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FLUORINE-FREE HYDROPHOBIC AND OLEOPHOBIC NONWOVEN

Abstract

The invention relates to fluorine-free hydrophobic and oleophobic nonwoven for use, for example, in automotive engine bays, and a method for making such nonwoven.

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Background/Summary

[0001] The invention relates to a fluorine-free hydrophobic and oleophobic nonwoven for use, for example, in automotive engine bays, and a method for making such nonwoven.

[0002] Nonwovens contribute to extend the lifetime of automobiles and make them safer, more comfortable, more cost-effective and more sustainable. The combination of reducing the weight of the car, lowering fuel consumption, provide advanced insulation, advanced sound absorption, fire retardancy and resistance to water, fuel, extreme temperatures and abrasion, are usually only possible with a combination of a fluorine-containing compound and a nonwoven, namely a fluorinated nonwoven fabric. Fluorinated nonwoven fabrics protect the engine compartment and prevent liquid absorption, block leakage of resin and promote slip in moulding forms. Examples of usage for a fluorinated nonwoven fabric, in an automotive, are as motor insulation, battery cover, headliner and underbody.

[0003] The textile industry is under pressure to remove hazardous chemicals from their products and supply chain. High on that list of chemicals is fluorine-containing compounds, which are being banned, e.g. by REACH regulation in EU. Because of per- and polyfluorinated substances resistance to both water and oil, they are extremely attractive in a number of industrial applications and consumer products such as automobiles. Per- and polyfluorinated substances are extremely persistent and experience high mobility in the environment. Potential adverse effects on human health and the environment are of concern and uses that result in release to the environment should be controlled.

[0004] Finding replacements for fluorine-containing compounds, while maintaining the same level of performance and durability, is not trivial. While there are many examples of superhydrophobic coatings, limited progress has been made towards highly oleophobic treatments.

[0005] A challenge in engineering oleophobic coatings stems from a fundamental limitation in materials. As typical surface tensions of hydrocarbon oils are in the range of 20-40 mN/m. The surface tension of a smooth oil repellent substrate must be around 20 mN/m. The requirement for low surface energy suggests that most commonly used materials are not intrinsically oleophobic and only few fluorinated materials can meet this prerequisite for oleophobicity, such as PTFE, fluorosilanes and fluoropolymers. Essentially, previously developed highly oleophobic treatments are based on low surface energy fluorinated materials.

[0006] Simple poly(dimethyl) siloxane (PDMS) finishes typically has a surface energy about 22-24 mN/m and does not provide an efficient oleophobic repellence because the surface energy is not low enough. In addition, because of the different nature of the substrates, the PDMS finishing can be problematic in terms of adhesion, uniformity and durability.

[0007] There is hence a need for a fluorine-free finish that has a high degree of oleophobicity and does not suffer the disadvantages of the known solutions.

[0008] The solution proposed by the present invention comprises a method for making a nonwoven fabric having hydrophobic and oleophobic properties, the method comprising the following steps: providing a nonwoven fabric comprising fibers; providing an aqueous colloidal solution comprising nanoscale SiO₂-particles, which is formed from an aqueous precursor solution comprising a SiO₂-producing substance; and applying the colloidal solution onto the nonwoven fabric to form a hydrophobic and oleophobic finish on fibers of the fabric and thereby impart hydrophobic and oleophobic properties.

[0009] A nonwoven fabric produced by such method comprises one or two surfaces having a hydrophobic and oleophobic properties, wherein the nonwoven fabric comprises fibers and wherein

a hydrophobic and oleophobic finish is present on fibers of the fabric, including or especially those exposed to the surface, thereby imparting hydrophobic and oleophobic properties to the fabric in general and the surface in particular, wherein the finish comprises a continuous or interrupted porous SiO₂-containing layer of nanoscale thickness.

[0010] Sol-gel processes are wet chemical processes that deposit nano-crystalline coatings. The special feature of sol-gel processes is that the creation of the coating starts from a liquid sol state, which is converted into a solid state by means of a sol-gel transformation. The sols used are dispersions of solid nanoparticles, which are dispersed in water, organic solvents or a mixture hereof. Sol-gel processes are mainly based on organometallic precursors, such as siloxanes. The sol-gel process start with a solution where different polymerization and condensation processes lead to the gradual formation of a solid phase network. A normal densified sol-gel coating results in a uniform coating.

[0011] In the present invention, the colloidal solution comprises nanoscale colloidal SiO₂ structures produced in a sol-gel process of the SiO₂-producing substance. Preferably, the SiO₂-producing substance is silicon alkoxide and undergoes hydrolysis and subsequent condensation reactions. Specifically, the molecules of the silicon alkoxide within the precursor solution undergo hydrolysis and condensate to form small SiO₂ particles. The SiO₂ particles continue to grow on the surface of the fibers and may touch one another and, through further condensation, crosslink with one another to form a gel structure.

[0012] The finish may have a thickness of 10 to 300 nm, preferably a thickness of 50 to 250 nm, and more preferably a thickness of 80 and 150 nm. The surface free energy of the coated fiber surfaces and the nonwoven surface in total is preferably lower than 24 mN/m, preferably lower than 22 mN/m, and most preferably around 20 mN/m, which is lower than a typical surface tension value for oil.

[0013] The porous SiO₂-containing layer preferably comprises structural elements from SiO₂, RSiO_{1.5}, and/or R₂SiO, where R=H, alkyl, aryl, epoxy-alkyl, or aminoalkyl.

[0014] The forming of the nonwoven is preferably from staple fibers and more preferable includes carding. The laydown of fibers on the conveyor of the production line preferably involves cross-laying the carded web.

[0015] The staple fibers preferably comprise between 50 wt % and 100 wt % synthetic fibers, wherein the remaining fibers, if any, may be cellulosic fibers like viscose, lyocell or hemp. Examples for suitable synthetic fibers comprise polypropylene, polyethylene, polyethylene terephthalate, polyacrylate, polyacrylonitrile, polyamide, or a mixture thereof.

[0016] The silicon alkoxide can, for example be a tetraalkoxysilane, an alkyltrialkoxysilane, a dialkyldialkoxysilane, or any mixture. Examples comprise tetraethoxysilane, trimethoxymethylsilane, dimethoxydimethylsilane, polydimethylsiloxane, vinyltrimethoxysilane, 3-aminopropyltrimethoxysilane, methacryloxypropyltrimethoxysilane, and 3-glycidyloxypropyltrimethoxysilane. Generally, alkyltriethoxysilanes and aminopropyltriethoxysilanes can be preferred.

[0017] The solvent of the aqueous precursor solution is preferably either water or a mixture of alcohol, preferably methanol, ethanol and/or isopropanol, and water. Further preferably, the precursor solution comprises a hydrolysis and condensation catalyst, preferably an acid.

[0018] The aqueous colloidal solution can typically be formed from the aqueous precursor solution by mixing the precursor solution and stirring at a temperature below 50° C., preferably between 15 and 30° C., for between 10 minutes and 24 hours, preferably between 30 minutes and 12 hours, more preferably between 1 and 6 hours.

[0019] In one embodiment, the solids content in the colloidal solution is between 0.1 and 15 wt %, preferably between 1 and 7 wt %. The average particle size of the colloids in the colloidal solution is between 1 and 500 nm, preferably between 5 and 300 nm, and more preferably between 20 and 150 nm.

[0020] In one embodiment, the colloidal solution further comprises a binder, preferably in the form of acrylic, acrylic-ester, melamine, thermoplastic or self-curable polymers.

[0021] Additionally the colloidal solution may further comprise a flame retardant, for example in the form of inorganic components including phosphorus-based salts and particles.

[0022] In one embodiment, the colloidal solution is applied onto the surface of the nonwoven fabric, preferably in-line, by spray application, coating or by foaming. Application via an in-line foaming application can be most preferred. The amount of colloidal solution applied to the nonwoven fabric, after drying, preferably is between 0.1 gram per square meter to 5 gram per square meter, more preferably between 0.5 gram per square meter to 2 gram per square meter.

[0023] The colloidal solution can be applied to the fabric in a dry state, e.g. after drying in case of using a wet-lay process or spunlacing, or in a semi-dried-state, e.g. after partial drying in case of using a wet-lay process or spunlacing. Drying preferably comprises passing the fabric through a drying oven. In one embodiment, the colloidal solution is continuously applied to the nonwoven fabric in-line after drying and before wind-up. Alternatively, the fabric can be wound up to form a fabric roll after its in-line formation and drying, subsequently unwound before applying the colloidal solution off-line.

[0024] In one embodiment, the method further comprises an in-line step of continuously and actively drying the fabric after the application of colloidal solution. Again, drying preferably comprises passing the fabric through a drying oven.

[0025] The speed, at which the nonwoven/nonwoven fabric travels through the production line on the conveyor belt, can be between 2 meters per minute and 70 meters per minute. More preferably, the speed of the line is between 5 meters per minute and 25 meters per minute.

[0026] Preferably, the nonwoven fabrics of the invention, which are modified for increased hydrophobicity and oleophobicity, can be used in automotive applications, for example as a motor insulation element, battery cover, headliner or underbody liner.

Description

[0027] Further details and advantages of the invention will become apparent from the working examples and figures described in the following. In the figures:

[0028] FIG. 1: shows a production line for carrying out a method of the invention;

[0029] FIG. 2: visual results for the inventive fluorine-free treatment;

[0030] FIG. 3: a microscopic image of the surface-facing fibers of a 30 wt % viscose and 70 wt % polyester nonwoven fabric on which the inventive fluorine-free treatment has been carried out; and

[0031] FIG. 4: a microscopic image of the surface-facing fibers of a 30 wt % viscose and 70 wt % polyester nonwoven fabric before the inventive fluorine-free treatment has been carried out.

EXAMPLE 1-COLLOIDAL SOLUTION PREPARATION

[0032] Production of an aqueous colloidal solution comprising nanoscale SiO₂-particles in a first embodiment:

[0033] 100 ml tetraethoxysilane, 400 ml water and 200 ml 0.01 N hydrochloric acid as a polycondensation catalyst are mixed at ambient temperature (20° C.) and stirred continuously (approx. 5 hours). The result is an aqueous silica sol-gel, with a solids content of approx. 4.5% and with an average particle size of 6 nm.

EXAMPLE 2-COLLOIDAL SOLUTION PREPARATION

[0034] Production of an aqueous colloidal solution comprising nanoscale SiO₂-particles in a second embodiment:

[0035] 40 ml tetraethoxysilane, 40 ml aminopropyltriethoxysilane, 20 ml 3-methacryloxypropyltrimethoxysilane and 400 ml water are mixed at ambient temperature (20° C.), wherein the SiO₂-forming precursors in the order tetraethoxysilane,

aminopropyltriethoxysilane and 3-methacryloxypropyltrimethoxysilane after in each case 3 hours stirring are added to the solvent H.sub.2O. Then, while stirring, the 200 ml 0.01 N hydrochloric acid carboxylic acid as a polycondensation catalyst is titrated. The result is an aqueous silica sol-gel with a solids content of approx. 6% and with an average particle size of 6 nm.

EXAMPLE 3-PRODUCTION

[0036] FIG. 1 illustrates a production line 100 that can be used for carrying out a method of the invention for making a hydrophobic and oleophobic nonwoven fabric.

[0037] The production line 100 comprises a number of stations subsequently arranged. The first station 110 is for fiber preparation and comprises means like a hopper feeder or the like for enabling a uniform feed of staple fibers to carding machine 120. From the carding machine 120, a perforated conveyor belt travels through the subsequent spunlacing station 130, which is followed in-line by a first drying station 140, a foam-application station 150 and a second drying station 160 before the finished dried nonwoven fabric is wound up onto a roll.

[0038] The carding machine 120 and subsequent spunlacing station 130 can be configured as generally known in the art. The fibers of the fibrous web formed from the laydown in station 120 can be conveyed on the conveyor belt at high speed of, for example, 5 meters per minute and 25 meters per minute, and be mechanically bonded by means of high energy water jets.

[0039] Next in line is the first drying oven 140, which dries the fabric that is wet from spunlacing.

[0040] Next in line is the foam-application station 150, which is representative for the key step of the inventive process. The nonwoven fabric enters the foam-application station 150 at unchanged travel speed. The foam-application station 150 comprises a foam application system suitable to uniformly apply at a rate sufficient high to apply between 0.1 and 2 gram per square meter dry content of the colloidal solution comprising nanoscale SiO.sub.2-particles.

[0041] The foam-application station 150 is followed by a drying station 160, which comprises a drying oven through which the chemistry loaded nonwoven fabric travels with unchanged speed for drying under elevated temperature. In a final in-line step, the dried nonwoven fabric is wound up to form large rolls of meters in width and up to kilometres in length. The rolls can be stored in a warehouse, shipped to different locations, and unwound for further processing.

EXAMPLE 4-PRODUCT TEST

[0042] A carded and spunlaced polymer fiber (100% PET) nonwoven fabric has been prepared.

[0043] For the inventive samples, an amount of 1.03 g/m.sup.2 of a colloidal solution of the invention based on solids content of SiO.sub.2 was spray-applied to the fabric and the fabric was dried in an oven (hot air 190° C.) for 15 minutes.

[0044] Reference samples comprised untreated samples and samples treated by a standard C6 fluoro chemical.

[0045] During the tests, carried out according to ISO 14419, 5 drops of 0.5 ml each of different liquids were deposited on the surface. The result was recorded after 10 seconds. The results are shown in Table 1 below.

TABLE-US-00001 TABLE 1 Surface tension Negative C-6 fluoro Fluorine-free Liquid (mN/m) reference chemical treatment Distilled water 72 Not OK OK OK Liquid no. 3 27.3 Not OK OK OK (n-hexadecane) Liquid no. 4 26.4 Not OK OK OK (n-tetradecane) Liquid no. 5 24.7 Not OK OK OK (n-dodecane) Liquid no. 6 23.5 Not OK OK OK (n-decane) Liquid no. 7 21.4 Not OK OK OK (n-octane) Liquid no. 8 19.8 Not OK Not OK Not OK (n-heptane)

[0046] Visual results for the inventive fluorine-free treatment are shown in FIG. 2. As apparent, the liquids 1 to 7, i.e. even liquids with a surface tension down to 20 mN/m, did not penetrate into the fabric due to the oleophobic properties imparted by the inventive treatment.

[0047] A microscopic image of the surface-facing fibers of the nonwoven fabric on which the inventive fluorine-free treatment has been carried out is shown in FIG. 3. A comparative picture of the same type of nonwoven, before the treatment has been carried out, is shown in FIG. 4.

[0048] The comparison demonstrates the result of the inventive treatment, namely the nanoscale

modified silica surface hierarchy on the nonwoven fabric fibers, which is produced by means of a sol-gel process. This structure imparts a surface tension around 20 mN/m and is thus both hydrophobic and oleophobic.

Claims

1. A method for making a nonwoven fabric having hydrophobic and oleophobic properties, the method comprising the following steps: providing a nonwoven fabric comprising fibers; providing an aqueous colloidal solution comprising nanoscale SiO₂-particles, which is formed from an aqueous precursor solution comprising a SiO₂-producing substance; and applying the colloidal solution onto the nonwoven fabric to form a hydrophobic and oleophobic finish on fibers of the fabric and thereby impart hydrophobic and oleophobic properties.
2. The method of claim 1, wherein the fibers are carded fibers.
3. The method of claim 1, wherein the fibers comprise 50 wt % to 100 wt % synthetic fibers.
4. The method of claim 1, wherein the SiO₂-producing substance is a silicon alkoxide.
5. The method of claim 1, wherein the solvent of the aqueous precursor solution is water or a mixture of alcohol and water.
6. The method of claim 1, wherein the aqueous precursor solution comprises a hydrolysis and condensation catalyst.
7. The method of claim 1, wherein the solids content in the colloidal solution is between 0.1 and 15 wt %.
8. The method of claim 1, wherein the colloidal solution is applied onto the surface of the nonwoven fabric by spray application, coating or by foaming.
9. The method of claim 1, wherein the amount of colloidal solution applied to the nonwoven fabric is between 0.1 g/m² and 5 g/m².
10. A nonwoven fabric comprising a surface having a hydrophobic and oleophobic properties, wherein the nonwoven fabric comprises fibers and wherein a hydrophobic and oleophobic finish is present on fibers of the fabric, thereby imparting hydrophobic and oleophobic properties to the fabric, wherein the finish comprises a continuous or interrupted porous SiO₂-containing layer of nanoscale thickness.
11. The nonwoven fabric of claim 10, wherein the layer has a thickness of 10 to 300 nm.
12. The nonwoven fabric of claim 10, wherein the surface free energy of the surface having a hydrophobic and oleophobic properties is 24 mN/m or lower.
13. The nonwoven fabric of claim 10, wherein the porous SiO₂-containing layer comprises structural elements from SiO₂, RSiO_{1.5}, and/or R₂SiO, where R=H, alkyl, aryl, epoxy-alkyl, or aminoalkyl.
14. An automotive article, said article comprising the nonwoven fabric according claim 10.
15. The method of claim 1, wherein the fibers are carded fibers and providing the nonwoven fabric includes carding and laydown of the carded web on a conveyor of a production line.
16. The method of claim 1, wherein the fibers are carded fibers and providing the nonwoven fabric includes carding and laydown of the carded web on a conveyor of a production line involving cross-laying the carded web.
17. The method of claim 1, wherein the fibers comprise 50 wt % to 100 wt % synthetic fibers and formed from polypropylene, polyethylene, polyethylene terephthalate, polyacrylate, polyacrylonitrile, polyamide, or a mixture thereof.
18. The method of claim 1, wherein the SiO₂-producing substance is a silicon alkoxide that is selected from one or more of a tetraalkoxysilane, an alkyltrialkoxysilane, a dialkyldialkoxysilane, or any mixture thereof, preferably alkyltriethoxysilanes or aminopropyltriethoxysilanes.
19. The method of claim 1, wherein the solids content in the colloidal solution is between 1 and 7 wt %.

20. The method of claim 1, wherein the amount of colloidal solution applied to the nonwoven fabric is between 0.5 g/m.² and 2 g/m.².
