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(71) Applicant: **EUROFIBRE S.p.A.**
37046 Minerbe (Verona) (IT)

(72) Inventors:
- **VACCARI, Bruno**
  37046 MINERBE (VERONA) (IT)
- **CONTE, Lino**
  35028 PIOVE DI SACCO (PADOVA) (IT)
- **ZAGGIA, Alessandro**
  35030 RUBANO (PADOVA) (IT)

(74) Representative: **Piovesana, Paolo**
Via F. Baracca, 5/a
30173 Venezia-Mestre (IT)

(54) NEEDLE-PUNCHING AID TO BE USED IN THE PRODUCTION OF NEEDLE-PUNCHED FELTS OF MINERAL WOOL, AND METHOD OF MANUFACTURING NEEDLE-PUNCHED FELTS

(57) A method for manufacturing a mechanically needle-punched felt consisting of mineral fibers such as glass, rock, slag, characterized in that the mechanical needle-punching step is carried out with a needle-punching aid consisting of graphite.

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Description

[0001] The present invention relates to a needle-punching aid to be used in the production of needle-punched felts of mineral wool, and to a method of manufacturing needle-punched felts.

[0002] Inorganic mineral fibers are manufactured by drawing, centrifugation, blowing or centrifugation/blowing processes of molten mineral masses.

[0003] The resulting mat has poor mechanical and structural properties which impair the possible applications thereof as sound and heat insulator, fire-resistant material, filtering medium.

[0004] In order to improve the structural and mechanical properties thereof, mineral wool mats can be impregnated with organic resins, for example based on phenol-formaldehyde-urea, acrylates, natural or other starches (generally defined as ligands) which are meant to form junction points between the felt fibers, thus imparting strength and elasticity.

[0005] However, this solution, which is optimal in low temperature applications (for example in the field of thermal insulation in construction), cannot be implemented in applications involving the use under conditions of high temperatures, such as in home stoves and for communities, junction boxes, heaters, insulation of equipment.

[0006] One of the basic requirements demanded for the inorganic fiber felts used for such applications is the substantial chemical stability at high temperatures to prevent or minimize the emission of substances which are potentially harmful to health. If the above-listed applications involve exposing the insulating felt to temperatures above 200°C-250°C, any organic binder would undergo an inevitable degradation process resulting in the formation of potentially toxic by-products, such as nitrogen oxides, isocyanates and aldehydes.

[0007] In order to avoid these drawbacks, a so-called "needle-punching" process is used, which allows to provide felts with satisfactory mechanical properties without having to resort to the use of organic binders.

[0008] This process involves obtaining the physical interconnection of the fibers of the mats by mechanical twisting, which mechanically orients the fibers and fastens them together.

[0009] The mechanical interconnection and the relevant link between the fibers are produced by needles with barbs which alternately pass through the mat. Needle-punched felts are a combination of mineral fibers mechanically interconnected to form a non-woven fabric which does not contain any chemical binder. They provide an excellent and high thermal insulation and thermal protection and can be safely used without changing properties at the following temperatures: fiber C up to 500°C, fiber E up to 650°C, rock wool fiber up to 700°C, silica fiber up to 800°C, ceramic fiber up to 1000°C.

[0010] Mineral fibers are however characterized by high fragility, and the mechanical stress induced by the action of the needles causes the fracture and the consequent breakage of the fibers, once again obtaining a product with inadequate mechanical properties. Another drawback of the needle-punching process is the production of a fine material which inevitably increases the dustiness of the article itself.

[0011] In order to obviate such a drawback, the needle-punching process is therefore carried out by adding a so-called "needle-punching aid" on the fiber, i.e. a substance having an essentially lubricant function which is intended to improve the tribological properties of the system by reducing the friction between the needle and the surface of the fibers and thus limiting the breakage of the fibers themselves.

[0012] With the needle-punching aid, when the needle penetrates inside the mat, it slides freely on the surface of the fibers, twisting them without breaking them.

[0013] Additionally, the use of the needle-punching aid reduces the formation of dust and fine material, thereby reducing the emission thereof when using and handling the felt.

[0014] The needle-punching aid is usually applied on the fibers output from the drawing machine using sprayers. In this step, the needle-punching aid should have low viscosity and low surface tension in order to facilitate the diffusion on the fibers. On the contrary, when the felt is subject to a needle-punching process, the aid should have a high viscosity to allow the weaving of the fibers and the stabilizing action.

[0015] In order to take into account all the requirements mentioned above, the needle-punching aids are based on mineral or natural oils, fatty acid derivatives, halogenated polyethers, fluorinated polyethers, fluoropolymers and mixtures thereof, and are in the form of emulsions, aqueous microemulsions and dispersions, solutions.

[0016] Although some of the needle-punching aids described in the prior art have limited the emission of substances which are potentially harmful to health, the release of aldehydes (in particular formaldehyde), isocyanates (in particular methyl isocyanate) and fluorinated substances (in particular perfluorinated and polyfluorinated acids, perfluoroisopropene, hydrofluoric acid) is not completely excluded.

[0017] Moreover, the use of natural and mineral oils as a needle-punching aid requires the emulsification or dispersion in water thereof before use. In order to obtain a sufficiently homogeneous and stable emulsion or dispersion, particularly effective surfactants are generally used, such as ethoxylated or propoxylated alcohols and phenols, sorbitan esters, alkyl polyglucosides, phosphate esters.

[0018] A drawback of these agents is the easy thermal decomposition when exposed to temperatures above 200°C.

[0019] Another approach is based on the use of aqueous dispersions of fluoropolymers. According to US 4654235, perfluoropolymers such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene polymers (FEP), polyvinylidene fluoride (PVDF) or fluoroelastomers such as vinylidene fluoride (VDF) and hexafluoropropylene copolymers, vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene terpolymers are applied as aqueous dispersion to substrates in order to obtain composites which are flexible and not brittle and show a low friction coefficient.

[0020] Historically, perfluoroethylene (PTFE) was produced by emulsion polymerization of tetrafluoroethylene. The surfactant of choice for this process was perfluorooctanoic acid ammonium salt. The use of PTFE dispersions therefore entailed the inevitable emission of perfluorooctanoic acid and salts thereof. As a result of the growing concern associated with the toxicity and persistence features and bioaccumulation of perfluorooctanoic acid and salts thereof, the curing process of PTFE is currently carried out using alternative surfactants with a lower impact.

[0021] An important advantage of using last-generation PTFE dispersions or perfluoropolyethers is the production of a fiberglass felt which does not release formaldehyde or PFOA and related compounds even if heated to about 500°C.

[0022] In the reference cited, however, no reference is made to the possible emissions of methyl isocyanate (MIC) which may result, at high temperatures, from organic precursors and from the ammonium ion present in the needle-punching aid. Methyl isocyanate is a highly toxic chemical and, therefore, very dangerous to human health.

[0023] EP 1022260 proposes, in particular, the use of aqueous emulsions of alkylaryl silicones and diaryl silicones as useful needle-punching aid for mineral wool.

[0024] These emulsions are claimed for releasing amounts of formaldehyde of less than 50 mg/kg of mineral fiber when exposed to temperatures of 350°C. Although this result represents a considerable improvement as regards the use of mineral oil-based emulsions, it does not conform to the requirements of aldehydes emissions set forth in the LGA certification "tested for contaminants".

[0025] EP2781635 B1 describes a needle-punching aid which does not release aldehydes (in particular formaldehyde), methyl isocyanate, perfluorooctanoic acid and salts thereof at temperatures above 350°C. The proposed needle-punching aid consists of an aqueous dispersion containing one or more perfluoropolyethers, one or more solvents and one or more alkaline metal salts. While this result represents a significant improvement over the prior art, it cannot ensure the absence of fluorinated compound emissions of any nature (including hydrofluoric acid) when the felt is exposed to temperatures greater than or equal to 350°C. It follows that a drawback common to needle-punching aids for the needle-punched felts described in the prior art is the release of toxic or irritant decomposition compounds when exposed to the typical temperatures of ovens, cookers and other domestic and industrial equipment.

[0026] It is the object of the invention to prepare a needle-punching aid for producing a felt which does not release significant amounts of toxic or irritating decomposition product, especially formaldehyde, methyl isocyanate, fluorine compounds of any kind (including hydrofluoric acid) at temperatures greater than or equal to 350°C.

[0027] According to the invention, said objects are achieved by a method for manufacturing a needle-punched felt as described in claim 1.

[0028] The present invention will be further described hereinafter in a preferred embodiment thereof, in two illustrative and non-limiting examples.

[0029] Graphite is known for its lubricating properties in the solid state, which thus allows to reduce the friction between two surfaces which slide relative to each other without requiring an oil or another liquid medium. Graphite consists of hexagonal planes essentially consisting of carbon whose relative distance is considerable and, therefore, the interaction strength between the planes is relatively low.

[0030] The reduction in the friction coefficient is due precisely to this laminar structure in which the layers, held together by weak forces, can slide over each other without offering particular resistance.

[0031] For the applications of the present invention, graphite can be used as a needle-punching aid both in solid form (for example in powder form), and in the form of an aqueous dispersion or dispersion in oil.

[0032] Graphite as a needle-punching aid can be applied on the fibers output from the drawing machine by means of sprayers or at any point of the production chain which precedes the mechanical needle-punching step.

[0033] Graphite is characterized by the absence of toxicity and its use both in powder form and as an aqueous dispersion or in solvent base allows to obtain an article which, in use, does not release substances potentially harmful to health in such concentrations as to be a hazard.

[0034] Aqueous graphite dispersions generally consist of at least two phases: a continuous phase, which forms the dispersant, and one or more dispersed phases (dispersed phase consisting of graphite). In order to obviate the natural destabilization and coalescence tendency of graphite dispersions, adjuvants may be used in their preparation, including surfactants, dispersants, thickeners and protective colloids. The role of adjuvants is essential not only to ensure adequate stability of the dispersion but also to obtain the rheological characteristics needed to apply the same dispersion by spraying. When graphite is used in the form of an aqueous dispersion, this can be applied by spraying in a uniform and homogeneous manner on the surface of the fibers output from the drawing chamber. The dispersion may contain a variable amount of graphite from a minimum of 0.05% by weight to a maximum dictated by the rheological characteristics of the dispersion itself which must, however, allow easy application thereof. For example, dispersions containing 0.1% - 5% by weight of graphite have optimal rheological characteristics to ensure a uniform spraying process and a degree of fiber surface coverage sufficient to reduce friction.

[0035] If graphite dispersions containing organic adjuvants are used, these can lead to the formation of by-products potentially hazardous to health once the article is in use at high temperatures. To prevent the emission of substances resulting from the thermal decomposition of additives in operation, it is possible to introduce, after the fiber spraying step, a heating step at temperatures above 150°C for a time sufficient to remove, by thermal decomposition, any organic residues employed as adjuvants for the preparation of the dispersion.

[0036] By using graphite or dispersions thereof as a needle-punching aid, formaldehyde and methyl isocyanate are detected, in the finished article, in lower concentration, at 10 mg/kg of glass fiber and 5 mg/kg of rock fiber, respectively, as regards formaldehyde, and 0.02 mg/kg of fiber as regards formaldehyde at temperatures up to 350°C. In addition, the same felts, when exposed to the above working conditions, do not emit any fluorinated substance or of an organic (such as polyfluorinated acids, perfluoroisopropene) or inorganic (hydrofluoric acid and salts thereof) nature.

[0037] Both natural graphite and synthetic graphite may be used, and the graphite particles used may have an average particle size ranging from 0.1 to 500 microns and preferably from 0.1 to 50 microns. The viscosity of the aqueous dispersion ranges from 100 to 1000 mPa.s and preferably from 500 to 600 mPa.s. Obtaining a uniform distribution of the graphite on the fiber surface is crucial in order to reduce the mutual friction between the fibers and thus promote their mechanical intertwining, thus reducing fractures and consequent increase of dustiness.

[0038] The use of other additives such as stabilizer oils, silicones, dyes can be contemplated with the application of graphite in powder form and as an aqueous or oil dispersion.

[0039] The following examples describe more in detail the invention without limiting the scope thereof.

EXAMPLE 1.

[0040] A composition was prepared for use as a needle-punching aid by diluting the dispersion TIMREX® LB 1300 of MERYS GRAPHITE AND CARBON in water.

[0041] 35.00 kg of the dispersion TIMREX® LB 1300 were diluted with 290 kg water to obtain a solution having a graphite content of about 2.9% (by weight).

[0042] The graphite diluted solution was then sprayed onto the glass fibers exiting the drawing machines. The fibers were conveyed in an oven heated at 130°C to facilitate evaporation of the water and any low-boiling products. The fibers mat thus formed was conveyed to the needle-punching process.

[0043] The felt of mineral wool obtained had an apparent density of about 78 kg/m^3 and a thickness of 25 mm and it was tested by TUV LGA Rheinland at 350°C to verify the release of aldehydes and methyl isocyanate using the ceramic tube furnace method.

[0044] The release of aldehydes and methyl isocyanate (MIC) from the felt of mineral wool complied with the requirements for aldehydes and MIC according to the "LGA-schadstoffgepruft" certification (LGA-tested for contaminants). The test results are shown in Table 1.

[0045] In addition, the hydrofluoric acid emissions determined by combustion with Wickbold method at 500°C followed by liquid ion chromatography according to DIN EN ISO 10304-1 remained below the detection limit.

Table 1. Test report for emissions at 350°C from mineral wool felt as described in example 1.

Contaminant	Unit of measure	Value	Limit value for the glass wool relating to the "LGA tested for contaminants" certification
Methanal (formaldehyde)	mg/kg	7.2	≤ 10
Ethanal (acetaldehyde)	mg/kg	2.9	≤ 10
Propanal	mg/kg	0.5	Total: ≤ 10
Butyraldehyde	mg/kg	0.2	
Pentanal	mg/kg	<0.1	
Methyl isocyanate (MIC)	mg/kg	<0.01	≤0.02

EXAMPLE 2

[0046] A composition was prepared for use as a needle-punching aid by diluting the dispersion TIMREX® LB 1300 of

MERYS GRAPHITE AND CARBON in water.

[0047] 29.00 kg of the dispersion TIMREX® LB 1300 of IMERYS GRAPHITE AND CARBON were diluted with 290 kg water to obtain a solution having a graphite content of about 2.5% (by weight).

[0048] The graphite diluted solution was then sprayed onto the glass fibers exiting the drawing machines. The fibers were conveyed in an oven heated at 300°C to facilitate evaporation of the water and any low-boiling products. The fibers mat thus formed was conveyed to the needle-punching process.

[0049] The felt of mineral wool obtained had an apparent density of about 78 kg/m^3 and a thickness of 25 mm and it was tested by TUV LGA Rheinland at 350°C to verify the release of aldehydes and methyl isocyanate using the ceramic tube furnace method.

[0050] The felt of mineral wool obtained had density and thickness similar to those reported in the previous examples and was tested by TUV Rheinland LGA Products at 350°C for the release of aldehydes and methyl isocyanate using the ceramic tube furnace method.

[0051] The release of aldehydes and methyl isocyanate (MIC) from the felt of mineral wool complied with the requirements for aldehydes and MIC according to the "LGA-schadstoffgepruft" certification (LGA-tested for contaminants). The test results are shown in Table 3.

[0052] In addition, the hydrofluoric acid emissions determined by combustion with Wickbold method at 500°C followed by liquid ion chromatography according to DIN EN ISO 10304-1 remained below the detection limit.

Table 2. Test report for emissions at 350°C from mineral wool felt as described in example 2.

Contaminant	**Unit of measure**	**Value**	**Limit value for the glass wool relating to the "LGA tested for contaminants" certification**
Methanal (formaldehyde)	mg/kg	1.8	≤ 10
Ethanal (acetaldehyde)	mg/kg	1.7	≤ 10
Propanal	mg/kg	0.17	Total: ≤ 10
Butyraldehyde	mg/kg	0.12	
Pentanal	mg/kg	<0.1	
Methyl isocyanate (MIC)	mg/kg	<0.01	≤ 0.02

[0053] From the foregoing it is apparent that the felt needle-punched with the needle-punching aid according to the invention has the following advantages, in particular:

- it complies with the emission requirements for aldehydes and MIC determined by the Criteria Catalog "LGA-tested for contaminants" for mineral fibers in cookers and ovens (2PfG S 0079/03:12),
- it has an emission of hydrofluoric acid below the combustion detection limit with Wickbold method at 500°C and determination with liquid ion chromatography according to DIN EN ISO 10304-1,
- it has an emission of PFOA, PFOS and other perfluorinated acids below the detection limit for the determination by LC-MS/MS even after heating at temperatures up to 500°C.

Claims

1. A method for manufacturing a mechanically needle-punched felt consisting of mineral fibers such as glass, rock, slag, **characterized in that** the mechanical needle-punching step is carried out with a needle-punching aid consisting of graphite.

2. A method according to claim 1, **characterized in that** graphite is applied in powder form.

3. A method according to claim 1, **characterized in that** graphite is applied in aqueous dispersion.

4. A method according to claim 1, **characterized in that** graphite is applied in oil dispersion.

5. A method according to claim 3, **characterized in that** the aqueous dispersion comprises a dispersed phase (graphite), a continuous phase (water), and any adjuvants such as surfactants, wetting agents, dispersing agents, thickeners and protective colloids, silicones, siloxanes and silanes, stabilizer oils, dyes.

6. A method according to claim 1, **characterized in that** the felt is heated before or after the needle-punching step at temperatures above 150°C.

7. A needle-punching aid for implementing the method according to claim 1, **characterized in that** it consists of graphite having dimensions in the range from 0.1 to 500 microns.

8. An aid according to claim 7, **characterized in that** the dimensions of the graphite particles are in the range from 0.1 to 50 microns.

9. A needle-punching aid for producing needle-punched felts according to claim 7, **characterized in that** the graphite content of the aid is in the range from 0.05% to 5% referred to the dry weight of the mineral fiber treated.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 17 6317

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	11 August 2017	Demay, Stéphane

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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