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- **Rissanen, Mikko**
02750 Espoo (FI)
- **Littunen, Kuisma**
53100 Lappeenranta (FI)
- **Rautalahti, Jaakko**
37630 Valkeakoski (FI)
- **Antila, Janne**
13100 Hämeenlinna (FI)

(71) Applicant: **UPM-Kymmene Corporation**
00100 Helsinki (FI)

(74) Representative: **Berggren Oy, Tampere**
Visiokatu 1
33720 Tampere (FI)

(72) Inventors:
• **Kosonen, Harri**
53300 Lappeenranta (FI)

(54) **A METHOD FOR MANUFACTURING A PAPER SUBSTRATE SUITABLE FOR A RELEASE LINER WITH HIGH CONTENT OF FUNCTIONAL VINYL GROUPS, AND PRODUCTS AND USES THEREOF**

(57) The invention relates to a method for manufacturing a paper substrate and product thereof which is suitable for binding silicone in a catalytic hydrosilation reaction, the paper substrate comprising a cellulose fiber-based paper and a polymeric primer layer, wherein the polymeric primer layer comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram of the polymer, such that the surface of the polymeric primer layer is hydrophobic. Advantageously, high-vinyl content polybutadiene obtainable from 1,2-addition polymerization reaction of 1,3-butadiene may be used in the polymeric primer layer.

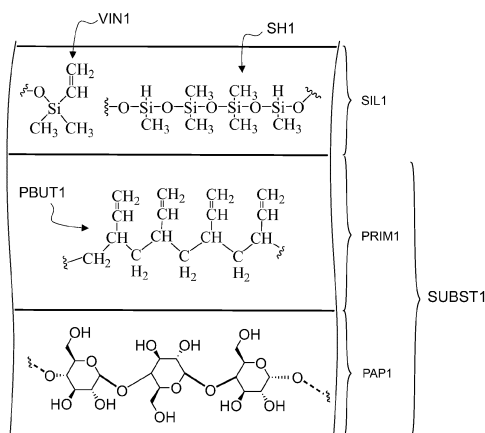


Fig. 6a

Description**Technical field**

5 **[0001]** The invention relates to a paper substrate that is suitable for binding silicone in a catalytic hydrosilation reaction containing a high vinyl content polymer. The invention further relates to a method for manufacturing such paper substrate. The invention further relates to use of high-vinyl content polybutadiene in a method for manufacturing a paper substrate containing a high vinyl content polymer.

10 **Background**

[0002] A release liner refers to a product comprising a paper substrate and a release layer (i.e. a cured release coating), such as a silicone-based release layer, applied on at least one side of the paper substrate. Release layers have a
15 dehesive surface facing away from the paper substrate, the surface energy level typically being in the range of 21 to 25 dynes/cm. The dehesive surface of the release layer may be used to protect adhesive material in contact with the dehesive surface.

[0003] Papers used as paper substrates for siliconizing, such as glassine or supercalendered kraft paper, are typically manufactured from bleached chemical pulp, such as bleached Kraft pulp, with an aim to provide dimensionally stable and dense paper surface able to reduce the surface penetration of a release coating, when the release coating is applied
20 on the paper surface. The surface penetration of the release coating can be further reduced by applying a coating (i.e. a primer layer) on the paper surface and/or calendaring the paper prior to applying the release layer. A primer layer typically applied on the paper surface is a surface coating. A conventional surface coating, also referred to as a "surface size", may improve the surface smoothness and reduce the porosity of the paper surface and thus act as a barrier between the release layer and the paper surface.

25 **[0004]** Release coatings based on silicone polymers are typically easy to apply and well-flowing. Uncured silicone polymers may penetrate easily into the pores of a paper, unless sufficient hydrophobicity is present at the paper surface. The curing of a silicone refers to a thermally induced cross-linking reaction of the silicone polymer once applied onto the substrate surface, which results into a cross-linked surface coating attached to the substrate surface. Release coatings have previously been cured by radiation, wherein the coating contains either an initiator in the formulation, such
30 as a photo initiator sensitive to ultra violet light, or the curing relies on high-energy radiation, such as an electron beam, producing sufficient amounts of energy to start the cross-linking reaction. The radiation cured layer functioned by either breaking chemical bonds and/or generating ions, which resulted into a cured silicone polymer based release layer, without the use of additional heat.

[0005] Thermally curable release coatings refer to specific type of release coatings, which are distinguished from radiation curable systems. Low temperature curable silicone polymer or "LTC" silicone polymer, refers to an addition-
35 curable polymer comprising silicone base polymer with functional vinyl groups and a cross-linker compound with silane hydride groups, which components are configured to cross-link in a catalytic hydrosilation reaction at a low temperature. In the presence of precious metal catalysts such as platinum or rhodium complexes, a silane hydride group undergoes an addition reaction with a vinyl group. The addition reaction is typically catalysed by a platinum catalyst. Platinum-
40 catalyzed addition reactions are fast, and the curing speed of the reaction can be controlled via the curing temperature. A low temperature in this context refers to a catalytic hydrosilation reaction temperature of less than 120°C, preferably in the range of 55 to 110°C, wherein the silane hydride groups and the functional vinyl groups form covalently cross-linked structures within the release coating, thereby forming the cured release layer. Novel fast-curing silicone polymers are often further designed to function with low amounts of platinum catalyst.

45 **[0006]** A problem with respect to the fast-curing silicone polymers is the relatively low anchorage of the release coating applied on the paper substrate. Further, due to the high volumes of release liner material produced, there is a constant aim to reduce the amounts of platinum catalyst from the current level in the range of 50 to 35 ppm to a lower level, such as to a level of 30 ppm or below. Due to the wide use of fast-curing silicone polymers in release liners, there is a constant need to save costs by using less platinum. Platinum is a very expensive catalyst material. In addition, the amount of
50 other reagents, such as silicone used for a release coating, is a cost factor to be minimized. A further challenge is the curing temperature, which refers to the minimum temperature wherein the silicone polymers begins to cross-link, such that a fixed layer structure with dehesive properties is obtained. The curing temperature should be maintained relatively low in order to save production costs due to heating. However, a very low curing temperature, e.g. below 45°C, may be problematic as the silicone polymers may then begin to cross-link prematurely, for example before it has been applied
55 on the paper substrate surface. The importance of such parameters is emphasized when the machine speed is increased.

[0007] Thus far, the anchorage of fast-curing silicone polymers on the paper substrate has been improved by using a primer layer containing chemically post-treated polymer, such as water soluble polyvinyl alcohol, which has been modified to contain functional vinylic groups. In the chemical post-treatment of polyvinyl alcohol, the reaction typically

takes place through the highly reactive hydroxyl group. A polymer containing hydroxyl groups is most often reacted with a compound that contains a carbonyl group. Carbonyl groups may be oxidized, and may undergo addition reactions under basic or neutral conditions. Hence, the modification of the polymer is performed by means of carbonyl group reactions with one or more hydroxyl groups of the polymer, thereby providing water soluble polymer modified to contain functional vinylic groups. Examples of carbonyl compounds are aldehydes, carboxylic acids, esters, anhydrides and acid halides. Examples of chemical post-treatment of polyvinyl alcohol by carbonyl group reactions are disclosed in publications WO 2009/147283 and WO 2011/104427, which disclose methods for grafting PVA polymer with organic molecule to provide the PVA polymer with vinylic functions.

[0008] A disadvantage related to chemical post-treatment of polyvinyl alcohol is, however, that when the amount of the carbonyl compound further containing a vinyl group in such a post-treatment reaction is increased, the solution quickly becomes highly viscous and increasingly less water-soluble. Hence, the solubility of the compounds significantly limits the amount of vinylic side groups that can be grafted into the PVA polymer. Attempts to increase the aldehyde content in the reaction solution dramatically increase the viscosity of the reaction solution such that the reactants will prematurely precipitate out of the solution. For example, when grafting polyvinyl alcohol, having a hydrolysis degree of 98 - 99 % and degree of polymerization of 1400, with undecylenic aldehyde (an aldehyde comprising 11 carbon atoms), the polymer typically becomes significantly less water-soluble already when undecylenic aldehyde is added to the reaction mixture more than 2% by weight, when expressed as grams of aldehyde compound per 100 grams of polyvinyl alcohol. The formed reaction product thus becomes highly viscous and very difficult to apply on a substrate surface as a coating. Hence the amount of vinylic side chains in a modified PVA polymer is maintained relatively low, which typically is necessitated by current high-speed release liner applications.

[0009] Due to the very limited amount of functional vinylic groups which can easily be grafted into a PVA polymer, previous solutions have not been able to provide a substrate without drawbacks in high-speed labelling applications. The higher the velocity in a labelling process is, the smaller is the acceptable amount of release liner silicone anchorage level defects.

Summary

[0010] A silicone-based release layer comprises a base polymer containing functional vinyl groups ($-\text{CH}=\text{CH}_2$) and a cross-linker compound containing silane hydride (Si-H) groups. Novel fast-curing silicones can have a more branched molecular structure than those of the previous generation. The branched molecular structure enables faster reaction kinetics when cross-linking the functional vinyl groups ($-\text{CH}=\text{CH}_2$) and the cross-linker compound containing functional groups with silane hydride (Si-H) bonds. Novel fast-curing silicones therefore require less time for the addition curing reaction to take place.

[0011] According to an aspect of the invention, a selectively addition-polymerized diene may be used to provide an oleophilic primer layer, which contains a polymer having high amounts of functional vinyl groups without styrene groups. The anchorage of a release layer to a paper substrate may thus be improved by providing a paper substrate having a primer layer surface containing a high amount of functional vinyl groups throughout the primer layer surface plane. A primer layer containing a high-vinyl content polymer provides an unprecedented means of improving the anchorage characteristics of a silicone-based release layer. In addition to fast curing silicone polymers which have been specifically referred to, the covalent attachment of other silicone polymers based on addition-curable cross-linker compound containing silane hydride bonds may also be improved.

[0012] A method for manufacturing polymer having high vinyl group content without a significant amount of hydroxyl groups may comprise selective polymerization of diene monomers. In particular, a method for manufacturing polymer having high vinyl group content may comprise reacting diene monomers having two or more vinylic groups in the presence of a catalyst selective for addition reaction. The percentage of the polymer repeat units containing a vinyl group may be adjusted by selecting the polymerization conditions and a suitable catalyst. A suitable catalyst is, for example, butyl lithium. The 1,3-butadiene monomer is highly selective for 1,2-addition reaction in the presence of butyl lithium, thereby producing high vinyl content polybutadiene that does not contain a significant amount of hydroxyl groups. High vinyl content polybutadiene may have a vinyl group content of up to 18,5 mmol/g, wherein the vinyl groups content represents the molality of the functional groups in the formed polymer.

[0013] The high amount of functional vinyl groups on a selectively addition-polymerized diene provides a composition which may be coated on a cellulose fiber-based paper, thereby providing a substrate improved anchorage properties toward silane hydride groups. A further advantage of such an oleophilic primer layer is the hydrophobicity of the surface. A hydrophobic primer layer may be used to resist the penetration of various substances, such as a water-based adhesive material, which may become into contact with the hydrophobic polymer coating. A hydrophobic polymer also evens out the characteristics of the whole surface, despite the existence of possible defects, such as holes, which may sometimes be present in the cellulose fiber-based paper.

[0014] Hydrophobic polymer coating, as such, has a poor adhesion to silicone. The silicone adhesion towards a

hydrophobic polymer coating is furthermore inversely related to the coating speed. When the coating and curing is performed at higher speed, there is less adhesion of the silicone towards the hydrophobic polymer coating. When the cellulose fiber-based paper is, however, coated with a primer layer which contains a non-polar polymer having high vinyl group content without a significant amount of hydroxyl group, the polymer has a tendency to be hydrophobic and avoids the hydrophilic surface of the cellulose fibre-based paper. While a hydrophobic polymer coating, as such, has a poor adhesion to silicone, the catalytic hydrosilation reaction enables chemical bonding of the silicone with the functional vinylic group present in the polymer. An advantage of the hydrophobic surface on the cellulose fiber-based paper is that less adhesive may penetrate through a release layer into the cellulose fibre-based paper beneath, when the paper substrate is used as release liner paper substrate. Thus, also the minimum amount of force required to detach a label or excess matrix material is reduced. A further effect of the hydrophobic surface on the cellulose fiber-based paper is that this enables the thickness of the release layer to be reduced, since the minimum amount of force required to detach a label from the release liner is dependent of the thickness of the release layer. The hydrophobic surface therefore facilitates the reduction of the amounts of silicone and platinum required for providing a release layer. A thinner release layer further enables a lower high-speed release value. Without a significant amount of hydroxyl groups in the polymer the vinyl groups thereby have a tendency to orientate away from a hydrophilic surface, such as cellulose fiber-based paper, when coated on such a surface. A particular advantage of a primer layer that contains functional vinylic groups in an amount of equal to or higher than 0.3 mmol/g, preferably an amount of equal to or higher than 0.5 mmol/g in the formed polymer is that the high amount of functional vinyl groups enables the use of very fast curing silicone compounds in the release coating. When the polymer contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram (mmol/g) of the polymer, this enables forming a tight, closed paper substrate with oleophilic properties on the surface. The cellulose fiber-based paper may be e.g. a coated paper having a grammage equal to or more than 38 g/m², for example in the range of 38 to 160 g/m². The formed paper substrate may therefore be arranged to have a tight, closed surface with oleophilic properties resembling those of a synthetic paper substrate surface. A synthetic material, such as polypropylene, conventionally tends to have a low surface energy level, and reduced anchorage of silicone to the substrate surface. However, as a significantly higher amount of vinyl groups compared to levels cited in the prior art can be provided on the paper substrate surface, this improves the anchorage of the silicone polymers cured via the polyaddition reaction.

[0015] While emulsions of styrene-butadiene copolymer (SBR) have been extensively used in coated papers due to low manufacturing cost, they in general are unsuitable for release liner primer layer applications. Styrene-butadiene copolymers for paper coatings, also denoted as SBR or SB-latex, are typically manufactured in the presence of emulsifying agents, such as surfactants like various soaps. The emulsifying agents are used to control the molecular weight and hence the viscosity of the formed copolymer product, but do not stay attached in the formation of copolymer and instead easily separate and float to the surface during manufacturing of the coating.

[0016] The polymerized diene comprising functional vinyl groups may further be arranged to contain unsaturated dicarboxylic acid or an anhydride or monoester thereof, such as maleic acid or maleic anhydride. Preferably, the polymeric primer layer having high amounts of functional vinyl groups, which is on top of the cellulose fiber-based paper, is without styrene groups. Thereby, a paper substrate having a surface without styrene groups may be obtained. The lack of styrene groups in the polymeric primer layer is related to the theoretical amount of functional vinyl groups obtainable on a polymer formed of monomers. Advantageously, the amount of functional vinyl groups in the polymer formed of monomers is maximized, which improves the hydrophobic properties of the polymer, as is the case with polybutadiene obtainable from 1,3-butadiene monomers by 1,2-addition polymerization. A further introduction of polar groups to the polymeric structure, such as the covalent grafting of unsaturated dicarboxylic acid, anhydride or monoester thereof, however, will consume said functional vinyl groups of the polymer. Polar groups which are covalently grafted to the vinylic groups of polymer structure therefore supercede part of the functional vinyl groups of the polymer. The amount of polar groups which have been covalently grafted to the polymer structure, however, may be used to control the hydrophobicity of the polymer, thereby selecting how the polymer behaves in water. A balance between the hydrophobic and hydrophilic properties of the polymer may be used to reduce problems commonly associated to emulsifying agents, which tend to separate easily and float to the surface. Such polar groups in the polymer composition may thus be arranged to modify the degree of hydrophobicity of the polymer composition. In particular, a polymerized diene may be arranged to contain hydrophilic groups to improve the water-solubility of the polymer composition, thereby facilitating the application of the polymer to a cellulose fiber-based paper layer. Namely, depending on the polymerization degree and the amount of hydrophilic groups in addition to the functional vinyl groups, the polymer composition may be water soluble or it may be applied as a water-based emulsion or water-based dispersion. Advantageously, the amount of unsaturated dicarboxylic acid or an anhydride or monoester thereof may be equal to or higher than 3 mol-% of the polymer. It is contemplated, that an amount of unsaturated dicarboxylic acid or an anhydride or monoester thereof in the range of 3 to 6 mol-% provides conditions suitable for a water-based emulsion. A water soluble polymer composition may be obtained, when the amount of unsaturated dicarboxylic acid or an anhydride or monoester thereof is equal to or higher than 20 mol-% and the solution has an alkaline pH, preferably a pH value above 8. Sodium salts may be used to improve solubility and

stability of the polymer composition. A method for manufacturing polymer having high vinyl group content may thus further comprise grafting unsaturated dicarboxylic acid or an anhydride or monoester thereof, such as maleic acid or maleic anhydride, into the polymer having high vinyl group content, thereby modifying the hydrophobicity of the polymer.

[0017] According to an aspect of the invention, there is provided a paper substrate that is suitable for binding silicone in a catalytic hydrosilation reaction, the paper substrate comprising

- a cellulose fiber-based paper and
 - a polymeric primer layer,
- wherein the polymeric primer layer comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram (mmol/g) of the polymer, such that the surface of the primer layer is hydrophobic. Functional vinyl groups present on the surface of the primer layer are capable to form covalent bonds with a silicone-based release layer which may be applied on top of the hydrophobic primer layer.

[0018] According to another aspect of the invention, there is provided a method for manufacturing a paper substrate that is suitable for binding silicone in a catalytic hydrosilation reaction, the method comprising

- providing a cellulose fiber-based paper and
- coating a polymeric primer on top of the cellulose fiber-based paper layer, thereby forming the paper substrate having a polymeric primer layer, wherein the polymeric primer layer comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram (mmol/g) of the polymer, such that the surface of the primer layer (PRIM1) is hydrophobic and the functional vinyl groups are capable to form covalent bonds with a silicone-based release layer (SIL1) applicable on top of the paper substrate (SUBST1).

[0019] Advantageously, the polymeric primer layer is made of or contains a polymerized diene compound comprising functional vinyl functional groups, such as high-vinyl content polybutadiene obtainable from 1,2-addition polymerization reaction of 1,3-butadiene.

[0020] Such a paper substrate could be used in a method for manufacturing a release liner, the method comprising

- providing a cellulose fiber-based paper and
- coating a polymeric primer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram (mmol/g) of the polymer on top of the cellulose fiber-based paper, thereby forming the paper substrate having a hydrophobic surface layer comprising functional vinyl groups
- coating the hydrophobic surface layer with a silicone-based release layer comprising silane hydride groups, and
- curing the silicone-based release layer by means of a polyaddition reaction, thereby anchoring silicone-based release layer comprising silane hydride groups to the hydrophobic surface layer comprising functional vinyl groups, thereby forming the release liner.

[0021] Thus, in addition, there is also provided a release liner comprising

- a cellulose fiber-based paper,
 - a hydrophobic surface layer that contains a polymerized diene, such as 1,2-addition polymerized polybutadiene, and
 - a silicone-based release layer applied on top of the hydrophobic surface layer,
- wherein the silicone-based release layer has been covalently anchored to the hydrophobic surface layer by means of a catalytic hydrosilation reaction.

[0022] High-vinyl content polybutadiene obtainable from 1,2-addition polymerization reaction may be used in a primer layer composition of a paper substrate suitable for binding silicone in a catalytic hydrosilation reaction. The polymerized diene compound may further contain unsaturated dicarboxylic acid or an anhydride or monoester thereof, such as maleic acid or maleic anhydride.

[0023] Advantageously, the polymeric primer layer contains a polymer comprising functional vinyl groups in an amount of equal to or higher than 2 millimoles per gram (mmol/g) of the polymer, preferably equal to or higher than 4 mmol/g, most preferably equal to or higher than 8 mmol/g. A higher amount of functional vinyl groups correlates directly with the hydrophobicity of the surface, thereby decreasing the surface energy, while still enabling silicone polymers to be cured via the polyaddition reaction. Experimental results have suggested that up to functional vinyl groups in an amount of 18.5 mmol/g of the polymer may be obtained on a primer layer applied on top of the cellulose fiber-based paper layer. Therefore, the amount of functional vinyl groups may be in the range of 0.5 to 18.5 mmol/g of the polymer, which amount represents the molality of the vinyl groups in the polymer.

[0024] The invention is further described in the independent and dependent claims.

Brief description of the drawings**[0025]**

- 5 Figure 1 shows, by way of an example, a polyaddition reaction of a fast-curing silicone polymer in the presence of a platinum catalyst,
- Figure 2 shows, by way of an example, a facestock laminate attached on a release liner, the facestock laminate containing a face layer and an adhesive layer,
- 10 Figure 3 shows, by way of an example, a primer layer containing a high vinyl content polymer applied on a cellulose fiber-based paper surface,
- Figure 4 shows, by way of an example, a method for manufacturing high vinyl content polymer from 1,3-butadiene monomers by 1,2-addition polymerization reaction in the presence of a selective catalyst,
- 15 Figure 5 shows, by way of an example, a method for modifying the hydrophobicity of a polymer containing functional vinyl groups in high amounts by grafting the polymer with unsaturated dicarboxylic acid, anhydride or monoester thereof,
- 20 Figure 6a shows, by way of an example, a product containing a cellulose fiber-based paper surface coated with a primer layer containing a high vinyl content polymer, prior to arranging a silicone cross-linking reaction to take place between the high vinyl content polymer and a fast-curing silicone polymer applied on top of the primer layer containing functional vinyl group,
- 25 Figure 6b shows, by way of an example, a product containing a cellulose fiber-based paper surface coated with a primer layer containing a high vinyl content polymer, after a silicone cross-linking reaction has taken place to at least some extent between the high vinyl content polymer and a fast-curing silicone polymer applied on top of the primer layer containing functional vinyl group.
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[0026] The drawings are schematic.

[0027] In the drawings, Sx and Sz denote orthogonal directions.

Detailed description

- 35 **[0028]** Reference is made to Figures 1 and 2. Fast-curing silicone polymers are typically cured via a polyaddition reaction. A silicone-based release layer SIL1 (as denoted in Figure 2) may be formed in a polyaddition reaction of a silicone base polymer containing a functional vinyl group VIN1 and a cross-linker compound SH1 containing silane hydride bonds. The functional vinyl group VIN1 may be an end group or it may be positioned elsewhere in the silicone base polymer. A polyaddition reaction refers to a silicone cross-linking reaction, wherein a silicone base polymer containing a functional vinyl group VIN1 is arranged to form a covalent bond with a cross-linker compound SH1 in the presence of a catalyst compound. The catalyst compound is typically a metal catalyst, such as platinum catalyst, abbreviated as Pt. Fast-curing silicone polymers typically cross-link already at a temperature equal to or less than 100°C, such as in the range of 60 to 100°C. The activation temperature range and reaction kinetics may be adjusted by selecting the chemical composition of the silicone base polymer containing a functional vinyl group VIN1 and the chemical composition of the cross-linker compound SH1. Compositions having a cross-linking temperature close to room temperature of 25°C are not preferred, since this would increase the risk of premature silicone cross-linking reaction, before the compounds have been applied on the substrate surface.
- 40 **[0029]** Reference is made to Figures 2 and 3. A release liner REL1 may comprise a cellulose fiber-based paper PAP1 which may be cellulose fiber-based, a release layer SIL1 formed of a silicone resin, and an oleophilic primer layer PRIM1 between the cellulose fiber-based paper PAP1 and the release layer SIL1. A release liner REL1 may be used as backing material for a facestock laminate FILM1. A facestock laminate FILM1 is used for manufacturing adhesive labels. In such manufacturing, some of the facestock laminate FILM1 may be made e.g. by cutting discrete labels LAB1 out of the facestock laminate FILM1. Adhesive labels LAB1 may be, for example, self-adhesive labels or pressure sensitive labels
- 45 **[0030]** The paper substrate SUBST1 for a release liner REL1 denotes a combination of at least a cellulose fiber-based paper PAP1 and a primer layer PRIM1 as applied on at least one side of the cellulose fiber-based paper PAP1. The
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primer layer PRIM1 is typically applied on the side or sides intended to be coated with the silicone-based release layer SIL1. Advantageously, the primer layer PRIM1 is an oleophilic primer layer containing a polymerized diene PBUT1 having vinylic functions, said polymerized diene PBUT1 being present in the composition of the oleophilic primer layer PRIM1. When forming a release liner REL1, the primer layer PRIM1 is formed between the cellulose fiber-based paper PAP1 and the silicone-based release layer SIL1.

[0031] A method for manufacturing a release liner REL 1 may comprise providing a cellulose fiber-based paper PAP1. Examples of commercial products typically used as a release liner paper substrate SUBST1 are coated papers, vegetable parchment, glassine and greaseproof paper. Typical examples of coated papers are Super Calandered Kraft paper (SCK) and glassine. Glassine in general refers to paper made of chemical pulp, typically having a coat weight (grammage) in the range of 50 to 150 g/m². Glassine paper has a good transparency level; for example a 60 g/m² glassine paper typically has a transparency level of at least 45, when measured with visible light (ISO 2469:1994). Other examples of coated papers are Clay Coated Kraft paper (CCK), Machine Finished Kraft paper (MFK) and Machine Glazed paper (MG). Coated papers may have a grammage equal to or more than 38 g/m², such as in the range of 38 to 160 g/m².

[0032] A method for manufacturing a release liner REL1 may further comprise applying a primer layer PRIM1 on a cellulose fiber-based paper PAP1 surface. The primer layer PRIM1 may contain high vinyl content polymer PBUT1, such as a polymerized diene comprising functional vinyl groups VIN1, which is applied as a coating on top of the cellulose fiber-based paper PAP1, thereby forming a paper substrate SUBST1. A paper manufacturer typically provides the cellulose fiber-based paper PAP1 as a paper substrate SUBST1 comprising the primer layer PRIM1.

[0033] The primer layer PRIM1 surface may be arranged to have hydrophobicity. When the primer layer PRIM1 is arranged to contain a polymer comprising a catenated carbon structure, such as a linear chain of carbons without hydroxyl groups, the non-polar nature of the polymer is increased. Such polymer, when applied on a primer layer surface, therefore provides hydrophobicity and may thus be oleophilic. A hydrophobic primer layer PRIM1 surface may improve the orientation of functional vinyl groups VIN1 towards the surface of the primer layer PRIM1, thereby promoting the formation of covalent bonds with a silicone-based release layer SIL1, after a release coating has been applied on top of the hydrophobic primer layer PRIM1. A paper substrate SUBST1 may thus be arranged to have an oleophilic primer layer PRIM1 applied on top of a cellulose fiber-based paper PAP1 and covalent connections will be formed during the cross-linking of silicone, wherein the silane hydride groups of the cross-linker react with the vinyl groups VIN1 of the high vinyl content polymer PBUT1.

[0034] A method for manufacturing a release liner REL1 may further comprise coating the oleophilic primer layer PRIM1 with a silicone-based release layer SIL1. The silicone-based release layer SIL1 may comprise a fast-curing silicone polymer comprising cross-linker compound with silane hydride groups. The silicone-based release layer SIL1 may be cured by a polyaddition reaction in the presence of a catalyst, thereby anchoring the polymerized diene of the oleophilic primer layer to the silicone-based release layer SIL1, thereby forming the release liner REL1. The hydrophobicity of the primer layer PRIM1 improves the spreading of the silicone polymer applied on the paper substrate SUBST1, thereby enabling reducing the amount of silicone polymer needed to form a silicone-based release layer SIL1. The silicone-based release layer SIL1 may be applied later than during or immediately after manufacturing the paper substrate SUBST1, for example during manufacturing of the face stock FILM1. Alternatively, the silicone-based release layer SIL1 may be applied on the paper substrate SUBST1 during or immediately after manufacturing the paper substrate SUBST1, such as in the same production process and/or production line. An additional advantage of the hydrophobicity is, that a thinner release layer SIL1 may be provided, thereby reducing the amount of silicone polymer needed to form the silicone-based release layer SIL1. This subsequently will reduce the amount of platinum catalyst needed. The silicone-based release layer may thereby remain thin, such as less than 1 micrometer in thickness. A hydrophobic (i.e. oleophilic) paper substrate surface therefore facilitates the even spreading of the uncured silicone polymer applied on the surface. When the release liner paper substrate contains a polymer comprising functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram of the polymer, the release layer SIL1 is more firmly bonded to the paper substrate. A hydrophobic primer layer may be used to resist the penetration of water-based or hot-melt adhesive material, which may be used in the manufacturing of a face stock FILM1 and may thus become into contact with the paper substrate SUBST1 surface. A hydrophobic polymer also evens out the characteristics, for example release characteristics, of the whole surface, despite the existence of possible defects, such as holes, which may sometimes be present in the cellulose fiber-based paper.

[0035] A removable facestock laminate FILM1 may be attached on a release liner REL1. The facestock laminate FILM1 may contain a face layer FACE1 and an adhesive layer ADH1 for attaching the facestock laminate FILM1 onto the release liner REL1 surface. The facestock laminate FILM1 may be used, for example to manufacture a label stock. Herein, a release liner REL1 carrying a plurality of adhesive labels is referred to as a label stock. A label stock is typically wound on a roll and used in a labelling process during which use the label stock is unwound as labels are needed.

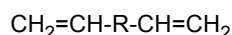
[0036] Figure 3 illustrates a primer layer PRIM1 containing a high vinyl content polymer PBUT1 applied on a cellulose fiber-based paper PAP1 surface SURF1. A high vinyl content polymer PBUT1 refers to a polymer comprising functional vinyl groups VIN1 in an amount of equal to or higher than 0.5 millimoles per gram (mmol/g) of the polymer. Advantageously,

the primer layer contains a polymer comprising functional vinyl groups in an amount of equal to or higher than 1 millimoles per gram (mmol/g) of the polymer, preferably equal to or higher than 2 mmol/g, most preferably equal to or higher than 4 mmol/g, such as equal to or higher than 8 mmol/g. The amount of functional vinyl groups may be, for example, in the range of 0.5 to 18.5 mmol/g of the polymer. A primer layer PRIM1 containing high vinyl content polymer PBUT1 is hydrophobic, as a large proportion of the functional vinyl groups VIN1 are present on the surface of the primer layer PRIM1. A higher amount of chains that end into functional vinyl groups correlates directly with the hydrophobicity of the surface, thereby decreasing the surface energy. Functional vinyl groups VIN1 present on the top surface of the primer layer PRIM1 (i.e. the surface facing away from cellulose fiber-based paper PAP1) are capable to form covalent bonds with a silicone-based release layer SIL1 which may be applied on top of the primer layer PRIM1. The primer layer PRIM1 may contain high vinyl content polymer PBUT1, such as polymerized diene.

[0037] Reference is made to Figure 4, illustrating an example of addition polymerization of 1,3-butadiene monomers.

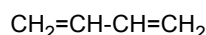
[0038] A polymerized diene may be formed from diene monomers containing two or more functional vinyl groups VIN1 ($-\text{CH}=\text{CH}_2$) by means of a catalytic addition polymerization reaction. By using a selective catalyst, the polymerized diene may be arranged to contain a very high amount of functional vinyl groups VIN1.

[0039] In general, the chemical structure of a diene may be of the form



, wherein R refers to an optionally present carbon chain which may be linear, branched or cyclic, and may further contain heteroatoms.

[0040] A particular example of a suitable diene monomer is 1,3-butadiene, having the chemical structure of



1,3 -butadiene can be polymerized in three different ways, referred to as *cis*-, *trans*- and *vinyl*-additions, which result in different forms of polybutadiene. The *cis* and *trans* forms may be obtained in 1,4-addition reactions. High vinyl content polybutadiene may be obtained from 1,3 -butadiene by selective polymerization, when the polymerization is 1,2-addition reaction of 1,3-butadiene.

[0041] 1,3-butadiene may be 1,2-addition polymerized in the presence of a selective catalyst, such as metallocene catalyst. A butyl lithium initiator as such may be used to provide 80-90 % of 1,4-addition product, as evidenced by Samotsvetov et al. (Butadiene polymerization in the presence of butyl lithium modified with sodium butylate, Polym Sci USSR 23 (1981) 100-107). However, when the reaction is done in the presence of 1,2-bis(piperidino)ethane, the selectivity towards 1,2-addition product may be up to 100%, as evidenced by Halasa, Lohr & Hall (Anionic polymerization to high vinyl polybutadiene, J Polym Sci Part A: Polym Chem 19 (1981) 1357-1360).

[0042] The letter n in Figure 4 refers to the amount of monomer units used to form a polymer. The reference sign CAT1, in turn, refers to the catalyst used for the polymerization reaction. The n may be, for example in the range of 10 to 10000, thereby providing a polybutadiene having a molecular weight in the range of 110 to 540000 g/mol.

[0043] Reference is made to Figures 5 and 6a and 6b. The oleophilic primer layer PRIM1 between the cellulose fiber-based paper PAP1 and the release layer SIL1 may further contain solubilizing agent between 3 mol-% and 20 mol-% of the polymer, such that the high vinyl content polymer PBUT1 comprising functional vinyl groups is water-dispersible or water-emulsifiable, when applied on top of the cellulose fiber-based paper PAP1. Further, the high vinyl content polymer PBUT1 may contain solubilizing agent in an amount equal to or higher than 20 mol-% of the polymer, such that the polymer comprising functional vinyl groups is water-soluble, when applied on top of the cellulose fiber-based paper PAP1. The solubilizing agent may be, for example, an unsaturated dicarboxylic acid or an anhydride or monoester thereof, such as maleic acid or maleic anhydride, which has been grafted into the high vinyl content polymer PBUT1 comprising the functional vinyl groups, as shown in Figure 5. Alternatively, an unsaturated carboxylic acid or an unsaturated acrylic containing a functional vinyl group may be used. The improved water-solubility of a polymer composition comprising the high vinyl content polymer PBUT1 facilitates the homogeneous application of the polymer composition on a cellulose fiber-based paper PAP1 surface. The silicone layer and excess cross-linker compound SH1 is thereby bonded covalently and more strongly to the substrate surface.

Example 1 - preparation of high-vinyl content polybutadiene

[0044] In an experiment, 400 g (7.4 mol) of 1,3-butadiene was weighted and subsequently dissolved in 1600 g of cyclohexane under nitrogen atmosphere, such that a clear solution containing 1,3-butadiene monomers was obtained. The temperature of the solution containing the 1,3-butadiene monomers was then adjusted to 30°C, and an initiator system comprising 0.17 g (2.65 mmol) of butyl lithium and 5.2 g (26.5 mmol) of 1,2-bis(piperidino)ethane was added, thereby providing a reaction mixture and reaction conditions selective for 1,2-addition reaction of 1,3-butadiene. The

reaction mixture was then agitated for 120 min with a mechanical stirrer, after which 2000 g of ethanol was added to stop the reaction and precipitate the polymer. The reaction product was purified by evaporating solvent and monomer residues at 50°C in vacuum. The purified polybutadiene had number average molecular weight of 150000 g/mol, analyzed by size exclusion chromatography (abbreviated as SEC), and included 99 mol-% of 1,2-addition product, when analyzed by nuclear magnetic resonance (abbreviated as NMR).

Example 2 - experimental data of high-vinyl content polybutadiene

[0045] Table 1 (below) demonstrates a correlation between vinyl percentage, i.e. the percentage of the polymer repeat units containing a vinyl group, and the vinyl group content (mmol/g). As can be seen from the Table 1, when 1,3-butadiene is 1,2-addition polymerized in the presence of a selective catalyst, a very high vinyl content may be obtained. A higher amount of functional vinyl groups in polybutadiene has been observed to correlate with higher hydrophobicity on coated cellulose fiber-based papers, thereby indicating that higher amounts of functional vinyl groups on the surface decrease the surface energy. When the vinyl content is very high, such as higher than 60 percent of the amount of polymer repeat units, the reaction conditions may be selected to produce polybutadiene having lower molecular weight. A lower molecular weight of the polybutadiene may be advantageous for reducing the risk of premature cross-linking of the polybutadiene repeat units.

[0046] Table 1. Comparison of vinyl group molality (mmol/g) between polymerized butadiene (polybutadiene) grades as a function of vinyl percent of polymer. The 'vinyl percent of polybutadiene' in this context refers to the percentage of the polymer repeat units containing a vinyl group. The 'vinyl content' in this context refers to the classification of the polybutadiene with respect to the vinyl content. Normal (conventional) catalyst and reaction route typically results to a butadiene having vinyl groups in the range of 1 to 2 percent of the amount of polymer repeat units. Upon butyl lithium catalyst and 1,2-bis(piperidino)ethane initiator system, polybutadiene having increased amount of vinyl groups may be obtained.

vinyl percentage of polybutadiene	vinyl group molality (mmol/g)	vinyl content
1	0.19	normal
2	0.37	normal
4	0.74	increased
6	1.11	increased
10	1.85	increased
20	3.70	increased
30	5.56	high
40	7.41	high
50	9.26	high
60	11.11	high
80	14.81	high
90	16.67	high

Comparative example 3 - vinyl group content obtainable by post-grafting polyvinyl alcohol

[0047] A comparative experiment was performed to demonstrate the level of vinyl group contents achievable by grafting polyvinyl alcohol with an organic molecule containing a functional vinyl group in an acetalization reaction. When grafting polyvinyl alcohol having a hydrolysis degree of 98 - 99 % and degree of polymerization of 1400 with 10-undecenal (an aldehyde comprising 11 carbon atoms), the polymer became significantly less water-soluble already when 10-undecenal was added 3 wt.-%, when expressed as grams of aldehyde compound per 100 grams of polyvinyl alcohol. The formed reaction product further became highly viscous and such that application of the reaction product on a substrate surface as a coating was not feasible by conventional coating means. The results of the comparative experiment are presented in Table 2 (below).

[0048] Table 2. Comparison of vinyl group contents in modified polyvinyl alcohol samples as a function of the aldehyde reactant content (10-undecenal, molecular weight of 168 g/mol). The 'degree of modification (wt-%)' refers to the mass

ratio (in percentages) of the aldehyde reactant in grams that has been reacted per 100 grams of the polyvinyl alcohol. The 'coatability' refers to the coatability of the reaction product to a cellulose fibre-based paper, wherein the formed polymer product is either easy to coat ('1') such that reaction product viscosity is low enough to apply by conventional coating means, or the polymer is difficult to coat ('2') such that that reaction product forms a viscose gel which is not easy to apply by conventional coating means, or the polymer has lost its coatability ('3') to such a degree that the reaction product could no longer be applied as a coating.

degree of modification (wt-%)	vinyl group molality (mmol/g)	coatability
0	0	1
1	0.06	1
2	0.12	2
3	0.17	3
3.5	0.20	3
4	0.23	3
5	0.28	3
10	0.55	3
15	0.79	3
20	1.01	3
25	1.21	3
30	1.41	3

NMR method to evaluate the quantity of functional vinyl groups

[0049] Proton nuclear magnetic resonance (^1H -NMR) analysis may be used to identify chemical structures from the chemical shift values δ of individual hydrogen atoms. Samples for ^1H -NMR analysis may be prepared by dissolving PBD into a suitable solvent, such as deuterated chloroform.

[0050] Further, integration of the ^1H -NMR spectra may be used to estimate vinyl group content of PBD samples. This can be accomplished by comparing areas of the peaks representing the terminal vinyl protons in 1,2-addition product ($\delta = 4.8$ ppm) and olefinic protons in 1,4-addition product ($\delta = 5.4$ ppm). The molality (mmol/g) of vinyl groups in the product can be calculated according to equation 1.

$$\text{Equation 1: } b_{1,2} = \frac{A_{1,2}}{A_{1,2} + A_{1,4}} \times \frac{1000 \frac{\text{mmol}}{\text{mol}}}{M_{BD}}$$

where $b_{1,2}$ represents the molality (mmol/g) of vinyl groups, $A_{1,2}$ and $A_{1,4}$ represent the integrated areas of the peaks representing terminal vinyl protons and 1,4-olefinic protons, respectively, and M_{BD} represents the molecular weight of butadiene.

[0051] For example, when in a tested polybutadiene sample the integrated area of the NMR spectra of 1,4-olefinic protons is 36 and the integrated area of the NMR spectra of the terminal vinyl protons is 1, the tested polybutadiene sample having a molecular weight of 54.09 g/mol, the tested polybutadiene sample has a molality of 0.5 mmol/g of vinyl groups, as demonstrated below using Equation 1:

$$b_{1,2} = \frac{1}{1 + 36} \times \frac{1000 \frac{\text{mmol}}{\text{mol}}}{54.09 \frac{\text{g}}{\text{mol}}} = 0.5 \text{ mmol/g}$$

[0052] For the person skilled in the art, it will be clear that modifications and variations of the product and the method

according to the present invention are perceivable. The figures are schematic. Any particular examples described above with reference to the accompanying drawings are illustrative only and not meant to limit the scope of the invention, which is defined by the appended claims.

Claims

1. A paper substrate (SUBST1) that is suitable for binding silicone in a catalytic hydrosilation reaction, the paper substrate (SUBST1) comprising
 - a cellulose fiber-based paper (PAP1) and
 - a polymeric primer layer (PRIM1),
 wherein the polymeric primer layer (PRIM1) comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram of the polymer, such that the surface of the polymeric primer layer (PRIM1) is hydrophobic.
2. A method for manufacturing a paper substrate (SUBST1) that is suitable for binding silicone in a catalytic hydrosilation reaction, the method comprising
 - providing a cellulose fiber-based paper (PAP1) and
 - coating a polymeric primer layer (PRIM1) on top of the cellulose fiber-based paper (PAP1), thereby forming the paper substrate (SUBST1), wherein the polymeric primer layer (PRIM1) comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 0.5 millimoles per gram of the polymer, such that the surface of the primer layer (PRIM1) is hydrophobic and the functional vinyl groups are capable to form covalent bonds with a silicone-based release layer (SIL1) applicable on top of the paper substrate (SUBST1).
3. The method according to claim 2, further comprising
 - polymerizing diene monomers comprising functional vinyl groups in an addition polymerization reaction, thereby forming the polymer that contains functional vinyl groups.
4. The method according to claim 3, wherein
 - the addition polymerization reaction is catalyzed by butyl lithium and, when necessary, in the presence of 1,2-bis(piperidino)ethane initiator system.
5. The method according to any of the claims 2 to 4, wherein the polymer that contains functional vinyl groups further contains solubilizing agent between 3 mol-% and 20 mol-% of the polymer, such that the polymer comprising functional vinyl groups is water-dispersible or water-emulsifiable, when applied on top of the cellulose fiber-based paper (PAP1).
6. The method according to any of the previous claims 2 to 4, wherein the polymer that contains functional vinyl groups further contains solubilizing agent in an amount equal to or higher than 20 mol-% of the polymer, such that the polymer comprising functional vinyl groups is water-soluble, when applied on top of the cellulose fiber-based paper (PAP1).
7. The method according to the previous claim 5 or 6, wherein the solubilizing agent is an unsaturated dicarboxylic acid or an anhydride or monoester thereof, such as maleic acid or maleic anhydride, which has been grafted into the polymer that contains functional vinyl groups.
8. The paper substrate (SUBST1) according to claim 1 or the method according to any of the claims 2 to 7, wherein the polymeric primer layer (PRIM1) comprises a polymer that contains functional vinyl groups in an amount of equal to or higher than 2 millimoles per gram of the polymer, preferably equal to or higher than 4 millimoles per gram of the polymer, most preferably equal to or higher than 8 millimoles per gram of the polymer.
9. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the polymer that contains functional vinyl groups is polybutadiene.

10. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the polymer that contains functional vinyl groups is high-vinyl content polybutadiene, which is an isomeric form of polybutadiene obtainable from 1,3-butadiene monomers by 1,2-addition polymerization.
- 5 11. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the cellulose fiber-based paper (PAP1) is coated paper having a grammage equal to or more than 38 g/m², for example in the range of 38 to 160 g/m².
- 10 12. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the polymeric primer layer (PRIM1) applied on top of the cellulose fiber-based paper (PAP1) is applied in an amount of 0.1 to 20 g/m², preferably in an amount of 1 to 5 g/m².
- 15 13. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the polymeric primer layer (PRIM1) applied on top of the cellulose fiber-based paper (PAP1) contains the polymer comprising functional vinyl groups equal to or more than 1 wt.%, such as in the range of 1 to 100 wt.% of the weight of the polymeric primer layer (PRIM1).
- 20 14. The paper substrate (SUBST1) or the method according to any of the previous claims, wherein the polymeric primer layer (PRIM1) applied on top of the cellulose fiber-based paper (PAP1) is without styrene groups.
- 25 15. Use of a high-vinyl content polybutadiene, which is an isomeric form of polybutadiene obtainable from 1,3-butadiene monomers by 1,2-addition polymerization, comprising functional vinyl groups in a primer layer composition of a paper substrate suitable for binding silicone in a catalytic hydrosilation reaction.

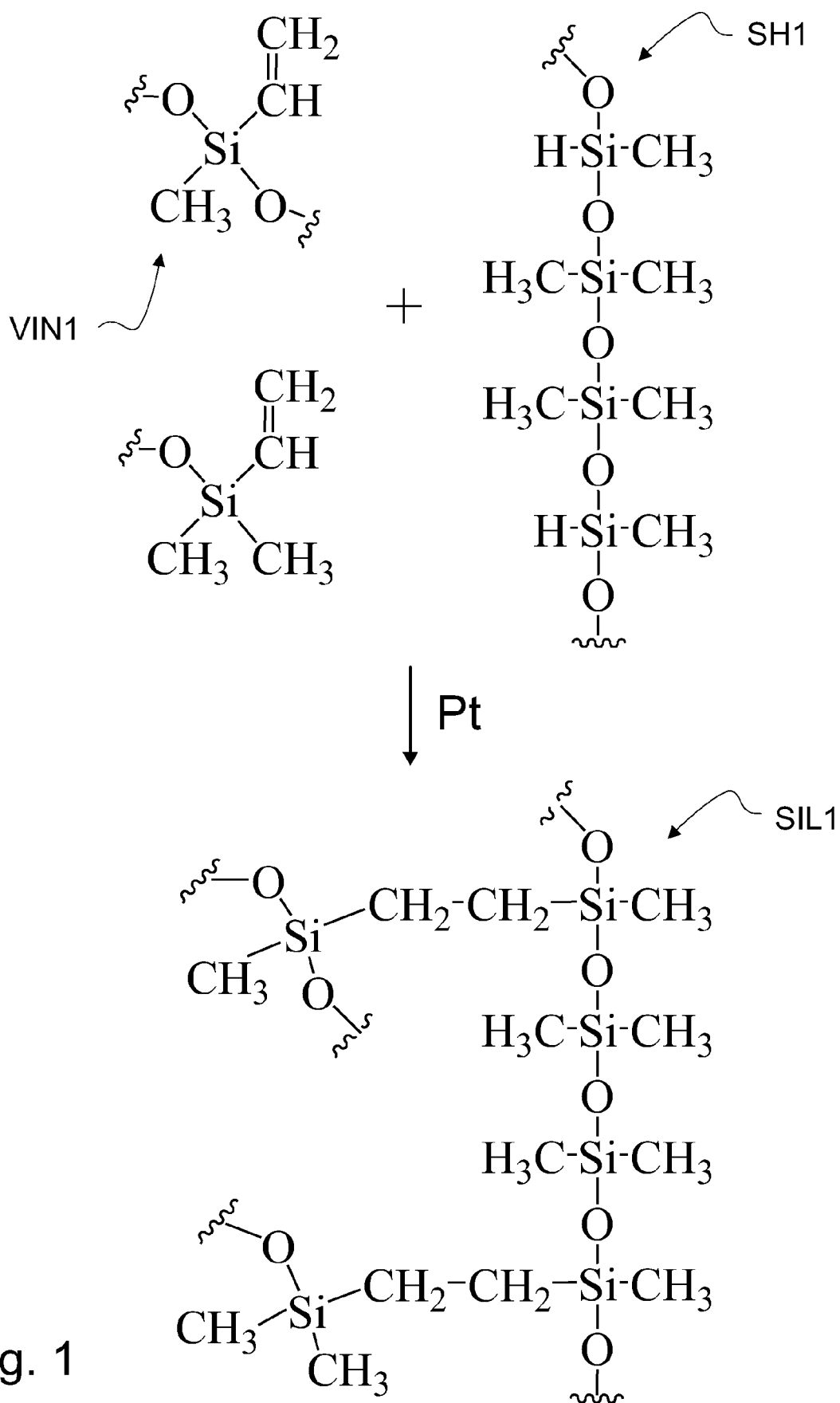


Fig. 1

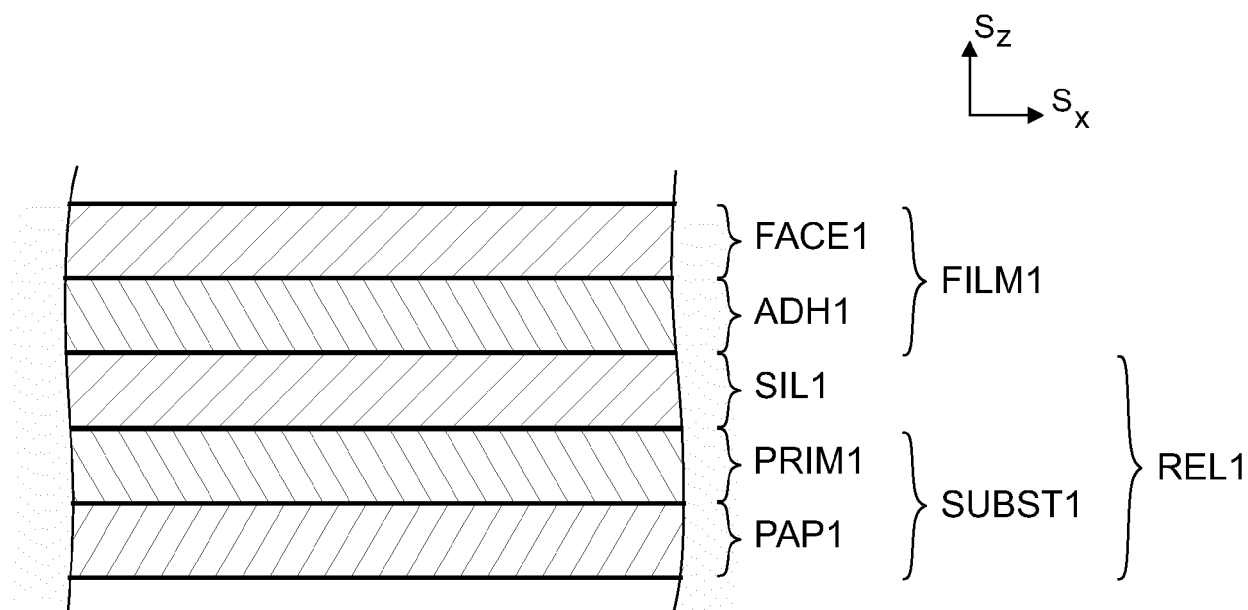


Fig. 2

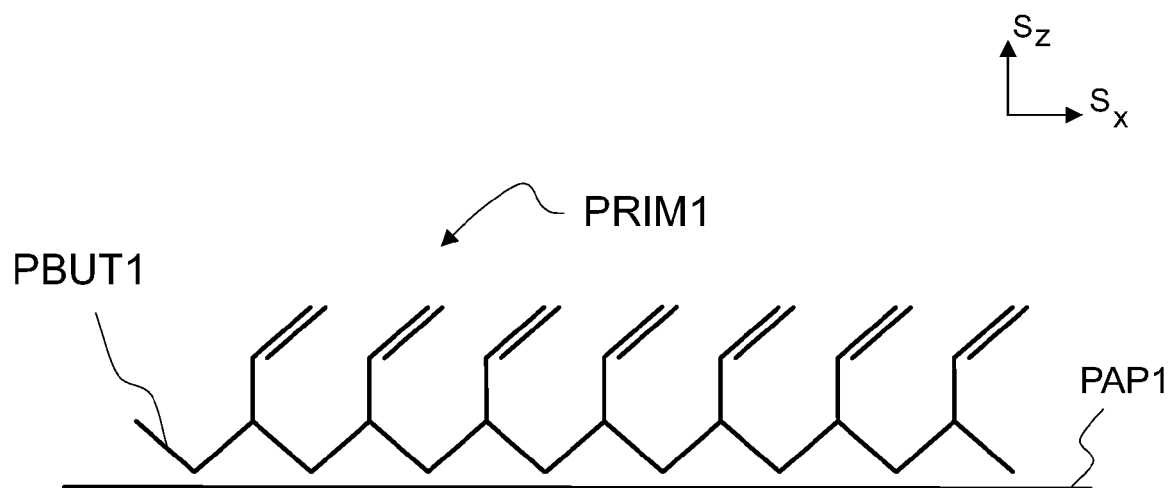
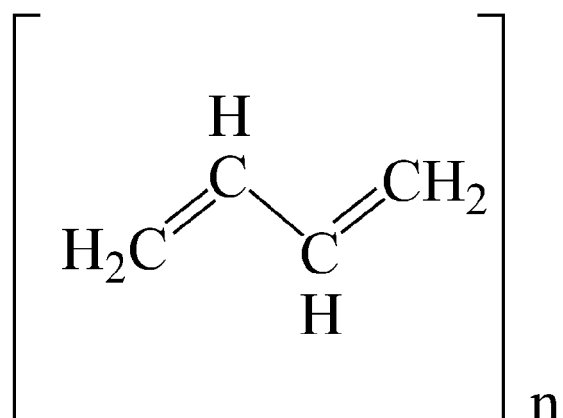


Fig. 3



1,2-addition
polymerization $\downarrow$ $\text{CAT1}^\oplus$

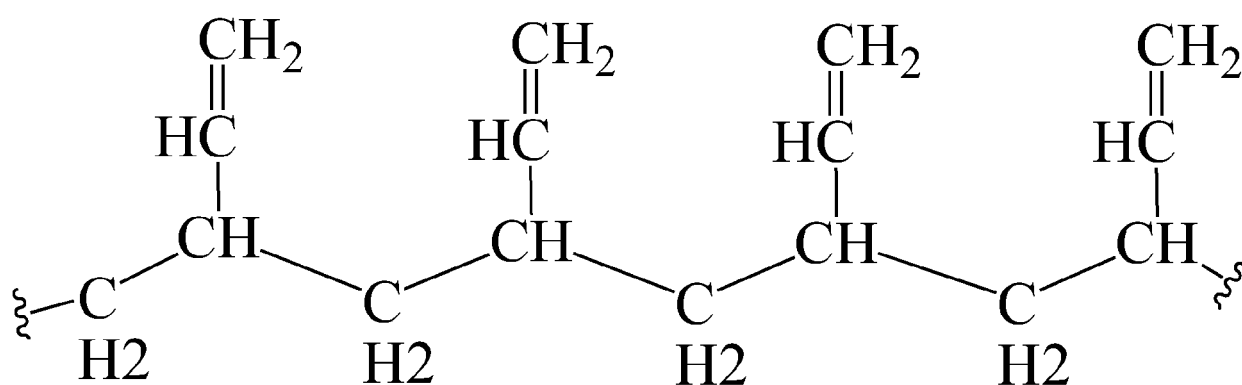


Fig. 4

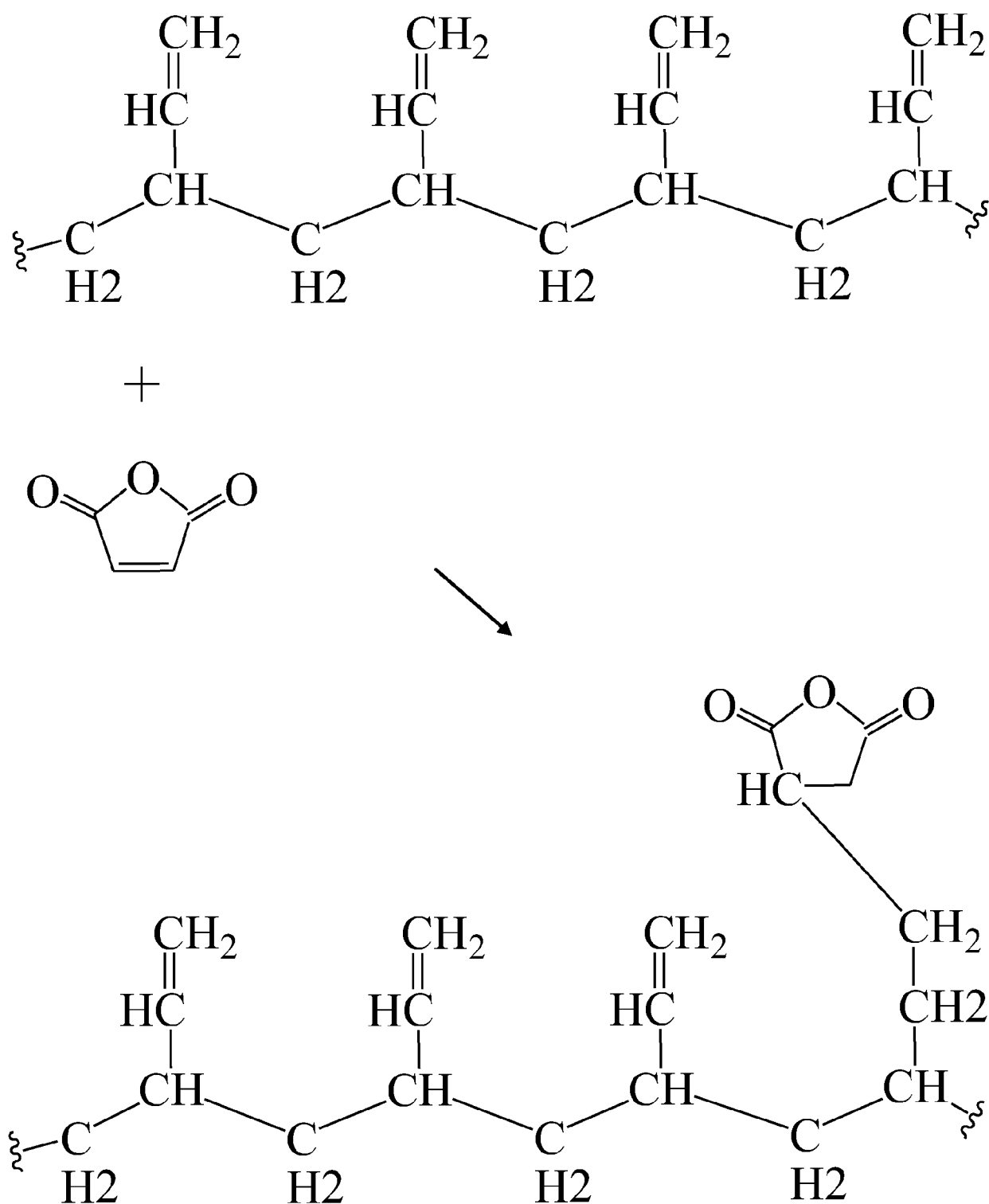


Fig. 5

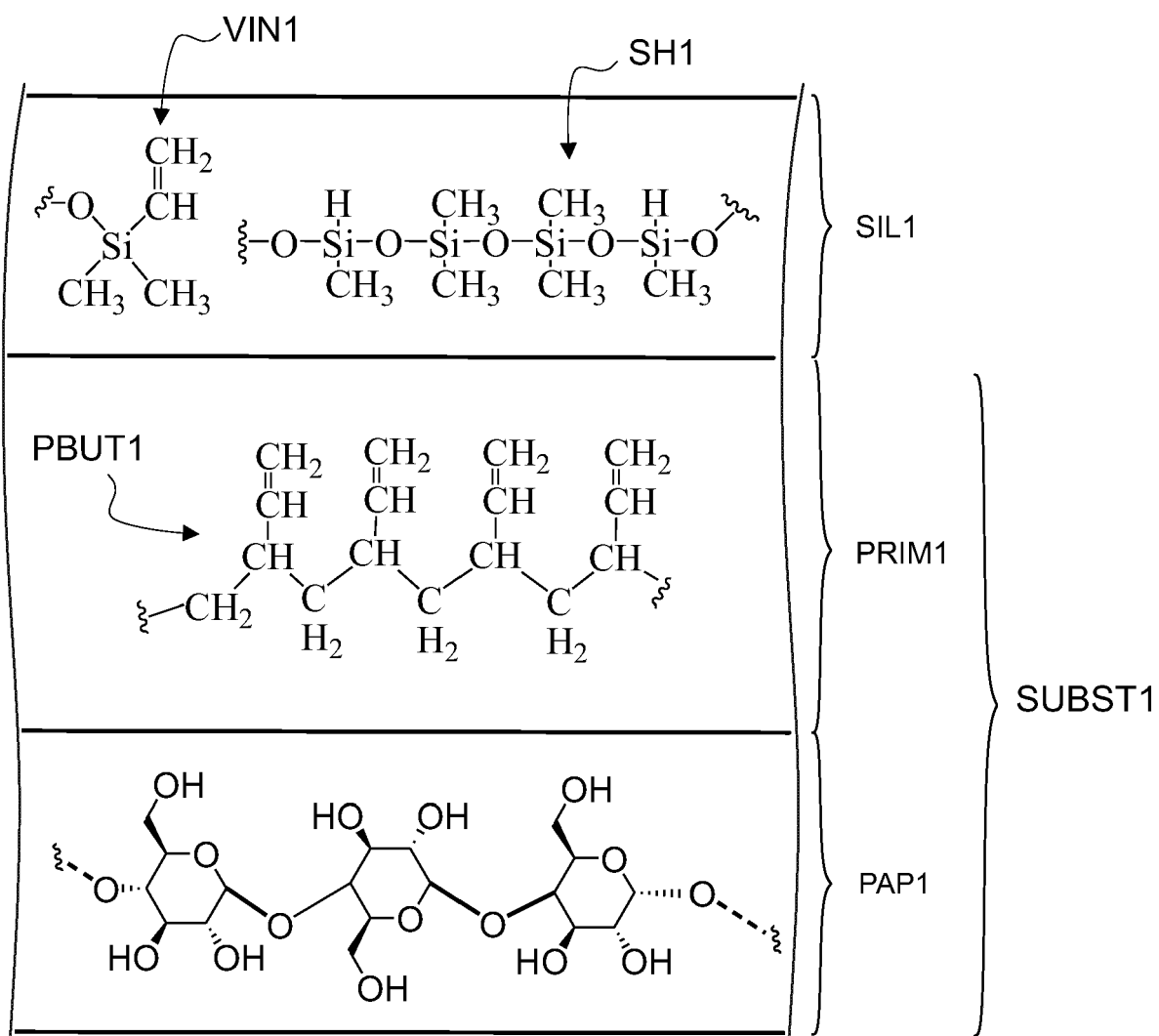


Fig. 6a

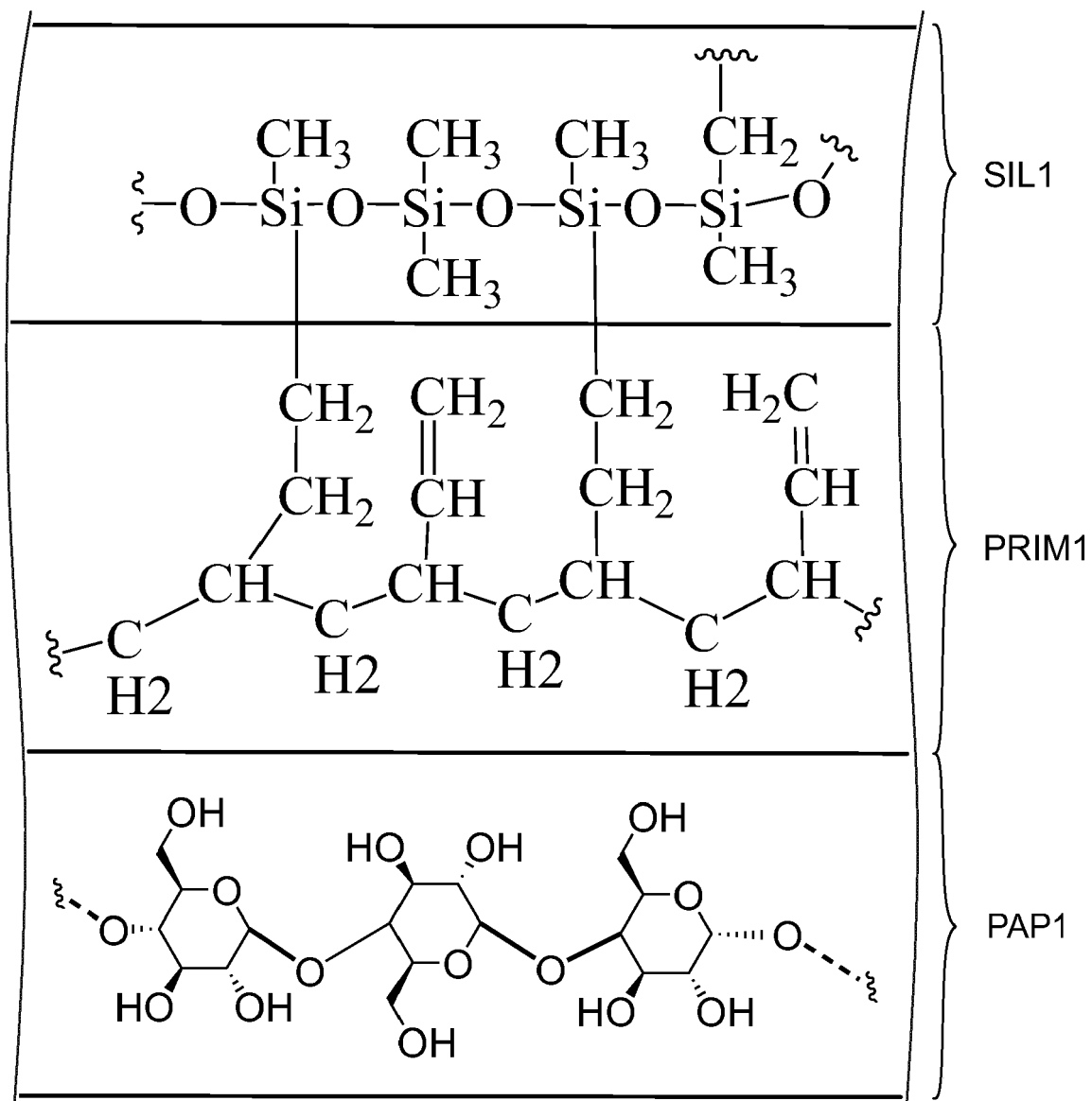


Fig. 6b



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