(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 781 635 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.09.2014 Bulletin 2014/39

(21) Application number: **14157479.8**

(22) Date of filing: **03.03.2014**

(51) Int Cl.:
D04H 1/4209 *(2012.01)* ***D04H 1/4218*** *(2012.01)*
D04H 1/46 *(2012.01)* ***D06M 15/53*** *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **18.03.2013 IT VE20130008**

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(54) Aqueous dispersion used as needling aid for producing needle mineral fiber felts and use of an aqueous dispersion

(57) An aqueous dispersion used as needling aid for producing needle mineral fiber felts characterized by comprising:
(a) at least one perfluoropolyether,
(b) at least one water-soluble polar aprotic solvent,
(c) at least one alkali metal salt chosen among lithium hydroxide, sodium hydroxide, potassium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, sodium bicarbonate, lithium bicarbonate, potassium bicarbonate, lithium chloride, sodium chloride, potassium chloride, lithium bromide, sodium bromide, potassium bromide, lithium fluoride, sodium fluoride, potassium fluoride, lithium iodide, sodium iodide, potassium iodide, lithium oxide, sodium oxide, potassium oxide and preferably lithium hydroxide, potassium hydroxide, lithium carbonate, potassium carbonate, lithium bicarbonate, potassium bicarbonate, lithium chloride, potassium chloride, lithium bromide, potassium bromide, lithium fluoride, potassium fluoride, lithium iodide, potassium iodide, lithium oxide, potassium oxide and most preferably potassium hydroxide, potassium carbonate, potassium bicarbonate, potassium chloride, potassium bromide, potassium fluoride, potassium iodide, potassium oxide and mixtures thereof,
(d) and the balance being water.

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Description

[0001] The present invention relates to an aqueous dispersion, comprising emulsions and microemulsions of perfluoropolyethers carboxylic salts, and its use as needling-aid for producing needle felts of mineral fiber glass wool.

[0002] Inorganic mineral fibers are manufactured by pulling, centrifugal, blowing or centrifugal/blowing processes of molten mineral masses in the form of interlocked fibers. Because of the brittleness of the fibers the resulting felt lacks structural strength compromising the possibility of use in application such as acoustic and thermal insulation, filter media, fireproofing material. To overcame this deficiency inorganic fiber felts are impregnated with an organic binder (usually a phenol-formaldehyde-urea or other organic resin) locking fibers together assuring optimal mechanical prope0rties when placed in use.

[0003] This solution is not usable when inorganic fiber felts are used for thermal insulation of ovens, cookers and mufflers both in household and industrial/institutional appliances. Inorganic fiber felts used for these applications must be chemically inert in order to exclude the release of any toxic or irritating chemical during use.

[0004] To avoid the use of a binder the so called "needling-process" or "needle-punching process" is used. This process produces felts by mechanically orienting and interlocking fibers of a spun mat. The mechanical interconnection and relative anchorage of fibers is produced by barbed needles which alternatively pass into and out of the mat. Fiber needle felts are a combination of mineral fibers mechanically intertwined to form a non-woven fabric which do not contain any organic binder. They give excellent high thermal insulation and thermal protection and they can be safely used at the following temperatures without changing properties: C fiber as high as 500 °C, E fiber 650 °C, rockwool fiber 700 °C, silica fiber 800 °C, ceramic fiber 1000°C.

[0005] The needling process produces considerable mechanical stresses on fibers which are brittle and can be fractured and broken by barbed needles with consequent loss of mechanical properties and production of dust.

[0006] The aforementioned considerations have led to the application of a needling-aid or finishing agent to fibers before the needling process.

[0007] The purpose of the needling-aid is to favor the sliding of the barbed needles into the fibers reducing thus friction. When the needle penetrates into the fiber-mat, part of the needling-aid moves from fibers onto the surface of the barbed needle facilitating its subsequent release from the mat. Furthermore, a certain reduction of mutual friction between fibers promotes mechanical interlocking.

[0008] An inevitable consequence of mechanical stresses induced by needling is the rupture of some fibers with consequent production of fine materials and powders. An additional advantageous effect of the needling-aid is to bound dusts thus avoiding their release during use.

[0009] Usually the needling-aid is applied on the chute of the spinning machine by means of a sprayer. At this step the needling-aid should have low viscosity and low surface tension in order to facilitate spraying, wetting and spreading onto the fibers. Conversely when the felt is subject to the needling process, the needling-aid should possess a high viscosity in order to consolidate the felt promoting fiber interlocking and dust binding.

[0010] To take into account all the aforementioned requirements needling-aids are based on mineral or natural oils, fatty acids derivatives, silicones, halogenated polyethers, perfluorated polyethers, fluoropolymers, mixtures thereof and the like in the form of aqueous emulsions, microemulsions and dispersions.

[0011] However, the use of needling aids described in the prior art has not completely ruled out the release of dangerous substances such as aldehydes, methylisocyanate (MIC), perfluorooctanoic acid (PFOA) upon heating of fiber felts.

[0012] The use of natural and mineral oils as needling-aids requires their emulsification or dispersion in water before use. In order to obtain a sufficiently homogeneous and stable emulsion or dispersion, large amounts of surfactants must be used. Particularly effective emulsifiers are ethoxylates or propoxylates alcohols and phenols, sorbitan esters, alkyl polyglucosides, phosphate esters. It is a drawback of these finishing agents that they readily decompose when exposed to high temperatures typical of ovens and cookers releasing aldehydes (notably formaldehyde).

[0013] Another approach is based on the use of aqueous dispersions of fluoropolymers. In accordance with US 4654235, perfluoroplastics such as polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene polymers (FEP), polyvinylidene fluoride (PVDF) or fluoroelastomers such as copolymers of vinylidene fluoride and hexafluoropropylene, terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene are applied as aqueous dispersions to substrates to obtain composites which are flexible and not brittle and which exhibit a low coefficient of friction. Many of the fluoroplastics and notably PTFE are produced by emulsion/dispersion polymerization using as dispersing aids salts of perfluorooctanoic acid (PFOA), notably ammonium perfluorooctanoate (APFOA). EPA and other international environmental agencies have been investigating PFOA and related compounds because they are persistent in the environment and bioaccumulable in human and animal body causing developmental and other adverse effects on laboratory animals. In accordance with Article 37 (4) of the Regulation (EC) N. 1272/2008 (CLP Regulation) the Committee for Risk Assessment (RAC) of the European Chemicals Agency (ECHA) has adopted an opinion on the proposal for harmonized classification of PFOA as suspected for causing cancer, damaging unborn children, causing harm to breast-fed children. It is a drawback of finishing agents containing PTFE or PTFE-derived perfluoroplastics the release to the environment

of PFOA and related compounds carried by fiber felts.

[0014] EP 0819788 teaches the use of aqueous dispersions of halogenated and preferably perfluorated polyethers and polyesters and alcohols as needling-aid additives. Perfluoropolyethers described have general formula CF_3-(O-$CF(CF_3)$-$CF_2)_n$-(O-$CF_2)_m$-O-CF_2-R_1 with R_1=-$COO^-NH_4^+$ or -$C(OH)_2$-CF_3 and n and m integers with n/m ranging from 20 to 40. An important advantage of the method proposed in the reference is the production of a fiber glass felt which does not release formaldehyde even if heated at approx. 500 °C. Furthermore the perfluoropolyethers used do not contain PFOA and related compounds. However in the cited document no reference is made to possible releases of methylisocianate (MIC) which may arise at high temperatures from organic precursors and the ammonium ion present in the needling aid. Methylisocianate is a highly toxic and irritating chemical extremely hazardous to human health.

[0015] EP 1022260 teaches the use of water emulsions of methyl phenyl silicone oils as useful needling-aids for mineral wool. These emulsions are claimed to release less than 50 mg of formaldehyde per kg of fibers when exposed to temperatures as high as 350 °C. Although this result represents a considerable improvement over the use of mineral oil emulsions it does not comply with the requirements for the emission of aldehydes according to the LGA certificate "LGA-schadstoffgerprüft" which prescribe, in the same conditions, a maximum concentration of 10 mg of formaldehyde per kg of fiber felt.

[0016] A common drawback of the needling-aids for needle felts described in the prior art is the release of toxic or irritating decomposition compounds when exposed to temperatures typical of ovens, cookers and other household and industrial applications.

[0017] The aim of the invention is to prepare a needling-aid for producing a needle felt which does not release any toxic or irritating decomposition product, notably formaldehyde, methylisocianate, perfluorooctanoic acid and salts thereof at temperatures up to 350 °C.

[0018] According to the invention this aim has been reached through an aqueous solution as described in claim 1.

[0019] The Applicant has surprisingly found that it is possible to solve the above technical problem by formulating a needling-aid following the specification indicated herein below.

[0020] The present invention is further clarified in three embodiment.

[0021] The neutralization of the carboxylic functional group makes the perfluoropolyethers having formula:

(I) $F\text{-}(R_f)_m\text{-}CF(CF_3)\text{-}R_2$

where

R_f= $CF(CF_3)$-CF_2-O,
R_2= -COO^- H^+, K^+, Li^+, Na^+ and mixtures thereof,
index m being an integer number selected so that the average molecular weight is between 500 and 100.000, or

(II) $CF_3\text{-}CF_2\text{-}CF_2\text{-}O\text{-}(R_f)_n\text{-}CF(CF_3)\text{-}R_2$

where :

R_f= $CF(CF_3)$-CF_2-O,
R_2= -COO^- H^+, K^+, Li^+, Na^+ and mixtures thereof,
index n being an integer number selected so that the average molecular weight is between 500 and 100.000,

water dispersible. The further addition of water-soluble polar aprotic solvents and optionally of polyether modified polydimethyl siloxanes helps to stabilize the perfluoropolyether dispersions.

[0022] The use of water dispersible perfluoropolyethers and optionally polyether modified polydimethyl siloxanes allows the elimination of non ionic, anionic, cationic or amphoteric hydrocarbon based surfactants which are recognized of being precursors of formaldehyde. Further the absence of ammonia, organic amines, urea and derivatives thereof as neutralizing agents of the carboxylic group or contaminants excludes the presence of any nitrogen source which can be a precursor for high-temperature formation of methylisocianate.

[0023] Formaldehyde and methylisocianate are detected in concentration lower than 8 mg and 0.02 mg per kg of fiber respectively in the final needle felts treated with needling-aid solutions prepared according to the present invention and exposed to temperatures up to 350 °C. Further, the same needle-felts when exposed to the aforementioned working conditions do not emit any PFOA or derivatives and precursors thereof.

[0024] Needling-aid solutions prepared according to the present invention have the additional advantage of using a solvent having a boiling point less than 150 °C, preferably less than 80 °C and more preferably less than 60 °C which

instantaneously evaporates as soon as the needling-aid solution is sprayed onto the glass fibers in the chute of the spinning machine. This is a crux to exclude the presence of traces of solvent on the finished product which can act as potential precursor for toxic or irritating thermal decomposition compounds during use.

[0025] Viscous aqueous dispersions disclosed in the present invention have the additional advantage that they are obtained in a homogeneous and translucent form only by gentle mixing of ingredients without requiring particular mixing devices such as high pressure homogenizers, turbo mixers or emulsifiers.

[0026] Viscous aqueous dispersions disclosed in the present invention have long shelf-life. They are physically stable for at least 6 months, and do not produce precipitation or flocculation in the temperature range from 5 °C to 50 °C.

[0027] The pH of the aqueous dispersions of the present invention is generally between 5 and 12, preferably between 6 and 11, most preferably between 7 and 10.

[0028] The dynamic viscosity of aqueous viscous dispersions disclosed in the present invention is generally between 1 mPa·s and 10000 mPa·s, preferably between 100 mPa·s and 5000 mPa·s, most preferably between 400 mPa·s and 2500 mPa·s.

[0029] A further object of the present invention is the preparation of a practically applicable needling-aid solution starting from the aforementioned viscous aqueous dispersions which are diluted with water to a final concentration of approx. 0.01% to 10% (weight percentage of perfluoropolyether) preferably from 0.05% to 2% (wt.) and most preferably from 0.1% to 1% (wt.) and then sprayed onto the mineral fibers coming out from the chute of the spinning machine.

[0030] The surface tension of needling-aid solutions prepared according to the present invention ranges from 12 $mN \cdot m^{-1}$ to 30 $mN \cdot m^{-1}$ depending on the perfluoropolyether formula and concentration. Low surface tension positively affects spreading and capillarity favoring the rapid and uniform coating of fibers with the perfluoropolyether solution. As a consequence the mutual friction between fibers and between fibers and barbed needles in the subsequent needling process is extremely reduced favoring mechanical interlocking of fibers without any appreciable fracture or breakage.

[0031] Owing to the small amount of solutions according to the present invention the cost of the finishing treatment is comparable or even lower than other traditional needling-aids.

[0032] The following Examples illustrate more in detail the invention without limiting the scope thereof.

EXAMPLE 1

[0033] A needling-aid composition was prepared in that 0,038 kg of potassium carbonate were dissolved into a mixture of 7,6 kg of demineralized or softened water and 1,824 kg of acetone where after 1,52 kg of a perfluoropolyether based on hexafluoropropylene commercially available under the designation Krytox 157 FS were added. The mixture was vigorously stirred until the achievement of a clear gel which was diluted with demineralized or softened water obtaining a translucent and stable solution having a perfluoropolyether content of approx. 4,25% (wt.).

[0034] 35,74 kg of the aforementioned composition were further diluted with 264 kg of tap water obtaining a solution having a perfluoropolyether content of approx. 0,5% (wt.).

[0035] The diluted perfluoropolyether solution was then sprayed onto the glass fibers in the chute of the spinning machine. Fibers were then conveyed in a tunnel heated at 130 °C in order to facilitate the evaporation of water and acetone. The fiber mat thus formed was conveyed to the needle-punching process.

[0036] The mineral wool felt obtained had a bulk density of 78 kg/m^3 and a thickness of 25 mm and it was tested by TUV Rheinland LGA Products at 350 °C for the release of aldheydes and methylisocyanate using the ceramic tube furnace method.

[0037] The release of aldheydes and methylisocianate (MIC) of the mineral wool felt comply with the requirements for aldehydes and MIC according to the "LGA-schadstoffgepruft" (LGA-tested for contaminants). Test results are reported in Table 1.

TABLE 1

Release of	**Dimension**	**Value**	**Limit value of the certificate "LGA tested for contaminants" for glass wool**
Formaldehyde	mg/kg	2.2	≤ 10
Acetaldehyde	mg/kg	1.4	≤ 10
Propanal	mg/kg	0.13	Total: ≤ 10
Butanal	mg/kg	<0.1	
Pentanal	mg/kg	<0.1	
Methylisocyanate (MIC)	mg/kg	<0.02	<0.02

EXAMPLE 2

[0038] A needling-aid composition was prepared in that 0,041 kg of potassium carbonate were dissolved into a mixture of 7,4 kg of demineralized water and 1,81 kg of acetone where after 1,5 kg of a perfluoropolyether marketed under the designation Cheminox® PO-7M-CA having an average molecular weight of ca. 1250 and purchased from Unimatec Co. were added. The mixture was vigorously stirred until the achievement of a clear gel which was diluted with softened water obtaining a stable solution having a perfluoropolyether content of approx. 4,21% (wt.).

[0039] 36,4 kg of the aforementioned composition were further diluted with 261 kg of tap water obtaining a solution having a perfluoropolyether content of approx. 0,5% (wt.) which has been sprayed onto the glass fibers in the chute of the spinning machine. Fibers were conveyed in a tunnel heated at 130 °C and subsequently to the needle-punching process.

[0040] The mineral wool felt obtained had a bulk density of 78/m^3 and a thickness of 20 mm and it was tested by TUV Rheinland LGA Products at 350 °C for the release of aldheydes and methylisocyanate using the ceramic tube furnace method.

[0041] The release of aldheydes and methylisocianate (MIC) of the mineral wool felt comply with the requirements for aldehydes and MIC according to the "LGA-schadstoffgepruft" (LGA-tested for contaminants). Test results are reported in Table 2.

TABLE 2

Release of	**Dimension**	**Value**	**Limit value of the certificate "LGA tested for contaminants" for glass wool**
Formaldehyde	mg/kg	1.8	≤ 10
Acetaldehyde	mg/kg	1.7	≤ 10
Propanal	mg/kg	0.17	Total: ≤ 10
Butanal	mg/kg	0.12	
Pentanal	mg/kg	<0.1	
Methylisocyanate (MIC)	mg/kg	<0.01	≤0.02

EXAMPLE 3

[0042] A needling-aid composition was prepared in that 0,05 kg of potassium carbonate were dissolved into a mixture of 4,95 kg of softened water and 1,5 kg of acetone. 0,025 Kg of a polyether modified polydimethyl siloxane marketed under the trade name Strucksilon 8005 where than added together with 1,5 kg of a Krytox 157 FS. The mixture was vigorously stirred until the achievement of a clear gel which was diluted with softened water obtaining a stable solution having a perfluoropolyether content of approx. 3,0% (wt.).

[0043] 50,1 kg of the aforementioned composition were further diluted with 260 kg of tap water obtaining a solution having a perfluoropolyether content of approx. 0,48% (wt.) which has been sprayed onto the glass fibers in the chute of the spinning machine. Fibers were conveyed in a tunnel heated at 130 °C and subsequently to the needle-punching process.

[0044] The mineral wool felt obtained had bulk density and thickness similar to those reported in previous examples and it was tested by TUV Rheinland LGA Products at 350 °C for the release of aldheydes and methylisocyanate using the ceramic tube furnace method.

[0045] The release of aldheydes and methylisocianate (MIC) of the mineral wool felt comply with the requirements for aldehydes and MIC according to the "LGA-schadstoffgepruft" (LGA-tested for contaminants). Test results are reported in Table 3.

TABLE 3

Release of	**Dimension**	**Value**	**Limit value of the certificate "LGA tested for contaminants" for glass wool**
Formaldehyde	mg/kg	4,5	≤ 10
Acetaldehyde	mg/kg	2,8	≤ 10

(continued)

Release of	Dimension	Value	Limit value of the certificate "LGA tested for contaminants" for glass wool
Propanal	mg/kg	0.37	Total: ≤ 10
Butanal	mg/kg	0.29	
Pentanal	mg/kg	<0.12	
Methylisocyanate (MIC)	mg/kg	<0.014	≤0.02

Claims

1. An aqueous dispersion used as needling aid for producing needle mineral fiber felts **characterized by** comprising:

(a) at least one perfluoropolyether,
(b) at least one water-soluble polar aprotic solvent,
(c) at least one alkali metal salt chosen among lithium hydroxide, sodium hydroxide, potassium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, sodium bicarbonate, lithium bicarbonate, potassium bicarbonate, lithium chloride, sodium chloride, potassium chloride, lithium bromide, sodium bromide, potassium bromide, lithium fluoride, sodium fluoride, potassium fluoride, lithium iodide, sodium iodide, potassium iodide, lithium oxide, sodium oxide, potassium oxide and preferably lithium hydroxide, potassium hydroxide, lithium carbonate, potassium carbonate, lithium bicarbonate, potassium bicarbonate, lithium chloride, potassium chloride, lithium bromide, potassium bromide, lithium fluoride, potassium fluoride, lithium iodide, potassium iodide, lithium oxide, potassium oxide and most preferably potassium hydroxide, potassium carbonate, potassium bicarbonate, potassium chloride, potassium bromide, potassium fluoride, potassium iodide, potassium oxide and mixtures thereof,
(d) and the balance being water.

2. An aqueous dispersion as claimed in claim 1 **characterised in that** perfluoropolyether has general formula

$$(I) \qquad F\text{-}(R_f)_m\text{-}CF(CF_3)\text{-}R_2$$

where

R_f= $CF(CF_3)\text{-}CF_2\text{-}O$,
R_2= $-COO^- H^+$, K^+, Li^+, Na^+ and mixtures thereof, index m being an integer number selected so that the average molecular weight is between 500 and 100.000.

3. An aqueous dispersion as claimed in claim 1 **characterised in that** perfluoropolyether has general formula

$$(II) \qquad CF_3\text{-}CF_2\text{-}CF_2\text{-}O\text{-}(R_f)_n\text{-}CF(CF_3)\text{-}R_2$$

where :

R_f= $CF(CF_3)\text{-}CF_2\text{-}O$,
R_2= $-COO^- H^+$, K^+, Li^+, Na^+ and mixtures thereof,
index n being an integer number selected so that the average molecular weight is between 500 and 100.000.

4. An aqueous dispersion as claimed in claims 2 and 3 **characterized in that** the perfluoropolyether consists of a mixture of (I) and (II).

5. An aqueous solution as claimed in claim 1 **characterised in that** the aprotic polar solvent is choosen between such as tetrahydrofuran, acetone, dimethylformamide, acetonitrile, dimethylsulfoxide and mixtures thereof.

6. An aqueous dispersion as claimed in claims and 3 **characterised in that** the number average molecular weight of perfluoropolyether is between 500 to 5000.

7. An aqueous dispersion according to claim 1, **characterized in that** the perfluoropolyether has a concentration from 0.005% to 50% (wt.).

8. An aqueous dispersion according to claim 1, **characterized in that** the polar aprotic solvent has a concentration from 0.005% to 50% (wt.).

9. An aqueous dispersion according to claim 1 **characterized in that** the alkali-metal salt or the alkali-metal salts mixture has a concentration from 0.005% to 5% (wt.).

10. An aqueous dispersion according to claim 1 **characterized in that** the alkali-metal salt or the alkali-metal salts mixture has a concentration from 0.01 % to 2.5% (wt.).

11. An aqueous dispersion according to claim 1 **characterized in that** the alkali-metal salt or the alkali-metal salts mixture has a concentration from 0.02% to 1.25% (wt.).

12. An aqueous dispersion according to any of claims 1 to 11 **characterised by** further comprising a polydimethylsiloxane having formula:

$$Si(CH_3)_3\text{-}O\text{-}\{Si(CH_3)[(CH_2)_3\text{-}O\text{-}(CH_2\text{-}CH(R_3)\text{-}O\text{-}R_4)]_p\text{-}O\}_q\text{-}(Si(CH_3)_2\text{-}O\text{-})Si(CH_3)_3$$

where R_3= -H, $-CH_3$

R_4= $-CH_3$, $-(CH_2)_3CH_3$, $CH_3C(O)$-
P= 1-50
q= 1-100

13. The use of an aqueous dispersion according to any one of claims 1 to 12 applicable onto mineral fibers based needle-felts.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 15 7479

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	11 June 2014	Demay, Stéphane

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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