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(56) Documents Cited:  
**GB 1478043 A** **GB 1174341 A**  
**WO 1987/001070 A** **US 4751249 A**

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(54) Title of the Invention: **Material**  
Abstract Title: **Syntactic foam**

(57) A low density syntactic foam comprises hollow glass microspheres encapsulated in a styrene based resin system, in which the volume fill of the microspheres is at least about 70%. The material is formed by forming a liquid mix of hollow glass microspheres including floater and sinker fractions and a styrene based resin system, pouring the liquid syntactic into a mould, vibrating the liquid syntactic and subsequently curing the liquid syntactic whilst controlling the gelation time of the liquid syntactic to separate out the floater and sinker fractions of the microspheres before gelation occurs to concentrate the volume fill of the floater fraction microspheres in a layer of the resulting cured syntactic foam and the volume fill of the sinkers fraction microspheres in another lower and resin-rich layer of the resulting cured syntactic foam and removing the resin rich layer containing the concentration of sinkers fraction.

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**MATERIAL**

5 This invention relates to a material and a method of making a material and more particularly to a syntactic foam and a method of making a syntactic foam for reducing the submerged weight of a subsurface/seabed structure or an underwater vehicle.

10 By reducing the density of the syntactic foam used in fabricating the body of the buoyancy elements, the overall weight of the buoyancy elements can be reduced, thereby reducing the volume of foam and product size required to provide the same uplift, which in turn reduces the overall cost of production of the buoyancy elements.. Reduction in product size for a given uplift may offer additional operational benefits such as reduced drag from ocean currents during operation or reduced dynamic loads from active sea states during launch of the subsurface structure or underwater vehicle.

15 Syntactic foams are typically referred to either as pure or composite. Pure syntactic foams comprise hollow glass microspheres encapsulated in a resin system, such as epoxy. Composite syntactic foams comprise a combination of large macrospheres typically of around 40mm diameter core which are encapsulated in a matrix of pure syntactic.

20 The macrospheres are of lower density than the pure syntactic of the same depth rating. They are also lower cost/kg. The use of macrospheres therefore produces buoyancy foams of lower density and lower cost than pure syntactics.

25 In certain cases the disadvantages of using composite syntactic foams outweigh the significant cost and density advantages. These include service depth limitation of around 4500MSW which is due to the limiting hydrostatic pressure resistance performance of the macrospheres in the composite syntactic, reduced mechanical strength compared to pure syntactics, greater susceptibility to mechanical damage from impacts and abrasion, greater buoyancy loss in service, an inability to modify the foam blocks after manufacture and during service and poorer cosmetics and dimension control as composite blocks have to be fairly rough moulded to essentially final

dimensions whereas pure syntactics can be CNC-machined to complex shapes and a fine finish.

5 Therefore pure syntactics are typically used for ROVs, AUVs and subsea work tools where these disadvantages of composite foams are of major importance.

Standard pure syntactics used in composite foams are relatively cheap but have the major disadvantage of a relatively high density which is a problem for subsea vehicles for example due to increased on-deck handling weight and increased size and therefore  
10 reduced manoeuvrability. Product development focus is therefore on reducing the pure syntactic density even if this involves a significant cost increase.

The density of a pure syntactic foam is dependent upon.

- 15 1. The strength of the resin matrix – a stronger matrix allows the use of lighter grades (lower collapse pressure) of microspheres by providing increased reinforcement;
2. The density of the resin matrix;
3. The density of the microsphere for a given pressure rating;
4. The volume fill of microspheres in the resin matrix.

20

The scope for using a stronger matrix is very limited as epoxy resins are amongst the strongest available.

25 Other resin matrices of similar or only slightly lower performance but of significantly lower density are available.

There is only a very limited range of standard glass microspheres available and the glass type used, which decides the microsphere strength, is essentially limited to fused soda lime borosilicate glass. There are premium grades of glass microsphere available, but at  
30 an excessive and unacceptable cost premium. These premium grades use essentially the same glass and process technology but deliver their superiority by having the non-buoyant “sinkers” fraction, which is always present after the manufacturing process, removed by a separate floatation step. The improvement i.e. reduction in density, from applying a floatation step to any microsphere grade, is very significant. However the

problem lies in practicality as floatation, separation, drying and anticaking protection are slow, costly and laborious steps.

5 There is a limit in the volume quantity of microspheres that can be added to a resin system and still maintain any sort of liquid characteristics e.g. the ability to pump – depending on the microsphere particle size distribution, this limit is typically 55-60 % by volume for example for an epoxy resin system and about 59-62% by volume for a styrene resin system.

10 The present invention aims to provide a syntactic foam material which has a low density and thus provides good buoyancy characteristics whilst also retaining the strength of a pure syntactic material at an acceptable cost.

15 The present invention also aims to provide a method of making a syntactic foam material which has a low density when compared to known pure syntactic materials.

20 According to one aspect of the invention there is provided a low density syntactic foam comprising hollow glass microspheres encapsulated in a styrene based resin system, in which the volume fill of the microspheres is at least about 70%.

25 Preferably the styrene is selected from t-butyl styrene or one or more isomers of methyl styrene.

Advantageously the styrene has a density of around 850-950KG/m<sup>3</sup> and relatively low viscosity of around 10-50MPa.s

30 Advantageously the syntactic foam further comprises trimethylolpropane trimethylacrylate to act as a cross-linker within the otherwise linear styrene polymer matrix.

Preferably the syntactic foam further comprises a coupler, a wetting agent, an accelerator and one or more catalysts.

Advantageously the coupler comprises , a methacryloxy functional trimethoxy silane, the wetting agent comprises unsaturated polar esters and fatty acid-modified polyamide salts, the accelerator comprises a 6% solution of cobalt naphthenate dissolved in styrene and the catalyst comprises methyl ethyl ketone peroxide and/or  
5 dibenzoyl peroxide.

Preferably the low density syntactic foam has a cured and finished density of between 395 to 600 KG/m<sup>3</sup>.

10 Advantageously the microspheres when added to the styrene based resin system comprise both a floater fraction and a sinker fraction to form a liquid syntactic. During production of the foam the floater fraction of the microspheres are concentrated in an upper layer of the syntactic foam and the sinker fraction are concentrated in a separate layer, typically a lower resin layer, by vibrating the liquid syntactic and subsequently  
15 curing the liquid syntactic whilst controlling the gelation time of the liquid syntactic to separate out the floater and sinker fractions of the microspheres before gelation occurs allowing the separated layer containing the sinker fraction of the microspheres to be removed.

20 According to a second aspect of the present invention there is provided a method of producing a low density syntactic foam comprising the step of forming a liquid mix of hollow glass microspheres including floater and sinker fractions and a styrene based resin system, pouring the liquid syntactic into a mould, vibrating the liquid syntactic and subsequently curing the liquid syntactic whilst controlling the gelation time of the  
25 liquid syntactic to separate out the floater and sinker fractions of the microspheres before gelation occurs to concentrate the volume fill of the floater fraction microspheres in a layer of the resulting cured syntactic foam and to concentrate he volume fill of the sinkers fraction microspheres in another lower and resin-rich layer of the resulting cured syntactic foam and removing the resin-rich layer containing the concentration of  
30 sinkers fraction.

According to a third aspect of the present invention there is provided a buoyancy material comprising a syntactic foam according to the first aspect of the present invention.

An embodiment of the present invention will now be described.

5 In order to prepare a block of finished material of approximately 750mm x 500mm x 150mm high, 30.7kg of t-butyl styrene is mixed with 1.38kg of a cross-linker trimethylolpropane trimethacrylate and a 0.15 kg of a coupler Silquest A174NT, 0.08kg of a wetting agent comprising unsaturated polar esters and fatty acid-modified polyamide salts and commercially available under the name EFKA 8503 and 0.009kg of an accelerator comprising 6% (as cobalt) solution of cobalt naphthenate dissolved in  
10 styrene commercially available as Accelerator R in a vacuum rated mixer equipped with a slow speed, low shear agitator.

The styrene has a density of around 850KG/m<sup>3</sup> and relatively low viscosity of around 10-50MPa.s.

15

To this is added 23kg of glass microspheres available from 3M as S38XHS with a density of 0.38 g/cc and a target crush strength (90% survival ) of 5,500 psi.

20 After evacuating the mixer to provide a vacuum the composition is mixed together. Thereafter the vacuum is released and 0.085kg of a catalyst such as commercially available Catalyst O comprising methyl ethyl ketone peroxide is added and the mixer is evacuated once more and the mixer agitator operated.

25 After the vacuum is released the discharge valve of the mixer is opened to allow the mix to flow down into a mould of internal dimensions 777mm x 530mm x 300mm high which is placed below the valve. Typically the filled height of the mould is around 222mm.

30 The filled mould is then transferred to a vibrating table sized for the mass of the filled mould and the table is vibrated for around 12 hours following which the mould is transferred to a cure oven operating at around 50 deg C. The condition of the material in the mould within the oven is monitored visually and the block can advantageously be demoulded when the block is still in a gelled state. It is expected that the block will be

solid after approximately 6 hours. The mould is removed from the oven and inverted to discharge the block. At this stage the height of the block is typically around 220mm.

5 During the mixing, vibrating and curing process, the block separates out into distinct layers. The heavy solid glass “sinters” fraction of the microspheres settles in a layer of resin at the bottom of the block of around 10mm thick. A clear resin layer of around 20mm thick forms above this bottom layer with the main syntactic foam layer forming above that. The main syntactic foam layer forms as a consolidated layer of around 180mm thick with an upper friable layer of around 10mm thick.

10

The addition of catalysts and accelerators in combination with control of the temperature of the process steps allows the cure characteristics and particularly the cure onset of the low viscosity styrene resins to be controlled to ensure that the period before gelation of the block is extended to enable maximum separation of the floater and sinker fractions of the microspheres into their respective layers within the block.

15

Whilst the heavy solid glass “sinters” fraction settle at the bottom of the block, the light, hollow “floaters” fraction of the microspheres rise to the top of the block to form a layer of solid cake of extremely high volume fill which is typically over 70% by volume. This is a volume fraction of microspheres in resin which cannot be produced by mixing and curing a standard resin and microsphere system.

20

The bottom 2 gelatinous layers of the inverted block which comprise the clear resin layer material and solids-laden lower material (the “sinker” fraction) are peeled or scraped off the syntactic block. The remaining block is then returned to the cure oven to complete a further cure process for around 12 hours after which the cured block is transferred to a post-cure oven operating at around 90 deg C for about 6 hours.

25

The block is then removed from the post- cure oven and allowed to cool slowly to ambient temperature under a thermal blanket. This cooling process typically takes at least 24 hours.

30

The upper friable surface of the block is then skimmed to remove around 10mm and the bottom surface is machined to produce a final block thickness of around 150mm. The

vertical sides of the block are machined to remove the thin layer of friable material and then to produce the final block dimensions as required with a density of around 490 kg/m<sup>3</sup>.

- 5 Whilst it may be possible to produce a syntactic foam from a standard epoxy resin system with a density of around 490 KG/m<sup>3</sup>, due to the limited pressure rating of the light microspheres necessary for such a system, the resulting foam will have a service depth rating of around 2000MSW as opposed to the service depth rating of around 6000MSW of the styrene based syntactic foams which can be produced in accordance  
10 with the present invention.

The syntactic foam of the present invention is provided by initial forming a liquid syntactic from a resin system and glass microspheres containing "sinkers" fraction at a maximum microsphere volume fill for liquid handleability which is typically 59-62% for  
15 styrene resins. This achieves the minimum possible syntactic foam density by utilising a low density, high stiffness resin system in a manufacturing process which simultaneously separates out the heavy, density-increasing "sinkers" fraction and also achieves maximum packing/consolidation of floating fraction microspheres in the syntactic foam layer which produces the elevations in volume fill of at least about 70%  
20 as noted above.

To further illustrate the advantages of the present invention, the following table gives the cured densities of a standard pure epoxy syntactic and a low density syntactic according to the present invention for a range of hollow glass microspheres.  
25



Table 1

Microsphere Density, kg/m <sup>3</sup>	Cured Density- 'Standard' Epoxy Syntactic Foam, kg/m <sup>3</sup>	Cured Density- 'Low Density' Styrene Syntactic Foam, kg/m <sup>3</sup>
250	595	395
290	645	435
320	665	450
380	695	490
420	720	565

5 In a further embodiment of the present invention the block is removed from the cure oven when in a fully solid state and the bottom 2 layers of pure resin and sinkers-containing resin are removed once fully cured and hard, for example by machining these layers off the block.

10 In the embodiment described, the styrene is t-butyl styrene but this may be replaced with one or more isomers of methyl styrene with a density of about 950 KG/m<sup>3</sup> to achieve the same advantageous volume fill of floater fraction of microspheres in the finished syntactic foam.

15

## CLAIMS

1. A low density syntactic foam comprising hollow glass microspheres encapsulated in a styrene based resin system, in which the volume fill of the microspheres is at least about 70%.  
5
2. A low density syntactic foam of claim 1, wherein the styrene is selected from t-butyl styrene or one or more isomers of methyl styrene.
- 10 3. A low density syntactic foam of claim 1 or 2, wherein the styrene has a density of around 850-950KG/m<sup>3</sup> and relatively low viscosity of around 10-50MPa.s.
4. A low density syntactic foam of any of claims 1-3 wherein the syntactic foam further comprises trimethylolpropane trimethylacrylate.  
15
5. A low density syntactic foam of any of claims 1-4, wherein the syntactic foam further comprises a coupler, a wetting agent, an accelerator and one or more catalysts.
6. A low density syntactic foam of claim 5, wherein the coupler comprises a methacryloxy functional trimethoxy silane, the wetting agent comprises unsaturated polar esters and fatty acid-modified polyamide salts, the accelerator comprises a 6% solution of cobalt naphthenate dissolved in styrene and the catalyst comprises methyl ethyl ketone peroxide and/or dibenzoyl peroxide.  
20
7. A low density syntactic foam having a cured and finished density of between 395 to 600 KG/m<sup>3</sup>.  
25
8. A low density syntactic foam substantially as hereinbefore described.
- 30 9. A method of producing a low density syntactic foam comprising the step of forming a liquid mix of hollow glass microspheres including floater and sinker fractions and a styrene based resin system, pouring the liquid syntactic into a mould, vibrating the liquid syntactic and subsequently curing the liquid syntactic whilst controlling the gelation time of the liquid syntactic to separate out the floater and sinker fractions of

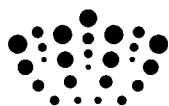
the microspheres before gelation occurs to concentrate the volume fill of the floater fraction microspheres in a layer of the resulting cured syntactic foam and concentrate the volume fill of the sinkers fraction microspheres in another lower and resin-rich layer of the resulting cured syntactic foam and removing the resin-rich layer containing the concentration of sinkers fraction.

5

10. A method of producing a low density syntactic foam substantially as hereinbefore described.

10 11. A buoyancy material comprising a syntactic foam according to any of claims 1-8.

15



**Application No:** GB1312288.2

**Examiner:** Mr Jason Scott

**Claims searched:** all

**Date of search:** 27 September 2013

**Patents Act 1977: Search Report under Section 17**

**Documents considered to be relevant:**

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1, 4, 7, and 11	WO 87/01070 A HUTCHINSON See whole document and especially claims 1 & 2 showing a syntactic foam with SBR and up to 80% by volume glass spheres.
X	1	US 4751249 A MPA See whole document and especially claim 1 showing a syntactic foam with up to 3.5 times the volume of microspheres to resin.
X	1	GB 1478043 A TBA See whole document and especially claim 1 and page 1, lines 73-80 teaching up to 75% glass microspheres for addition to syntactic foam.
X	1	GB 1174341 A MINNESOTA MINING & MFG See whole document and especially claim 1 and page 1, lines 80-82.

**Categories:**

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>X</sup> :

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Worldwide search of patent documents classified in the following areas of the IPC

C08J; C08L
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The following online and other databases have been used in the preparation of this search report

WPI, EPODOC
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**International Classification:**

Subclass	Subgroup	Valid From
C08J	0009/32	01/01/2006
C08L	0025/04	01/01/2006