Title: NANOSTRUCTURED REPELLENT FIBROUS MATERIAL

Abstract: The invention presents a composition, a method and a use for a novel surface treatment approach for fiber-based substrates, where the surface characteristics of the fiber material can be regulated. The method is based on the production of a nanocoating, utilizing controllably thin and possible self-organizing polymer materials, in conjunction of fiber substrate. As the advantageous applications areas of the invention, can be mentioned a regulation of adhering and impregnation of the surfaces of fibrous substrates.
Nanostructured release paper

The present invention concerns a method and a composition according to patent Claim 1, for modification of fibrous substrate material. An object of the invention is to provide a novel repellent, and regulated by surface adhesion characteristics, fibrous material with a novel composition and a method, where a polymer component is spread on the surface of the fibers. Particularly, the object of the invention is to provide cellulose based fiber material composition, which has the character described previously. Further particular object of the invention is to provide a material composition applicable as backing paper of labels so-called release paper, which has advantageous and regulating release characteristics, is easy and advantageous to prepare, in addition, is recyclable and can be prepared among others from recycled fibers if needed.

Due to the structure of fibrous materials, they usually have tendency to absorb foreign liquid, gel-like or gluey substances, generally fluids, on their surface or inside the fiber structure for example under the influence of capillary forces. Structure of the surface is usually also irregular. Consequently, in the preparation of fiber materials, such as paper or paper board, is traditionally used surface coating methods by which the surface of the material can be modified for instance to smooth, capillary penetration can be hindered, or for example adhesion of glue substances can be regulated. As examples can be mentioned coated printing paper, where the surface of the fiber material is blocked and smoothened with latex type mixtures of polymer and filler and typically with 1-5 µm layer thicknesses. Used substances are for example styrene-butadiene-latex, starch, polyvinyl alcohol and fillers such as kaolin, silica, titanium dioxide pigment, just to mention a few.

Furthermore, if the surface is to be made more repellent in character according to a present level of technique, it is possible to coat paper by separate layer of polysiloxane or siliconize the surface of the paper.

However, to achieve advantageous end result in these technologies, it is required to use relatively large amounts of modifying substances such as polymers, which is a cost lifting factor, increasing the preparation steps, in addition hindering factor for recycling. It is like
this particularly, if it is necessary to use relatively expensive components such as silicone to provide particularly good surface repellency.

Due to the physically and chemically heterogenic nature of paper, base paper has to be modified with different manners, so that the quality of fiber material satisfies the requirements of the end application. The goal is to controllably adjust the capillary penetration and absorption of the solvents or other fluids such as gluey substances or pastes into the paper fibers and pores between the fibers. One of the most important physical methods for modification is calendering of a paper, where the fibers are packed into more compact network with the help of temperature and pressure treatment. Traditionally, printing surface is chemically improved with polymer containing pigment coating, whose thickness is typically 1-5 µm. With the aid of the pigment coating, the surface of the paper is filled up by covering the holes of the loose fiber network and the pores and the roughness by pigments. In known methods, polymer acts as a binder, whose most important task is to bind the pigment particles together and bind the coating layer to backing paper.

The polymer used as a binder, can be in water, both in liquid or dispersed state. Structurally, the polymers can be either homopolymers or random-copolymers. As water-soluble polymers, it is typically used among others polyvinyl alcohol and carboxymethylcellulose. Dispersion polymers are synthetic latex or starch based coatings. These are among others styrene-butadiene, acrylate and vinyl acetate based latex.

Usually, the spreading into the surface of the paper occurs with a roller, but in recent years, new coating methods have been developed, such as curtain coating and spray coating, which require novel characteristics of the polymers used as coatings.

In the concept of the present invention, we have surprisingly observed, that the ability of fiber material, such as paper or paper board, to bind into its surface or absorb liquid or viscous flowing substances such as glues or oily substances, can be influenced with entirely novel manner by using nanotechnical approach. Particularly in the invention, the surface of the cellulose based fiber substrates, such as surface of paper and paper board, but also as an essential factor, the inner parts of the structure, are modified by bringing them into contact with small amounts of polymers. Polymers in this concept can be
structurally homogenic homopolymers or copolymers or they can be structurally amphiphilic block polymers. The polymer applied in small amounts as a nanocoating on the surface of the fibers has been spread, according to the invention, on the surface of the fiber structure, and at least partly impregnated into it from a dilute aqueous solution, from an emulsion formed in water or from a dispersion formed in water.

Homogenic polymers according to the invention are typically soluble in water or dispersible homo- or copolymers, such as advantageously polyvinyl acetate, polyvinyl alcohol or biopolymers such as lactic acid based polymers.

Amphiphilic polymers are block polymers, which contain a hydrophilic and correspondingly a hydrophobic block. Owing to the unique structure, interaction of different blocks of the amphiphilic polymers with nonpolar or polar solvents or liquids is very different. To avoid unfavourable interactions, molecules usually form self-organized structures in solutions. Thus, amphiphiles have a long history as industrial surfactants.

An important application of amphiphiles is as emulsifiers and stabilizers for emulsions. As emulsifier, the hydrophobic end of the amphiphile dissolves into hydrophobic compound and hydrophilic end reaches out to water phase. Block copolymers are also used in pharmacy. Self-organized structures can enclose hydrophobic drug substances, and thus add their solubility in water. Because micelles in aqueous solution can dissolve hydrophobic compounds, amphiphiles can also be used for extraction of organic molecules from water phase. Thus, the use of organic solvents can be avoided.

In the present invention, the application field of amphiphilic polymers is broaden towards fibrous materials, particularly natural fiber based fiber materials such as paper and paper board, very particularly release papers used as the backing layers of labels or stickers. Thus, the invention provides water-soluble, colloidal or micellar form of amphiphilic block copolymers in water, which are capable of, by their fiber coating ability, even coating ability at nano level and furthest by the self-organization of amphiphilic polymers, influencing the release characteristics and adhesion characteristics of fiber material. The polymer is spread out on the surface of the paper as highly dilute aqueous solution, emulsion or dispersion, whereat the polymer is possible to be applied evenly as a small concentration, as water is removed during the drying stage.
In Figures 1 and 2 is presented the principle of how the amphiphilic polymers can organize on the surface of fiber material such as paper.

More accurately said, mainly distinctive to the method according to the invention, is what is presented in the feature section of Claim 1.

Remarkable advantages are obtained with the invention. Thus, by using nanotechnic approach, the adhesion ability, capillary absorption and release ability can be influenced with amphiphilic polymers by already very small concentrations. Owing to the amphiphilic nature, the block copolymers can orientate on the surface of the fiber material or on its constituents such as individual fibers or filler particles, and through this, the hydrophobic blocks of the polymer can orientate outward form the surface and restrict the penetration of both water and solvent based liquids or viscous fluids. Simultaneously, the water-soluble block of the polymer anchors the polymer on the surface of the fiber.

Next, the invention is undertaken for examination more carefully through detailed explication referred to enclosed figures.

Figures 1 and 2 represent diagrammically the behaviour of the block copolymer on the surface of the paper, in Figure 3 is represented the four possible structure variations of amphiphilic polymer.

Amphiphilic polymers are copolymers, which can be structurally linear block copolymers, graft copolymers or star copolymers. Possible structure variations are presented in Figure 3. Amphiphilicity results from the different polarities of the polymer blocks. In a limited sense, the other block of the amphiphilic copolymer, is hydrophilic, water-soluble and the other is hydrophobic, insoluble in water.

An analogous polymer structure, according to the invention, is such where the water-soluble polymer is modified with a hydrophobic molecule, a technique from which as an example one can mention modified polyethylene oxide (PEO), whose ends are linked by \( n \)-octadecenylsuccinic anhydride (OSA) molecules using the hydrophobic blocks.
The preparation of amphiphilic polymers and their characteristics are described among others in following publications: US patent publications 6.887.962, 6.538.091 and 6.624.262; Vlcek et al, Polymer 46 (2005), ss. 4991-5000; Sugiyama et al, Polymer 44 (2003), ss. 4157-4164; Dworak et al., Reactive and Functional Polymers 42 (1999), ss. 31-36; Chognot et al., Journal of Colloid and Interface Science 268 (2003), ss. 441-447 and Kurian et al., Journal of Polymer Science: Part A : Polymer Chemistry 38 (2000), ss. 3200-3209.

Advantageous ways to prepare linear amphiphilic block structures are for example synthesis of macromonomers through condensation reaction, through formation of urethane, utilizing the chemistry of silicon such as with the aid of hydrosilylation reaction or utilizing living radical polymerization, just to mention a few examples.

Commercial manufacture of the block copolymers, composed of vinyl monomers, has been expensive until lately, difficult and restricted to rather limited group of monomers. Traditionally, such block copolymers are prepared through living anionic and cationic polymerization mechanism by adding the monomers in sequence into the reaction mixture. Weakness of the method has been very low reaction temperatures and sensitivity of growing anionic chain to polar groups.

A new method, so-called living radical polymerization, has been developed for the preparation of vinyl monomeric block copolymers. The reactions can be performed at room temperature in the living radical polymerization, and the method is not as sensitive to polar groups as the traditional living polymerization methods.

Advantageously in the invention, one uses homogenic homo- or copolymer or alternatively amphiphilic block copolymer material, which is applied on the surface of the substrate in the form of aqueous based liquid, emulsion, colloidal mixture or dispersion, in particular the polymer is dissolved or dispersed in water. Block copolymer can be structurally di- or tri-block copolymer. As mentioned above, block copolymer contains typically both water-soluble (hydrophilic) and water-unsoluble (hydrophobic) blocks.

The hydrophilic block of the amphiphilic can be any water-soluble polymer, in which a hydrophobic block can be attached by reaction. As examples of the hydrophilic block can
be mentioned polyethylene oxide, vinyl pyrrolidone, hydroxyl ethyl methacrylate, polyvinyl alcohol in addition polyacrylic acid, and as hydrophobic blocks n-octadecenyl succinic anhydride, styrene, methyl methacrylate, vinyl acetate, polysiloxane or silicon compound and polyolefin or copolymer of monomer units typical to them.

In addition, the polymer mixtures described here can be applied accordingly to the invention.

Frequently, one wants to prepare linear block structures, whereat polyethylene oxide is used as the hydrophilic block. The reactive groups in PEO are solely hydroxyl groups at the end of the chain, thus it is easy to prepare linear block copolymers from it. Other used hydrophiles in amphiphiles are among others poly(4-vinyl pyrrolidone), polymethacrylic acid and polyacrylic acid, but these polymers have to be modified into reactive by means of the chain transfer agents, or the block structure is to be prepared via living radical mechanism. In addition to or instead of the polyethylene oxide, polyalkylene oxides are possible in the implicated polymer structures.

In an advantageous application, for example polyethylene oxide works as the hydrophilic block and the octadecenyl succinic anhydride as the water-insoluble block, which are connected to each other by the reaction of octadecenylsuccinic anhydride with the hydroxyl groups at the end of the PEO.

Further, as an advantageous amphiphilic block copolymer according to the invention, can be mentioned a form of:

\[
\begin{align*}
\text{Si-O} & \quad \overset{\text{I}}{} \\
\text{R}_1 & \\
\text{R}_2
\end{align*}
\]

di- or tri-block copolymer formed from polysiloxane and polyalkenyl oxide, where the blocks are connected to each other by hydrosilylation reaction, and where the proportion of the polysiloxane units is advantageously 40% - 1% and the proportion of polyalkenyl units is advantageously 60% - 99%, and where R1 and R2 are the same or lower alkyl or phenyl group, whereas the lower alkyl or phenyl group can be substituted or unsubstituted.
Advantageously, this block copolymer composes of poly(di-methyl siloxane) (PDMS) and polyethylene oxide. Further, R1 and R2 can also be a type of polyalkenyl oxide, partly or entirely.


Water solubility of amphiphilic polymers or their tendency to form micelles in water phase depends on the type of the block and the length. In the case of polyethylene oxide modified with octadecenylsuccinic anhydride or octadecenylsuccinic acid anhydride, for example the water solubility level can be adjusted by molar mass of polyethene. The longer the block of polyethylene oxide, the better such an amphiphilic polymer is soluble in water.

In the case of polyethylene oxide and polydimethyl siloxane, the block length choice and the mutual ratio of substances, contributes essentially if the copolymer is soluble in water, forms micelles in it or is insoluble in water, but is dispensable in it.

Proportions of blocks can vary in a large scale. Typically, the proportion of hydrophobic components is amphiphilic block copolymers is 1-85 wt-%, advantageously 5-40 wt-% and correspondingly the hydrophilic components 15-99 wt-%, advantageously 60-95 wt-%.

Typical molar mass of the polymer is 500 - 500 000g/mol, advantageously 1000 - 50 000g/mol.

By means of the amphiphilic block copolymers according to the invention, the surface of the paper is not need to be filled, as in the traditional coating technique, but the polymers are applied evenly on the surface of the fibers, whereas they at least partly prevent the penetration of liquid or viscous fluids or pastes into the fiber material such as paper. Fiber material constituents such as on the surface of the fiber, the polymers are capable of
forming even or partly even layer. Actually, certain roughness of the surface is, yet surprisingly according to the invention, observed to be an advantageous feature as the adjusting parameter of the release force of foreign substances, such as glue substances.

The polymer is applied on the surface of the substrate by roll coating, curtain coating or spray coating or by some other corresponding way, typically as water dispersion or liquid, as mentioned above.

The amount of the polymer of the surface is small and it does not block up the surface of the paper. Typical use amounts of amphiphilic polymers are under 3 g/m², but generally on the surface of the substrate, one applies approximately 0,001 - 10 g/m², advantageously approximately 0,005 - 5 g/m²; in particular approximately 0,01 - 3 g/m², of the polymer or amphiphilic block copolymer.

By the previously presented method, the paper or paper board can be further treated for example by calendering it, always according to the application. It is also according to the invention, a nanocoating precoated fiber materials by self-organizing amphiphilic polymers to modify the repellence of the surface, so for example follow-up treatment of surface glued paper to improve its properties by applying on its surface a thin layer of polyethylene oxide modified with octadecenylsuccinic anhydride, or block or branched copolymer of polyethylene oxide and polysiloxane.

One application form according to the invention is also such, where the amphiphilic block copolymer, advantageously the block of polydimethyl siloxane or graft copolymer with polyethylene oxide is used as a blend component with surface glue containing essentially polyvinyl alcohol, advantageously with a proportion of 0,01 - 20wt-% from the total polymer mass to improve the release characteristics in the preparation of release paper. Also in this case the tendency of the amphiphilic polymer to a self-organization occurring on the surface is exploited, however in a novel surprising approach according to this invention.

The treatment according to the invention enables, however the use of paper without the need of performing any other treatments, than possibly calendering.
Calendering can be performed as online calendering or offline calendering, for example by using online-softcalander or offline-supercalander.

The square mass of the paper to be treated can be 50 - 450 g/m². Usually, the square mass of the backing paper of paper is 30 - 250 g/m², advantageously 30 - 80 g/m², with paper board is 90 - 400 g/m².

Polymer compositions according to the invention can be used in very small amounts per area unit. In an advantageous embodiment of the invention, by using the amphiphilic polymer, a self-organized, at least partly almost monomolecular polymer nanocoating is formed on the surface of the fiber material constituents, such as on the surface of the fibers or fillers. The adhesion characteristics of paper are changed by means of the polymer material, in accordance with the characteristic demands of the release papers of labels.

Using the polymers according to the invention, in the concept of fibrous substrates, it is surprisingly observed the roughness of surface to be highly significant in adjusting the adhering of foreign substances on the surface, for example the adhering of glue substances on the surface of fiber material, particularly for example when aiming at to tailor the release force of glue labels from the release paper. The release force of the glue labels can be regulated within large boundaries by means of regulating the surface unevenness, thus the surface roughness, of the fiber materials treated with the polymers according to the invention. It has been observed, that by adjusting separately two parameters, the natural repellence level of the polymer and the roughness level of the surface, the release force is adjustable within a very large range. Advantageous combinations of the natural adhesion of the polymer and the roughness of the surface are according to the invention.

By the natural repellence of the polymer, one means the selection of polymer composition, where the polysiloxanes usually represents one of the most repellent edge points. The repellence of the surface can be described, for example with the contact angle of water or the surface energy values. By the roughness of the surface, one means for example unevenness of the surface by atom force microscopy, which can be typically extent of 0.1 - 50µm, and for example in the embodiment of paper materials, it can be typically 1 - 5µm. The more even the surface is and the smaller the values of surface roughness are, the bigger release force values are obtained. Conversely it has been observed, that even the
fiber material coated by polyvinyl alcohol accordingly to the invention, advantageously paper, shows very low release force values of the glue substances when the surface roughness is bigger, advantageously over 5 microns. Such a behaviour has been generally named from other context as "Lotus" effect, which has now consequently shown to be provided by the composition and the method according to the invention, onto the surface of fibrous materials, as for example onto the surface of the paper.

The fiber material according to the invention is any fiber substrate, but advantageously natural fiber mass or cellulose based fiber material such as cellulose mass, paper, paper board, paper made from recycled fiber, fabric, fiber fabric, other natural fiber masses such as flax fiber mass, plates or fabrics from synthetic fiber, or three-dimensional objects from mentioned thereof, and there can be present, in addition to fiber material, other components such as fillers. From the fillers can be mentioned minerals such as calcium carbonate and kaolin. Particularly advantageously the invention is suitable for the treatment of paper and paper board paths and sheets. Product fibers can be virginal fibers or recycled fibers. In particular advantageously, the base paper is untreated, but it is also possible to modify the surface glued paper web or sheet.

It has also been observed, that in the composition and method according to the invention, it is sometimes advantageous to target temperature and/or pressure treatment into the material, for example calendering, after the coating. By this one can be influence the degree of surface roughness or evenness, and also the spreading of the polymer component on the fiber surfaces, and thereafter also promote the self-organization when using amphiphilic polymers. If the polymer composition is such, that is has been in the beginning with an emulsion or dispersion in water, it is possible after the removal of water to spread the possibly remained polymer particles better onto fiber surface and thus, promote the repellence of fiber structure.

Completely particular advantage of the invention is the possibility to prepare release sheets used as backing paper of labels without that there would be a separate silicozining phase in the conjunction. Then, it is also possible to provide accordingly to the invention a release paper, which can be recycled without that the silicon would hinder the recycling, and which can also be prepared from the recycled fiber.
Following non-exclusive application examples describe the invention:

**Example 1**
**Preparation of** PEO-b-OSA-copolymer

Polyethene oxide (20 g; 2 mmol) and n-octadecenylsuccinic anhydride (5.3 g; 15.1 mmol) are placed in a laboratory bottle, where a nitrogen flow is directed. The mixture is heated at 130 °C for 6 h. Product mixture is dissolved in water and extracted four times with equivalent amount of dichloromethane. Dichloromethane phase is collected and the solvent is removed under vacuum in a rotavapor. The product polymer is recovered by dissolving the evaporation residue again into dichloromethane and precipitating with diethyl ether. The product is separated form the solution by filtration. Finally, the product is dried under vacuum at room temperature for 8 h.

**Example 2**
**Preparation of** PEO-b-OSA-copolymer

Polyethene oxide (20 g; 3,33 mmol) and n-octadecenylsuccinic anhydride (3,5 g; 9,98 mmol) are placed in a laboratory bottle, where a nitrogen flow is directed. The mixture is heated at 130 °C for 6 h. Product mixture is dissolved in water and extracted four times with equivalent amount of dichloromethane. Dichloromethane phase is collected and the solvent is removed under vacuum in a rotavapor. The product polymer is recovered by dissolving the evaporation residue again into dichloromethane and precipitating with diethyl ether. The product is separated form the solution by filtration. Finally, the product is dried under vacuum at room temperature for 8 h.

**Example 3**
**Preparation of** PEO-b-OSA-copolymer

Polyethene oxide (20 g; 5 mmol) and n-octadecenylsuccinic anhydride (7,9 g; 22,54 mmol) are placed in a laboratory bottle, where a nitrogen flow is directed. The mixture is heated at 130 °C for 6 h. Product mixture is dissolved in water and extracted four times with equivalent amount of dichloromethane. Dichloromethane phase is collected and the solvent is removed under vacuum in a rotavapor. The product polymer is recovered by dissolving
the evaporation residue again into dichloromethane and precipitating with diethyl ether. The product is separated from the solution by filtration. Finally, the product is dried under vacuum at room temperature for 8 h.

Example 4
Preparation of PEO-b-OSA-copolymer

Polyethene oxide (20 g; 10 mmol) and n-octadecenylsuccinic anhydride (15.7 g; 44.79 mmol) are placed in a laboratory bottle, where a nitrogen flow is directed. The mixture is heated at 130 °C for 6 h. Product mixture is dissolved in water and extracted four times with equivalent amount of dichloromethane. Dichloromethane phase is collected and the solvent is removed under vacuum in a rotavapor. The product polymer is recovered by dissolving the evaporation residue again into dichloromethane and precipitating with diethyl ether. The product is separated from the solution by filtration. Finally, the product is dried under vacuum at room temperature for 8 h.

Example 5
Preparation of monofunctional PEO macroinitiator

Solution are made from polyethene oxide monomethyl ether (20 g; 4 mmol) and propynyl chloride (1.1 g; 12 mmol) into dichloromethane. The reaction vessel is placed in an ice bath where a nitrogen flow is directed. Polyethene oxide solution is added to the reaction vessel and propynyl chloride is added dropwisely into the reaction vessel during an 1 hour. Thereafter, the reaction vessel is moved at room temperature and the temperature of the reaction mixture is let to equilibrate during 18 hours. Finally, triethyl amine dissolved in dichloromethane is added dropwisely into the reaction mixture, until the mixture turns into alkaline. The solution is filtrated, half of the solvent is removed under vacuum and the macroinitiator is precipitated by cold diethyl ether. The macroinitiator is recovered by filtration and dried under vacuum overnight.

Example 6
Preparation of difunctional PEO macroinitiator
Solution are made from polyethene oxide monomethyl ether (20 g; 2 mmol) and propynyl chloride (1.1 g; 12 mmol) into dichloromethane. The reaction vessel is placed in an ice bath where a nitrogen flow is directed. Polyethene oxide solution is added to the reaction vessel and propynyl chloride is added dropwisely into the reaction vessel during a 1 hour. Thereafter, the reaction vessel is moved at room temperature and the temperature of the reaction mixture is let to equilibrate during 18 hours. Finally, triethyl amine dissolved in dichloromethane is added dropwisely into the reaction mixture, until the mixture turns into alkaline. The solution is filtrated, half of the solvent is removed under vacuum and the macroinitiator is precipitated by cold diethyl ether. The macroinitiator is recovered by filtration and dried under vacuum overnight.

**Example 7**

**Preparation of block polymer of polyethylene oxide and polydimethyl siloxane; PEO-ended tri-block copolymer**

Dehydrated alpha-vinyl ether polyethylene oxide (PEO), whose molar mass is 10 000 g/mol was weighted 50 g into a three-neck flask. In addition, 1.88 g of alpha, omega-bis(dimethylsilylhydride) polydimethyl siloxane (PDMSDIH) Mn = 750 g/mol is weighted into same vessel and 30 wt-% of distilled dry toluene.

Reaction solution was stirred with magnetic stirrer 200 rpm and dry oxygen was directed thought the solution to avoid the deactivation of the catalyst. Reaction xoluiton was warmed to 50°C, thereafter the catalyst (Pt(O) divinyltetramethylsiloxane complex) was added into the solution through septum. The amount of platinum was 30 ppm calculated from the amount of start materials. Thereafter, the polymerization was monitored by IR, until the reactions were finished, which was observed as a disappearance of the peak at 2130 cm⁻¹. This took approximately 4 h. After finishing the polymerization, toluene was distilled from the solution by increasing temperature at 65°C and decreasing the pressure to 5 bars during 1 h.

**Example 8**

**PDMS-PEO-PDMS - Tri-block copolymer**
Dehydrated alpha-vinyl ether polyethylene oxide (PEO) whose molar mass is 10 000g/mol was weighted 40g into a three-neck flask. In addition, 5.74g of alpha, omega-bis(dimethylsilylhydride) polydimethyl siloxane (PDMSDIH) Mn = 750g/mol is weighted into same vessel and 30wt-% of distilled dry toluene. Because the amount of dimethylsilylhydride groups was in excess in the reaction, the dimethylsilyl groups were obtained in the both ends of the end product.

Reaction solution was stirred with magnetic stirrer 200 rpm and dry oxygen was directed thought the solution to avoid the deactivation of the catalyst. Reaction solution was warmed to 50°C, thereafter the catalyst (Pt(O) divinyltetramethylsiloxane complex) was added into the solution through septum. The amount of platinum was 30 ppm calculated from the amount of start materials. Thereafter, the polymerization was monitored by IR, until the reactions were finished, which was observed as a disappearance of the peak at 2130cm⁻¹. This took approximately 4 h. After finishing the polymerization, toluene was distilled from the solution by increasing the temperature at 65°C and decreasing the pressure to 5 bars during 1 h.

**Example 9**

**Preparation of repellent fiber material with PVA**

5 wt-% of polyvinyl alcohol (Mw = 30 000g/mol) was dissolved in water as dilute aqueous solution. Uncoated fine paper was spray coated by air-pressured spraying apparatus. The paper sample was dried at heat cabinet at 40°C for 2 h. The amount of polymer in the paper was measured and it was observed to be 0.9g/m². The adhesion of the prepared paper to glue label was observed to be much lower than in the comparison test of uncoated fine paper, where a part of the paper structure delaminated and got stuck on the glue label. In the case of the coated paper, the fibers were not observed to adhere on the glue surface after release.

**Esimerkki 10**

**Preparation of repellent fiber material using PEO modified with octadecenylsuccinic anhydride**
3 wt-% of PEO modified with octadecenylsuccinic anhydride was dissolved in water. A series of spray coatings onto the uncoated fine paper was performed in a same way as in Example 9, but varying the amount of coating solution. The amount of polymer in the dried fine paper was estimated 0.2, 0.5 and 1.0 g/m².

Clearly lower release force of glue label was detected with all these samples than in the comparison label release test of uncoated fine paper.

**Example 11**

**Paper coating by amphiplilic block**

1...5 wt-% aqueous solution, emulsion or colloidal mixture or dispersion was made from the dried amphiphilic block copolymer. Coated sheet was weighted before the coating and 8h after coating. Aqueous solution was sprayed with air pressure on the surface of the paper sheet. Coating amount was adjusted with the solution volume. Wet sheet was transferred in the oven, where it was dried at 120°C for 5 min. The coating amount was determined by the weights of uncoated and coated sheets and also by the coated area.

**Example 12**

**Preparation of repellent fiber material using PEO-PDMS-block copolymers**

PEO-PDMS-block copolymers, according to 7 and 8, were made by using dilute aqueous solutions containing 5 wt-% of the polymer.

These mixtures were applied onto the surface of the fine paper according to the technique described in Example 9.

The samples were dried and the release force tests of glue labels were made. Clearly lower release force of glue labels was detected than in the uncoated comparison paper. No wood fibers detached from the surface of the treated samples onto the adhesive coated surface unlike from the surface of untreated comparison sample.
Example 13
Preparation of repellent fiber material using graft structured PDMS modified as hydrophilic.

Dilute 5wt-% and 10 wt-% aqueous solutions of modified PDMS grades were made according to table below:

<table>
<thead>
<tr>
<th>grade</th>
<th>molar mass</th>
<th>water solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABCRDBE 814</td>
<td>10000g/mol</td>
<td>+</td>
</tr>
<tr>
<td>ABCR DBP 732</td>
<td>20000g/mol</td>
<td>+</td>
</tr>
<tr>
<td>ABCR CMS 626</td>
<td>5000g/mol</td>
<td>+</td>
</tr>
</tbody>
</table>

These solutions were applied onto the uncoated fine paper according to description in Example 9. The samples were dried and measured by weighting, so that the amounts of polymers were 0.3 and 0.6g/mol.

The tests describing the release force of glue labels were performed and the release forces were observed to be much lower that in the comparison sample.

Example 14
Release paper having a large surface roughness

A coating experiment according to example 9 was made, but in a way that the fiber material was a paper board with unevenness of 10µm.

The release force was observed to be particularly low in the release test of adhesive labels, and no substance remained on the glue surface from the release paper.

Example 15
Mixture of polysiloxane and PVA modified as polar.

10wt-% aqueous solution of polyvinyl alcohol (PVA) was prepared. In it, one dissolved 20% of ABCR DBP-732 polymer according to Example 12, which is PDMS grafted with polyethylene oxide and is water-soluble and amphiphilic.
A coating of a fine paper was performed from the aqueous solution with the polymer amount on the level of 2g/m². The paper was dried.

Decreased adhesion was clearly observed, when compared to similarly coated PVA coated fine paper, but without the silicon component.
Claims

1. Essentially cellulose based foreign substances repellent release paper composition, characterized in that there is on the surface of the material components spread a small amount of polymer, which is either:
   A) water-soluble, colloids or micelles composing, or water dispersed polymer, or mixture of polymers
   or
   B) amphiphilic linear, branched, or star shaped block or graft copolymer, wherein is present:
   hydrophilic blocks (a) and hydrophobic blocks (b).

2. A composition according to Claim 1, characterized in that a water-soluble, colloids or micelles forming, or water dispersed homogenic polymer (A) is advantageously polyethylene oxide, polyvinyl alcohol, polyvinyl pyrrolidone, poly(hydroxyethyl methacrylate), water-soluble polysaccharide, polyacrylamide, polyvinyl acetate, lactic acid based biopolymer, or a copolymer composed of monomer units thereof, or a mixture of these, not excluding other analogous.

3. A composition according to claim 1, characterized in that the hydrophilic block (a) of the amphiphilic polymer (B) is advantageously polyethylene oxide, polyvinyl alcohol, polyvinyl acetate, polyvinyl pyrrolidone, poly(hydroxyethyl methacrylate), water-soluble polysaccharide, polyacrylamide, or a copolymer composed of monomer units thereof, or a mixture of these polymers, not excluding other analogous water-soluble polymers or combinations thereof.

4. A composition according to claim 1, characterized in that the hydrophobic blocks (b) of the amphiphilic polymer (B) are a type of hydrophobic parts of a molecule or polymer chains, and are advantageously hydrocarbon chains such as paraffins, polyolefins, fatty acids, or polysiloxanes, blocks originated from octadecenylsuccinic anhydride, polystyrene, or polymethyl methacrylate, just to mention a few phobic blocks, not excluding similarly behaving polymeric or oligomeric homo or copolymer block structures or phobic molecule blocks.
5. A composition according to Claim 1, characterized in that the hydrophobic block (b) of the amphiphilic block copolymer (B) is a form of:

$$\text{R}_1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{R}_2$$

polysiloxane, where R1 and R2 are the same, or different lower alkyl or phenyl group, whereat the lower alkyl or phenyl group can be substituted or unsubstituted.

6. A composition according to Claim 1, characterized in that the amphiphilic block copolymer is a form of:

$$\text{R}_1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{R}_2$$

a di- or tri-block copolymer composing of polysiloxane and polyalkenyl oxide, where the proportion of polysiloxane is advantageously 40%-1% and the proportion of polyalkenyl oxide is advantageously 60-99%, and where R1 and R2 are the same or different lower alkyl or phenyl group, whereat the lower alkyl or phenyl group can be substituted or unsubstituted. Advantageously this polymer consists of poly(di-methyl siloxane) and polyethylene oxide. Further, R1 and R2 can be a type of polyalkenyl oxide, partly of entirely.

7. A composition according to Claim 2, characterized in that the polymer coating is provided by applying or impregnating a water-soluble, colloids or micelles in water forming, or water dispersed polymer or mixture thereof with water onto fiber based material by roller coating, spray coating, curtain coating or other analogous method and thereafter removing water.

8. A composition according to Claim 1, characterized in that the polymer is particularly on the surface of fiber constituents or fiber material or it is spread evenly onto the surfaces of structure parts of a fiber material, such as advantageously fibers or fillers, throughout the entire material as a thin layer or as micellaric or dispersed particles.
9. A composition according to Claim 1 characterized in that the amount of used polymer component (A) or (B) in the fiber material composition is 0.005 - 1 g/ m², advantageously 0.3 - 1 g/ m² in the preparation of paper.

10. Some of the above compositions according to claims characterized in that amphiphilic polymer (B) has formed a self-organized nanocoating onto the surface of fiber material constituents, such as advantageously onto the surface of the fibers or fillers.

11. A composition according to Claim 1 characterized in that a repellent, adhering ability regulating characteristic or lowering impregnation on the fiber material characteristic is formed on the fiber material, advantageously on the paper, which composes of one or many of the following substance group: glue substances, label glues, solvents and solutions, fats or waxes.

12. A composition according to Claim 1, characterized in that the fiber material is essentially cellulose based such as paper, paper board, cellulose plate, paper or paper board or mass made form recycled fiber, fabric, natural fiber mass, such as advantageously flax fiber mass, or plate or fabric made from synthetic fibers, such as fiber fabric, or three-dimensional kappale form mentioned above and there can also be other components such as fillers.

13. A composition according to Claim 1, characterized in that the release force of glue substances, such as labels, tapes, glue masses and similar thereof, from the fiber material can essentially diminished, when the surface of the fiber material, advantageously paper, contains unevenness or pores in a size range of 0.5 - 50 µm, advantageously 5-10 µm.

14. A method for the preparation of foreign substance repellent release paper, characterized in that a small amount of a polymer is spread on the surface of the material constituents, which composes of:
   A) soluble, colloids or micelles forming, or water dispersed homogenic homo- or copolymer polymer or a mixture of the polymers thereof, not excluding other similar water-soluble polymers or compositions thereof,
B) amphiphilic linear, branched, or star shaped block or graft copolymer, which contains: hydrophilic blocks (a) and hydrophobic blocks (b).

15. A method according to Claim 14, characterized in that the polymer (A) or (B) is coupled in the fiber material as dilute water based solution, emulsion or dispersion, where the polymer concentration in the solution is advantageously 1 - 15wt-% and water is removed after the association.

16. A method according to Claim 14, characterized in that the polymer coating is provided by a water-soluble, colloids or micelles in water forming, or water dispersed polymer or mixture thereof with water onto the fiber based material by roller coating, spray coating, curtain coating or other analogous method by applying or impregnating and thereafter removing water.

17. A method according to Claim 14, characterized in that the structure and characteristics of the polymer treated fiber material can be changed, improve the polymer spreading on the fiber surfaces, in addition, promote the self-organization of amphiphilic polymers by temperature and/or heat treatment the fiber material, such as by calendering.

18. A method according to Claim 14, characterized in that the amphiphilic block copolymer (B), advantageously block copolymer of polydimethyl siloxane and polyethylene oxide, is used as mixture component of surface glue containing fundamentally polyvinyl alcohol, advantageously by proportion of 0,01 - 20wt-% from the polymer mass to improve the release characteristics in the preparation of paper.

19. A method according to Claim 14, characterized in that the release force of gluey material, such as advantageously glue label or tape, can be decreased from the polymer treated fiber material, when the surface of the fiber substrate contains unevenness or pore structures of 0,5 - 50µm.
20. A method according to Claim 14, characterized in that the release sheet of glue label, glue containing sheet, tapes or glue masses and similar products, used on the back side of the products, can be prepared without separate siliconizing stage.

21. A use of a fiber material according to Claim 1 and a method according to Claim 14 in the adjustment of the adhering of the glue substances to different surfaces and to provide adjustment on the surface repellence and material impregnation of paper, paper board, natural fiber based sheets, fabrics and other similar substrates or objects, in particular the use in the preparation of release papers, such as in the concept of backing papers for labels and tapes.
Fig. 1
Di-block copolymer

Tri-block copolymer

Star-shaped copolymer

Graft copolymer

Fig. 3
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8: D21H, B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Fl, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC-Internal, WPI

c. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 99/1 1683 A1 (MINNESOTA MINING &amp; MFG) 11 March 1999 (1.1.03.1999), Claims 1, 13, 16, page 8, lines 18-23, page 12, lines 25-28, example 7</td>
<td>1.3-5, 8-12, 14-18, 20, 21</td>
</tr>
<tr>
<td>X</td>
<td>WO 2004/085561 A2 (OMNOVA SOLUTIONS INC et al.) 07 October 2004 (07.10.2004), page 2, page 13 lines 13-18, page 15, lines 4-19, page 16, lines 24-27, page 17, lines 14-24</td>
<td>1.3-6-8-12, 14-16, 18, 20, 21</td>
</tr>
<tr>
<td>X</td>
<td>US 6541 109 B1 (KUMAR RAMESH C et al.) 01 April 2003 (01.04.2003), claims 1 and 2, column 4, line 30 - column 5, line 21, column 8, line 30 - column 9 line 8, column 9 lines 51-65, column 14, line 40 - column 15, line 15</td>
<td>1.3-6-8-12, 14-16, 18, 20, 21</td>
</tr>
<tr>
<td>X</td>
<td>US 2005/01 19391 A1 (MASON GEOFF et al.) 02 June 2005 (02.06.2005), paragraphs [0012], [0015]-[0024], [0056], [0058], [0064]-[0069]</td>
<td>1.2, 9, 14, 18</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
12 March 2007 (12.03.2007)

Date of mailing of the international search report
22 March 2007 (22.03.2007)

Name and mailing address of the ISA/FI
National Board of Patents and Registration of Finland
P.O. Box 1160, FI-00101 HELSINKI, Finland
Facsimile No. +358 9 6939 5328

Authorized officer
Heimo Koskinen
Telephone No +358 9 6939 500
<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>JP 11290777 A (OJI PAPER CO) 26 October 1999 (26.10.1999), (abstract) Patent Abstract of Japan, Retrieved from EPOQUENET/BNS</td>
<td>1, 2, 7-9, 11, 12, 14-18, 20, 21</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family members(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>WO 99/1 1683 A1</td>
<td>11/03/1999</td>
<td>AU 9372998 A</td>
</tr>
<tr>
<td>WO 2004/085561 A2</td>
<td>07/10/2004</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 200351 1540T T</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1230314 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 3224600 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1490549 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2480825 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 200321 6939 A1</td>
</tr>
<tr>
<td>JP 11323778 A</td>
<td>26/11/1999</td>
<td>None</td>
</tr>
<tr>
<td>JP 11290777 A</td>
<td>26/10/1999</td>
<td>None</td>
</tr>
<tr>
<td>Classification of Subject Matter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Int.Cl.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D21H 27/00</strong> (2006.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D21H 77/33</strong> (2006.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D21H 21/16</strong> (2006.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D21H 19/32</strong> (2006.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B32B 7/06</strong> (2006.01)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>