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(54) METHOD OF PREPARING FOAMED SOLID AMINO-FORMALDEHYDE FURFURYL ALCOHOL RESINS

(71) We, KONINKLIJKE EMBAL-
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 Dutch company, of Amsterdamseweg 206,
 Amstelveen, the Netherlands, do hereby declare
 the invention, for which we pray that a patent
 may be granted to us, and the method by
 which it is to be performed, to be particularly
 described in and by the following statement:—

The present invention relates to a method
 of preparing foamed solid amino-formaldehyde
 furfuryl alcohol resins by polymerizing a fur-
 furyl alcohol-containing amino-formaldehyde
 liquid resin composition in the presence of an
 acid.

In British Patent 942,845, a method of
 preparing such foamed solid amino-formalde-
 hyde furfuryl alcohol resins is disclosed,
 wherein a furfuryl alcohol-containing amino-
 formaldehyde composition is polymerized in
 the presence of a strong acid. Due to their
 low thermal conductivity in combination with
 non-flammability as determined by older
 flammability tests, such as ASTM 1692, the
 products obtained by this method are suitable
 for thermal insulation. However, they cannot
 be considered as non-flammable when tested
 by more recent and more severe flammability
 tests such as the NEN 1076, part C, flash-
 over test, since they are not able to pass this
 test with a class 1 rating.

Description of the NEN 1076, part C test
 relating to flash-over and flammability.

1. Purpose.

This part comprises a method for deter-
 mination of the flash-over intensity, in order
 to be able to determine the contribution of
 materials to the occurrence of flash-over and
 their flammability. Materials are classified
 according to their flash-over intensity.

2. Principle.

To determine the flash-over intensity, two
 samples to be tested are erected vertically and
 parallel to each other in a test box. They are
 exposed to such an amount of heat that flash-

over, if possible, occurs from one test sample
 to the other. The amount of heat applied per
 second and per square centimetre to the surface
 of the test sample to give flash-over in exactly
 15 minutes, determines the classification. This
 heat is called the flash-over intensity and can
 be considered as a measure of the contribution
 to flash-over and the non-flammability of the
 test material.

3. Test samples.

3.1 Dimensions.

The test samples should have an area of
 300 millimetres × 300 millimetres; the
 thickness of the test samples should be the
 normal thickness of the material.

3.2 Number.

The number of test samples necessary to
 determine the flash-over intensity is norma-
 lly ten.

4. Preparation of the test samples.

Materials should be subjected to testing in
 the condition in which they are used in prac-
 tice. Before testing, the moisture content of the
 test samples should be in equilibrium with air
 at a temperature of 10 to 20°C and a relative
 humidity of 55 to 65%. If competent authori-
 ties judge it necessary, the flash-over intensity
 of a few test samples should be determined
 after being submitted to one or more ageing-,
 weathering- or other tests.

To determine the flash-over intensity, an
 apparatus is used as shown in the accompany-
 ing drawings, in which:

Figure 1 is a vertical section of such appara-
 tus (on line I—I of Figure 3),

Figure 2 is a horizontal section of the
 apparatus shown in Figure 1 on line II—II
 of Figure 3, and

Figure 3 is an elevation of the apparatus as
 viewed from the right hand side of Figure 1
 with the right hand side panel 15 and test
 sample 14 removed.

The apparatus comprises a generally box-like enclosure made from asbestos panels 1 having a thickness of 34 millimetres. Horizontally mounted in a central vertical plane of the enclosure are a series of twelve quartz rods 2 on each of which is spirally wound an electrical heating wire formed of chromium-nickel steel and having a diameter of 0.6 mm. The ends of the windings are connected to a source of electric current. The energy output of the heating elements (that is the heating wire-wound quartz rods) can be expressed in cal/cm² sec. and is found by dividing the energy supplied expressed in calories per second, by the area of the plane containing the heating elements, 900 cm².

The test samples 14 are clamped between steel supports 3 and loose panels of asbestos 15 having a thickness of 34 mm, such an assembly being provided on each side of the plane containing the heating elements. Strips of asbestos 12 having a thickness of 10 mm are attached to each of the vertical side edges of the asbestos panels 15 so that the test sample 14 is separated from the associated asbestos panel 15 by an air cavity of 10 mm width. One of the test samples is exposed to 9 gas flames issuing from apertures 5 in a gas supply tube 16. Each aperture 5 has a diameter of 1 mm and the apertures are spaced from each other a distance of 30 mm. The gas supply is adjusted so that the flames have a length of 20 mm; the flames are directed perpendicularly to the test sample. The gas supply pipe is positioned at a height of 75 mm above the bottom of the box. An electrical resistance wire 4 which glows when supplied with current through terminals located on the outside of the box, is provided to ignite the gas flames.

The temperature is measured at two points in the box. Firstly in the centre of the box by means of a thermocouple 6 and at a distance of 5 mm from the test sample which is not exposed to the gas flames by a thermocouple 7. The apparatus also comprises a vent hole 8 in the bottom of the box, a chimney 9 at the top of the box, thermocouple tubes 10 and 11 (for the thermocouples 7 and 6 respectively), and an observation window 13.

6. Procedure.

The test box is first warmed up to a constant temperature by means of the gas jets, this initial heating being monitored by means of the thermocouple 6. The test sample which

is not exposed to the gas flames is affixed in place with its associated asbestos panel 15 and the other test sample is placed so that it partially closes the box, but does not touch the gas flames. As soon as the inside temperature has risen to 60°C, the second test sample and its associated asbestos panel 15 are secured in place to close the box, and the electric power supply to the heating wires on the rods 2 is switched on. When testing materials which develop extinguishing gases (so-called self-extinguishing materials), the gas ignition wire 4 (power consumption 20 Watts) is also connected to a power supply, so that the gas flames are immediately re-lit if they should be put out. When testing materials which distort or melt, wire netting (mesh size 12 mm, thickness 0.8 mm) is sandwiched between the steel supports 3 and the test samples, or the samples are glued (if possible) on to an asbestos panel having a thickness of at least 3 mm in order to prevent sagging. The temperature indicated by thermocouple 7 is noted at least every minute until flash-over occurs, or for a maximum time of 30 minutes from the time when the second test sample was fully secured. When testing materials which melt and drip to the bottom of the box during the test, the same procedure is used.

Flash-over may be observed visually by looking through the observation window 13 or may be deduced from the temperature change of thermocouple 7. Flash-over may be assumed if the test sample which is not exposed to the gas flames is burning or, if it is not visibly burning, the temperature of thermocouple 7 has risen by 15°C or more within 1 minute.

Using an energy supply of 0.05 cal/cm² sec., if flash-over has occurred within or exactly 15 minutes, the test is completed. If the energy supply is more than 0.05 cal/cm² sec. and a flash-over time has been found in the first test of less than or more than 15 minutes, then the test has to be repeated using other amounts of energy supply until from two or more tests, by graphic interpolation or extrapolation, the exact amount of energy supply at which flash-over occurs in exactly 15 minutes, can be deduced.

7. Classification.

Materials can be classified with respect to their flash-over intensity, F, as shown in the following table.

TABLE

Class I	$F \geq 0.4 \text{ cal/cm}^2 \text{ sec.}$	Material does not contribute to flash-over
Class II	$0.2 < F < 0.4 \text{ cal/cm}^2 \text{ sec.}$	Material contributes slightly to flash-over
Class III	$0.05 \leq F < 0.20 \text{ cal/cm}^2 \text{ sec.}$	Material contributes appreciably to flash-over
Class IV	$F < 0.05 \text{ cal/cm}^2 \text{ sec.}$	Material contributes strongly to flash-over

The testing of several commercially available thermal insulation materials showed that none of them passed the NEN flash-over test. The non-flammable materials disclosed in our British Specification 1411567 were also tested and were not able to pass the NEN flash-over test with a class 1 rating.

Boron compounds are known to improve the performance of various foams in fire tests, such as ASTM 1692, ASTM D 653-44, ASTM E 162 radiant panel test, or the Butler chimney flammability test for cellular plastics. The latter is described in detail in the *Journal of Cellular Plastics*, November 1967.

In the *Journal of Cellular Plastics*, September 1970, pages 215 et seq., Carlos J. Hilado et al describe the effect of boric acid, boric anhydride, sodium borate, zinc borate, and a number of organic boron compounds, on the flammability of rigid polyurethane foams. The boron compounds were used in concentrations of up to 40% by weight based on the polymer. It was found that although the boron compounds may reduce the burning rate and the extent of burning, none of the compositions were non-flammable or free of flash-over.

In U.S. Patent 3,740,358 it is disclosed that boric acid, boric oxide, and boron polyol complexes can be used to render a phenolic foam non-punking.

The punking property of phenolic foams is the property of continuing to glow and burn without a visible flame despite the removal of the external heat source. Although the boron compounds disclosed in U.S. Patent 3,740,358 may render a phenolic foam non-punking, the foam will still be combustible and be liable to flash-over when subjected to the above NEN test.

Since there is a serious demand for materials meeting the high requirements of the NEN test, and current as well as future regulations in this field will require a foam material for use in buildings to be free of flash-over as determined by the NEN test and tests comparable therewith, such as Williamson's Corner

Test and the Factory Mutual Channel Test, it is highly desirable to develop materials which have the required property.

We have now surprisingly found that certain foamed solid amino-formaldehyde furfuryl alcohol resins can be modified by the inclusion of boron compounds therein to provide cellular thermal insulation materials suitable for use in the building industry which pass the NEN flash-over test with a class 1 rating.

According to the present invention, we provide a method of preparing a foamed solid amino-formaldehyde furfuryl alcohol resin, which comprises polymerising a furfuryl alcohol-containing amino-formaldehyde liquid resin composition, the amine portion of the resin being one or more of urea, thiourea and melamine and the resin having an amine: formaldehyde molar ratio of from 1:1 to 1:5, and the liquid resin composition containing 15 to 90% by weight of free or bound furfuryl alcohol and a sufficient amount of a boron compound, said amount being at least 10%, based on the weight of the liquid resin composition, so that the foamed product obtained passes the muffle furnace test (as herein defined) at 500°C, the polymerization being effected in the presence of a blowing agent and an acid which is compatible with the liquid resin composition so that a substantially homogenous mixture is maintained during polymerization.

The present invention also comprises a foamed solid-amino-formaldehyde furfuryl alcohol resin made by the method according to the invention.

The muffle furnace test referred to herein is carried out as follows:

The muffle furnace test.

Apparatus.

The muffle furnace test is carried out in a laboratory horizontal muffle furnace (type Nr. 170 from Heracus, Germany) having a depth of 300 mm, a width of 170 mm and a height of 100 mm, all these dimensions being the interior furnace dimensions. The furnace is heated by means of electric heating elements

having a total consumption of 3000 Watts. The temperature is controlled by means of a thermostat capable of regulating the temperature inside the furnace with an accuracy of approximately 7.5°C in the range of from 500 to 550°C.

A jig for mounting the test samples during the test consists of a flat rectangular frame made from 9 mm stainless steel tubing. The outside dimensions of the frame are 160 × 250 mm. On one of the short sides of this frame, a cubicle sample holder made from thin stainless wire mesh is mounted. This wire mesh holder is in the shape of a box having internal dimensions of 32 × 32 × 32 mm, and is open upwards and towards the centre of the frame.

From the bottom of the sample holder extends a small iron-Konstantan thermocouple protected by a 2.5 mm diameter stainless steel tube. When the foam sample to be tested is placed in the sample holder, this thermocouple is in the centre of the sample and records the temperature in the centre of the sample.

Another thermocouple is placed just outside the centre of the left side of the sample holder. This thermocouple is unprotected and records the furnace temperature very close to the surface of the sample during the test. Both thermocouples are made from very thin wires (maximum 0.25 mm) to assure rapid response during the test.

A 1.5 mm bore stainless steel tube is provided which passes from the frame behind the sample holder and the end of the tube is bent horizontally over the sample holder so that the tip is 25 mm from the top of the sample. During the test, natural gas is fed through this tube to give a horizontal pilot flame 10 mm long and spaced 25 mm above the top of the sample. This flame ignites any flammable material given off from the sample during the test.

The two thermocouples are connected to a two point recorder with a full scale deflection of 250 mm, a sensitivity of 2 mV per cm, and a paper speed of 60 mm/min.

Also an event marker is provided, which allows the operator to mark the start and stop of any flashing or burning occurring during the test.

Calibration.

Prior to any test, the furnace should have been at the test temperature with the furnace door open for at least 6 hours.

A small cube, 30 × 30 × 30 millimetres, of mineral wool, density 60 kg/m³, is placed in the sample holder. The jig is pushed into the furnace so the sample holder is in the correct position close to the back wall of the furnace.

The temperature of the two thermocouples is now recorded and corrections in the furnace temperature are made if necessary. When

the conditions are correct, the temperature recorded in the centre of the dummy sample will be equal to said temperature $\pm 6^\circ\text{C}$.

After calibration, the jig is removed from the furnace and allowed to cool below 200°C before any test sample is placed in the sample holder.

Test samples.

The test samples have the dimensions 30 × 30 × 30 millimeters.

Before testing, the moisture content of the test samples should be in equilibrium with air having a temperature of 18–22°C and a relative humidity of 55 to 65%.

Test procedure.

The sample is placed in the sample holder and pressed down until the thermocouple is in the centre of the sample. If necessary, a small hole should be previously bored in the sample for this thermocouple.

The pilot flame is ignited and the jig is rapidly pushed into the furnace so that the sample is in the correct position close to the rear wall of the furnace and a mark is made on the recorder to indicate the start of the test.

The sample is now closely observed and any burning of sample or flashing of volatiles around the sample is recorded with the event marker.

The test is continued for at least 5 minutes, or for materials with which the temperature in the centre of the sample rises above the furnace temperature, until the centre temperature is again falling. The maximum temperature reached during the test is noted.

After the test, the jig is removed from the furnace and allowed to cool below 200°C before being used for the next test.

Evaluation of test results.

A sample showing no flashing or burning when the test is carried out at 500°C or higher is considered to have passed the muffle furnace test. We have found, in practice, that all materials that pass the muffle furnace test at 500°C or higher will pass the NEN flash-over test (i.e. will be graded Class 1 according to the above classification) and that all materials that fail the muffle furnace test at 500°C will not pass the NEN flash-over test (i.e. will not fall into Class 1). The muffle furnace test at 500°C can, therefore, be taken as equivalent to Class 1 of the NEN 1076, part C test.

It has been found that among the materials passing the muffle furnace test at 500°C, a further selection can be made based on the maximum temperature recorded during the test. Those materials showing lower maximum temperatures, such as temperatures below about 550°C, generally show better performance in other fire tests, and hence such

materials are particularly preferred.

The furfuryl alcohol-containing amino-formaldehyde liquid resin used as starting material may be a liquid amino-formaldehyde furfuryl alcohol resin or a solution of an amino-formaldehyde resin in furfuryl alcohol. The furfuryl alcohol content of the starting material may also be provided by a furfuryl alcohol prepolymer, such as are commercially available as "furan resins". Such furan resins are generally prepolymers in which the furfuryl alcohol monomer units are bonded together with loss of the alcohol group, that is they consist of a chain of furan rings linked together by methylene groups. The amount of such prepolymers which may be present depends on the amount and nature of the boron compound used, on the nature of the amino-formaldehyde resin, and on the degree of polymerisation of the furfuryl alcohol prepolymer. Generally it is preferred to less than 40% by weight of furfuryl alcohol in this form.

As indicated above, the furfuryl alcohol-containing amino-formaldehyde resin used is one in which the amine:formaldehyde molar ratio is from 1:1 to 1:5 and which contains from 15 to 90% by weight of free or bound furfuryl alcohol. Preferred resins are those in which the amine:formaldehyde molar ratio is from 1:1.5 to 1:4, more preferably from 1:1.5 to 1:2.5, or even more preferably from 1:1.7 to 1:2.1, and which contain from 25 to 70%, more preferably 25 to 50%, even more preferably 30 to 40%, by weight of free or bound furfuryl alcohol. The more preferred ranges of the amine:formaldehyde molar ratio give the optimum balance between the fire resistance and mechanical properties of the resulting foamed product, and the more preferred ranges of the proportion of furfuryl alcohol give the optimum balance between foaming characteristics and fire resistance.

Resin compositions that, in the absence of a boron compound, can be converted into a foam showing substantially no second exotherm at 200°C, for example a maximum temperature of about 225°C, when tested by the second exotherm test as hereinafter described, are preferred.

Resin compositions that in the presence of at least 10% of a boron compound, based on the weight of the resin, can be converted into a foam showing substantially no second exotherm at 200°C, for example a maximum temperature of about 225°C, when tested by the second exotherm test, are very useful.

The second exotherm test referred to herein is carried out as follows.

A sample is cut with dimensions of 6 × 6 × 6 cm. The sample is placed in the middle of an oven, the temperature of which is kept at 200°C. A thermocouple is inserted in the middle of the sample and the temperature of the foam is recorded. In foams having a second exotherm, the temperature of the foam will

rise above 200°C and the maximum temperature is noted.

Formulations which develop low exotherms generally require less boron compound to be free from flash-over, whereas foams having highly exotherms can be made free of flash-over only if a larger amount or a more effective type of boron compound is used.

The boron compounds that may be used may be inorganic or organic. Boric acid and boric oxide are preferred, but borax, boric acid esters, boron tribromide, boron trichloride, boron nitride, boron phosphate, boron trifluoride etherate, boron trifluoride methanol and boron trifluoride monoethylamine may also be used, and also complexes of boric acid with polyhydroxyl compounds and mixtures of boron compounds.

In carrying out the method according to the invention a variety of blowing agents and combinations of blowing agents may be used, for example Freon 113 (Trade Mark), Arcton 11 (Trade Mark), dimethoxyethane, methylenechloride, 1,1,1-trichloroethane or pentane. They are generally used in minor amounts, for example from 2 to 40% by weight, based on the resin.

Suitable surfactants for use in the method according to the invention are those typically used in polyurethane and urea formaldehyde foams, for example silicone-based surfactants, such as DC 193 manufactured by Dow Corning, and non-silicone-based surfactants, such as LK 221 manufactured by Air Products Ltd. A surfactant is generally used in a minor proportion such as 0.005 to 5% by weight, based on the resin, depending on the efficiency of the specific surfactant or blend of surfactants.

Suitable compatible acids for use in the method are, for example ortho-phosphoric acid, polyphosphoric acid and sulphuric acid. An oxy-acid of phosphorus is generally preferred, if desired in combination with another acid, such as sulphuric acid or para-toluene sulphonic acid, but an oxy-acid of phosphorus can be used as the sole acidic catalyst. If desired, the acid may be used in combination with an alcohol or hydroxy-aldehyde, such as glucose. A preferred combination is aqueous phosphoric acid containing 30—90% by weight of H_3PO_4 and up to 50% by weight of glucose. The catalyst is generally used in a minor proportion such as from 2 to 20% by weight, based on the resin.

Preferred alcohols for use in combination with the acid catalyst are 1,4-butanediol and propane-2-ol; other preferred alcohols are the polyglycols.

Conventional polymerization and foaming procedures are employed in preparing the foams of the present invention. The polymerization may, for example, be effected by bringing the starting materials together at ambient temperature or within the range of

10 to 40°C, and mixing them intimately. The mixing may be done at atmospheric pressure or at an elevated pressure up to 20 atmospheres or higher. The blowing agent and other additives, if used, may be added to the starting materials or as a separate stream during the mixing. The reaction mixture is then poured into open or closed moulds and allowed to polymerize into the final solid state.

The polymerization may be started at ambient temperature and pressure or heat may be applied to or extracted from the mould to initiate or control the initial rate of polymerisation. During polymerization, the heat of reaction will increase the temperature of the mixture and the blowing agent(s) will expand the material into the desired foamed state. The temperature during the reaction may rise up to between 40 and 130°C. After the initial setting of the foam material, cure may be completed by maintaining the material at an elevated temperature for a period of time of from 15 minutes to 10 hours depending upon the reactivity of the starting materials.

It appears that completion of the foaming reaction is essential if the product obtained is to perform well in fire tests and this completion is only obtained if the resin and the acid used are sufficiently compatible so as to be able to form an homogeneous mixture during foam formation.

If the resin and the acid have insufficient compatibility, or if during the reaction they become wholly or partly incompatible and separate out into macrophases, then the reaction will not go to completion and the foam will have a second exotherm reaction and show poor performance in fire tests.

The relationship between the fire resistance of the products obtained according to the invention and known fire-resistant foams suitable for use in the building industry is shown in Figure 4 of the accompanying drawings. Figure 4 is a diagram in which various levels of fire resistance are shown as the ordinate and

different groups of foamed resins are shown as the abscissae.

Level I of the ordinate represents the inherent fire resistance of the foamed material itself (that is without the addition of any boron compound), level II represents the fire resistance obtainable by incorporating a boron compound in the foamed resins of groups A and C and a small proportion of the foamed resins of group B, this level of fire resistance corresponding to the self-extinguishing classification of ASTM 1692, and level F—F' represents fire resistance such that the foamed resin passes the muffle furnace test at 500°C (corresponding to Class 1 of the NEN 1076, part C test). Along the abscissae, group A are phenolic resins, group B are amino-formaldehyde furfuryl alcohol resins, and group C are other foamed resins.

In order that the invention may be more fully understood, the following examples are given by way of illustration. Of these examples, 1.1—1.3, 2.1, 2.3, 2.4, certain of the parts of Example 4 (as explained therein), 5.1—5.4, 7, 8.1, 8.3, 10.2, 10.3, 11.1, 12.4, 13.1, 14.2—14.9 and 14.14—14.16 are not in accordance with the invention and are given for the purpose of comparison; the remaining examples are in accordance with the invention. All parts and percentages mentioned in the examples are by weight unless the contrary is stated; UFF stands for urea-formaldehyde furfuryl alcohol (resin).

Example I.

A series of foams was prepared using the formulations stated in Table I. The foams were tested according to the NEN 1076, part C test. The test results are stated as the time elapsed before a flash-over occurs at an energy input of 0.4 cal/cm².sec. The requirement for a class 1 rating in the test is that this time should exceed 15 minutes. In addition, results of muffle furnace tests and second exotherm tests are stated.

TABLE 1.1

Foam No.	1.1	1.2	1.3	1.4	1.5
1) UFF resin	60	60	60	100	100
2) Furan resin	40	40	40		
Silicone surfactant (DC 193)	1	1	0.8	1	1
Boric acid	30	30	25	35	35
Borax	—	—	—	2	3
Blowing agent (Freon 113)	6	6	6	6	1
3) Fyrepruffe			25		
Catalyst:					
Orthophosphoric acid (89% aqueous soln.)	9.1	7.2	—	9.7	9.4
Polyphosphoric acid	—	—	10	—	—
Isopropanol	—	—	6	—	—
1.4 Butanediol	2.6	—	—	—	—
Methanol	—	2	—	—	—
Water	2.6	2.0	—	4	5.2
Glucose	9.7	10.2	—	10.7	10.4
Muffle furnace test 500°C, flash +/-	+	+	+	—	—
2nd exotherm at 200°C, °C	450	227	442	206	206
NEN 1076 part C test, time to flash-over (min., sec.) at 0.40 cal/cm ² sec.	8.40	13.50 and 15.30	12.35	>18	>25
at 0.5 cal/cm ² sec.				>15	
at 0.6 cal/cm ² sec.				>15	

- 1) The UFF used to make each of foams 1.1–1.5 had a urea:formaldehyde molar ratio of 1:2.3. The UFF used for foams 1.1–1.3 contained 28.4% of furfuryl alcohol; that used for foams 1.4 and 1.5 contained 56.1% of furfuryl alcohol. These UFF resins were obtained from Borden Chemical Co.
- 2) Furan resin available under Trade Mark "Synphorm P490".
- 3) A commercial fire retardant containing ammonium phosphate and ammonium sulphate.

Foam 1.1 did not pass the muffle furnace test nor the NEN 1076 test although it contained 30 parts boric. This is consistent with the high amount of furan resin used in the preparation of the foam, which makes it difficult to obtain a complete cure, as is evident from the high temperature reached in the second exotherm test.

Foam 1.2 was made with a different catalyst and the second exotherm was much lower. This foam showed a very brief flash in the muffle furnace test and almost passed the NEN test.

Foam 1.3 shows that a conventional fire retardant cannot produce the desired effect. Finally foams 1.4 and 1.5 show the superior performance in the NEN 1076 test of urea-formaldehyde-furfuryl alcohol resin foams to

which sufficient boric acid has been added to make them pass the muffle furnace test at 500°C.

Example II.

Foamed materials were prepared using the formulations given in table 2.1. The resin blend was pumped to a mixing chamber in which it was intimately mixed with the catalyst. The mixture was poured into a mould and allowed to expand. The foams were post-cured at 70°C for 15 minutes (foam 2.1) or at 60°C for 2 hours (foams 2.2—2.5). Samples were cut and tested by the second exotherm test and the muffle furnace test as described above. Finally the foams were tested by the NEN 1076, part C flash-over test.

Test results are given in table 2.2.

TABLE 2.1

Foam No.	2.1	2.2	2.3	2.4	2.5
Borden TM1 a)	57.7	70	70		
Borden FRD 511 a)		30	30	100	
Borden FRD 530 a)					100
Furan resin	34.0				
Furfuryl alcohol	8.3				
Glucose	40				
Boric acid		20	10		20
DC 193 b)	0.2				1
Pluronic f 88 c)		1	1		
Dowfax a 11 d)				4	
Freon 113 e)	2.5	6	6		4
Freon 11 e)		4	4		5
Dimethoxymethane	1.25				
Dichloromethane	1.25				
Pentane				10	
Catalyst:					
o-phosphoric acid, 45%		6	6		5
Tetraphosphoric acid	7.8				
Isopropanol	5.8				
Ammonium chloride, 25%				4	

Footnotes to Table 2.1.

- a) the UFF designated TM 1 had a urea:formaldehyde (U:F) molar ratio of 1:1.7 and contained 46.0% furfuryl alcohol; that designated FRD 511 had a U:F ratio of 1:1.8 and contained 47.0% furfuryl alcohol; and that designated FRD 530 had a U:F ratio of 1:2.1 and contained 36.6% furfuryl alcohol. These UFF resins were obtained from Borden Chemical Co.
- b) silicone surfactant from Dow.
- c) Trade Mark; surfactant from BASF, Wyandotte.
- d) Trade Mark; surfactant from Dow.
- e) halogenated hydrocarbons from du Pont.

TABLE 2.2

Foam No.	2.1	2.2	2.3	2.4	2.5
Muffle furnace test at					
550°C flash/burn, sec.		16-32	8-118	6-87	10-121
T max. in °C		570	595	690	600
515°C flash/burn, sec.		-	22-120	5-183	14-123
T max. in °C		530	585	690	575
508°C flash/burn, sec.	flash + burn	-	89-132	19-157	-
T max. in °C		535	565	630	560
495°C flash/burn, sec.			99-131		
T max. in °C			570		
2nd exotherm at 200°C max. temp.	435	200	210		
NEN 1076					
performance	class 2	class 1	class 2	class 2	class 1
time to flash over at 0.2 cal/cm ² sec.				more than 16 min.	
0.4 cal/cm ² sec.	6 min. 45 sec.	more than 16 min.	7 min. 25 sec.	1 min.	more than 16 min.
0.6 cal/cm ² sec.		more than 16 min.			4 min. 45 sec.

Foam 2.1 contained no boron compound and failed both in muffle furnace test and in the NEN 1076 test.

Foam 2.2 contained 20% of boric acid and

passed the muffle furnace test both at 525°C and at 508°C and hence also the NEN 1076 test with a very high performance.

Foam 2.3 contained 10% of boric acid which

with this resin composition gave failure both in the muffle furnace and in the NEN 1076 test.

From the combined results with these two foams, we conclude that only a slight increase in boric acid is required in order to improve foam 2.3 so that it would pass the tests.

Foam 2.4 was made from a resin composition free of furan resin, but even so the fire performance in the absence of a boron compound was very poor.

Foam 2.5 was made from another urea-formaldehyde-furfuryl-alcohol resin and contained 20% boric acid. It passed the muffle furnace test at 508°C and, as expected, also the NEN 1076 test.

It will be apparent from the results of Example I and II that there is a good correlation between the muffle furnace test and the NEN 1076 test.

Example III.

A foamed material was prepared from a blend consisting of the following ingredients.

Urea-formaldehyde-furfuryl alcohol resin 100 parts.

Silicone surfactant 1.5 parts.

Boric acid 15 parts.

n-Pentane 10 parts.

This urea-formaldehyde-furfuryl alcohol resin had an average U:F:F molar ratio of 1:2.0:0.67; it contained 32.0% furfuryl alcohol and had a viscosity of 5400 cp at 25°C.

The blend was pumped into a mixing chamber where it was intimately mixed with 12—13 parts of an acid catalyst consisting of 50% orthophosphoric acid. The mixture was introduced into heated moulds having the dimensions 85 × 95 × 10 cm and allowed to rise and cure. After 30 min. in the moulds, the foam blocks were placed in a cabinet heated to 50°C with circulating air and left overnight to cure and dry completely.

Samples of 6 × 6 × 6 cm were cut and tested in the second exotherm test (SET) at 200°C as described above.

Samples were also tested in the muffle furnace test at 540°C.

Finally the foam was tested in the NEN 1076, part C flash-over test.

The test results are given in table 3.1.

TABLE 3.1.

Foam No.	3.1	3.2
Maximum temperature second exotherm test at 200°C max. temp.	210	210
Muffle furnace test at 540°C flash	no flash	no flash
max. temp. in °C	545	565
flash-over test NEN 1076, part C,		
time to flash at 0.40 cal/cm ² sec.	more than 30 min.	more than 30 min.
time to flash at 0.50 cal/cm ² sec.	6 min. 42 sec.	
time to flash at 0.60 cal/cm ² sec.	4 min. 34 sec.	3 min. 53 sec.
Light transmission percent at 0.40 cal/cm ² sec.	90	96
Rating	class 1	class 1

Foams 3.1 and 3.2 are the same in composition, apart from a slight variation in the catalyst content.

This example shows the use of a resin composition which with 15% boric acid will pass

the muffle furnace test at a temperature of 540°C.

As expected, the foams also passed the NEN 1076 test with a class 1 rating.

A series of foams was prepared using the following formulation.

These resins were obtained from Borden Chemical Co.

In the absence of furfuryl alcohol prepolymer, the addition of 20% boric acid will make the foam pass the muffle furnace test. As the content of furfuryl alcohol prepolymer is increased, higher levels of boric acid are required to obtain the desired MFT performance.

(a) Each of the UFF resins used in foams 4.1—4.6 had a U:F ratio of 1:2.3; their contents of furfuryl alcohol were as follows:

TABLE 4.1.

	5	10	15	20	25	30	40	50	60
Boric acid									
UFF resin	100	100	100	100	—	100	100	100	100
Synphorin P490	—	—	—	—	—	—	—	—	—
MFT Flashing 550°C	+	+	+	—	—	—	—	—	—
Max. temp. in MFT 550°C	580	580	570	560	—	550	—	—	550
Max. temp. in SET 200°C	220	216	216	213	—	211	—	—	210

TABLE 4.2.

Boric acid	30
UFF resin	95
Synphorm P490	5
MFT Flashing 550°C	-
Max. temp. in MFT 550°C	560
Max. temp. in SET 200°C	212

TABLE 4.3.

Boric acid	20	25	30	60
UFF resin	90	90	90	90
Synphorm P490	10	10	10	10
MFT Flashing 550°C	+	-	-	-
Max. temp. in MFT 550°C	560	570	555	550
Max. temp. in SET 200°C	220	215	211	208

TABLE 4.4.

Boric acid	20	30	40	60
UFF resin	80	80	80	80
Synphorm P490	20	20	20	20
MFT Flashing 550°C	+	-	-	-
Max. temp. in MFT 550°C	590	565	560	560
Max. temp. in SET 200°C	219	211	215	216

TABLE 4.5.

Boric acid	30	40	50	60
UFF resin	70	70	70	70
Synphorm P490	30	30	30	30
MFT Flashing 550°C	+	+	-	-
Max. temp. in MFT 550°C	600	570	570	570
Max. temp. in SET 200°C	213	226	220	221

TABLE 4.6.

Boric acid	30	50	60
UFF resin	60	60	60
Synphorm P490	40	40	40
MFT Flashing 550°C	+	+	+
Max. temp. in MFT 550°C	610	610	615
Max. temp. in SET 200°C	223	222	253

Example V.

Foams were prepared using a conventional technique from an aqueous solution of a commercial urea-formaldehyde resin (vide U.S. Patent 3,006,871), that is a solution of 100

parts of Urecoll 270, BASF having a U:F ratio of 1:1.7, in 100 parts of water. Foams were made using this solution and the formulations stated below.

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TABLE 5.1.

Foam No.	5.1	5.2	5.3	5.4
Ureacoll 270, 50% aqueous soln.	200	200	150	300 1)
Water	100	100	50	—
Surfactant	3	3	2.5	2
Furfuryl alcohol	50	50	25	25
Boric acid		30		30
9.7% aq H_3PO_4	50	50	50	20
MFT (550°C) flash +/-	+	+	+	+
MFT (550°C) T. max. °C	660	715	590	670

1) 2 parts Ureacoll 270 dissolved in 4 parts water.

It will be apparent from these results that all the foams failed the MFT and the high temperatures recorded in the test show that a sufficient degree of cure has not been achieved by using this technique of foam preparation.

In such cases, the addition of boric acid is not able to remove the flash-over characteristic from the foam.

Example VI.

A foam (Foam 6) was prepared using a solution of 40 parts of a commercial urea-formaldehyde resin (Ureacoll 270, BASF) having a U:F molar ratio of 1:1.7 dissolved in 60 parts of furfuryl alcohol. To 100 parts of this solution, were added

- 10 parts of water
- 1 part of surfactant (DC 193)
- 30 parts of boric acid
- 2 parts of Freon 133, and, as a catalyst,
- 64 parts of 59% aqueous o- H_3PO_4 .

The foam was allowed to rise and cure. When tested in the muffle furnace test (550°C), the foam did not flash, the maximum temperature recorded being 575°C.

Example VII.

This example is intended to show that the addition of boric acid is, in itself, not sufficient to render a foam non-flashing, although the particular foam showed no second exotherm. The foam must also be prepared from urea-formaldehyde and furfuryl alcohol.

A polyurethane foam was prepared by reacting 50 parts of a commercial polyether polyol RF 33 from Lancro Chemicals with 70 parts of a polyisocyanate in the presence of 15 parts blowing agent and the usual surfactant and catalyst additives. The foam had a density of 35 kg/m³. It had no second exotherm, but burned vigorously with production of heavy smoke in the 550°C muffle furnace test.

A similar foam was prepared with the addition of 30 parts of boric acid. The foam had a density of 21.5 kg/m³, had no exotherm, and burned violently in the muffle furnace test, both at 550 and at 500°C.

Example VIII.

A UFF resin having a U:F molar ratio of 1:2.6 and containing 31.0% furfuryl alcohol, was prepared according to Example 1 of British Specification 942,845. From this resin foams were prepared according to the formulations stated in Table 8.1, which also contains the test results obtained.

TABLE 8.1.

Foam	8.1	8.2	8.3	8.4
UFF resin	100	100	100	100
Furfuryl alcohol	-	-	-	5
Surfactant DC 193	1	1	1	1
Water	-	-	-	5
Freon 113	1	1	-	-
Sodium bicarbonate	-	-	6	5
Boric acid	-	30	-	30
o-H ₃ PO ₄ , 59% aq. soln.	12	15	-	-
o-H ₃ PO ₄ , 66.5% aq. soln.	-	-	22	22
Muffle furnace test (550°C), flash +/-	+	-	+	-
Max. temp. °C	640	560	690	575
2nd exotherm test (200°C), °C	-	206	208	204

It will be seen from these results that only foams containing boric acid and having no second exotherm at 200°C will pass the muffle furnace test at 550°C.

British Specification 1,248,756 having a U:F:F molar ratio = 1:3:6.0 and containing 37.2% furfuryl alcohol. Foams were prepared using this resin with the formulations stated in Table 9.1, which also contains the test results obtained.

Example IX.

A. UFF resin was prepared according to

TABLE 9.1.

Foam No.	9.1	9.2	9.3
UFF resin	100	100	100
Furfuryl alcohol	20	30	40
Boric acid	36	39	42.5
Surfactant (DC 193)	1.2	1.3	1.45
Blowing agent (Freon 113)	1.2	1.3	1.45
o-H ₃ PO ₄ , 89% aq. soln.	9.6	6	6
Water	4.8	3	3
2nd exotherm test at 200°C, max. temp. °C	211	208	211
Muffle furnace test at 550°C, flash +/-	-	-	-
Max. temp. °C	600	595	605

All foams were free of a second exotherm and passed the muffle furnace test.

Example X.

5 A UFF resin was prepared according to British Specification 1,248,756, having a

U:F:F molar ratio = 1:3:1 and containing 34.4% furfuryl alcohol. From this resin foams were made using the formulations stated in Table 10.1. The test results obtained are also stated in the table.

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TABLE 10.1.

Foam No.	10.1	10.2	10.3	10.4
UFF resin	100	100	100	100
Surfactant (DC 193)	1	1	1	1
Freon 113	1	1	1	1
Boric acid	30	10	-	30
Glucose			20	
Catalyst:				
o-H ₃ PO ₄ , 89% aq. soln.	8	8	8	8
Water	4	4	4	4
glucose	-	-	-	10
2nd exotherm test (200°C), max. temp. (°C)	208	208	225	206
Muffle furnace test (550°C), flash +/-	-	+	+	-
Max. temp., °C	585	580	715	600

The foams containing 30 parts of boric acid and having no second exotherm at 200°C, passed the muffle furnace test.

Example XI.

15 Foams were prepared using a resin similar to the one used in Example X, but having a U:F:F molar ratio = 1:3:2 and containing 51.5% furfuryl alcohol.

20 Table 11.1 sets out the formulations used and the test results obtained.

Table 11.1.

Foam No.	11.1	11.2
UFF resin	100	100
Surfactant (DC 193)	1	1
Blowing Agent (Freon 113)	1	1
Boric acid	-	30
Catalyst:		
o-H ₃ PO ₄ , 89% aq. soln.	8	8
Water	4	4
Glucose		10
2nd exotherm test, (200°C) °C	219	210
Muffle furnace test 550°C, flash +/-	+	-
Max. temp., °C	555	560

Example XII.

Preparation of glyoxal-boric acid complex: 193.5 g of 30% aqueous glyoxal (1 mole) was blended with 61.8 g boric acid (1 mole) and heated to 85-90°C for one hour and cooled to room temperature. A white precipitate was formed, which was filtered off, washed and dried. Yield was 68.3 g.

Four foams were prepared using the following formulation:

100 parts urea-formaldehyde furfuryl alcohol resin with an average U:F:F molar ratio of 1:1.8:0.6 and containing 31.0% furfuryl alcohol,
1.5 parts silicone surfactant (Dow Corning DC 193).
10 parts n-pentane,
25 parts boron compound, and
12-17 parts catalyst containing 50% phosphoric acid.

The type of boron compound and test results obtained are shown in Table 12.1.

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TABLE 12.1.

Foam No.	12.1	12.2	12.3	12.4
Trimethoxy-boroxine	25			
Sodium tetraborate		12.5		
Boric acid		12.5		
Glyoxal/boric acid complex			25	
Second exotherm at 200°C	205	215	207	212
Muffle furnace test 505°C, flash +/-	-	-	-	+
Max. temp. during test, in °C	540	515	505	532

Foam 12.4, which contained no boron compound, is included as a control. It flashed and burned in the muffle furnace test and did not pass the NEN 1076 test. The other foams showed no burning in the muffle furnace and passed the NEN 1076 test.

Example XIII.

Foams were prepared using a resin similar to the one used in Example X, but having a U:F:F molar ratio of 1:3:6 and a furfuryl alcohol content of 75.9%.

Table 13.1 sets out the formulations used and the test results obtained.

Table 13.1.

Foam No.	13.1	13.2
UFF resin	100	100
Surfactant (DC 193)	1	1
Freon 113	1	1
Boric acid	—	30
Glucose	20	
Catalyst:		
o/H ₃ PO ₄ , 89% aq. soln.	8	8
Water	4	4
Glucose, dissolved		10
2nd exotherm test (200°C), °C	223	210
Muffle furnace test, 550°C, flash +/-	+	—
Max. temp., °C.	740	580

Example XIV.

A series of foams was made by reacting 100 parts of a commercial urea-formaldehyde furfuryl alcohol resin (Borden TM1) having a U:F molar ratio of 1:2.3 and containing 55.4% furfuryl alcohol, with 1 part of a surfactant (DC 193), and 6 parts of a blowing agent (a mixture of 1,1,1-trichloroethane and

dichloroethane in a 1:2 weight ratio) in the presence of 10 parts of ortho-phosphoric acid (specific gravity 1.5) as catalyst. In addition the formulations contain filler and/or water as stated in Table 14.1.

In foams 14.11 to 14.17, the 10 parts of o—H₃PO₄ (s.g. 1.5) were replaced by 9 parts 6NH₄SO₄.

TABLE 14.1

Foam No.	14.1	14.2	14.3	14.4	14.5	14.6	14.7	14.8	
Boric acid	30	-	-	-	20	-	-	10	
Glucose	-	-	30	20	-	-	10	-	
Talc	-	30	-	-	-	20	-	-	
Water	-	-	-	-	-	-	-	-	
Muffle furnace test 550°C, flash +/-	-	+	+	+	+	+	+	+	
Max. temp., °C	555	675	700	670	550	670	665	625	

Foam No.	14.9	14.10	14.11	14.12	14.13	14.14	14.15	14.16	14.17
Boric acid	-	30	30	30	30	-	-	-	30
Glucose	-	-	-	-	-	30	-	-	-
Talc	10	-	-	-	-	-	30	-	-
Water	-	4	6	8	2	4	4	-	-
Muffle furnace test 350°C, flash +/-	+	-	-	-	-	+	+	+	-
Max. temp., °C	635	585	560	570	560	700	690	700	570

It will be apparent from this table that the foams containing 30 parts of boric acid passed the muffle furnace test.

WHAT WE CLAIM IS:—

1. A method of preparing a foamed solid amino-formaldehyde furfuryl alcohol resin, which comprises polymerising a furfuryl alcohol-containing amino-formaldehyde liquid resin composition, the amine portion of the resin being one or more of urea, thiourea and melamine and the resin having an amine: formaldehyde molar ratio of from 1:1 to 1:5, and the liquid resin composition containing 15 to 90% by weight of free or bound furfuryl alcohol and a sufficient amount of a boron compound, said amount being at least 10%, based on the weight of the liquid resin composition, so that the foamed product obtained passes the muffle furnace test (as herein defined) at 500°C, the polymerisation being effected in the presence of a blowing agent and an acid which is compatible with the liquid resin composition so that a substantially homogenous mixture is maintained during polymerisation.

2. A method according to claim 1, in which the liquid resin composition used as starting material is one that, in the absence

of a boron compound, can be converted into a foam showing no second exotherm at 200°C when tested as herein described.

3. A method according to claim 1, in which the liquid resin composition used as starting material is one that in the presence of at least 10% of a boron compound, based on the weight of the liquid resin composition, can be converted into a foam showing no second exotherm at 200°C when tested as herein described.

4. A method according to any of claims 1 to 3, in which the liquid resin composition contains 25 to 70% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.5 to 1:4.

5. A method according to any of claims 1 to 3, in which the liquid resin composition contains 25 to 50% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.5 to 1:2.5.

6. A method according to any of claims 1 to 3, in which the liquid resin composition contains 30 to 40% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.7 to 1:2.1.

7. A method according to any of claims 1 to 6, in which the boron compound is boric acid.

TABLE 14.1

Foam No.	14.1	14.2	14.3	14.4	14.5	14.6	14.7	14.8	
Boric acid	30	-	-	-	20	-	-	10	
Glucose	-	-	30	20	-	-	10	-	
Talc	-	30	-	-	-	20	-	-	
Water	-	-	-	-	-	-	-	-	
Muffle furnace test 550°C, flash +/-	-	+	+	+	+	+	+	+	
Max. temp., °C	555	675	700	670	550	670	665	625	

Foam No.	14.9	14.10	14.11	14.12	14.13	14.14	14.15	14.16	14.17
Boric acid	-	30	30	30	30	-	-	-	30
Glucose	-	-	-	-	-	30	-	-	-
Talc	10	-	-	-	-	-	30	-	-
Water	-	4	6	8	2	4	4	-	-
Muffle furnace test 350°C, flash +/-	+	-	-	-	-	+	+	+	-
Max. temp., °C	635	585	560	570	560	700	690	700	570

It will be apparent from this table that the foams containing 30 parts of boric acid passed the muffle furnace test.

5 WHAT WE CLAIM IS:—

1. A method of preparing a foamed solid amino-formaldehyde furfuryl alcohol resin, which comprises polymerising a furfuryl alcohol-containing amino-formaldehyde liquid resin composition, the amine portion of the resin being one or more of urea, thiourea and melamine and the resin having an amine: formaldehyde molar ratio of from 1:1 to 1:5; and the liquid resin composition containing 15 to 90% by weight of free or bound furfuryl alcohol and a sufficient amount of a boron compound, said amount being at least 10%, based on the weight of the liquid resin composition, so that the foamed product obtained passes the muffle furnace test (as herein defined) at 500°C, the polymerisation being effected in the presence of a blowing agent and an acid which is compatible with the liquid resin composition so that a substantially homogenous mixture is maintained during polymerisation.

2. A method according to claim 1, in which the liquid resin composition used as starting material is one that, in the absence

of a boron compound, can be converted into a foam showing no second exotherm at 200°C when tested as herein described.

3. A method according to claim 1, in which the liquid resin composition used as starting material is one that in the presence of at least 10% of a boron compound, based on the weight of the liquid resin composition, can be converted into a foam showing no second exotherm at 200°C when tested as herein described.

4. A method according to any of claims 1 to 3, in which the liquid resin composition contains 25 to 70% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.5 to 1:4.

5. A method according to any of claims 1 to 3, in which the liquid resin composition contains 25 to 50% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.5 to 1:2.5.

6. A method according to any of claims 1 to 3, in which the liquid resin composition contains 30 to 40% by weight of free or bound furfuryl alcohol and has an amine:formaldehyde molar ratio of from 1:1.7 to 1:2.1.

7. A method according to any of claims 1 to 6, in which the boron compound is boric acid.

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8. A method according to any of claims 1 to 7, in which the initial mixture contains from 10 to 60% of the boron compound, based on the weight of the liquid resin composition.

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9. A method of preparing a foamed solid amino-formaldehyde furfuryl alcohol resin substantially as herein described with reference to foams numbered 1.4, 1.5, 2.2, 2.5, 3.1, 3.2, 6, 8.2, 8.4, 9.1—9.3, 10.1, 10.4, 11.2, 12.1—12.3, 13.2, 14.1, 14.10—14.13 and 14.17 of the Examples.

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10. A foamed solid amino-formaldehyde furfuryl alcohol resin when prepared by the method claimed in any of the preceding claims.

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