantly greater than that of a closed cell polymeric foam.

- 15 [0008] Closed cell insulation materials like polyurethane / polyisocyanurate (PUR/PIR), extruded polystyrene (XPS) and phenolic foams (PF) offer superior insulation values in comparison to MMMW. Closed cell polymeric foams are formed by expanding a blowing agent, which generally has a low thermal conductivity, in a polymeric resin or pre-polymeric reactants which will react to form a polymeric resin. The foam cells contain the blowing agent, whose low thermal conductivity imparts excellent insulating properties
- 20 to the foam. The closed cell structure of the foam ensures these gases cannot escape from the product.

[0009] A scanning electron microscopy photograph of a typical closed cell structure of a phenolic foam is shown in Figure 1.

- 25 [0010] Historically, phenolic resins have been the preferred thermosetting resins to use for foam insulation requiring low toxicity, low smoke emission and self-extinguishing capability in a fire situation. Phenolic foams are known to combine excellent fire performance with superior thermal insulation values at a commercially viable cost price, without requiring flame retardants additives which may be deleterious in terms of toxicity. In contrast, foams such as PIR or XPS have inferior fire performance which precludes
- 30 their use in certain applications, and in order to meet minimum fire performance standards in other applications, the use of significant levels of flame retardants are required.

[0011] While improved fire performance can be achieved by using flame retardants (FRs), the use of flame retardants is sometimes not preferred. This is due to various

concerns. One main concern is that flame retardants may have other undesired effects on the foam.

5 [0012] For example some flame retardants (FRs), in particular liquid flame retardants, may plasticise foam cells. Plasticising foam cells can lower foam compressive strength particularly at higher ambient temperature. Plasticising foam cells may allow low thermal conductivity blowing agent within the foam cells to diffuse out of the foam cells thus adversely affecting the thermal conductivity of the foam. Such effects are experienced with phenolic foams and liquid flame retardants.

10 [0013] Some solid flame retardants, particularly micronized flame retardants tend to adversely affect foam thermal conductivity with time. This depends on the chemical nature of the particular flame retardant, and the amount of it added to the foamable composition.

[0014] There is also a concern about toxicity of some flame retardants.

15 [0015] Hence, when a flame retardant is added to an insulating foam, this is done as a compromise between improved fire performance but with the acceptance that the improved fire performance is achieved with a deleterious effect on thermal insulation performance and also with the acceptance that there are now toxicity concerns because of the presence of the flame retardant.

20 [0016] The most important chemical families of flame retardants are those based on bromine, chlorine, phosphorus, nitrogen, antimony, certain metal salts and hydrates of inorganic hydroxides.

25 [0017] A flame retardant should inhibit or even suppress the combustion process. Flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of the burning process, e.g. during heating, ignition, flame spread, or decomposition of a material.

30 [0018] As blowing agent (which may be flammable) may be released from foam cells at a temperature in excess of the blowing agent boiling point temperature for example at 100°C or higher, flame retardants need to function around this temperature also. Some flame retardants, for example, aluminium trihydrate, have higher decomposition temperatures at which they release their water of hydration content, and as such the flammable blowing agent will be released before the flame retardancy effect of the flame retardant can be effected. For this reason, such a flame retardant will have only a limited effect in reducing the spread of the flames and the reaction to fire.

[0019] Many common flame retardants are brominated compounds. Some brominated products can have a negative environmental and health impact, and are now being phased out by various environmental initiatives worldwide. Accordingly, it would be desirable to have alternative insulation products which have excellent insulation performance and fire performance which do not require the use of such brominated flame retardants.

[0020] Figure 2 shows heat release development as a function of time in a real fire situation. The risk of casualties in a fire can be reduced if the initial area where heat release is fuel controlled can be extended. In the case of buildings comprising façades, the façade construction and the materials used therein, can significantly impact fire growth.

[0021] To determine the fire performance of insulation materials, a wide range of fire tests have been developed. The main issue with these tests is that there is limited correlation between the performances of a material in many of these fire tests with the actual fire performance of the material in a real fire. The main reason is that the intensity of the heat is very difficult to simulate on a smaller scale. Examples of standardized small-scale fire tests include EN13823, ISO 13785-1, ISO 21367 and PN-B-02867. Standardized large scale fire tests include DIN 4102-20, ISO 9705, SP105, BS8414-1, MSZ 14800-6, LePIR-II, JIS A 1310 and NFPA 285.

[0022] The fire behaviour of a closed cell insulation material can be categorized into two categories, namely: "reaction to fire" and "resistance to fire". The first category is an indicator of the rate at which a fire spreads after a material is ignited by a heat source. The second category indicates the resistance against fire propagation through the foam insulation material.

[0023] When a closed cell foam is exposed to a heat source, the temperature of the gas inside the foam cells will increase. As the temperature increases, the volume of the gas increases leading to increased pressure in the cells and ultimately, the cell walls will rupture with the release of the cell gas.

[0024] When the blowing agent in the cell gas is flammable, the gas released from the product will ignite and generate heat. This effect can accelerate the spread of a fire, reducing the time between the initial ignition and the full development of the fire.

[0025] The rupture of the cell walls can start to occur at temperatures of above about 100°C, causing the formation of combustible decomposition gases from the chemical foam matrix.

[0026] The release of flammable blowing agent, and its subsequent combustion increases the temperature of the foam matrix, and accelerates its decomposition. This results in an increased rate of fire propagation.

5 [0027] Polyurethane, polyisocyanurate and phenolic laminate foams are generally manufactured with a surface protection layer called a facer. Fire resistant facers can delay the release of cell gas in the very early stages of a fire. Gas tight facers which are applied to a foam core are particularly efficacious at protecting the foam core in a fire. Examples of gas tight facers include (unperforated) aluminium foil and steel sheet facers.

10 [0028] For polyisocyanurate foams for example, aluminium foils with a thickness of around 30 microns (in some cases even up to 200 microns) may be used as facers on polyisocyanurate foam cores, to improve the fire performance of the insulation product.

15 [0029] For phenolic foams however, these gas tight facers are not generally used in the production process, because water which is generated during the phenolic resin condensation polymerization process needs to be removed, to avoid the formation of voids in the foam matrix. A gas tight facer which is applied during foam manufacture would prevent such water removal. Gas tight facers can be applied to a phenolic foam after the water is removed in the production process, by secondary bonding but this is cost inefficient.

20 [0030] In many fire performance standard test methods, products are tested without removal of the facer. However, the use of a facer will only help to prevent the spread of the fire in the case of a limited heat/ignition source, for example a trash can which has caught fire. The ability of a facer to prevent or stem the spread of a more developed fire is limited. In relation to the resistance to fire, facers will not offer protection because an aluminium foil will burn away in a matter of seconds.

25 [0031] The presence of the facer on a polymeric foam can skew the outcome of the performance of the foam in a small-scale fire test, to an extent which does not translate to the performance of the foam in a large-scale test. Accordingly, the most realistic approach which simulates a foam insulation product's performance in an actual fire, is to test the foam core instead of the complete insulation product which includes the facer.
30 The most reliable approach to obtain a realistic assessment of the performance of an insulation product including the facer is probably to conduct a large-scale fire test. The disadvantage of these large-scale fire tests is that they are very expensive, and conducting such tests is time consuming. Furthermore, there is a limited availability of suitable test rigs for carrying out such tests.

[0032] A wide variety of small scale and large-scale fire tests are being used to simulate actual fire performance.

[0033] Examples of laboratory fire tests are the "Cone Calorimeter Heat Release test" (ISO 5660-1), "the Limiting Oxygen Index" (LOI) test (ISO 4589-2), "the Heat of Combustion" test (ISO 1716) and the "Ignitability of Products Subjected to Direct Impingement of Flame test" (ISO 11925-2).

[0034] The problem with most of these laboratory scale fire tests is there is a very limited correlation with the fire performance of a material tested in such a laboratory test, to its actual fire performance in a large-scale fire test, or indeed in a real fire situation. Firstly, in some of these experiments, the product is not exposed to a flame but to an alternative heat source. Secondly the power of the heat source is much lower compared to an actual fire situation.

[0035] For example, in test method EN ISO 11925-2, "Reaction to fire tests - Ignitability of building products subjected to direct impingement of flame - Part 2: Single-flame source test", the product to be tested is exposed to a small flame that is comparable to a cigarette lighter flame. The foam, facer and edges of the insulation product are exposed to this flame for 15 to 30 seconds. The flame height should be smaller or equal to 150 mm. Due to the small flame used in this test, the correspondence with the product's performance in an actual fire situation is limited.

[0036] In the Limiting Oxygen Index test (LOI) ISO 4589-2, a small test sample is supported in a vertical glass column and a slow stream of known composition oxygen/nitrogen mixture is introduced into the glass column. The upper end of the sample is ignited and the specimen is observed for the duration of the burning and the burn length of the specimen is noted. The calibrated mixture of oxygen and nitrogen is varied and the test is continued with additional specimens until the minimum concentration of oxygen (as a percentage) that will just support combustion is found. The higher the LOI, the lower the flammability. Air contains approximately 21% oxygen and therefore any material with an LOI of less than 21% will probably support burning in an open-air situation.

[0037] The LOI value is a basic property of the material but provides insufficient information about how the material will actually react to burning in an open atmosphere. The LOI test has no direct relationship with an actual fire where materials ignite. The LOI test only studies extinguishing behaviour in an oxygen rich (or deficient) gas mixture with nitrogen.

[0038] Notwithstanding the foregoing, large scale fire testing and some small-scale fire tests such as EN13823, ISO 13785-1, ISO 21367 and PN-B-02867 provide much more reliable information with respect to the fire performance of a product in a real fire situation.

- 5 **[0039]** A particularly useful evaluation method to assess the fire performance of an insulation material in a real fire situation is the Single Burning Item (SBI) test (EN13823). This test method involves measuring flame spread length, average rate of heat release (HRR_{av}), total heat release (THR) after “t” seconds, propensity to produce flaming drips and the rate of smoke production (SPR). The test procedure simulates the performance
10 of insulation products fixed to the walls and ceiling of a small room where the single burning ignition source in the corner of the room is a nominal 30 kW heat output. The burner is comparable to a waste-paper basket on fire in the corner of a room. Accordingly, EN13823 is a test method which simulates a real fire situation and thus provides very useful information regarding the fire performance of an insulation material
15 in a real fire situation.

- [0040]** The performance of the specimen is evaluated for an exposure period of 20 minutes. During the test, the heat release rate (HRR) is measured by using oxygen consumption calorimetry. The smoke production rate (SPR) is measured in the exhaust duct based on the attenuation of light. The fall of flaming droplets or particles is visually
20 observed during the first 600 seconds of the heat exposure on the specimen. Lateral flame spread is also measured.

- [0041]** The fire performance of a material is assessed in EN13823 by monitoring the rate of fire growth and the rate of smoke production after threshold values for the average heat release rate, total heat release rate, average smoke production rate and total smoke
25 production rate have been exceeded beyond defined reference values in the specification.

- [0042]** The fire performance classification parameters of the SBI test are fire growth rate index (FIGRA), lateral flame spread (LFS), and total heat release at 600 seconds (THR_{600s}). Additional classification parameters are defined for smoke production as
30 smoke growth rate index (SMOGRA) and total smoke production at 600 seconds (TSP_{600s}), and for flaming droplets and particles according to their occurrence during the first 600 seconds of the test.

[0043] It will be appreciated that the SBI test is very different from a test where there is a simple total calorific value test. A total calorific value is expressed over the full

duration of the test and the maximum heat generated during that test. In particular the calorific value does not correlate to values obtained by SBI testing such as values obtained by FIGRA testing.

5 **[0044]** The performance of closed cell thermal insulation foams in the SBI test varies considerably, depending inter alia on the chemical type of foam resin being tested, the type of blowing agent retained in the foam and the presence or absence of flame retardants.

10 **[0045]** The Euroclass system for evaluation of the fire performance of building materials involves the classification of building materials into seven classes based on their reaction-to-fire properties. The classes are as follows: A1, A2, B, C, D, E and F. The Euroclass system classifies the fire performance of materials based on their performance in several standard test methods including: EN ISO 11925-2; EN13823; EN ISO 1716 and EN ISO 1182. Products in the Euroclass “A” classes include inorganic and ceramic products with little or no organic material. Examples of products in the
15 Euroclass B class include gypsum boards with thin facing materials. The classification of closed cell insulation products varies depending on the nature of the organic polymer resin from which the foam is formed, the type of blowing agent and the presence or absence of flame retardants. As outlined above, the phenolic resin matrix of a phenolic foam is inherently less flammable than the resin matrices in polystyrene, polyurethane
20 or polyisocyanurate foams. While achieving Euroclass “A” classification for closed cell foams formed from thermoset or thermoplastic resins may not be possible, it would be desirable to provide closed cell foams achieving Euroclass “B” or as a minimum Euroclass “C” classification, which also deliver excellent thermal insulation performance. These and other desires are solved by the present invention.

25 **[0046]** In this respect it is important to note that there are clear differences between “reaction to fire” and “resistance to fire”. In particular a material with good “reaction to fire” properties does not necessarily have a good “resistance to fire” and *vice versa*.

[0047] While specific standard tests are described herein the difference between the two can be considered in simple conceptual terms as follows.

30 **[0048]** “Resistance to fire” is a measure of the time which is needed for a fire to burn the insulation material away. This aspect of a fire is of interest when there is a fire in a room and the time to reach the next room is of importance. Take the example of two rooms separated by a wall insulated with a phenolic foam. The first room is on fire and the second room is occupied by people. The fire resistance of the wall construction will

determine how long it will take until the wall construction perishes. This time is of interest because it will give people the time to leave the building without being harmed.

5 [0049] "Reaction to fire" however is a different measure which indicates how fast the fire spreads. This aspect of a fire is the rate at which the fire propagates. So take the example where a trash bin catches fire and sets the room on fire. When people are present in the room a slow fire propagation rate is important as it will give people the time to leave the room. In relation to foam insulation material, reaction to fire is a very important property.

10 [0050] As an example in general the resistance to fire for PIR foams is very good as the product forms a very tight char layer. However the reaction to fire is relatively poor. For this reason PIR foams are not preferred for facades for example, but are a relative good solution for other applications where reaction to fire is not so critical, for example in flat roof application.

15 [0051] So there remains a need to provide a foam insulation which has improved, such as preventative and restricting, properties in a reaction to fire test. In the present application reaction to fire properties are determined by SBI, in particular FIGRA tests.

Summary of the Invention

20 [0052] In one aspect, the present invention provides a phenolic foam formed from a foamable phenolic resin composition, and a blowing agent,

the phenolic foam comprising 1 to 5 % by weight of red phosphorus based on the weight of the phenolic foam wherein said phenolic foam has a density of from 10 kg/m³ to 100 kg/m³, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA_{0.2MJ} of 120 W/s or less, when measured according to EN13823 and a thermal conductivity of 0.023 W/m.K or less, at 10°C, in accordance with EN 13166:2012. Desirably the phenolic foam has a thermal conductivity of 0.20 W/m.K or less, at 10°C, in accordance with EN 13166:2012.

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[0053] The present invention provides closed cell foams which can achieve Euroclass "B" or as a minimum Euroclass "C" classification, which also deliver excellent thermal insulation performance. This is a substantial step forward as increases in fire performance often comes with a loss in insulation performance as discussed above.

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5 [0054] The red phosphorus not only acts as a flame retardant it may also act as a formaldehyde scavenger. For example in a foam of the invention the formaldehyde emissions from the foam may be up to 50% lower as compared to a control foam which is the same phenolic foam without any red phosphorus particles being present in the foam. Such emissions are tested in accordance with EN16516.2017.

10 [0055] The use of a blowing agent in the production of a phenolic foam, is generally a negative factor in relation to the reaction to fire. The current invention overcomes this issue, for a phenolic foam which includes a very effective flame retardant. This is particularly so in combination with a specified density and/or specified moisture content. Such foams have especially good reaction to fire.

15 [0056] The foam suitably has a density of from about 15 kg/m³ to about 60 kg/m³, such as from about 20 kg/m³ to about 50 kg/m³, suitably of from about 24 kg/m³ to about 48 kg/m³. In particular it has been found that a foam having a density such as from 34.5 kg/m³ to 40 kg/m³; such as from 35 kg/m³ to 39 kg/m³, for example from 36 kg/m³ to 38 kg/m³ gives desirable fire performance for example in relation to reaction to fire. Such densities give desirable fire performance for example a FIGRA_{0.2MJ} value of 120 W/s or less, when measured according to EN13823.

20 [0057] Without wishing to be bound by any theory the densities set out above such as those with densities above 34.5 kg/m³ have cell walls which are sufficiently strong to withstand the rapid increase of the cell pressure in the first stage of a fire. When a foam product is exposed to a flame, the temperature will increase rapidly with an increase in cell pressure as result. The cells in the foam only have a limited ability to withstand this pressure increase. The stronger the cell walls, the longer they can resist the pressure. Rupture of the cell walls will have an important contribution to the flame spread with
25 blowing agent compositions which are flammable. Rupture of the first cells will trigger a domino effect as the heat released by ignition of the cell gas will potentially destroy a new series of cells. On the other hand higher densities are undesirable as the higher mass will negatively impact thermal performance.

30 [0058] A phenolic foam of the invention may comprise 2 to 5 parts by weight of red phosphorus based on 100 parts by the weight of the cured phenolic foam. For example it may comprise 3 to 4 parts by weight of red phosphorus based on 100 parts by the weight of the cured phenolic foam.

[0059] The blowing agent may comprise at least one of the following:

at least one saturated or unsaturated C₃-C₆ hydrocarbon;

at least one saturated or unsaturated C₃-C₆ compound that is substituted at least once by one or more of fluorine and chlorine for example isopropyl chloride.

[0060] Desirably the blowing agent comprises at least one of isopropyl chloride or a saturated C₃-C₆ hydrocarbon such as pentane for example isopentane.

5 **[0061]** A foam of the invention may have a FIGRA_{0.2MJ} of 110 W/s or less, for example 100 W/s or less, such as 90 W/s or less when measured according to EN13823.

[0062] A phenolic foam of the invention may comprise 2 to 4 parts by weight of red phosphorus based on 100 parts by weight of the phenolic foam. Unless otherwise stated all references to the phenolic foam refer to the final cured product.

10 **[0063]** Desirably the blowing agent comprises at least one of hydrofluoroolefin or chlorinated hydrofluoroolefin.

[0064] The blowing agent may comprise at least one of the following:

at least one saturated or unsaturated C₃-C₆ hydrocarbon;

15 at least one saturated or unsaturated C₃-C₆ compound that is substituted at least once by one or more of fluorine and chlorine for example isopropyl chloride.

[0065] For example the blowing agent may comprise a blend of at least one of hydrofluoroolefin or chlorinated hydrofluoroolefin with a C₃-C₆ hydrocarbon such as pentane for example isopentane.

20 **[0066]** A foam of the invention may have a FIGRA_{0.2MJ} of 100 W/s or less, for example 90 W/s or less, such as 80 W/s or less, such as 70W/s or less when measured according to EN13823.

[0067] A foam of the invention desirably has a compressive strength of at least 95kPa.

25 **[0068]** In a foam of the invention it is desirable that the red phosphorus is in particulate form for example micronized form. For example the red phosphorus may be in particulate form with a number average particle size in the range from 0.5 µm to 10 µm for example as observed by scanning electron microscopy. See **Figure 5** which is a representative SEM image of a phenolic foam with red phosphorus particles dispersed therein and having the number average particle size set out above and present in the amount stated above.

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[0069] Desirably each of the at least one hydrofluoroolefin and the at least one chlorinated hydrofluoroolefin have a thermal conductivity of 0.0135 W/m.K or less at 10°C.

5 **[0070]** The present invention provides a foam that incorporates a flame retardant that does not have major toxicity concerns, that improves fire performance but does not compromise the insulation performance of the foam. Red phosphorus can act in both gas and condensed phases at the same time.

10 **[0071]** It has been surprisingly found that the presence of 2 to 5 % by weight of red phosphorus of particle size 0.5 to 10 µm pre-dispersed in phenolic resin prior to the addition of surfactant, blowing agent and acid catalyst, reduces fire growth rate (FIGRA) whilst maintaining stable foam thermal conductivity. The red phosphorus has relatively low oral toxicity, LD50 is 15,000mg/kg in rats.

15 **[0072]** The red phosphorus may have a coating layer on its surface. The red phosphorous may have a coating layer comprising a metal oxide and/or metal hydroxide and/or a resin. Suitably the coating may comprise a phenol resin such as a phenol formaldehyde resin. Suitably the coating may comprise aluminium hydroxide. Desirably the red phosphorus has a coating layer comprising phenol formaldehyde and/or aluminium hydroxide. In the invention, the red phosphorus used may have different coatings, but preferred coatings, including those on the red phosphorous of the
20 Examples below, are phenol formaldehyde and/or aluminium hydroxide.

[0073] Suitably, each of the at least one hydrofluoroolefin and the at least one chlorinated hydrofluoroolefin have a thermal conductivity of 0.0125 W/m.K or less. For example, each of the at least one hydrofluoroolefin and the at least one chlorinated hydrofluoroolefin have a thermal conductivity of 0.0125 W/m.K or less at 25°C.

25 **[0074]** The foam may have 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.

30 **[0075]** The foam desirably 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.

[0076] The cells of the foam may have an average cell diameter in the range of from 50 to 250 µm, such as in the range of from 80 to 180 µm.

[0077] Suitably, the foam has a thermal conductivity of 0.020 W/m·K or less, suitably of 0.018 W/m·K or less, desirably 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.

- 5 **[0078]** The foam may have a limiting oxygen index of 34% or more, preferably 35% or more, suitably 36% or more, such as 37% or more as determined in accordance with ISO 4589-2.

[0079] Suitably, the foam has a stable moisture (water) content of from 3% to 5% by weight added when determined at 23 (± 2)°C and a relative humidity of 50 (± 5)% in
10 accordance with EN12429:1998 - Thermal insulating products for building applications: conditioning to moisture equilibrium under specified temperature and humidity conditions.

[0080] If stable moisture content exceeds 5% there is a risk of thermal conductivity of the foam increasing with age in application. If the stable moisture content is below 3%,
15 then FIGRA may increase. So an optimum stable moisture content of phenolic foam can assist in obtaining low FIGRA without compromising low thermal conductivity over an extended time period in its insulation application.

[0081] The at least one chlorinated hydrofluoroolefin may be selected from 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) and 1-chloro-2,3,3,3-tetrafluoropropene
20 (HCFO-1224yd).

[0082] The HCFO-1233zd may be the E or Z isomer, or a mixture thereof, i.e. the HCFO-1233zd may be HCFO-1233zd(E), HFCO-1233zd(Z) or a mixture thereof. For example, the HCFO-1233zd may comprise 90 wt.% or more (such as 95 wt.% or more) HCFO-1233zd(E), or the HCFO-1233zd may comprise 90 wt.% or more (such as 95
25 wt.% or more) HCFO-1233zd(Z). Desirably, the HCFO-1233zd comprises 95 wt.% or more HCFO-1233zd(E).

[0083] The HCFO-1224yd may be the E or Z isomer, or a mixture thereof, i.e. the HCFO-1224yd may be HCFO-1224yd(E), HFCO-1224zd(Z) or a mixture thereof. For example, the HCFO-1224yd may comprise 90 wt.% or more (such as 95 wt.% or more) HCFO-1224yd(E), or the HCFO-1224yd may comprise 90 wt.% or more (such as 95wt.%
30 or more) HCFO-1224yd(Z). Desirably, the HCFO-1224yd comprises 95wt.% or more HCFO-1224yd(Z).

[0084] The at least one hydrofluoroolefin desirably comprises 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz). The HFO-1336mzz may be the E or Z isomer, or a mixture

thereof, i.e. the HFO-1336mzz may be HFO-1336mzz(E), HFO-1336mzz(Z) or a mixture thereof. For example, the HFO-1336mzz may comprise 90wt.% or more (such as 95wt.% or more) HFO-1336mzz(E), or the HFO-1336mzz may comprise 90wt.% or more (such as 95wt.% or more) HFO-1336mzz(Z). Desirably, the HFO-1336mzz
5 comprises 95wt.% or more HFO-1336mzz(Z). The at least one alkyl halide may for example comprise isopropyl chloride.

[0085] The at least one (saturated) C₃-C₆ hydrocarbon may comprise butane, for example isobutane, and/or pentane, desirably isopentane.

[0086] The at least one unsaturated C₃-C₆ hydrocarbon may comprise butene and/or
10 pentene.

[0087] Suitably, each blowing agent used has a thermal conductivity of 0.0125 W/m.K or less at 25°C. If a blend of blowing agents is used then it will be appreciated that one or more blowing agents in that blend may not have a thermal conductivity of 0.0125 W/m.K or less at 25°C. In such a case it is desirable that the blend used has a thermal
15 conductivity of 0.0125 W/m.K or less at 25°C.

[0088] Suitably the at least one hydrofluoroolefin or at least one chlorinated hydrofluoroolefin or the at least one alkyl halide or the at least one chlorinated alkene wherein each of the at least one hydrofluoroolefin or the at least one chlorinated hydrofluoroolefin or the at least one alkyl halide or the at least one chlorinated alkene
20 have a thermal conductivity of 0.0125 W/m.K or less at 25°C; and the at least one C₃-C₆ hydrocarbon are blended. For example, the blowing agent components i.e. the at least one hydrofluoroolefin, the at least one chlorinated hydrofluoroolefin, the at least one alkyl halide or the at least one chlorinated alkene and the at least one C₃-C₆ hydrocarbon may be blended prior to being mixed with the phenolic resin.

[0089] The present invention also provides a phenolic foam formed by foaming and curing a phenolic resin foamable composition comprising a phenolic resin, a surfactant, an acid catalyst, a blowing agent, and 2 to 5 % by weight of red phosphorus based on the weight of the phenolic foam, wherein said phenolic foam has a density of from 10 kg/m³ to 100 kg/m³, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA_{0.2MJ} of 120 W/s or less (such as
30 110 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 and wherein the phenolic foam has a thermal conductivity of 0.023 W/m.K or less, at 10°C, in accordance with EN 13166:2012.

[0090] The blowing agent may comprise at least one hydrofluoroolefin and at least one chlorinated hydrofluoroolefin; and said blowing agent further comprising at least one C₃-C₆ hydrocarbon.

5 [0091] The at least one chlorinated hydrofluoroolefin may comprise 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) and/or 1-chloro-2,3,3,3-tetrafluoropropene (HCFO-1224yd).

[0092] The at least one hydrofluoroolefin may comprise 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz).

10 [0093] The at least one C₃-C₆ hydrocarbon may comprise butane, preferably isobutane, and/or pentane, preferably isopentane.

[0094] Suitably, 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.

15 [0095] The phenolic resin suitably 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.

20 [0096] Suitably, 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. The phenol may be a substituted phenol such as cresol. Naturally occurring phenols may be used including naturally occurring phenolic macromolecules. Other aldehydes may be used including dialdehydes such as glyoxal. The molar ratio above may be adjusted to take account of aldehyde functionality

[0097] The water content of the phenolic resin foamable composition may be in the range of from about 5 wt.% to 12 wt.%, such as from 5 wt.% to 10 wt.%, for example 7 to 10% wt.% based on the total weight of the phenolic resin foamable composition.

25 [0098] The phenolic resin used to form the phenolic resin foamable composition of the present invention, may have a water content in the range of from about 7.5 wt.% to about 14 wt.% i.e. in its uncured state.

30 [0099] The phenolic resin may have a viscosity of from about 2,500 mPa·s to about 18,000 mPa·s when measured at 25°C, such as from about 3500 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.

[00100] The blowing agent is suitably present in an amount of from about 5 to about 20 parts by weight per 100 parts by weight of the phenolic resin.

[00101] The phenolic foam of the present invention may further comprise an inorganic filler. For example, calcium carbonate may be added, as a filler and/or to increase pH. The higher pH value of the foam ensures less residual acid, with benefits for example that metallic material in contact with the phenolic foam is at reduced risk of corrosion.

5 The calcium carbonate may be added to the foamable composition forming the phenolic foam of the invention.

[00102] The invention concerns a phenolic foam that contains 2 to 5 parts by weight of micronized (0.5 μ m to 10 μ m particle size) red phosphorus flame retardant present in 100 parts of the cured phenolic foam which results in foam insulation products having

10 excellent fire resistance properties, and low smoke emissions defined by FIGRA (0.2MJ threshold) <150W/s and SMOGRA <20 m²/s², stable insulation performance (<0.023 W/m.K), and a high closed foam cell content, (>85%). A further aspect of the invention is that the presence of 2 to 5 parts by weight of micronized (0.5 to 10 μ m particle size) red phosphorus flame retardant present in 100 parts by weight of the phenolic foam

15 results in phenolic foam insulation products having reduced formaldehyde emissions from phenolic foam articles by 30 to 60% as measured by EN717-1 / EN16516 / ISO16000-11.

[00103] The foam may have a compressive strength in the range of from about 95 kPa to about 200 kPa as determined in accordance with EN826.

20

Brief Description of the Drawings

[00104] Figure 1 shows a scanning electron micrograph of a closed cell phenolic foam.

[00105] Figure 2 shows heat development as a function of time in a real fire situation

[00106] Figure 3 is a schematic of the SBI test set-up of EN13823.

25 [00107] Figure 4 shows the impact of temperature on the thermal conductivity (λ value) of phenolic foams blown with three different weight ratio blends of 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) and isopentane.

[00108] Figure 5 is a representative SEM image of a phenolic foam with red phosphorus particles dispersed therein and having the number average particle size set out above

30 and present in the amount stated above. This foam is the same as that of Example 3 below.

Definitions

[00109] The phrase “at least one X selected from the group consisting of A, B, C, and combinations thereof” is defined such that X includes: “at least one A” or “at least one B” or “at least one C”, or “at least one A in combination with at least one B”, or “at least one A in combination with at least one C” or “at least one B in combination with at least one C” or “at least one A in combination with at least one B and at least one C”.

[00110] The phrase “Y may be selected from A, B, C and combinations thereof” implies Y may be A, or B, or C, or A+B, or A+C, or B+C, or A+B+C.

[00111] The term “blowing agent” is defined as the propelling agent employed to blow the foamable composition for forming a foam. For example, a blowing agent may be employed to blow/expand a resin to form a foam.

Properties

[00112] Suitable testing methods for measuring the physical properties of phenolic foam are described below.

15 (i) Foam Density:

This was measured according to BS EN 1602:2013 - Thermal insulating products for building applications - Determination of the apparent density.

(ii) Thermal Conductivity of the Foam:

20 A foam test piece of length 300 mm and width 300 mm was placed between a high temperature plate at 20°C and a low temperature plate at 0°C in a thermal conductivity test instrument (LaserComp Type FOX314/ASF, Inventech Benelux BV). The thermal conductivity (TC) of the test pieces was measured according to EN 12667: “Thermal performance of building materials and products - Determination of thermal resistance by means of guarded hot plate and heat flow meter methods, Products of high and medium thermal resistance”.

(iii) Thermal Conductivity of the Foam after Accelerated Ageing:

30 This was measured using European Standard BS EN 13166:2012 - “Thermal insulation products for buildings - Factory made products of phenolic foam (PF)” - Specification Annex C section 4.2.3. The thermal conductivity is measured after exposing foam samples for 25 weeks at 70°C and stabilisation to constant weight at 23°C and 50% relative humidity. This thermal ageing serves to provide an estimated thermal conductivity for a period of 25 years at ambient temperature. Alternatively, aged thermal

conductivity may be measured after exposing foam samples for 2 weeks at 110°C and stabilisation to constant weight at 23°C and 50% relative humidity.

(iv) pH:

The pH was determined according to the standard BS EN 13468.

5 (v) Closed cell Content:

The closed cell content may be determined using gas pycnometry. Suitably, closed cell content may be determined according to ASTM D6226 test method.

(vi) Foam Friability:

Friability is measured according to test method ASTM C421 – 08(2014).

10 (vii) Imaging Foam

A piece of foam was roughly cut measuring approximately 20 mm x 10 mm from one coated surface to the other. From this piece, the surfaces were trimmed with a razor blade to approximately 8 mm square. The foam was then snapped sharply to reveal a clean surface and most of the sample was removed to leave a thin (~1 mm) slice.

15 The slice was fixed onto an aluminium sample stub using a double sided conducting sticky tab.

The samples were then given a thin (~2.5 Angstroms) conducting coat of gold/palladium using a Bio-Rad SC500 sputter coater. The reason for coating the sample is (a) to add a conducting surface to carry the electron charge away and (b) to increase the density to give a more intense image. At the magnifications involved in this study the effect of the coating is negligible.

20 The samples were imaged using an FEI XL30 ESEM FEG Scanning Electron Microscope under the following conditions: 10kV accelerating voltage, working distance ~10mm, spot size 4, and Secondary Electron Detector. Images were saved at the following magnifications x350, x1200 and x5000 and saved as .tiff files to disc. The images at x350 show the general size distribution of the cells and higher magnifications at x1200 and x5000 show the nature of the cell surfaces.

25 Images acquired at x350 magnification for both samples typically show a size range of ~100 to 200 microns. In the preparation of the foam samples for evaluation by electron microscopy, the manual snapping of the foam sample - to create a surface to examine - can induce some damage at the cell walls.

The images collected at x1200 and x5000 magnification are substantially free of defects and holes.

(viii) Average Cell Diameter

A flat section of foam is obtained by slicing through the middle section of the thickness of the foam board in a direction running parallel to the top and bottom faces of a foam board. A 50-fold enlarged photocopy is taken of the cut cross section of the foam. Four straight lines of length 9 cm are drawn on to the photocopy. The number of cells present
5 on every line is counted and the average number cell number determined according to JIS K6402 test method. The average cell diameter is taken as 1800 μm divided by this average number.

(ix) Resin Viscosity

The viscosity of a resin employed in the manufacture of a foam of the present invention
10 may be determined by methods known to the person skilled in the art for example using a Brookfield viscometer (model DV-II+Pro) with a controlled temperature water bath, maintaining the sample temperature at 25°C, with spindle number S29 rotating at 20 rpm or appropriate rotation speed and spindle type or suitable test temperature to maintain an acceptable mid-range torque for viscosity reading accuracy.

15 (x) % Water Content of Phenolic Resin

To dehydrated methanol (manufactured by Honeywell Speciality Chemicals), the phenol resin was dissolved in the range of 25% by mass to 75% by mass. The water content of the phenol resin was calculated from the water amount measured for this solution. The instrument used for measurement was a Metrohm 870 KF Titrino Plus.
20 For the measurement of the water amount, Hydranal™ Composite 5, manufactured by Honeywell Speciality Chemicals was used as the Karl-Fischer reagent, and Hydranal™ Methanol Rapid, manufactured by Honeywell Speciality Chemicals, was used for the Karl-Fischer titration. For measurement of the titre of the Karl-Fischer reagent, Hydranal™ Water Standard 10.0, manufactured by Honeywell Speciality Chemicals,
25 was used. The water amount measured was determined by method KFT IPol, and the titre of the Karl-Fischer reagent was determined by method Titer IPol, set in the apparatus.

(xi) Phosphorus Content in Phenolic Foam

The concentration of phosphorus in phenolic foam can be determined by any suitable
30 analytical method. One method for determining the concentration of phosphorus in phenolic foam is the use of inductively coupled plasma optical emission spectrometry (ICP-OES). The procedure for determining the concentration of phosphorus with ICP-OES is as follows:

Prior to use, all glass and plasticware was acid washed in 1.5M hydrochloric acid
35 overnight before being rinsed with MilliQ (grade 1 deionised water). All reagents were

Primar Plus Trace Metal Grade (Fisher Scientific). A shredded foam sample was dried in an oven for 1hr at 70°C before being cooled in a desiccator. 0.1g (+/-0.01g) of foam was weighed out into a 55ml Teflon microwave digestion tube. To the tube, 4.5ml of 68% nitric acid, 1ml of 37% hydrochloric acid and 0.5ml of 30% hydrogen peroxide were added and the sample was allowed to react for 10 minutes and for the effervescence to subside. Replicates of the sample and a procedural blank, consisting of the above reagents and no foam, were processed in parallel. The tubes were sealed with a PTFE pressure seal, capped and transferred to a CEM Mars 5 digestion microwave system fitted with a sample carousel. The microwave digester was heated to 190°C over 10 minutes and held at 190°C for a further 15 minutes before being allowed to cool to room temperature. The digested sample was transferred into a 15ml centrifuge tube and a 1ml aliquot was subsequently diluted with 4ml of MilliQ water to achieve a solution of 20% acid concentration. An aliquot of this solution was then diluted down to 2% acidity and filtered through a 0.45µm surfactant-free cellulose acetate filter. The filtered sample was run for phosphorus on a Thermo ICAP Duo ICP 6300 ICP-OES elemental analyser. The instrument was calibrated using a seven-point calibration in the range 0.5-20mg/l.

Instrument precision was measured by 3 injections of the same sample and the relative standard was found to be 0.244% of the mean. All samples were blank-corrected and the results were as follows:

% Phosphorus in Cured Phenol Foam Results	Total P conc. (mg/g)	% Phosphorus by weight in foam
Table 6 Examples 1 & 2 Foam Sample (i)	28.629	2.8629
Table 6 Examples 1 & 2 Foam Sample (ii)	27.607	2.7607
Table 6 Examples 1 & 2 Foam Sample (iii)	28.984	2.8984
Mean concentration	28.407	2.8407

Table A

(xii) Fire Performance of the Foam

[00113] A schematic of the SBI test set-up of EN13823 is shown in Figure 3. The test samples consist of two walls (formed of the material to be tested) mounted to form a vertical 90° corner. The dimensions of the walls are as follows:

Short wall - 1.5 m high by 0.5 m long

Long wall - 1.5 m high by 1.0 m long

[00114] A propane burner is positioned in the base of the corner formed by the specimen, with a horizontal separation of 40 mm between the edge of the burner and the lower edge of the specimen.

[00115] The rate of air flow extraction is set at 0.6 m³/s. A sampling probe is installed in the extraction duct, to measure the concentration of CO_x and O₂ of the fire effluent gases passing through. The rate of heat release is continuously calculated by means of the *Oxygen Consumption Method*. The obscuration of light caused by the smoke in the fire effluent passing through the exhaust duct is determined by a white light lamp and photocell system.

[00116] At the outset of the test procedure, baseline data (e.g. temperature at various points in the test set-up) are recorded for three minutes. The burner is then ignited and a 30 kW flame impinges upon the test specimen for 21 minutes. The performance of the specimen is evaluated over a period of 20 minutes.

[00117] Fire growth rate (FIGRA) indices are defined as the maximum of the quotient of the average heat release as a function of time:

$$FIGRA = (1000) \times \max. \frac{HRR_{av}(t)}{(t - 300)}$$

FIGRA is the fire growth rate index, in watts per second;

$HRR_{av}(t)$ is the average of heat release rate for $HRR(t)$ in kilowatts;

$HRR(t)$ is the heat release rate of the specimen at time t , in kilowatts;

Max. [a(t)] is the maximum of a(t) within the given time period

NOTE: Consequently, specimens with an HRR_{av} value of not more than 3 kW during the total test period or a THR value of not more than 0.2 MJ over the total test period, have a $FIGRA_{0.2MJ}$ equal to zero. Specimens with an HRR_{av} value of not more than 3 kW during the total test period or a THR value of not more than 0.4 MJ over the total test period, have a $FIGRA_{0.4MJ}$ equal to zero.

[00118] The quotient is calculated only for that part of the exposure period in which threshold levels for HRR_{av} and THR have been exceeded. If one or both threshold values of a FIGRA index are not exceeded during the exposure period, that FIGRA index is equal to zero. Two different THR -threshold values are used, resulting in $FIGRA_{0.2MJ}$ and $FIGRA_{0.4MJ}$. The moments in time that the threshold values are exceeded are defined as:

- (a) First moment after $t = 300$ s at which $HRR_{av} > 3\text{kW}$
- (b) First moment after $t = 300$ s at which $THR > 0.2$ MJ and/or $THR > 0.4$ MJ

[00119] The total heat release (*THR*) is measured over the first 10 minutes (*THR_{600s}*) after ignition of the burner.

[00120] EN13823 defines smoke growth rate index (SMOGRA) as the maximum of the quotient for the average smoke production rate as a function of time. The quotient is calculated only for that part of the exposure period in which threshold levels of average smoke production rate *SPR_{av}* and total smoke production rate *TSP* have been exceeded. If one or both threshold values are not exceeded during the exposure period, SMOGRA is equal to zero.

$$SMOGRA = (10000) \times \max. \frac{SPR_{av}(t)}{(t - 300)}$$

- 10 **SMOGRA** is the smoke growth rate index in square metres per square second;
- SPR_{av}(t)* is the average smoke production rate *SPR(t)* of the specimen in square metres per second;
- SPR(t)* is the smoke production rate of the specimen, in square metres per second;
- max.[a(t)]* is the maximum of *a(t)* within the given time period;
- 15 **TSP(t)** is the total smoke production of the specimen in the first 600s of the exposure period within $300s \leq t \leq 900s$ (m²).

Note: Consequently, specimens with a *SPR_{av}* value of not more than 0.1 m²/s during the total test period or a *TSP* value of not more than 6 m² over the total test period have a *SMOGRA* value equal to zero.

- 20 **[00121]** The moments in time that the threshold values are exceeded are defined as:

- (a) First moment after $t = 300$ s at which $SPR_{av} > 0.1$ m²/s
- (b) When "t" is between 300 s to 1500 s, $TSP(t) > 6$ m²

- [00122]** The SMOGRA index is determined during the full duration of the test. The total smoke production *TSP₆₀₀* is measured over the first 10 minutes after burner ignition (i.e. between 300 and 900 seconds).

[00123] As outlined above, the SBI test is comparable to a waste-paper basket on fire in the corner of a room.

[00124] Examples of the fire performance of different commercial available foam insulation materials tested according EN13823 is given in Table 1.

FOAM TYPE	Compressive Strength (kPa)	Blowing Agent Used	Declared Lambda Value (W/m.K)	EN13823 (test performed with foam core, no facings)					EN 11925-2	Euroclass
				FIGRA (0.2MJ) (W/s)	FIGRA (0.4MJ) (W/s)	THR (MJ)	SMOGRA (m ² /s ²)	TSP (m ²)		
XPS (high compressive strength)	700	unknown	0.035 to 0.037						<150	E
XPS (low compressive strength)	200	unknown	0.033 to 0.037						>150	F
PIR (1)	150	Cyclopentane /isopentane	0.022	697	298	4.75	61	62	<150	D

PIR (2)	150	Cyclopentane /isopentane	0.022	736	348	5.36	47	67	<150	D
PIR (3)	150	HCFO- 1233zd(Z)	0.019	1102	815	5.20	46	46	<150	E
Phenolic	100	Isopropyl chloride /isopentane	0.020	232	128	4.4	1	40	<150	C
Note: To test the fire performance of the foam core, the facer is removed and the surface is sanded to remove any remaining facer materials, which can influence the test. The boards are mounted in line with the test standard EN 15715 to the incombustible substrate prior to testing.										

Table 1

[00125] Before the test on the foam core, the foam sample is conditioned at 23°C 50% Relative Humidity in accordance with EN13823 and then the facer was peeled from the foam surface as carefully as possible. Any remaining facer is removed carefully by sanding with a very fine abrasive paper.

5 **[00126]** Phenolic foams typically have the best fire rating of any foam insulation products. The fire retardancy of a foam will be impacted by the nature of the blowing agent used to expand the foam and which is retained within the cells of the foam. As discussed above, the thermal insulating performance of a foam also depends significantly on the blowing agent, and the thermal conductivity thereof. Chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs)
10 represent a class of blowing agent with the highly desirable combination of low thermal conductivity and excellent fire performance. However, the use of such blowing agents is being phased out due to their negative environmental impact, in particular, their high ozone depletion potential and high global warming potential. Hydrocarbon blowing agents, which have low environmental impact, have been employed as a replacement blowing agent for CFCs and
15 HFCs but hydrocarbons are inherently higher in thermal conductivity than CFCs or HFCs and they are also flammable. Over the last 10 years, hydrofluoroolefins and chlorinated hydrofluoroolefins have emerged as a class of blowing agent with a combination of low thermal conductivity, good fire performance and low environmental impact.

[00127] Hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) are unsaturated
20 short-chain haloolefins, which have been introduced as alternatives to saturated hydrofluorocarbons (HFCs) as foam blowing agents, due to their ultra-low GWP (Global Warming Potential) and zero ODP (Ozone Depletion Potential).

[00128] With the introduction of HFOs (hydrofluoro olefins), and hydrochlorofluoroolefins (HCFOs), a range of blowing agents is now available to improve fire performance. A key
25 advantage of these particular blowing agents is their low thermal conductivity in the gas phase and favourable environmental performance.

[00129] HCFOs are also preferred as a blowing agent, due to their low thermal conductivity in the gas phase and their compatible solubility with phenolic resins.

[00130] HFOs tend to have slightly higher thermal conductivity values in the gas phase than
30 HCFOs.

[00131] Table 2 below gives an overview of the main blowing agents referred to in this patent.

Table 2

Commercial name/ IUPAC name	MW (g/mol)	BP °C	vapour pressure (bar, 20°C)	Thermal Conductivity (mW/m·K) at 25 °C	dipole moment (D)	solubility in water (g/kg)	Flammability	ODP	GW
Hydro(chloro) fluoroolefins									
HCFO-1224yd(Z) (Z)-1-Chloro-2,3,3,3-Tetrafluoro-propene	148	14	1.51*	12.2		0.34	none	0	<1
HFO-1336mzz(Z) cis-1,1,1,4,4,4-Hexafluoro-2-butene	164	33	0.72	10.7	3.19	3.8	none	0	5
HFO-1336mzz(E) (E)-1,1,1,4,4,4-Hexafluoro-2-butene	164	7.5	2	11.5				0	7
HCFO-1233zd(E) trans-1-chloro-3,3,3-trifluoropropene	131	19	1.06	10.5	1.44	1.9	none	0	5
HFO-1234ze(E) trans-1,3,3,3-tetrafluoro-propene	114	-19	4.9	13	1.44	0.037	none	0	6
HFO-1234yf 2,3,3,3-tetrafluoro-propene	114	-30	6.1	14	2.54	0.2	yes	0	4
Perfluorochemicals									
Perfluoro(4-methyl-2-pentene) Perfluoro(4-methyl-2-pentene)	300	49	0.355				none	0	
Perfluoropropene Hexafluoro-propene	150	-28	6.3			0	none	0	0.25
Perfluoroethylene Tetrafluoro-ethene	100	-76.3	32.4				yes	0	0.02
Perfluoro-1,3-butadiene Hexafluoro-1,3-butadiene	162	6	0.8			0	yes	0	0.03
Perfluorocyclo-hexene Decafluoro-cyclohexene	262	52						0	
Perfluorobenzene Hexafluorobenzene	186	80.1	0.11				high	0	
Chlorofluorocarbons									
CFC-11 trichlorofluoromethane	137	23.7	0.883	8.2	4.1	1.1	none	1	475
hydrochlorofluorocarbons									
HCFC-141b	117	32.2	0.69	9.8	4.32	4	none	0.1	725

[00132] When considering what blowing agent to use when manufacturing a foam, the end use application of the foam must be taken into consideration, and in general, the properties of the blowing agent must align with the end use application. Important properties of a given blowing agent which may be considered during the selection process include: the thermal conductivity in the gas phase, the boiling point, compatibility with the chemical matrix, flammability, toxicity and price.

[00133] One of the most important criteria is the thermal conductivity (or lambda) of each blowing agent component (comp). A simple model to estimate the insulation value of a binary gas mixture containing component A and component B is:

$$\lambda_{mix} = 0.5 * \frac{\lambda_{comp A} * \lambda_{comp B}}{\lambda_{comp A} * X_{comp B} + \lambda_{comp B} X_{comp A}} + 0.5 * (\lambda_{comp A} * X_{comp A} + \lambda_{comp B} X_{comp B})$$

where:

λ_{mix} is the thermal conductivity of the mixture of the blowing agent components A and B

$\lambda_{comp A}$ is the thermal conductivity of blowing agent component A

$\lambda_{comp B}$ is the thermal conductivity of blowing agent component B

$X_{comp A}$ is weight fraction of component A in the blowing agent mixture

$X_{comp B}$ is weight fraction of component B in the blowing agent mixture.

[00134] This model can also be used to estimate the thermal conductivities of more complex blowing agent mixtures by initially calculating the thermal conductivity of two components in a blend of blowing agents and then employing the λ_{mix} for the binary blend as a lambda input value for the mixture of the binary blend with a third blowing agent.

[00135] The cell gas inside a foam cell can start to condense when the foam temperature is at or below the boiling point of the blowing agent. The standard average temperature (T_{mean}) for lambda measurement of a foam according to the European standard EN 12667 for example is 10°C. In the heat flow meter, the temperature settings of the plates are 10°C above and below this T_{mean} . The point at which the cell gas starts to condense will have an important impact on the thermal conductivity of the product.

[00136] Figure 4 shows the impact of the temperature on the thermal conductivity of phenolic foams blown with three different weight ratio blends of 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) and isopentane.

[00137] Blowing agents are generally selected to try to avoid condensation above 10°C in order to prevent condensation in the cells of the foam when in use. Condensation causes a reduction in insulation performance.

[00138] Blowing agents can also be categorized in terms of flammability. ISO817
5 classifies blowing agents in terms of their flammability.

Table 3

Class	Category	Examples
1	Non-flammable	HFO-1336mzz(Z) HCFO-1233zd(E)
2L	Low flammability	HFO-1234yf HCFO-1234ze(E) HFC-32
2	Flammable	HFC-152a
3	High flammability	Propane isomers Butane isomers Pentane isomers Isopropyl chloride

[00139] There are several main parameters that characterize the level of flammability (1, 2L, 2, and 3) of a blowing agent including the burning velocity (BV), the upper and
10 lower flammability limits (UFL and LFL), the minimum ignition energy (MIE), and the heat of combustion (HOC):

- 1) BV, burning velocity: is the speed at which a flame propagates.
- 2) LFL, lower flammability limit: is the minimum concentration of a gas or vapour that is capable of propagating a flame within a homogenous mixture of that gas
15 or vapour and air.

- 3) UFL, upper flammability limit: is the maximum concentration of a gas or vapour that is capable of propagating a flame within a homogenous mixture of that gas or vapour and air.
- 4) MIE, minimum ignition energy: indicates how much energy must be in an ignition source (e.g. spark or naked flame) to initiate ignition of a gas or vapour.
- 5) HOC, heat of combustion: is the energy released as heat when a specific amount of a substance undergoes complete combustion under standard conditions.

[00140] A class 3 blowing agent, will have an LFL which is significantly lower and a BV which is significantly higher than those of a class 2L blowing agent. The use of HCFOs and HFOs as blowing agents in phenolic foam should therefore facilitate the manufacture of insulation products having excellent fire performance. The present inventors have found that surprisingly this is not the case.

[00141] The present inventors prepared and investigated the fire performance and thermal conductivity of various blowing agents in phenolic foam with red phosphorus pre-dispersed in the foamable phenolic resin mix and found particular blowing agents which may be used to form thermal insulating phenolic foam having surprisingly excellent thermal conductivity values and fire performance. This effect is observed is for various blowing agents as described herein and in particular in relation to ternary blends of blowing agents described herein.

Resin Preparations

Resin A Preparation

[00142] To a reaction vessel was added on a weight basis (pbw = parts by weight) 50.0 pbw phenol, 1 to 4 pbw water and 0.9 ± 0.2 pbw of 50% potassium hydroxide at 20°C. The temperature was raised to 70 to 76°C and 35 ± 2 pbw of 91% paraformaldehyde was added slowly over 1 to 3 hours to dissipate the heat of the reaction exotherm. The temperature was then raised to, and maintained in the range of from 82 to 85°C until the viscosity of the resin reached 7,500 mPa·s +/- 1500 mPa·s. Cooling was commenced whilst adding 0.3 pbw of 90% formic acid to neutralize pH. When the temperature has reduced to below 60°C, the following items were sequentially added: 2 to 6 pbw polyester polyol plasticiser, and 3 to 6 pbw of

urea. When urea has dissolved then 2 to 5 pbw of ethoxylated castor oil (surfactant) are mixed in at 30 to 40°C. The resulting phenolic resin composition Resin A contained 10 to 13 wt. % water, less than 4 wt. % free phenol, and less than 1 wt. % free formaldehyde.

5 **Resin P Preparation**

To a reaction vessel was added on a weight basis (pbw = parts by weight) 50.0 pbw phenol, 1 to 4 pbw water and 0.9 ± 0.2 pbw of 50% potassium hydroxide at 20°C. The temperature was raised to 70 to 76°C and 35 ± 2 pbw of 91% paraformaldehyde was added slowly over 1 to 3 hours to dissipate the heat of the reaction exotherm. The temperature was then raised to, and maintained in the range of from 82 to 85°C until the viscosity of the resin reached 7,500 mPa·s $\pm$ 1500 mPa·s. Cooling was commenced whilst adding 0.3 pbw of 90% formic acid to neutralize pH. When the temperature reached 70 $\pm$ 3 °C, water was vacuum distilled to give a water content of 7.9 to 8.4% as measured by Karl Fisher analysis. When the temperature is below 60°C, the following items were sequentially added: 2 to 6 pbw polyester polyol plasticiser, and 3 to 6 pbw of urea. When urea has dissolved then add 7.6 $\pm$ 1.5 parts of 50% $\pm$ 2% aqueous solution of red phosphorus and mix until uniformly dispersed. Then 2 to 5 pbw of ethoxylated castor oil (surfactant) are mixed in at 30°C to 40°C. The resulting phenolic resin composition, Resin P, has 10 to 13 wt. % water content, less than 4 wt. % free phenol, and less than 1 wt. % free formaldehyde.

[00143] Phenolic Foam Preparation

A general procedure for the manufacture of phenolic foam boards is described in Comparative Example (CE) 1 below

Comparative Example 1 (CE 1) – Blowing Agent (BA) is isopropyl chloride : isopentane (IPC : iP 80 $\pm$ 5 : 20 $\pm$ 5 by weight)

[00144] To 110 $\pm$ 5 pbw of Resin A at 15°C to 19°C was added with mixing at 300 $\pm$ 100rpm 5 $\pm$ 2 pbw of calcium carbonate powder until calcium carbonate is uniformly dispersed. The said blended resin mix is pumped to a high speed mixer where 9 $\pm$ 3 pbw

of iPC : iP blowing agent at 1 to 3°C. and 20 +/-3 pbw of 2 : 1 weight ratio toluene sulfonic acid : xylene sulfonic acid catalyst at 8 to 15°C is quickly mixed into the resin blend. High speed mixing at 1000 to 4000 rpm is used to achieve intimate mixing so that a foamable composition is produced. Then said foaming resin composition was discharged to a suitable facing such as non-woven glass mat at a predetermined foamable resin flow rate to give the desired final foam cured density, such as 35 kg/m³, at the desired foam thickness such as 20 to 150mm. Then the foamable mixture is carried by a moving horizontal conveyor belt into a conventional slat-type double conveyor foam lamination machine. The oven may have a uniform temperature such as 70°C or may include several different temperature zones. Just before entering the foam lamination machine, a top facing is then introduced on to the foaming resin composition. The moving foam material passes through the heated oven press where the rising foam is pressurised at 40 to 50 kPa at a fixed gap to give the required foam board thickness. The foam expansion and initial curing in the oven press is for between 4 and 15 minutes. The partially cured foam that exits from the lamination machine is cut to a required length. The foam board is then placed in a secondary oven at 70°C to 90°C until fully cured. Table 4 gives details of a foam board manufactured using such a method.

Comparative Example 6 (CE 6) – Blowing Agent (BA) is isopropyl chloride : isopentane (iPC : iP 80+/-5 : 20+/-5 by weight) containing half the amount of red phosphorus that was used in Resin P in Examples Ex1 to Ex6 identified as Resin “P/2”).

Table 4	CE 1	CE 6
	IPC : IP (80 : 20)	IPC : IP (80 : 20)
Phenolic Resin “A”	111	0
Phenolic Resin “P / 2”	0	111
Acid Catalyst	21	21
isopropyl chloride	7.6	6.8
isopentane	1.9	1.7
Sample thickness (mm)	84	100
Initial lambda (W/m-K)	0.0182	

110°C aged 2 weeks lambda (W/m·K)	0.0189	
Foam density Kg/m ³	35.8	
Foam stable water content %	3.7	
Compressive strength at first crack (kPa)	120	
FIGRA 0.2 MJ (W/s)	232	132
FIGRA 0.4 MJ (W/s)	128	
THR t = 600 s (MJ)	4.4	3.1
SMOGR (m ² /s ²)	1	10.1
TSP t = 600 s (m ²)	40	71
EuroClass	Cs2d0	Cs2d0

Comparative Example 2 (CE2) – Blowing Agent is HCFO-1233zd (E)

- [00145] Here the same procedure as was used as outlined in Comparative Example 1 except the blowing agent was changed to 14.8 parts by weight of HCFO-1233zd (E) blowing agent at 1 to 3°C. The foam board produced had a density of 35.6 kg/m³.

Comparative Example 3 (CE3) – Blowing Agent is HCFO-1233zd(E) : IP (70:30)

[00146] Same as CE2 except the blowing agent is 8.47 pbw of HCFO-1233zd(E) and 3.63 pbw of isopentane.

- 10 **Comparative Example 4 (CE4) – Blowing Agent is HCFO-1233zd(E) : HFO-1336mzz (Z) (95:5)**

[00147] Same as CE2 except that the blowing agent is 13.18 pbw HCFO-1233zd(E) and 0.76 pbw HFO-1336mzz (Z).

Comparative Example 5 (CE5) – Blowing Agent is HCFO-1233zd (E): HFO-1336mzz (Z): isopentane (65:5:30)

- 15 [00148] Same as CE2 except that the blowing agent is 7.5 pbw of HCFO-1233zd(E), 0.58 pbw of HFO-1336mzz (Z) and 3.47 pbw of isopentane.

Table 5	CE2	CE3	CE4	CE5
	HCFO (100)	HCFO : HC (70 : 30)	HCFO : HFO (95 : 5)	HCFO : HFO : HC (65 : 5 : 30)
Phenolic Resin A (pbw)	111	111	111	111
Acid Catalyst (pbw)	21	21	21	21
HCFO-1233zd E (pbw)	14.8	8.47	14.4	7.5
HFO-1366mzz (pbw)	0	0	0.76	0.58
isopentane (pbw)	0	3.63	0	3.47
Sample thickness (mm)	84	84	84	84
Initial lambda (W/m.K)	0.0160	0.0176	0.0159	0.0177
110°C aged 2 weeks lambda (W/m.K)	0.0168	0.0189	0.0166	0.0187
Foam density Kg/m ³	36.6	36.2	36.5	35.9
Foam stable water content %	3.8	3.7	4.1	4.2
Compressive strength first crack (kPa)	112	135	119	135
FIGRA 0.2 MJ (W/s)	394	237	272	157
FIGRA 0.4 MJ (W/s)	394	237	272	85
THR t = 600 s (MJ)	15.64	16.06	17.72	4.65
SMOGR (m ² /s ²)	30.3	16.3	19.9	4.1
TSP t = 600 s (m ²)	112	88	114	55
EuroClass	Ds2d0	Cs2d0	Ds2d0	Cs2d0

Example 1 (Ex1) – Blowing Agent is HCFO-1233zd (E) IP (95:5) by weight

[00149] Same as CE2 except that the resin used was Resin P and the blowing agent was 13.8 parts of HCFO-1233zd (E), and 0.73 parts of isopentane.

Example 2 (Ex2) – Blowing Agent is HCFO-1233zd (E) : IP (95:5) by weight

- 5 [00150] Same as Ex1 to assess the reproducibility of the SBI fire testing. So the blowing agent was 13.8 pbw of HCFO-1233zd (E), and 0.73 pbw of isopentane.

Example 3 (Ex3) – Blowing Agent is isopropyl chloride, iPC : IP (80:20) by weight

[00151] Same as Ex 1 except that the blowing agent was 6.8 pbw of isopropyl chloride) and 1.7 pbw of isopentane.

- 10 **Example 4 (Ex4) - Blowing Agent is isopropyl chloride, iPC : IP (80:20) by weight**

[00152] Same as Ex 1 except that the blowing agent was 6.8 pbw of isopropyl chloride) and 1.7 pbw of isopentane.

Example 5 (Ex 5) - Blowing Agent is isopropyl chloride, iPC : IP (80:20) by weight

- 15 [00153] Same as Ex 1 except that the blowing agent was 6.8 pbw of isopropyl chloride) and 1.7 pbw of isopentane.

Example 6 (Ex 6) - Blowing Agent is isopropyl chloride, iPC : IP (80:20) by weight

[00154] Same as Ex 1 except that the blowing agent was 7.9 pbw of isopropyl chloride) and 2.0 pbw of isopentane.

Table 6	Ex1	Ex2	Ex3	Ex4	Ex5	Ex6
	HCFO1233zd : iP (95 : 5)	HCFO1233zd: iP (95 : 5)	iPC : iP (80 : 20)	iPC : iP (80 : 20)	iPC : iP (80 : 20)	iPC : iP (80 : 20)
Phenolic Resin "P" (pbw)	111	111	111	111	111	111
Acid Catalyst (pbw)	21.7	21.7	21.5	21.5	21.5	21.5
HCFO-1233zd E (pbw)	13.8	13.8	0	0	0	0
IPC (isopropyl chloride) (pbw)	0	0	6.8	6.8	6.8	7.9
HC (isopentane) (pbw)	0.73	0.73	1.7	1.7	1.7	2.0
Sample thickness (mm)	100	100	100	100	100	40
Initial lambda (W/m.K)	0.0165	0.0162	0.0184	0.0179	0.0181	0.0181
110°C aged 2 weeks lambda (W/m.K)	0.0176	0.0173	0.0197	0.0198	0.0196	0.0197
Foam density Kg/m ³	36.5	36.5	41.4	36.6	37.4	
Foam stable water content %	4.2	4.2				
Compressive strength first crack (kPa)	112	112	124	113	109	
FIGRA 0.2 MJ (W/s)	68.3	68.0	52.2	83.3	85.0	84.6
FIGRA 0.4 MJ (W/s)	30.6	35.3	26.6	39.8	46.1	56.1
THR t = 600 s (MJ)	2.14	2.04	2.07	2.40	2.47	2.83
SMOGRA (m ² /s ²)	13.4	12.00	9.27	4.46	3.64	9.08
TSP t = 600 s (m ²)	98.8	93.8	81.4	55.8	52.9	87.5
EuroClass	Bs2d0	Bs2d0	Bs2d0	Bs2d0	Bs2d0	Bs2d0

Discussion of Comparative Examples and Examples

[00155] The physical properties and fire performance of the foams in the comparative examples and examples are illustrated in Tables 4, 5 and 6.

[00156] The blowing agent in CE1 is a blend of isopropyl chloride and isopentane, in an 80:20 weight ratio blend by weight. CE1 exhibits desirable initial and aged thermal conductivity values, and the fire performance classifies the foam of CE1 as a Euroclass C product. CE6 is the same chemical composition as CE1 except that half the weight of red phosphorus has been introduced into the foamable phenolic resin compared to Ex 1 to Ex6 inclusive. This results in half the weight of red phosphorus in the cured foam. In the cured foam there is a substantial reduction in the FIGRA 0.2 MJ value, though not enough to achieve a Euroclass B fire rating.

[00157] The blowing agent in CE2 is entirely HCFO-1233zd (a non-flammable class 1 blowing agent in accordance with ISO817). The initial and aged thermal conductivity of CE2 are excellent, however, the fire performance results of CE2 are inferior to values expected for when a non-flammable blowing agent is used. High FIGRA 0.2 MJ and FIGRA 0.4 MJ values were observed when a foam board of CE2 was assessed in BS EN 13823. Accordingly, despite the use of a non-flammable blowing agent, the fire performance of CE2 is worse than that of CE1 which comprises flammable isopentane and flammable isopropyl chloride. CE2 is classified as a Euroclass D fire growth rate product with Class "C2" smoke emissions and "d0" no dripping observed.

[00158] CE3 comprises a blowing agent blend of HCFO-1233zd and isopentane, and exhibits desirable performance for initial and aged thermal conductivity values, and an improvement in fire performance in comparison to CE2. However, despite this improvement CE3 is classified as a Euroclass C product rather than Euroclass B.

[00159] CE4 comprises a blowing agent blend of HCFO-1233zd and HFO-1336mzz. HFO-1336mzz is also classified as a non-flammable Class 1 blowing agent in accordance with ISO 817. The initial and aged thermal conductivity values of CE4 are excellent. Despite having 2 non-flammable blowing agents, the FIGRA 0.2 MJ and FIGRA 0.4 MJ values are surprisingly greater than those observed for CE3 that contains flammable isopentane.

[00160] CE5 comprises a ternary blowing agent blend of HCFO-1233zd, HFO-1336mzz and isopentane. Despite the inclusion of highly flammable isopentane, the desired low initial and low aged thermal conductivity values remain almost constant but significantly, there is a dramatic improvement in the fire performance, albeit the FIGRA 0.2 MJ value remains above 150 W/s.(Euroclass C)

[00161] In contrast, Examples E1 to E6 demonstrate that a FIGRA 0.2 MJ value of less than 150 W/s can be achieved when a specific ternary blend of a chlorinated hydrofluoroolefin, a hydrofluoroolefin and a hydrocarbon is employed in the phenolic foamable chemical blend along with

2 to 5 parts by weight of micronized, (0.5 to 10 μ m particle size), red phosphorus based on 100 parts by weight of cured phenolic foam which results in foam insulation products having excellent fire resistance properties, and low smoke emissions defined by FIGRA (0.2MJ threshold) <150W/s and SMOGRA <20 m²/s², . Indeed, each of Examples E1 to E6 demonstrate a FIGRA 0.2 MJ value of less than 120 W/s, and so are classified as having a desirable Euroclass B fire performance rating. This is achieved without deleteriously impacting the low thermal conductivity of the foam. The invention concerns stable insulation performance (<0.023 W/m.K), and a high closed foam cell content, (>85%).

[00162] The blowing agent used to form the phenolic foams of the invention may comprise at least one chlorinated hydrofluoroolefin, or at least one hydrofluoroolefin or at least one alkyl halide or at least one chlorinated alkene present and at least one C₃-C₆ hydrocarbon and combinations thereof. The at least one chlorinated hydrofluoroolefin or at least one alkyl halide or at least one chlorinated alkene or combinations thereof is desirably present in an amount of from about 62 wt.% to 95 wt.% based on the total weight of the blowing agent. The hydrofluoroolefin is desirably present in an amount of from about 5 to 15 wt.% based on the total weight of the blowing agent. The at least one C₃-C₆ hydrocarbon is desirably present in an amount of from 4 to 25 wt.% based on the total weight of the blowing agent.

[00163] As evidenced by comparing CE1 without red phosphorus in the foam, to CE6, which has half the optimum amount as is present in "Resin P", there is a substantial improvement in the FIGRA 0.2MJ value obtained for CE6 despite the presence of highly flammable isopropyl chloride and isopentane being present in the phenolic foam. However, with this reduced amount of red phosphorus present in the foam only Euroclass C is achieved. To achieve Euroclass B, the red phosphorus weight amount in foam needs to be in the range used in Examples 1 to 6 derived from "Resin P". If excessive amounts of red phosphorus are added, beyond 5 parts by weight of red phosphorus in 100 parts by weight of cured foam, then the SMOGRA values will increase and there is a risk that low stable thermal conductivity will be compromised with time. The proposed range for the amount of red phosphorus, 2 to 5 parts with particle size 0.5 to 10 μ m to be present in 100 parts by weight of cured phenolic foam and the particle size ensures the requirement for stable thermal conductivity and improved fire resistance. If too much red phosphorus is added to the foamable resin mix, then there are possible foam manufacturing issues when mixing due to the excessive high chemical blend viscosity. Historically improved foam fire resistance has been achieved by the presence of organic or inorganic phosphorus compounds in the foam. The concentration of phosphorus per unit weight is higher in red phosphorus than in other organic or inorganic phosphorus containing compounds. To obtain 2 to 5 parts by weight of phosphorus per 100 parts of cured phenolic foam would require much higher loadings of these other phosphorus compounds. Such higher additions would plasticise foam cells if the organophosphorus compound was a liquid or could

damage foam cells during the mechanical foam mixing process if the organophosphorus compound is a solid. The adverse effect on the insulation foam is undesirable higher thermal conductivity

[00164] For example, ammonium polyphosphate particles at 5 parts / 100 parts of uncured phenolic resin raises initial and aged foam lambda. Table 7 below shows the unit weight of elemental phosphorus is higher than other phosphorus based compounds permitting less flame retardant to be needed in the cured foam and so thermal conductivity is not compromised. .

<u>Chemical Name</u>	<u>Chemical Structure</u>	<u>% Elemental Phosphorus</u>	<u>Physical Form</u>	<u>Molecular Weight</u>
50% Aqueous Red Phosphorus	P	50.0	Dispersion	31
Diphenyl Phosphine	(C6H5)2-PH	16.6	Liquid	186.2
Diphenyl Phosphine Oxide	(C6H5)2-P(H)=O	15.3	Solid	202.2
Diphenyl Phosphate	(C6H5O)2-P(OH)=O	12.4	Solid	250.2
Diphenyl Phosphite	(C6H5O)2-P(H)=O	13.3	Liquid	234
Diethyl Phosphite	(C2H5O)2-P(H)=O	22.4	Liquid	138.1
Triphenyl Phosphine	(C6H5)3-P	11.8	Solid	262.3
Triphenyl Phosphine Oxide	(C6H5)3-P=O	11.1	Solid	278.3
Triphenyl Phosphate	(C6H5O)3-P=O	9.5	Solid	326.3
Triphenyl Phosphite	(C6H5O)3-P	10	Liquid	310
Triethyl Phosphine oxide	(C2H5)3-P=O	23.1	Solid	134.2
Triethyl Phosphate (TEP)	(C2H5O)3-P=O	17.0	Liquid	182.2
Triethyl Phosphite	(C2H5O)3-P	18.6	Liquid	166.2
Diethyl ethyl phosphonate DEEP	(C2H5O)2-P=O C2H5	15.3	Liquid	202
Tris (2-chloropropyl) phosphate TCPP	(Cl-CH2CH2-O)3-P(CH3)=O	9.5	Liquid	327.6
TMCP		9.4	Liquid	
Chlorinated phosphate ester				
Ammonium Polyphosphate	-(NH4PO3) _n - n>1000	31.5	Solid	
Ammonium Phosphate	NH4H2PO4	26.9	Solid	115

Table 7

[00165] Typically 2 to 5 parts by weight of red phosphorus per 100 parts by weight of cured phenolic foam are needed to obtain Euroclass Class B foam insulation products with an appropriate blowing agent blend and surfactant type.

[00166] However, if the amount of hydrocarbon exceeds about 25 wt.% of the blowing agent composition, the fire performance of the foam could be negatively impacted, and the attainment of a Euroclass B foam is not possible. Furthermore, as evidenced by CE2 and CE4, if less than about 5 wt.% hydrocarbon is present, the fire performance is also deleteriously impacted.

[00167] If less than about 3 wt.% hydrofluoroolefin is present, the fire performance of the product declines, and if greater than about 20 wt.% hydrofluoroolefin is present, the thermal conductivity of the foam product increases.

[00168] Accordingly, optimal thermal insulation performance and fire performance is achieved, when the blowing agent comprises the aforementioned ternary blend.

[00169] In the foams of the invention the % friability is below 30% for example below 25% as measured according to test method ASTM C421 – 08(2014).

[00170] A further desirable aspect of the invention is that the presence of 2 to 5% by weight of micronized (for example 0.5 to 10 μ m particle size) red phosphorus flame retardant present in 100 parts by weight of cured phenolic foam results in phenolic foam insulation products having reduced formaldehyde emissions from phenolic foam articles by 30 to 60% as measured by EN717-1 / EN16516 / ISO16000-11. Table 8 below shows the formaldehyde scavenging effect of red phosphorus present in phenolic foam regardless of blowing agent type.

Sample Details	Phenolic Resin	Blowing Agents	Test Chamber Size	Loading Factor (m ² /m ³)	Formaldehyde Emission (μ g/m ³)
100mm Phenolic Foam Board with 25 μ m perforated foil - glass mat facings	Resin "P"	80:20 by weight iPC : iP	1m ³	1.0	98
80mm Phenolic Foam Board with 25 μ m perforated foil-glass mat facings	Resin "A"	80:20 by weight iPC : iP	1m ³	1.0	200
110mm Phenolic Foam Board with 25 μ m perforated foil-glass mat facings	Resin "A"	80:20 by weight iPC : iP	1m ³	1.0	170
100mm Phenolic Foam Board with 25 μ m perforated foil-glass mat facings	Resin "P"	HCFO1233zd : iP (85 : 15)	1m ³	1.0	24
90mm Phenolic Foam Board with 25 μ m perforated foil glass mat facings	Resin "A"	HCFO1233zd : iP (85 : 15)	1m ³	1.0	160

Table 8

[00171] As outlined above, the at least one chlorinated hydrofluoroolefin is present in an amount of from about 65 wt.% to about 92 wt.% based on the total weight of the blowing agent used to form the phenolic foam of the present invention. Preferably, the chlorinated hydrofluoroolefin is present in an amount of from about 72 wt.% to about 92 wt.% based on the total weight of the blowing agent. More preferably, the chlorinated hydrofluoroolefin is present in an amount of from about 72 wt.% to

about 88 wt.% based on the total weight of the blowing agent, even more preferably the chlorinated hydrofluoroolefin is present in an amount from about 72 wt.% to about 82 wt.% based on the total weight of the blowing agent.

5 [00172] The at least one hydrofluoroolefin is present in an amount of from about 5 wt.% to about 20 wt.% based on the total weight of the blowing agent used to form the phenolic foam of the present invention. Preferably, the hydrofluoroolefin is present in an amount of from about 5 wt.% to about 15 wt.%, such as from about 8 wt.% to about 14 wt.% based on the total weight of the blowing agent.

10 [00173] The C₃-C₆ hydrocarbon is present in an amount of from about 4 wt.% to about 25 wt.% based on the total weight of the blowing agent used to form the phenolic foam of the present invention. Preferably, the C₃-C₆ hydrocarbon is present in an amount of from about 5 wt.% to about 20 wt.%, such as from about 8 wt.% to about 18 wt.% based on the total weight of the blowing agent.

[00174] Suitably, the chlorinated hydrofluoroolefin is selected from HCFO-1233zd and HCFO-1224yd.

15 [00175] The chlorinated hydrofluoroolefin may be HCFO-1233zd-(E) and/or HCFO-1233zd-(Z). For example, the 1233zd may be at least 90 wt.% of the E-isomer (HCFO-1233zd-(E)), such as at least 95 wt.% of the E-isomer (HCFO-1233zd-(E)).

[00176] The hydrofluoroolefin is suitably HFO-1336mzz. The HFO-1336mzz may be HFO-1336mzz-(Z) and/or HFO-1336mzz-(E). For example, the HFO-1336mzz may be at least 90 wt.% of the Z-isomer (HFO-1336mzz-(Z)), such as at least 95 wt.% of the Z-isomer (HFO-1336mzz-(Z)).

20 [00177] Suitably, the C₃-C₆ hydrocarbon is a propane, butane, pentane, hexane or isomer thereof. More suitably, the C₃-C₆ hydrocarbon comprises a butane and/or a pentane. Preferably, the butane comprises isobutane. Preferably, the pentane comprises isopentane.

25 [00178] Advantageously, each of the foams of Examples 1 to 6 demonstrate stable low thermal conductivity over extended time and temperature exposure, and excellent fire performance. Each of the foams of examples 1 to 6 are Euroclass B products.

[00179] The words “comprises/comprising” and the words “having/including” when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

30 [00180] It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

Claims

1. A phenolic foam formed from a foamable phenolic resin composition, and a blowing agent,

the phenolic foam comprising 1 to 5 % by weight of red phosphorus based on the weight of the phenolic foam wherein said phenolic foam has a density of from 10 kg/m³ to 100 kg/m³, a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a FIGRA_{0.2MJ} of 120 W/s or less, when measured according to EN13823 and a thermal conductivity of 0.023 W/m.K or less, at 10°C, in accordance with EN 13166:2012.

2. A phenolic foam according to Claim 1 wherein the phenolic foam comprises 2 to 5 % by weight of red phosphorus based on the weight of the phenolic foam.

3. A phenolic foam according to any preceding claim wherein the blowing agent comprises at least one of the following:

at least one saturated or unsaturated C₃-C₆ hydrocarbon;

at least one saturated or unsaturated C₃-C₆ compound that is substituted at least once by one or more of fluorine and chlorine for example isopropyl chloride.

4. A phenolic foam according to any preceding claim wherein the blowing agent comprises at least one of isopropyl chloride or a saturated C₃-C₆ hydrocarbon such as pentane for example isopentane.

5. A phenolic foam according to any preceding claim wherein the blowing agent comprises a blend of isopropyl chloride and a saturated C₃-C₆ hydrocarbon such as pentane for example isopentane.

6. A phenolic foam according to any preceding claim wherein the foam has a FIGRA_{0.2MJ} of 110 W/s or less, for example 100 W/s or less, such as 90 W/s or less when measured according to EN13823.

7. A phenolic foam according to any preceding claim wherein the blowing agent comprises at least one of hydrofluoroolefin or chlorinated hydrofluoroolefin.

8. A phenolic foam according to Claim 7 wherein the blowing agent further comprises at least one of the following:

at least one saturated or unsaturated C₃-C₆ hydrocarbon;

at least one saturated or unsaturated C₃-C₆ compound that is substituted at least once by one or more of fluorine and chlorine atoms for example isopropyl chloride.

9. A phenolic foam according to Claim 7 or 8 wherein the blowing agent comprises a blend of at least one of hydrofluoroolefin or chlorinated hydrofluoroolefin with a C₃-C₆ hydrocarbon such as pentane for example isopentane.

10. A phenolic foam according to any preceding claim wherein the foam has a FIGRA_{0.2MJ} of 100 W/s or less, for example 90 W/s or less, such as 80 W/s or less, such as 70W/s or less when measured according to EN13823.

11. A phenolic foam according to any preceding claim wherein the foam has a compressive strength of at least 95kPa.

12. A phenolic foam according to any preceding claim wherein the red phosphorus is in micronized form.

13. A phenolic foam according to any preceding claim wherein the red phosphorous is in particulate form with a number average particle size in the range from 0.1 µm to 25 µm, for example 0.25 µm to 15 µm, such as 0.5 µm to 10 µm.

14. 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.

15. 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.

16. 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 µm, suitably in the range of from 80 to 180 µm.

17. The phenolic foam according to any preceding claim, wherein said foam has a 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.

18. The phenolic foam according to any preceding claim, said foam having a limiting oxygen index of 34% or more, optionally 35% or more, suitably 36% or more, such as 37% or more as determined in accordance with ISO 4589-2.

19. The phenolic foam according to any preceding claim, wherein said foam has a stable moisture content of from 3% to 8%, for example 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.

20. The phenolic foam according to any of Claims 7 to 19, 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).

21. The phenolic foam according to any of Claims 7 to 20, wherein the at least one hydrofluoroolefin comprises 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz).

22. The phenolic foam according to any preceding claim, wherein the hydrocarbon comprises at least one butane, suitably isobutane, and/or at least one pentane, for example isopentane.

23. A phenolic foam formed by foaming and curing a phenolic resin foamable composition comprising a phenolic resin, a surfactant, an acid catalyst, a blowing agent, and 1 to 5 % by weight of red phosphorus based on the weight of the phenolic foam, wherein said phenolic foam has a density of from 10 kg/m^3 to 100 kg/m^3 , a closed cell content of at least 85% as determined in accordance with ASTM D6226 and wherein said foam has a $\text{FIGRA}_{0.2\text{MJ}}$ of 120 W/s or less (such as 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 and wherein the phenolic foam has a thermal conductivity of 0.023 W/m.K or less, at 10°C , in accordance with EN 13166:2012.

24. The phenolic foam according to claim 23, wherein the blowing agent comprises at least one hydrofluoroolefin and at least one chlorinated hydrofluoroolefin; and said blowing agent further comprises at least one $\text{C}_3\text{-C}_6$ hydrocarbon.

25. The phenolic foam according to claim 24 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).

26. The phenolic foam according to any Claim 24 or Claim 25, wherein the at least one hydrofluoroolefin comprises 1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz).

27. The phenolic foam according to any of Claims 24 to 26, wherein the at least one C₃-C₆ hydrocarbon comprises at least one butane, suitably isobutane, and/or at least one pentane, optionally isopentane.
28. 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.
29. The phenolic foam according to any preceding claim wherein the phenolic resin composition comprises a phenolic resin that 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.
30. The phenolic foam according to any preceding claim 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.
31. The phenolic foam according to any preceding claim 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.
32. The phenolic foam according to any preceding claim wherein the phenolic resin has a water content in the range of from about 7.5 wt.% to about 14% such as about 10 wt.% to about 14 wt.% based on the weight of the phenolic resin.
33. The phenolic foam according to any preceding claim, 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.
34. The phenolic foam according to any preceding claim wherein, 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.
35. 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.

36. The phenolic foam according to any preceding claim having a density of from about 15 kg/m³ to about 60 kg/m³, such as from about 20 kg/m³ to about 50 kg/m³, suitably of from about 24 kg/m³ to about 48 kg/m³.

37. The phenolic foam according to any preceding claim wherein the foam has a density from 34.5 kg/m³ to 40 kg/m³; such as from 35 kg/m³ to 39 kg/m³, for example from 36 kg/m³ to 38 kg/m³.