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

(11) **EP 3 636 833 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.04.2020 Bulletin 2020/16

(21) Application number: **18199296.7**

(22) Date of filing: **09.10.2018**

(51) Int Cl.:
D21H 27/00 *(2006.01)* ***D21H 27/06*** *(2006.01)*
D21H 19/20 *(2006.01)* ***D21H 19/32*** *(2006.01)*
D21H 19/60 *(2006.01)*

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

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

(72) Inventors:
- **Kosonen, Harri**
  53300 Lappeenranta (FI)
- **Rissanen, Mikko**
  02750 Espoo (FI)
- **Littunen, Kuisma**
  53100 Lappeenranta (FI)
- **Rautalahti, Jaakko**
  37630 Valkeakoski (FI)
- **Antila, Janne**
  13100 Hämeenlinna (FI)

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

(54) **A PAPER SUBSTRATE COMPRISING VINYL ALCOHOL OLIGOMERS MODIFIED TO CONTAIN CATENATED CARBON STRUCTURES WITH FUNCTIONAL VINYL GROUPS**

(57) The invention relates to a method for manufacturing a paper substrate suitable for binding silicone in a catalytic hydrosilation reaction and products thereof, wherein the paper substrate contains an acetal compound that contains catenated carbon structures with functional vinyl groups, wherein the acetal compound is based on oligomeric vinyl alcohol. The oligomeric vinyl alcohol may be used to adjust the rheology of an aqueous solution such that an aldehyde that contains a functional vinyl group and a catenated carbon structure of at least 4 carbon atoms may be grafted with high efficiency.

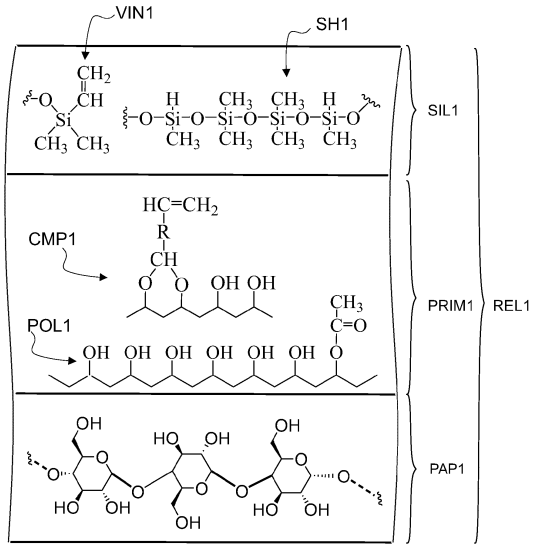


Fig. 4

EP 3 636 833 A1

Description

Technical field

[0001] The invention relates to a paper substrate suitable for binding silicone in a catalytic hydrosilation reaction and to a method for manufacturing such paper substrate. The invention further relates to use of oligomeric vinyl alcohol in a method for manufacturing a paper substrate and to products thereof.

Background

[0002] Release liners comprising cellulose fiber-based support layers are widely used as non-blocking backing material for self-adhesive products, such as self-adhesive labels. A typical cellulose fiber-based support layer suitable for use on release liner paper substrate is an industrially manufactured paper, which is manufactured from chemical pulp, such as bleached Kraft pulp. The purpose of a cellulose fiber-based support layer is to provide dimensionally stable and dense surface, on which a primer layer and a release coating may be applied. A typical example of an industrially manufactured paper that is used in a release liner is glassine paper.

[0003] Reference is made to Figures 1 and 2. A label stock refers to multiple labels LAB1 on a release liner REL1. A label stock may be formed of a label laminate web FILM1 by cutting the label laminate web FILM1 with a die cutting roll DIE1 and stripping excess matrix material MTX1 away from the release liner REL1, such that the labels LAB1 remain attached on the release liner REL1. When detaching a label LAB1 or excess matrix material MTX1 from the release liner REL1, the strength of the bonding between the adhesive ADH1 layer and the release layer SIL1 resists the separation of the adhesive ADH1 layer from the release layer SIL1. Release value refers to the minimum amount of force F_N required to detach a label LAB1 or excess matrix material MTX1 from the release liner REL1. Modern high-speed labelling applications, which may operate at a very high velocity up to tens of thousands of labels dispensed per hour, demand that the release liner has a sufficiently low and stable high-speed release value, such that the dispensing of labels from the release liner may proceed without interruptions. The higher the velocity in a labelling process is, the smaller is the acceptable amount of deficiency in the anchorage level of the release layer SIL1 towards the paper substrate SUBST1. This requirement is enhanced as the base weight (grammage) of the cellulose fiber-based paper used in high-speed release liner applications is decreasing, both in the paper substrates and in the face material, which may also be cellulose fiber-based paper. The reduced base weight therefore leads also to lighter label laminate web FILM1 and subsequently weaker excess matrix material MTX1, which needs to be stripped away from the release liner REL1 with lower amount of force FN than before to avoid breaking the matrix material MTX1.

[0004] A paper substrate SUBST1 is used herein to denote a coated cellulose fiber-based support layer, comprising a cellulose fiber-based support layer PAP1 and a primer layer PRIM1. Up to 35% by weight of the primer layer composition may consist of binder material. A mixture for coating a cellulose fiber-based support layer in general comprises water-soluble binders capable of forming a film, such as starch, polyvinyl alcohol (hereafter referred to also as PVA or polyvinyl alcohol) and carboxymethyl cellulose (hereafter referred to also as CMC). The paper substrate SUBST1 serves as a surface for a subsequent release coating applied on the coated cellulose fiber-based support layer, which release coating is then cured to form a release layer SIL1. Self-adhesive products may be manufactured by coating the release layer SIL1 of the formed release liner REL1 with an adhesive, thereby forming an adhesive layer ADH1 and subsequently adjoining a face material FACE1 on the adhesive layer ADH1 surface, thereby forming the label laminate web FILM1.

[0005] Thermally curable release coatings refer to specific type of release coatings, which are distinguished from radiation curable systems. Low temperature curable silicone compound or "LTC" silicone compound, refers to an addition-curable compound comprising a cross-linker component with silane hydride groups and a silicone polymer with functional vinyl 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 catalyzed by a platinum catalyst. Platinum-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.

[0006] Due to wide use of fast-curing silicone compounds in release liners, there is a need to save costs by using less platinum. Platinum is a very expensive catalyst material. A problem with respect to the fast-curing silicone compounds is the relatively low anchorage of the release coating towards the paper substrate, if the amount of platinum catalyst is reduced 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, even as low as 10 ppm. Further, due to the high volumes of paper substrate produced on paper machine there is an aim to reduce the silicone curing time, which is why fast curing silicones have been introduced to the markets. The silicone curing time, however, should not adversely affect the relative rub-off values of the release layer, which should remain

consistent over time, since a release liner may be stored for a period prior to its use. This sets requirements for the paper substrate, which should promote long-term stable anchorage of the silicone to the paper substrate at low platinum levels, while enabling the use of fast curing silicone compounds, which are advantageous in reducing the high-speed release values.

[0007] In the past, the anchorage of a release coating containing a silicone compound towards a paper substrate has been improved by using a primer layer containing a water-soluble polymer such as polyvinyl alcohol, which polymer has been grafted to contain functional vinyl groups. Thus far disclosed solutions, however, have either reported a long reaction time or have been very restricted in the degree of modification.

[0008] Publication WO 2011/104427 suggests functionalizing a PVA polymer that contains hydroxyl functionalities with undecylenic aldehyde. According to the publication, this functionalization of the PVA polymer can be done in a water-based process, before the modified PVA polymer is deposited on a cellulose fiber-based support layer. A disadvantage of the water-based reaction of the PVA polymer is, however, that while water is a suitable solvent for certain grades of PVA polymer, for each grade of water-soluble PVA polymer, an increase in PVA concentration is accompanied by a rise in solution viscosity. A high degree of viscosity quickly impedes the reaction dynamics and eventually causes flocculation or micelle formation.

[0009] Further to this, solvation of the PVA polymer to water is also slow and highly temperature-dependent, which limits the available reaction conditions. In addition, the organic molecule presented in the prior art is not water soluble, unlike the PVA polymer. Undecylenic aldehyde is commercially available, but the molecule is in an organic phase. As the density of undecylenic aldehyde is lower than the density of water, the reactant easily remains floating on the surface of an aqueous solution, despite stirring of the solution during the reaction. Therefore, the reaction of a mixture containing PVA polymer and undecylenic aldehyde is a two-phase reaction. To contact each other, the reactants need to reach over a phase interface, which reduces the reaction efficiency.

[0010] The prior art only discloses working examples wherein undecylenic aldehyde as an organic molecule has been added to a reaction mixture in the range of 1.4 to 1.6 wt.-% (grams of undecylenic aldehyde per 100 grams of polyvinyl alcohol), which does not disclose the vinyl group molality in the formed compound. At a higher PVA and/or undecylenic aldehyde concentration the reaction solution rapidly becomes highly viscose, despite vigorous stirring. At higher concentrations, the rapidly increasing viscosity therefore prevents efficient grafting of the organic molecule. Further, this prevents a subsequent application of the formed reaction product on a substrate surface as a coating composition. Therefore, industrial use of the reaction at higher reactant contents according to WO 2011/104427 is not feasible. The prior art discloses a solution that has a maximum limit to the amount of organic molecule, which may be grafted onto a PVA polymer. This limit is set to a relatively low level. The amount of functional vinyl groups grafted on a modified PVA polymer disclosed in the prior art is not optimal for a release liner which is used in modern high-speed release liner applications, wherein higher bonding strength and lower release values are needed between the paper substrate and the release layer. This requirement is enhanced as the base weight (grammage) of the paper substrate used in high-speed release liner applications with labels is decreasing. The reduced base weight leads to also lighter label laminate web and subsequently weaker excess matrix material, which need to be stripped away from the release liner with lower amount of force than before.

Summary

[0011] The invention addresses the above disclosed problems by providing means to change the rheology of the aqueous solution upon grafting the organic molecule. This enables the production of a coating composition comprising high amount of vinyl groups. Novel fast-curing silicone compounds, in particular, may require less time for the addition curing reaction to take place. A paper substrate comprising a cellulose fiber-based support layer and a coated primer layer containing a high amount of vinyl groups thus provides an unprecedented means of improving the release characteristics of a subsequent release layer applicable on the primer layer.

[0012] The rheology of the aqueous solution upon grafting the organic molecule may be controlled by using oligomeric vinyl alcohol. Oligomeric vinyl alcohol has a considerably lower hydrocarbon chain length and subsequently a lower molecular weight than a PVA polymer. When referring to oligomeric vinyl alcohol, the weight average molecular weight, hereafter referred to as $\overline{M}_w$, is less than 1000 g/mol. The weight average molecular weight represents the mean average weight of the oligomeric vinyl alcohol, weighted according to weight fractions. A water-based acetalization reaction of an organic molecule comprising both an aldehyde group and a functional vinyl group, may therefore be performed at a higher efficiency. In particular, higher acetalization efficiency may be obtained with an organic molecule that has a terminal vinyl group and a catenated carbon structure containing at least 4 carbon atoms, preferably at least 5 carbon atoms. Preferably, the organic molecule is an aldehyde which contains a linear chain of 5 to 15 carbon atoms and which ends into a terminal vinyl group, such as 10-undecenal. The length of the catenated carbon structure, which preferably is a linear hydrocarbon chain, is advantageous for reducing the polarity of the formed acetal compound. Thereby, a

cellulose fiber-based support layer may be coated with a compound based on oligomeric vinyl alcohol which contains unprecedently high amount of vinyl groups grafted onto the compound. This enables using lower amounts of platinum catalyst and fast curing silicone compounds, which facilitates the manufacturing of a release liner with improved release characteristics.

[0013] According to an aspect of the invention, there is provided a paper substrate which is suitable for binding silicone in a catalytic hydrosilation reaction, the paper substrate comprising

- a cellulose fiber-based support layer and
- a primer layer that contains a compound based on oligomeric vinyl alcohol,

wherein the compound contains a catenated carbon structure grafted onto oligomeric vinyl alcohol, and wherein the catenated carbon structure

- contains a chain of at least 4 carbon atoms,
- terminates into an acetal at the first end of the chain, and
- terminates into a functional vinyl group at the other end of the chain,

and wherein the vinyl group molality of the compound is equal to or higher than 0.2 millimoles per gram of the compound, thereby providing a hydrophobic effect to the primer layer surface. Preferably, the catenated carbon structure with functional vinyl group contains at least 5 carbon atoms, more preferably in the range of 5 to 15 carbon atoms. Preferably, the primer layer contains functional vinyl groups in an amount of equal to or higher than 0.3 millimoles per gram, more preferably equal to or higher than 0.4 millimoles per gram, most preferably equal to or higher than 0.5 millimoles per gram of the compound, up to 1.41 millimoles per gram of the compound.

[0014] According to another aspect of the invention, there is provided means to produce a release liner which comprises a paper substrate as disclosed above, and a release layer based on a silicone compound that has been applied on the paper substrate.

[0015] The term 'catenated carbon structure' is used to denote a series of bonded carbon atoms, wherein the carbon atoms are bonded to other carbon atoms. Carbon is known to be suitable for catenation, which herein refers to the formation of chain having interconnecting carbon-carbon bonds. Catenated carbon structures may also be referred to as 'catenae'. A catenated carbon structure in this context includes a hydrocarbon chain. A catenated carbon structure may also comprise substituents, such as oxygen, hydrogen or alkane or alkene groups, such as a vinyl group. The catenated carbon structure may have 4 or more interconnecting carbon atoms in a series. Preferably, the catenated carbon structure of an organic molecule is a hydrocarbon chain having at least 7 carbon atoms, more preferably 11 carbon atoms, and which terminates into an aldehyde at the first end of the chain and into a functional vinyl group at the other end of the chain.

[0016] On a primer layer, after the acetalization reaction with the oligomeric vinyl alcohol, the catenated carbon structure terminates into an acetal at the first end of the chain. The low $\overline{M}_w$ of the oligomeric vinyl alcohol facilitates the covalent bonding of a high amount of catenated carbon structures to the oligomeric vinyl alcohol, such that on the surface of the paper substrate, the formed compound renders the primer layer hydrophobic and enables to produce a paper substrate surface that contains a vinyl group molality of equal to or higher than 0.2 millimoles per gram of the compound. The primer layer may contain functional vinyl groups for example in the range of 0.20 to 1.41, preferably in the range of 0.23 to 1.21, most preferably in the range of 0.28 to 1.01 millimoles per gram of the compound.

[0017] The abbreviation 'mmol/g' used hereafter denotes millimoles per gram of the compound based on oligomeric vinyl alcohol, unless otherwise stated. The abbreviation therefore denotes the molality of vinyl groups in the compound, which has been formed in a water-based acetalization reaction of the dissolved oligomeric vinyl alcohol and the reactant, which is an organic molecule that contains at least 4 carbon atoms and comprises both an aldehyde group and a functional vinyl group.

[0018] The high amount of organic molecules which contain a catenated carbon structure may be used to provide a hydrophobic surface on a cellulose fiber-based support layer. A catenated carbon structure, linear hydrocarbon in particular, is non-polar and therefore the oligomeric vinyl alcohol, when grafted to contain high amounts of such catenated carbon structures before coating onto a cellulose fiber-based support layer surface, has a tendency to avoid the hydrophilic surface of the cellulose fiber-based support layer beneath, which contains hydroxyl groups. The hydrophobic effect is dependent of the amount of linear chains grafted onto the oligomeric vinyl alcohol. The non-polar, catenated carbon structures that end into a terminal vinyl group may also acts as a surfactant. While a hydrophobic oligomeric vinyl alcohol, as such, may have a poor adhesion to silicone, the catalytic hydrosilation reaction enables chemical bonding of the silicone. A compound based on the oligomeric vinyl alcohol comprising a high vinyl group content of equal to or above 0.2 mmol/g of the compound based on oligomeric vinyl alcohol on the surface of the cellulose fiber-based support layer

has been observed to be advantageous in providing a hydrophobic effect to the cellulose fiber-based support layer surface. The increased amount of non-polar catenated carbon structures reduces the effect of the hydroxyl groups present in the polyvinyl alcohol and on the cellulose fiber-based support layer surface. When the paper substrate has a more hydrophobic primer layer, the amount of a release coating containing silicone compound may be reduced. Less amount of release coating requires less platinum catalyst for curing to take place. Preferably, the primer layer contains catenated carbon structures with functional vinyl groups in an amount of equal to or higher than 0.3 mmol/g of the compound based on oligomeric vinyl alcohol, since the molality of catenated carbon structures with functional vinyl groups on the cellulose fiber-based support layer surface has been observed to correlate with high-speed release value, such that a higher molar amount provides a lower and more stable release value, particularly in high-speed labelling applications. Most preferably, the primer layer contains catenated carbon structures with functional vinyl groups in an amount of equal to or higher than 0.5 mmol/g of the acetal compound, as this enables to further reduce the thickness of the release layer. A particular advantage of the hydrophobic surface on the cellulose fiber-based support layer is that less adhesive may penetrate through a release layer into the primer layer beneath, when the cellulose fiber-based support layer is used as part of a release liner paper substrate. A primer layer having a hydrophobic surface or barrier may be arranged to repel the adhesive. 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 support layer 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. The silicone-based release layer may thereby remain thin, such as less than 1 micrometer in thickness. A thinner release layer enables also reduction of the thickness of the cellulose fiber-based support layer, which is needed as a backing to give strength for the release layer. The release value is therefore dependent of the behavior of the whole release liner wherein both the paper substrate comprising the cellulose fiber-based support layer and the viscoelastic behavior of the release layer determine the release properties. A particular advantage of a primer layer that contains catenated carbon structures with functional vinyl 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 of the acetal compound is that the high amount of functional vinyl groups enables the use of very fast curing silicone compounds in the release coating.

[0019] On a primer layer, the catenated carbon structure is thus configured to promote hydrophobicity and further configured to contain a functional vinyl group in one end, which vinyl group is suitable for catalytic hydrosilation reaction. At the other end, the catenated carbon structure is covalently bonded into the primer layer by having an acetal connectivity to the moiety of the compound, which is based on oligomeric vinyl alcohol. Acetal connectivity of the catenated structure at one end enables the formation of the compound based on oligomeric vinyl alcohol in a water-based reaction. Further, the formed compound may be purified from the reaction solution prior to coating the compound on a cellulose fiber-based support layer.

[0020] A hydrophobic surface facilitates the even spreading of the uncured silicone polymer applied on the surface. When the release liner paper substrate comprises acetal compounds that contain catenated carbon structures with functional vinyl groups in an amount of equal to or higher than 0.2 millimoles per gram of the acetal compound, the release layer is this more evenly spread and firmly bonded to the paper substrate. A hydrophobic primer layer may further be used to resist the penetration of water-based or hot-melt adhesive material, which may be used in the manufacturing of a label laminate web and may thus become into contact with the paper substrate surface. A hydrophobic acetal compound 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 support layer.

[0021] The method for manufacturing a paper substrate which is suitable for binding silicone in a catalytic hydrosilation reaction may comprise at least the steps of

- providing a water-based solution containing dissolved oligomeric vinyl alcohol,
- adding reactant which is an organic molecule that contains at least 4 carbon atoms and comprises both an aldehyde group and a functional vinyl group into the water-based solution containing the dissolved oligomeric vinyl alcohol,
- reacting the reactant with the dissolved oligomeric vinyl alcohol in a water-based acetalization reaction, such that a compound based on the oligomeric vinyl alcohol is formed, wherein the compound contains a catenated carbon structure grafted onto oligomeric vinyl alcohol, and wherein the catenated carbon structure

    - contains a chain of at least 4 carbon atoms,
    - terminates into an acetal at the first end of the chain, and
    - terminates into a functional vinyl group at the other end of the chain, and

  coating the compound on a cellulose fiber-based support layer as a primer layer, thereby forming the paper substrate suitable for binding silicone in a catalytic hydrosilation reaction, wherein the amount of functional vinyl groups in the

primer layer is equal to or higher than 0.2 millimoles per gram of the compound.

When necessary, the pH of the water-based solution may be adjusted to be acidic, such as in the range of 1.5 - 2.5.

[0022] A further issue addressed by a primer layer that contains high amounts of oligomeric vinyl alcohol with functional vinyl groups is the migration of uncured silicone compounds. When coating a paper substrate with a fast-curing silicone compound, the component comprising silane hydride groups is added in excess amount relative to the amount of the component comprising vinyl groups to ensure a proper cross-linking between the two components that cures the coating into a release layer. However, due to the excess amount of silane hydride groups, all these groups are not cured in the catalytic hydrosilation reaction. The uncured silane hydride groups may later migrate into the cellulose fiber-based support layer. While a conventional film-forming primer layer may provide some barrier effect, the unreacted cross-linker has despite a film-forming primer layer been observed to migrate through the primer layer and to the opposite side of the cellulose fiber-based support layer underneath the primer layer. Industrially manufactured cellulose fiber-based support layers, such as glassine papers, are never completely closed or impermeable and may contain some openings or pores, thereby allowing the uncured cross-linker compound to penetrate the cellulose fiber-based support layer and reach the opposite side of the release liner, thereby contaminating the adjacent surface of the label laminate web on a reel. Upon contact with the label laminate web, the uncured cross-linker compound may smear portions of the face material surface and subsequently cause problems with printing quality, such as poor intensity of the printed surface, especially when the face material is a filmic face substrate, such as polyethylene, polypropylene, polyethylene terephthalate or a similar synthetic thermoplastic polymer, which are widely in use. Advantageously, therefore, the primer layer may contains a compound based on oligomeric vinyl alcohol, wherein the compound comprises catenated carbon structures with functional vinyl groups in an amount of equal to or higher than 0.2 millimoles per gram, preferably equal to or higher than 0.3 millimoles per gram, most preferably equal to or higher than 0.5 millimoles per gram of the acetal compound, such as in the range of 0.20 to 1.41 millimoles per gram of the compound based on oligomeric vinyl alcohol. A high vinyl group molality of equal to or above 0.23 mmol/g is also efficient in binding unreacted cross-linker component, when the cross-linker component is added in excess stoichiometric amount. A high vinyl group content of equal to or above 0.23 mmol/g of the compound on the surface of the paper substrate may thus be configured to bind release coating components and thereby used to increase the printing intensity of a filmic face material, such as polyethylene, polypropylene, polyethylene terephthalate, polylactic acid or a similar film-forming thermoplastic polymer. The amount of functional vinyl groups may be measured by an iodometric titration method from the acetal compound formed in the acetalization reaction.

[0023] Oligomeric vinyl alcohol may be obtained from polyvinyl alcohol by means of controlled chain scission, for example with Fenton's reagent. Oligomeric vinyl alcohol has specific characteristics, which may be used to provide a composition containing a high amount of grafted catenated carbon structures with vinyl groups on a cellulose fiber-based support layer, the paper substrate thus formed comprising remarkably high amount of functional vinyl groups, which functional vinyl groups are available for a subsequent release coating. Such a paper substrate is particularly suitable for use as a release liner paper substrate for fast-curing silicone compounds, which require high bonding strength between the release layer and the coated cellulose fiber-based support layer.

[0024] Oligomeric vinyl alcohol may be used to provide an acetal compound based on the oligomeric vinyl alcohol, having a low $\overline{M}_w$, such as a $\overline{M}_w$ of less than 1000 g/mol, preferably in the range of 440-880 g/mol. The number of repeat units in an oligomer is typically in the range of 4 to 22. In context of oligomeric vinyl alcohol, it has been observed that the number of repeat units is preferably in the range of 10-20. The low $\overline{M}_w$ of the oligomeric vinyl alcohol may be used to suppress the rise of viscosity of a solution during a water-based acetalization reaction. Viscosity in this context refers to the property of a fluid that resists a force tending to cause the fluid to flow. The flow behavior of oligomeric vinyl alcohol in water is therefore related to the viscosity of the solution during a water-based acetalization reaction. The flow behavior of oligomeric vinyl alcohol in water may further be controlled by selecting the degree of hydrolysis of the oligomeric vinyl alcohol grade. Therefore, the viscosity η of the water-based solution containing the vinyl alcohol oligomer may be low, such as less than 20000 mPa·s, during the water-based acetalization reaction.

[0025] For practical reason, the viscosity of the water-based solution containing the vinyl alcohol oligomer should be less than 8000 mPa·s, when measured as Brookfield viscosity at 100 rpm. Experimental results have demonstrated that industrial applicability of PVA modified with undecylenic aldehyde in an acetalization reaction is limited by the solution viscosity. In practice, in on-line coating processes suitable for paper mills, a coating composition having a viscosity higher than 8000 mPa·s does not permit sufficient pumping on a coating machine, the viscosity thereby limiting the use of PVA modified with undecylenic aldehyde in an acetalization reaction as a coating composition.

[0026] Lower viscosity of the water-based solution during a water-based acetalization reaction enables increasing the dry matter content of the water-based solution. Therefore the vinyl alcohol oligomer may be dissolved to a less amount of water, which provides a reaction at a higher concentration and at a high conversion efficiency. A higher dry matter content in the formed reaction product is advantageous, since this enables coating of the reaction product on a cellulose

fiber-based support layer as a primer layer at high concentration. A high dry matter content in the coating composition requires less amount of drying.

[0027] The effect of the molecular weight to the rheology of the solution has been observed in particular with respect to water-based and acid catalyzed acetalization reactions, wherein the oligomeric vinyl alcohol enables a higher amount of organic molecules having a vinyl group to be grafted onto the oligomer. Hence, when manufacturing the paper substrate, a coating composition containing a higher amount of catenated carbon structures with functional vinyl groups which have been grafted onto the compound based on oligomeric vinyl alcohol may be applied on a surface of a cellulose fiber-based support layer, thereby forming a primer layer containing high amount of catenated carbon structures and a high vinyl group molality. A paper substrate containing catenated carbon structures with high amount of functional vinyl groups may be used to improve the anchorage of a release coating containing fast-curing silicone compound. The high density of functional vinyl groups on the paper substrate surface provides more anchoring points which are suitable for cross-linking reactions with silane hydride groups present in fast-curing silicone compounds, that may be applied on the paper substrate.

[0028] The viscosity of oligomeric vinyl alcohol has a significant effect on the flow behavior of the solution. When maintaining a relatively low degree of viscosity in the reaction mixture, the oligomeric vinyl alcohol may be arranged to react at a higher efficiency with an organic molecule comprising both an aldehyde and a vinyl function in a water-based acetalization reaction, such that a high conversion of the aldehyde to an acetal product is obtainable. This has not been possible in the past, since the high average molecular weight of polyvinyl alcohol has rapidly caused rise in viscosity of the reaction mixture, when the molar fraction of the reactants in the reaction mixture has been increased. In particular, when comparing an acetalization reaction of an organic molecule and oligomeric vinyl alcohol to an acetalization reaction of the organic molecule and polymeric PVA, it has been observed that the oligomeric vinyl alcohol may be arranged to provide a higher modification degree, thereby resulting into a primer layer containing more functional vinyl groups per surface area unit of the cellulose fiber-based support layer.

[0029] The affinity of the primer layer containing the acetal compound towards the cellulose fiber-based support layer may further be increased by selecting the degree of hydrolysis of the oligomeric vinyl alcohol. Advantageously, the degree of hydrolysis of the oligomeric vinyl alcohol is above 70%, preferably equal to or higher than 80%. The degree of hydrolysis of the oligomeric vinyl alcohol may be in the range of 70-99%, advantageously in the range of 85 to 99%. When the degree of hydrolysis of the oligomeric vinyl alcohol is below 70%, the solubility to water diminishes drastically. However, the hydrophobicity increases, when the solubility to water diminishes. The degree of hydrolysis in the oligomeric vinyl alcohol may thus be used to select the affinity of the oligomeric vinyl alcohol towards a hydrophilic layer, such as a further polymer containing layer containing a polymer having capability to provide barrier properties for the cellulose fiber-based support layer, such as polyvinyl alcohol, starch, and/or carboxymethyl cellulose.

[0030] Reference is made to the vinyl group molality disclosed above. The degree of hydrolysis in the oligomeric vinyl alcohol may be selected such that a water-based reaction of oligomeric vinyl alcohol with 10-undecenal yields an acetalized reaction product comprising a catenated carbon structure, wherein the reaction product has a very high vinyl group molality. The lower viscosity of the solution during a water-based acetalization reaction further enables higher dry matter content of the starting material oligomeric vinyl alcohol to be used. At a higher concentration of 10-undecenal in a solution having relatively low viscosity, the acetalization reaction may proceed further and yield a compound based on oligomeric vinyl alcohol comprising 10-undecylenic groups acetalized into the structure, wherein the compound thus contains vinyl group molality of equal to or more than 0.20 mmol/g, preferably equal to or more than 0.23 mmol/g, such as equal to or more than 0.3 mmol/g, or more than 1.4 mmol/g of the compound.

[0031] By maintaining the viscosity of the water-based fraction in the reaction at a lower level, the grafting reaction with the organic molecule may be arranged to proceed further, thereby obtaining a higher amount of catenated carbon structures with functional vinyl groups into the formed reaction product. The lower viscosity of the reaction mixture further facilitates the mixing of the reactants, thereby allowing the reactants to be better in contact with each other, despite possible phase layer interfaces. This is the case in particular, when a non-water-soluble organic molecule, such as 10-undecenal, is used. The amount of stirring correlates with the amount of surface area available for chemical reactions; the better the mixing of the reactants during the reaction is, the higher is the probability of the participating functional groups to be in contact for a reaction to take place. Hence, a paper substrate having a higher density of catenated carbon structures with functional vinyl groups per unit area of the primer layer surface may be obtained.

[0032] By maintaining the viscosity of the water-based fraction in the reaction at a lower level, the grafting reaction with the organic molecule may further be arranged to proceed towards a more complete reaction conversion, the reaction conditions may be arranged to yield more of the acetalized reaction product from the amount non-acetalized starting materials. The higher conversion of reactants to a reaction product has a further effect of reducing the amount of unreacted reactant present in the reaction mixture after the reaction has taken place. Therefore, there is less need for purification of the reaction mixture of unreacted reactant which could be recycled, for example. By maintaining the viscosity of the reaction at a lower level such that the reaction product remains in a solution, the acetalized reaction product is easier to purify. The purification would be much more challenging from a highly viscose gel. The method thereby provides a

clear advantage over the prior art by facilitating purification, increasing the process safety and the recyclability of the process chemicals.

[0033] The invention is further described in the independent and dependent claims.

Brief description of the drawings

[0034]

Figure 1 illustrates, by way of an example, a method for manufacturing a label stock from a label laminate web by cutting the label laminate web with a die cutting roll and stripping excess matrix material away from the release liner, such that the labels remain attached on the release liner,

Figure 2 illustrates, by way of an example, a cross-dimensional view of a label stock, which comprises a label laminate web on a release liner,

Figure 3 illustrates, by way of an example, a cross-dimensional view of a release liner comprising a paper substrate and a release layer,

Figure 4 illustrates, by way of an example, a cross-dimensional view of a release coating containing fast-curing silicone compound applied on top of a paper substrate comprising a cellulose fiber-based support layer and a primer layer containing a compound based on oligomeric vinyl alcohol, wherein the compound contains a catenated carbon structure which terminates into an acetal at the first end of the chain, and into a functional vinyl group at the other end of the chain,

Figure 5 illustrates, by way of an example, a schematic reaction, wherein organic molecule comprising both an aldehyde group and a functional vinyl group is reacted in a water-based acetalization reaction with oligomeric vinyl alcohol, such that a compound based on the oligomeric vinyl alcohol is formed, wherein the compound contains catenated carbon structures with functional vinyl groups grafted onto the oligomeric structure,

Figure 6 is comparative experimental data demonstrating the effect of molecular weight to water-based acetalization reaction solution viscosity (mPa·s) and vinyl group molality (mmol/g), when 10-undecenal has been used as the reactant.

[0035] Figures 1 to 5 are schematic.
S_x and S_z represent orthogonal directions in the figures.

Detailed description

Release liner

[0036] Reference is made to Figures 3 and 4. A release liner REL1 refers to a thin multilayer structure having width, length and thickness dimensions. A release liner REL1 having a multilayer structure comprises at least a paper substrate SUBST1 and a release layer SIL1, such as a silicone-based release layer, applied on at least one side of the paper substrate SUBST1. A paper substrate SUBST1 is used herein to denote a coated cellulose fiber-based support layer, wherein the cellulose fiber-based support layer PAP1 has been coated from at least one side with at least one primer layer PRIM1.

Primer layer

[0037] Reference is made to Figures 3 and 4. A primer layer PRIM1 in this context refers to a layer coated on a cellulose fiber-based support layer PAP1. A paper substrate SUBST1 may contain one or more primer layers. A primer layer PRIM1 is typically configured to reduce the porosity of the support layer surface, thereby improving the smoothness of the paper substrate SUBST1 surface. An example of a primer layer PRIM1 is a polymer containing layer. When the primer layer PRIM1 is a polymer containing layer, it is typically applied as a coating composition on the cellulose fiber-based support layer PAP1, when manufacturing the paper substrate SUBST1. A conventional technical effect of a polymer containing layer is to reduce the surface penetration of a subsequent release layer applied on the paper substrate SUBST1. Polyvinyl alcohol, starch, and/or carboxymethyl cellulose are typically unmodified polymers POL1 having a film-forming nature which are widely used to provide a barrier between the release layer SIL1 and the cellulose fiber-

based support layer PAP1 surface.

[0038] The primer layer PRIM1 may contain an acetal compound CMP1 based on oligomeric vinyl alcohol having a low $\overline{M}_w$, such as a $\overline{M}_w$ of less than 1000 g/mol, and wherein the acetal compound CMP1 has been formed in a water-based acetalization reaction with an organic molecule comprising both an aldehyde group and a functional vinyl group, such that the acetal compound CMP1 based on the oligomeric vinyl alcohol on the primer layer PRIM1 contains functional vinyl groups. Alternatively, the acetal compound CMP1 based on oligomeric vinyl alcohol may be coated on a cellulose fiber-based support layer PAP1 independently of any other polymer containing layer, such as a layer containing polyvinyl alcohol, starch, and/or carboxymethyl cellulose.

Cellulose fiber-based support layer

[0039] The cellulose fiber-based support layer PAP1 refers to a paper containing cellulose fibers, which paper is suitable for use as a layer of a release liner. When manufacturing paper suitable for a release liner, the pulp is typically derived from a chemical pulping process. Chemical pulping disintegrates the structure of the wood with strong chemicals in a cooking process, thereby producing fibrous material with a very high cellulose fiber content of equal to or higher than 70 wt.%, preferably equal to or higher than 80 wt.%, most preferably equal to or higher than 90 wt.%. A chemical pulping process removes nearly all the lignin and at least part of the hemicelluloses, while preserving well the fiber structure and length. Examples of chemical pulping processes are, for example, the sulphite pulping process or the Kraft pulping process. The Kraft pulping process uses sodium sulphide and alkali to degrade and dissolve the lignin. The remaining lignin in the chemical pulp, while only in residual amounts of less than 5 wt.%, may still cause darkening of the pulp. The remaining lignin can be further removed through bleaching processes, thereby providing bleached chemical pulp. The first bleaching steps are further delignification stages, whereas the later steps are brightening stages, in which the brown-color inducing chromophores are removed, thereby increasing the pulp whiteness and brightness. Bleached chemical pulp typically contains lignin in an amount of less than 2 wt.%, preferably less than 1 wt.%, most preferably less than 0.5 wt.% of the bleached chemical pulp. Bleaching is typically used to improve the brightness and whiteness of the pulp. In papers used for release liners, a high transparency level of the paper is desirable. The Kraft process, in particular, decreases considerably the amounts of hemicelluloses, lignin, wood extractives and inorganics in the pulp material such that only residual traces of these compounds remain; thereby bleached Kraft pulp may be denoted as essentially 'lignin free'.

[0040] In this context, a paper suitable for use as a layer of a release liner refers to paper manufactured on a paper machine. In release liner manufacturing, paper quality and suitability for coating with a silicon compound may be determined based on the smoothness, density, porosity and transparency of the paper. Typical characteristics of a paper suitable for use as a layer of a release liner are smoothness of at least 900 sec/min (ISO 5627), density of at least 1.0, such as in the range of 1.0 to 1.2, wherein the density refers to grammage (ISO536) per thickness (ISO534), porosity equal to or less than 15000 pm/Pas (ISO11004) and transparency of equal to or higher than 40%, preferably equal to or higher than 44% when the paper grammage is less than 70 g/m^2, or equal to or higher than 28%, preferably equal to or higher than 33% when the paper grammage is equal to or higher than 70 g/m^2 (ISO2470), the parameter values corresponding to ISO standards referred in parentheses.

[0041] In practice, paper types lending themselves for release liner applications are vegetable parchment, greaseproof paper, coated papers and glassine. Of these, glassine is preferred for industrial manufacturing of high-quality release liner, due to the mechanical properties of the paper obtained in the manufacturing process.

[0042] Conventionally, the paper may have been made essentially of bleached chemical pulp, such as bleached Kraft pulp. While hardwood is advantageous for increasing the brightness of the paper, softwood having a longer average fiber length is typically used together with the hardwood in bleached Kraft pulp to improve the internal bond strength and facilitate the formation of the paper web. The combination of bleached chemical pulp comprising hardwood and softwood may also be used to improve the burst strength and tensile strength of the paper.

[0043] Glassine is paper typically made of bleached chemical pulp, having a grammage in the range of 30 to 160 g/m^2. When producing glassine paper, the pulp is refined to obtain a fiber fineness, which enables a dense, nearly unporous, paper surface to be obtained. Such a surface is resistant to air and liquids such as oil and water. When manufacturing glassine paper, the pulp slurry is first refined to a high level, the formed paper web is then pressed and dried, and a coating layer containing conventional sizing polymers having a film-forming nature such as unmodified polyvinyl alcohol, starch, and/or carboxymethyl cellulose is applied on the paper surface to provide barrier properties. Glassine is calendered with a multi-nip calender or a supercalender before or after applying the coating layer, to obtain a product having high density surface, high impact strength, high tear resistance and transparency. The coating layer may be applied as a separate layer or together with a compound based on oligomeric vinyl alcohol that contains functional vinyl groups.

Release layer

[0044] Reference is made to Figure 4. The release layer SIL1 is formed of a release coating applied on the paper substrate surface. The release coating is typically applied as an uncured composition, which is a liquid polymer resin that is subsequently cured to form the release layer SIL1. A cured release layer SIL1 has a non-blocking surface. The surface energy level of a cured release layer SIL1 is typically in the range of 21 to 25 dynes/cm. The non-blocking surface of the cured release layer SIL1 may be used to protect adhesive material of a label laminate web FILM1 from premature adhesive bonding.

[0045] The release layer SIL1 may comprise fast-curing silicone compound. A fast-curing silicone compound comprises a cross-linker component SH1 with silane hydride groups and silicone polymer VIN1 with functional vinyl groups, which components SH1, VIN1 are configured to cross-link in a catalytic hydrosilation reaction, preferably with a low amount of platinum-based catalyst.

Organic molecule

[0046] Reference is made to Figures 4 and 5. An organic molecule MOL1 in this context refers to a reactant. An organic molecule has a chemical structure which is defined by number or carbon atoms and functional groups. An organic molecule MOL1 suitable for grafting oligomeric vinyl alcohol in this context further refers to a small molecule comprising a catenated carbon structure that terminates into an aldehyde at the first end of the chain and into a functional vinyl group at the other end of the chain. The organic molecule MOL1 should have a catenated carbon structure having a carbon chain length of at least 4 carbon atoms. The symbol R in Figure 4 is used to denote the part of the organic molecule which separates the functional vinyl group and the aldehyde group of the organic molecule MOL1 from each other such that the catenated carbon structure of the organic molecule MOL1 contains at least four carbon atoms. A catenated carbon structure having a chain length of less than 4 carbon atoms in the organic molecule MOL1 hydrocarbon chain may lead to interference with the oligomeric vinyl alcohol OLG1 during the grafting reaction. A catenated carbon structure having a chain length of equal to or less than 15 carbon atoms is preferred, as a longer chain length may lead to chain folding problems. Therefore, a suitable organic molecule MOL1 for a paper substrate has a catenated carbon structure, preferably a hydrocarbon chain, containing at least 4 carbon atoms, preferably in the range of 5 to 15. Preferably, the catenated carbon structure is aliphatic. More preferably, the catenated carbon structure is acyclic. When the catenated carbon structure is linear or branched, steric hindrances are better avoided. When the catenated carbon structure is a hydrocarbon, the non-polar effect of the carbon chain is very high. A catenated carbon structure, however, may also comprise substituents, such as oxygen, hydrogen or functional alkane or alkene groups, such as vinyl group. The organic molecule MOL1 is most preferably a terminally unsaturated aldehyde having a general formula CH_2=CH-$(CH_2)_n$-CH=O, wherein n = 1 to 12. Examples of preferred organic molecules MOL1 are those having a chain length comprising 5 to 12 carbon atoms, such as 10-undecenal having a formula CH_2=CH-$(CH_2)_8$-CH=O, 4-pentenal having a formula CH_2=CH-$(CH_2)_2$-CH=O, and 2,2-dimethyl-4-pentenal having a formula CH_2=CH-$CH_2C(CH_3)_2$-CH=O. Preferably the organic molecule MOL1 is 10-undecenal or 2,2'-dimethyl-4-pentenal, such that the acetalized compound comprises a hydrocarbon chain that contains 11 or 5 carbon atoms in a row, respectively. Of these, the preferred is 10-undecenal, which is a commercial fine chemical available in industrial amounts.

[0047] When the organic molecule is reacted in a water-based acetalization reaction with oligomeric vinyl alcohol, the selection of the organic molecule further depends of the desired substitution degree of the oligomeric vinyl alcohol upon the grafting reaction. A terminally unsaturated aldehyde having a shorter hydrocarbon chain has a better water-solubility and may therefore be used to provide a higher efficiency in the grafting reaction. The higher water solubility allows the reagent to be better in contact with the oligomeric vinyl alcohol. A shorter hydrocarbon chain length of the organic molecule therefore may increase the probability of the participating functional aldehyde groups to be in contact with hydroxyl groups of the oligomeric vinyl alcohol, such that a water-based acetalization reaction may take place at a high efficiency. The oligomeric vinyl alcohol further improves the coatability of the formed acetal compound based on oligomeric vinyl alcohol.

[0048] When each organic molecule contains a single vinyl group, the mass ratio of the reactant to the oligomeric vinyl alcohol corresponds to the vinyl group molality b_{vin} of the formed compound according to equations 1a and 1b below:

$$Equation\ 1a:\ mass\ ratio = R_m = \frac{mass\ of\ organic\ molecule}{mass\ of\ oligomeric\ vinyl\ alcohol}$$

$$Equation\ 1b:\ \ vinyl\ group\ molality = \ b_{vin} = \frac{1000\frac{mmol}{mol} \times \frac{R_m}{M_{ald}}}{1 + R_m \times \frac{M_{ald} - M_{H2O}}{M_{ald}}}$$

In the equations 1a and 1b (above), the mass ratio R_m refers to the amount of the aldehyde reactant in grams that is reacted per 100 grams of the oligomeric vinyl alcohol. The mass ratio R_m may also be expressed as degree of modification and the units given in percent by weight (wt.-%) of the oligomeric vinyl alcohol. When an aldehyde group reacts with two hydroxyl groups of the oligomeric vinyl alcohol in an acetalization reaction, a water molecule is eliminated from the formed compound based on the oligomeric vinyl alcohol. Water molecule has a molecular weight M_{H2O} of 18 g/mol. The molecular weight of the organic molecule containing the aldehyde group is referred to as M_{ald}.

[0049] In practice, for example, when the mass ratio R_m of 10-undecenal having molecular weight of 168 g/mol to oligomeric vinyl alcohol is 0.035 (equals to 3.5 wt.-% degree of modification), the vinyl group molality b_{vin} in the formed compound is calculated as follows:

$$vinyl\ group\ molality = \ b_{vin} = \frac{1000 \times \frac{0.035}{168}}{1 + 0.035 \times \frac{168 - 18}{168}} = 0.20\ mmol/g$$

[0050] Table 1 (below) shows correlation between degree of modification and coatability of the composition in a paper coating process. The experimental study was comparative and used polyvinyl alcohol having an average molecular weight higher than 50000 g/mol. The results demonstrate a rapid rise in viscosity of the modified polymer, when the amount of 10-undecenal increases. In contrast, with a compound based on oligomeric vinyl alcohol, the coatability is preserved to a higher degree of modification, up to a vinyl group content of 1.41 mmol/g, when 10-undecenal is used as the organic molecule in the acetalization reaction.

Table 1. Comparison of vinyl group contents (molality) 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 fiber-based support layer, 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 content ** (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

(continued)

degree of modification (wt.-%)*	vinyl group content ** (mmol/g)	coatability
30	1.41	3
* calculated according to Equation 1a. ** calculated according to Equation 1b.		

Oligomeric vinyl alcohol

[0051] Polyvinyl alcohol is commercially manufactured from polyvinyl acetate via hydrolysis. The main structure and degree of polymerization of polyvinyl alcohol is established already when the vinyl acetate monomers are polymerized. Polymerization in this context refers to the rapid chain extension reaction connecting the used individual monomer units together into a compound having a high $\overline{M}_w$, which consists of a large number of monomer units covalently bound together in the polymerization reaction. A polymer hence refers to a product directly obtainable by a polymerization reaction. The polymerized chains, when emerging, are 'live' only for a very short period and extend rapidly to their full length as polymers, the chain extension then terminating. The chain extension is also most efficient immediately after chain emergence, when available monomers for chain extension are most abundant.

[0052] Oligomeric vinyl alcohol may be formed from fully or partly hydrolyzed polyvinyl alcohol. Oligomeric vinyl alcohol compound may be used, in particular, to reduce the viscosity behavior of an aqueous solution. Oligomeric chains have a low number of repeat units, thereby reducing the tendency for entanglement.

[0053] The oligomeric vinyl alcohol compounds useful in the practice of this invention have flow and viscosity characteristics which permit use of the compound as part of a coating composition applicable on a cellulose fiber-based support layer. Advantageously, oligomeric vinyl alcohol has a $\overline{M}_w$ of less than 1000 g/mol, preferably in the range of 100 to 950 g/mol, advantageously in the range of 440 to 880 g/mol. The number of repeat units may be in the range of 4 to 22. A method to manufacture oligomeric vinyl alcohol may comprise, for example, reduction of the molecular weight of polyvinyl alcohol by controlled chain scission. Oligomeric vinyl alcohol may be produced, for example, by treating polyvinyl alcohol with Fenton's reagent. In this method, hydrogen peroxide (H_2O_2) and iron salt, which in this context refer to Fenton's reagent, are used to produce highly oxidizing reaction conditions to a solution containing dissolved polyvinyl alcohol, whereby the polyvinyl alcohol can be broken down into short, oligomeric fragments in a controllable manner. The pH of the solution and the amounts of hydrogen peroxide and iron salt may be used to control the degradation rate of the polyvinyl alcohol into oligomeric vinyl alcohol.

[0054] A method to manufacture oligomeric vinyl alcohol by means of chain scission may comprise

- dissolving polyvinyl alcohol into water, thus producing an aqueous solution containing dissolved polyvinyl alcohol,
- adjusting the temperature of the aqueous solution to be in the range of 20 to 40°C,
- adjusting, when necessary, the acidity of the aqueous solution, such that the pH of the aqueous solution is equal to or less than 6, preferably in the range of 3-5, thereby forming an acidic solution,
- adding iron salt catalyst, such as aqueous solution of $FeSO_4$, into the acidic aqueous solution, and then
- adding slowly oxidizing agent, such as aqueous solution of H_2O_2, into the acidic aqueous solution.

[0055] A higher concentration of the Fenton's reagent improves the reaction kinetics and facilitates the degradation of the PVA. The degradation reaction with Fenton's reagent typically occurs at a temperature in the range of 20 to 40°C and when the pH of the solution is between pH 3 and pH 6. A low pH value below 3 may inhibit the reaction. Advantageously the reaction temperature is in the range of 25 to 30°C. At a temperature higher than 40°C the reaction efficiency declines, which is due to the accelerated decomposition of H_2O_2 into oxygen and water. Sequential addition of the hydrogen peroxide may be necessary to moderate the rise in temperature, which may occur as the oxidation reaction proceeds. Aqueous solutions of $FeSO_4$ typically contains residual H_2SO_4, which has the effect of decreasing the solution pH. Similarly, the addition of H_2O_2 has the effect of decreasing the solution pH. In concentrated polymer solutions it may thus be necessary to perform the oxidation in steps while monitoring the pH of the solution, such that after each step the pH of the solution is adjusted upwards, when necessary, for example with an aqueous solution of sodium hydroxide (NaOH). Stepwise addition of the hydrogen peroxide facilitates to maintain the pH of the solution above 3, such as in the range of 4 to 5, while the reaction proceeds. The oxidation reaction time may be selected on the basis of the desired oligomer length to be obtained. A typical reaction time for Fenton's reagent is less than 3 hours, such as in the range of 15 to 120 minutes. However, the reaction time may be extended, if needed.

[0056] Experimental conditions suitable for treating polyvinyl alcohol with Fenton's reagent have been disclosed, for example, by Dvořáčková and Dung ("Degradation of polyvinyl alcohol (PVA) by Fenton process", 13th International

Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2009, Hammamet, Tunisia, 16-21 October 2009), wherein 100 ml samples of commercial polyvinyl alcohol (MOWIOL 5-88) at a concentration of 200 to 15000 mg/liter were placed in 250 ml bottles and sulfuric acid was added to each bottle such that pH 4 was reached, then ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and an aliquot of aqueous solution of H_2O_2 (Fluka AG, 35% w/w, in water) was added to the dissolved PVA solution. The reaction solutions were stirred rapidly at 25°C and samples were taken at 10, 20, 30, 60, 90 and 120 minute time points from the reaction solution. Each sample that was taken was treated by a 1M solution of NaOH such that a pH 9 was reached. The insoluble phase formed thereby was removed by filtration or centrifuging. The samples prepared had molar ratio of PVA : Fe^{2+} : H_2O_2 in the range of 1:2:0.2 to 1:20:2. The reaction products were analyzed by means of an UV-VIS spectrophotometer (660 nm).

[0057] The oligomeric vinyl alcohol formed by controlled chain scission may purified, for example, by dissolving the precipitated reaction product into water and precipitating it in acetone. The purification procedure may be repeated, if needed.

[0058] An advantage of the controlled chain scission is, that the molecular size and structure, and hence the performance characteristics, can be controlled in a predictable and understandable manner. The starting material, i.e. the polyvinyl alcohol, may further be selected to comprise desired properties, such as branching, which properties may be provided also on the oligomeric vinyl alcohol formed from the polymer. The oligomeric vinyl alcohol may thereby have functional characteristics, which due to the lower molecular weight differ from the characteristics of conventional polymeric PVA. The oligomeric vinyl alcohol may thus be provided with desired functionality.

[0059] Alternatively, vinyl acetate monomers may be oligomerized from vinyl acetate monomers in the presence of suitable initiator and chain transfer agent. Reference is made herein to the publication US20030050394 A1, which discloses an exemplary method for producing oligomeric vinyl acetate by radical polymerization of vinyl acetate monomers in the presence of di-*tert*-butyl peroxide as initiator and using isopropanol (2-propanol) as a chain transfer agent. The formed vinyl acetate oligomer may be partially saponified in the presence of a base catalyst and an inert solvent, thereby forming oligomeric vinyl alcohol having a desired amount of hydroxyl groups. The degree of oligomerization may be experimentally determined by the ratio of monomer (i.e. vinyl acetate) to chain transfer agent. Suitable initiators for the oligomerization are common free-radical polymerization initiators, such as dibenzoyl peroxide or 2,2'-azo-bis-isobutyronitrile. Advantageously, however, di-*tert*-butyl peroxide is used as the initiator because the tert-butanol that is produced during the initiation can easily be removed from the reaction mixture by distillation. Concentrations of 0.5 to 4 mol.%, with respect to the amount of vinyl acetate are generally suitable, as the degree of oligomerization is affected only slightly by the concentration of initiator. Isopropanol is a preferably used chain transfer agent, which also acts as a solvent and can easily be removed by distillation after the reaction. The boiling point of the chain transfer agent may be selected as the reaction temperature. The method enables manufacturing of oligomeric vinyl alcohol wherein the number of repeat units may be less than 30, preferably in the range of 2 to 15, most preferably 6 to 12.

[0060] A still alternative method to manufacture oligomeric vinyl alcohol is free radical polymerization of vinyl acetate monomers in the presence of a chain transfer agent such as chloroform and subsequent hydrolysis of the thereby formed oligomeric vinyl acetate, thereby forming oligomeric vinyl alcohol. Reference is made herein to the article written by Semsarzadeh and Mirzaei (Iranian Polymer Journal, 12 (1), 2003, 67-75), which discloses an exemplary method for producing oligomeric fractions of vinyl acetate. When the above-referred method is modified by reducing the concentration of the monomer used as a reagent, shorter oligomeric fractions of vinyl acetate may be produced. The oligomeric vinyl acetate can be hydrolyzed into oligomeric vinyl alcohol. However, due to the use of chloroform as both solvent and chain transfer agent, this method is not the preferred option for manufacturing oligomeric vinyl alcohol.

Acetalization reaction

[0061] Reference is made to Figure 5, which illustrates, by way of an example, a water-based acetalization reaction of an organic molecule MOL1 comprising both an aldehyde group and a functional vinyl group with oligomeric vinyl alcohol OLG1, such that an acetal compound CMP1 based on the oligomeric vinyl alcohol OLG1 is formed, wherein the acetal compound CMP1 contains functional vinyl groups grafted onto the oligomeric structure. Acetalization reaction as disclosed herein refers to a reversible chemical reaction comprising an acid catalyst, such as sulphuric acid, that is used to provide acidic condition to a water-based medium, thereby initiating a reaction wherein two hydroxyl groups of the oligomeric vinyl alcohol OLG1 are reacted with the aldehyde group of the organic molecule MOL1 which in acidic conditions leads to the formation of an acetal compound CMP1.

[0062] When providing acidic conditions (pH in the range of 1.5 to 2.5) and a reaction mixture containing relatively low amount of organic molecules compared to a relatively high amount of water, the balance of the acetalization reaction is on the acetal side, thereby providing acetal compound CMP1 wherein two hydroxyl groups of the oligomeric vinyl alcohol have been covalently bonded to the carbonyl group of the aldehyde. The water-based acetalization reaction may be performed in 1 hour or less, such as in the range of 20 to 60 minutes. The reaction temperature may be above room temperature, such as in the range of 20 to 99°C. Preferably the reaction temperature is above 50°C, as a higher reaction

temperature correlates with accelerated reaction kinetics. The acetalization reaction may be terminated by adjusting the solution pH to 7, for example by addition of a suitable neutralizing agent, such as sodium hydroxide. The neutralization step which terminates the acetalization reaction is preferably followed by a purification with acetone precipitation. Purification removes unreacted reactant and any by-products, such as inorganic salts, formed due to the neutralization step from the acetalized reaction solution.

[0063] Coating of the cellulose fiber-based support layer with unpurified acetalized reaction solution may result in further, undesired reactions on the surface of the cellulose fiber-based support layer. This may cause problems in novel high-speed release liner applications, wherein higher bonding strength and lower release values are needed between the paper substrate and the release layer.

Acetalization reaction efficiency

[0064] When 10-undecenal is used in a water-based acetalization reaction, the reaction is not complete and the unreacted reactant is readily detectable by its distinct odor. The efficiency of the acetalization reaction with respect to the organic molecule may be further evaluated by means of an analytical method, for example by means of gas chromatography from the acetalized reaction solution.

[0065] Analytical method to evaluate the efficiency of the acetalization reaction from a reaction solution or from a paper substrate surface may comprise

- providing a sample of unreacted solution containing oligomeric vinyl alcohol and an amount of organic molecule
- providing a sample of the same solution after an acetalization reaction, the solution thereby comprising acetal compound in addition to any unreacted organic molecule,
- drying both samples at a temperature of 40°C, and
- sealing each dried sample hermetically into a container, such as a glass bottle,
- heating the hermetically sealed samples in the containers in a temperature of 200°C for 1 hour, and after heating,
- analyzing the evaporated compounds from each heated sample by means of gas chromatography,

thereby allowing detection of any evaporated material in gaseous form from the samples. By comparing the resulting peaks to each other and to a known reference peak, the amount of evaporated starting material may be determined. The method therefore may be used to determine the amount of unreacted reactant in a solution. The amount of reacted reactant may be further determined by modifying the analytical method above such, that the solution after an acetalization reaction is first purified by acetone precipitation and the purified product is then hydrolyzed in an acidic aqueous solution such that the reactant regains the aldehyde form. By measuring the amount of the reactant in the aldehyde form from the acidic aqueous solution, the efficiency of the acetalization reaction may be verified from the purified acetal compound.

[0066] The analytical method may be performed, for example, with HeadSpace-GC-MDS equipment, wherein e.g. unreacted 10-undecenal may be detected by its specific retention time, i.e. the time needed for this specific component to flow through the separation column of the gas chromatography device. Analytical comparison of an unreacted solution and reacted solution may thus be used to provide a comparison, wherein the amount of unreacted 10-undecenal in the acetalization reaction is calculated from the integrated surface areas of the peaks of a solution before and after an acetalization reaction.

[0067] Alternatively, or in addition, proton nuclear magnetic resonance (^{1}H-NMR) analysis may be used to identify the presence of functional groups from the chemical shift value δ of the reactants and from the obtained reaction products. Samples for the ^{1}H-NMR analysis may be prepared, for example, by dissolving 1 to 10 mg of the reactant or the formed reaction product in 1 ml of DMSO-d6 solvent and measuring standard ^{1}H spectrum with 16 scans for each of the prepared NMR samples with a suitable analysis device, e.g. Bruker AVANCE -series spectrometer (400 Hz). Signals typical for a vinyl group may be detected in the region between δ = 4.8 to 6.0 ppm, approximately. For instance, the quantification of 10-undecenal can preferably be done by using the peak at δ = 5.7 to 5.9 ppm. The methine proton adjacent to the hydroxyl group (CH_2-C<u>H</u>(OH)-CH_2) on the backbone of oligomeric vinyl alcohol is located at δ = 3.8 to 3.9 ppm and can be used as a point of reference. Molar fraction of vinyl groups per vinyl alcohol unit can be determined using the ^{1}H-NMR spectrum by calculating the relative peak areas for one proton from both vinyl group and PVA backbone. In addition, when collecting and analyzing NMR samples prepared from solutions before and after an acetalization reaction, the NMR results may further be used to determine how much of the aldehyde reactant has been consumed in the acetalization reaction. The degree of substitution (DS) can be quantified by equation 2.

$$\text{Equation 2: } DS = \frac{A_1}{A_2/2}$$

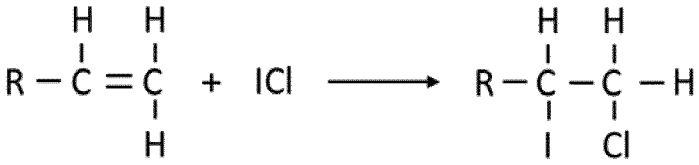
where A_1 is the area of the peak representing one vinyl proton and A_2 is the area of the peak representing one backbone proton.

Iodometric titration method for measuring the amount of functional vinyl groups of the acetal compound formed in the acetalization reaction

[0068] Iodometric titration in this context refers to a method based on the Wijs method according to standard ISO 3961:2009(E) wherein a known excess of iodine monochloride is added to a sample, which results in a reaction between the iodine monochloride and any double bonds present in the sample. The quantity of iodine monochloride that has reacted with the double bonds present in the sample is determined by reacting the remaining residual iodine monochloride with a known excess of potassium iodide to form iodine, the stoichiometric quantity of which is then determined by titration with a solution of sodium thiosulphate of known concentration. From this, an iodine value of the sample is obtained that specifies the amount of iodine in grams that can formally be added to the double bonds in a known amount of the sample and from which the quantity of double bonds in the sample may then be determined. Vinyl groups are double bonds and low molecular weight polyvinyl alcohol, as such, does not contain double bonds. Therefore, iodometric titration is a specific method that can be used to investigate the amount of vinyl groups present in a sample of acetalized polyvinyl alcohol and to determine the vinyl group molality of the sample.

[0069] In particular, the iodometric titration method based on the Wijs method may be used to measure the total number of vinyl double bonds present in a sample of oligomeric vinyl alcohol compound that has been acetalized with an aldehyde that contains a functional vinyl group, such as 10-undecenal or 2,2'-dimethyl-4-pentenal. The iodometric titration method is based on a measured volume of iodine monochloride in acetic acid (Wijs solution) which may be added to the reaction solution containing the acetalized oligomeric vinyl alcohol compound, whereby the iodine monochloride reacts according to Equation 3 (below) with the double bonds of the vinyl groups present in the oligomeric vinyl alcohol compound that has been acetalized such that the electrophilic addition reaction produces a dihalogenated single bond, of which one carbon has bound an atom of iodine.

Equation 3:



[0070] The iodine monochloride is a light-sensitive reagent and needs to be stored and incubated in the dark. After 1-hour incubation in the dark, the quantity of iodine that has reacted in the electrophilic addition reaction is determined by adding a measured volume of potassium iodide solution (15%, weight/volume) to the reaction solution, which causes the remaining unreacted iodine chloride in the reaction solution to form molecular iodine according to Equation 4 (below).

Equation 4: $ICl + KI \rightarrow KCl + I_2$

[0071] The liberated molecular iodine is then titrated against a standard solution of 0.1N sodium thiosulphate, whereby the stoichiometric quantity of molecular iodine may be calculated according to Equation 5 (below).

Equation 5: $I_2 + 2Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_2O_4$

[0072] The iodometric titration thus enables to determine an iodine value, which is a measure of the amount of iodine in grams that have reacted with the functional vinyl groups in a known amount of the oligomeric vinyl alcohol compound, as presented in Equation 6 (below).

Equation 6: $$Iodine\ value = \frac{(B-A)N \times 12{,}7 \frac{g}{100\ g}}{m}$$

where A is thiosulfate consumption in milliliters of a test sample (oligomeric vinyl alcohol compound that has been acetalized), B is thiosulfate consumption of a blank sample containing only the measured volume of iodine monochloride in acetic acid and the measured volume of potassium iodide solution, N is the normality (mol/l) of the thiosulfate solution and m is the mass in grams of the test sample (oligomeric vinyl alcohol compound that has been acetalized). When the

iodometric titration method is used to compare iodine values of multiple polyvinyl acetal samples that contain functional vinyl groups, a sample containing only the low molecular weight polyvinyl alcohol used in the acetalization reaction may be used as a blank sample, instead. Blank samples containing only low molecular weight polyvinyl alcohols may also be used if the samples have been obtained from different types of low molecular weight polyvinyl alcohols.

[0073] The vinyl group molality b_{vin} (mmol/g) can be determined according to Equation 7 (below), which equation is a simplified version obtainable from the Equation 6 (above):

$$\text{Equation 7: } b_{vin} = \frac{(B-A)N}{m}$$

[0074] As an example, when the thiosulfate consumption of a 2.5 g test sample of oligomeric vinyl alcohol compound that has been acetalized in iodometric titration is 35 milliliters, the thiosulfate consumption of a blank sample is 48 milliliters and the normality of the thiosulfate solution is 0.1 mol/l, the vinyl group molality of the test sample is 0.52 mmol/g, as demonstrated below by using the formula of Equation 7:

$$\frac{(48\ ml - 35\ ml) \times 0{,}1\ mol/l}{2.5\ g} = 0.52\ \frac{mmol}{g}$$

[0075] Below is provided an example method for measuring the quantity of functional vinyl groups from a reaction solution containing modified oligomeric vinyl alcohol, which has been reacted with undecylenic aldehyde.

[0076] The reaction solution is first cleaned by purification, which comprises:

- collecting aqueous reaction solution containing modified oligomeric vinyl alcohol which has been reacted with undecylenic aldehyde,
- adding the aqueous reaction solution to acetone with constant stirring such that a 5:1 ratio of acetone to the aqueous reaction solution is reached, thereby obtaining a precipitate containing the modified oligomeric vinyl alcohol and a filtrate containing the undecylenic aldehyde which has not reacted,
- separating the precipitate from the filtrate by filtering, and
- drying the thereby obtained precipitate at 60 °C for 16 h

, thereby obtaining an amount of dry modified oligomeric vinyl alcohol, which may be weighted to determine the mass of the dry modified oligomeric vinyl alcohol in grams.

[0077] The quantity of functional vinyl groups (i.e. the vinyl group molality) may then be measured by iodometric titration method, which comprises:

- adding a known mass of dry modified oligomeric vinyl alcohol into distilled water such that a 10% (w/v) mixture is formed and stirring the mixture at ambient temperature or heating as necessary until a clear solution is obtained, thereby obtaining an aqueous solution containing the modified oligomeric vinyl alcohol,
- collecting a 25 ml aliquot of the aqueous solution containing the modified oligomeric vinyl alcohol into an empty flask
- adding 25 ml of iodine chloride in acetic acid (Wijs solution) into the aliquot, thereby obtaining a test sample solution
- adding 25 ml of iodine chloride in acetic acid (Wijs solution) into another flask containing 25 ml of distilled water, thereby obtaining a blank sample solution
- incubating the test sample solution and the blank sample solution in the dark for 1 h,
- adding 15 ml of potassium iodide solution (15%, w/v) into each of the test and blank sample solutions, respectively, while thoroughly stirring the solutions,
- adding starch as indicator and titrating the test and blank sample solutions with 0.1 N sodium thiosulfate
- calculating the iodine value, which corresponds to the known mass of the dry modified oligomeric vinyl alcohol and which is directly proportional to the quantity of functional vinyl groups present in the dry modified oligomeric vinyl alcohol, which has been reacted with undecylenic aldehyde.

[0078] The starch indicator is added before the titration to visualize the end-point, which is observed as fading of the dark blue or purple color of the solution.

Determination of molecular weight

[0079] The $\overline{M}_w$ of oligomeric vinyl alcohol compounds can be determined by gel permeation chromatography (GPC) combined with static light scattering. The $\overline{M}_w$ is measured from re-acetylated specimens by methods known from the literature, for example in a pyridine/acetic anhydride mixture. The $\overline{M}_w$ represents the mean average weight of the oligomeric vinyl alcohol compound.

Viscosity measurements

[0080] The term viscosity herein refers to a measure of the internal friction occurring in the displacement of two adjacent liquid layers, as defined in standard DIN 51 550. Viscosity is a property of a fluid that resists the force tending to cause the fluid to flow. Viscosity of a polymer solution is dominated by short-range attractive intermolecular forces within the solution. The viscosity behavior of a solution during a reaction may be measured with a viscometer. Unless otherwise stated, the values refer to viscosity η given in units of mPa·s (millipascal-second) according to the international system of units (SI). The viscosity values have been determined by using a Brookfield viscometer from aqueous solutions having a temperature of 25°C at 100 rpm, according to the manufacturer's instructions.

Comparative experimental data of the effect of molecular weight of the polymer to the solution viscosity

[0081] Reference is made to Figure 6, which illustrates the results of a comparative experimental study, wherein the viscosity was measured from water-based acetalization reaction products as a function of modification degree, using 10-undecenal as reactant. The vertical axis in Figure 6 represents the viscosity value of the reaction mixture in millipascal-seconds (mPa·s) on a logarithmic scale. The horizontal axis in Figure 6 represents the vinyl group molality b_{vin} (mmol/g).

[0082] In the comparative experimental study, the viscosity η was measured as a function of the vinyl group molality b_{vin} from reaction solutions denoted as samples A, B, C, D, E or F. Each sample A, B, C, D, E and F contained polyvinyl alcohol of a specific grade. The specific grade refers to the degree of hydrolysis and the degree of polymerization of the polyvinyl alcohol. Table 2 (below) discloses the characteristics of the grades of polyvinyl alcohol used in samples A-F. Samples A, B, C, D and E represented fully hydrolyzed grades having a degree of hydrolysis equal to or higher than 97%, whereas sample F was a partially hydrolyzed grade having a degree of hydrolysis of 88%, respectively. All samples thereby contained functional hydroxyl groups. Different grades of polyvinyl alcohol were selected to compare the effect of the polymer grade to the solution viscosity during a water-based acetalization reaction with the same reactant (10-undecenal). Sample A was a reference sample containing commercial polyvinyl alcohol with a degree of hydrolysis of 98%, the degree of polymerization $\overline{P}_w$ of ca. 2800 and a $\overline{M}_w$ of ca. 125000 g/mol.

Table 2. $\overline{M}_w$ (g/mol) and degree of polymerization $\overline{P}_w$ of the polyvinyl alcohol grades used in the comparative experimental study.

Sample	$\overline{M}_w$ (g/mol)	$\overline{P}_w$
A	125000	2800
B	61000	1400
C	47000	1000
D	27000	600
E	16000	360
F	14000	270

[0083] Each sample A-F was prepared in the same manner by mixing polyvinyl alcohol into water and heating and stirring the mixture for 2 hours at 90°C until a solution was obtained that contained a 12% solids content (i.e. dry matter content) and subsequently adjusting the pH of the solution with sulfuric acid. The pH of the solution was measured to be 1.5 prior to adding 10-undecenal, which was used as the reactant for the water-based acetalization reaction. The solution was stirred vigorously during the synthesis to ensure a reaction with the reactant, which was not water-soluble. The synthesis was continued for 25 minutes at a temperature of 90°C and the pH was then adjusted to 7 by adding sodium hydroxide (1M solution). The solution containing the reaction product was subsequently allowed to cool down to room temperature before measurement of the viscosity of the sample thus prepared.

[0084] The viscosity was measured from the samples A-F at different vinyl group molalities, which correlated with the

amount of the reactant that was reacted with the polyvinyl alcohol. As an example, sample B at a vinyl group molality of 0.09 mmol/g correlates with a 1.5 wt.-% degree of modification.

[0085] As can be observed from Figure 6, when the polyvinyl alcohol was unmodified, the viscosity of samples A and B was already ca.1000 mPa·s or higher. This was likely due to the relatively high $\overline{M}_w$ of over 60000 g/mol and relatively high degree of polymerization $\overline{P}_w$ of ca.1400 or higher.

[0086] The leftmost dashed vertical line p1 denotes a sample with a vinyl group molality of 0.06 mmol/g. At this degree of modification, the viscosity of sample A was already 50000 mPa·s, whereas the viscosity of sample B was ca.1200 mPa·s.

[0087] Next to the dashed vertical line p1, the vertical line denotes a vinyl group molality of 0.12 mmol/g. At this degree of modification, the viscosity of sample A was too high for measurement. The viscosity of sample B had also increased rapidly and was already around 7200 mPa·s, which had a significant effect on the flow behavior of the solution. When the degree of modification of sample B was 0.15 mmol/g. the viscosity of the solution had already risen to 26000 mPa·s, which rendered the sample unsuitable for coating on a cellulose fiber-based support layer by conventional means used in the industry.

[0088] The dashed vertical line p2 denotes a vinyl group molality of 0.17 mmol/g. At this degree of modification, the viscosity of sample B was already ca.100000 mPa·s and the viscosity of sample C was already ca.20000 mPa·s.

[0089] The dashed vertical line p3 denotes a vinyl group molality of 0.42 mmol/g. At this degree of modification, the viscosity of fully hydrolyzed sample E was already above 10000 mPa·s. The viscosity of the partially hydrolyzed sample F, on the other hand, was ca.3000 mPa·s.

[0090] The comparative experimental study demonstrates how the viscosity η behaved as a function of vinyl group molality in the samples A-F, when 10-undecenal was used as a reactant. The examples 1 to 4 below illustrate in practice how the invention may be carried out and present some advantageous effects that the use of a compound based on oligomeric vinyl alcohol may provide on a paper substrate primer layer. In the examples, the abbreviation w/v denotes weight per volume, whereas the abbreviation w/w denotes weight per weight. The modified oligomeric vinyl alcohol refers to a compound based on oligomeric vinyl alcohol that has been modified to contain vinyl groups.

EXAMPLE 1

Preparation of oligomeric vinyl alcohol by Fenton oxidation

[0091] In an experimental study, 18 grams of commercial polyvinyl alcohol (Poval® 10-98 grade) was dissolved into hot water having a temperature of 95°C, such that an aqueous solution of polyvinyl alcohol having 18% solids content (i.e. dry matter content) was obtained, wherein the solution, after cooling to a temperature of 25°C, had a Brookfield viscosity of 3040 mPa·s, when measured at 100 rpm. The temperature and pH of the solution were then adjusted to 30°C and 4, respectively. Subsequently, the solution was subjected to Fenton oxidation reaction by adding an amount of 1.87 grams of aqueous iron(II) sulfate solution (1% w/v) and 2.49 grams of aqueous hydrogen peroxide (30% w/w) into the solution. The mixture thus obtained was then stirred for 16 hours, thereby allowing the polyvinyl alcohol to degrade into oligomeric vinyl alcohol by means of a controlled chain scission of the polymer. The chain scission reaction was stopped by adjusting the pH of the mixture to 7. The obtained reaction product was an oily solution of oligomeric vinyl alcohol wherein the solution, at a temperature of 25°C, had a Brookfield viscosity of 75 mPa·s, when measured at 100 rpm.

EXAMPLE 2

Preparation of oligomeric vinyl alcohol by polymerization

[0092] In another experimental study, a mixture of 80 grams of vinyl acetate and 745 grams of isopropanol were stirred under nitrogen flow for 60 minutes. To this mixture, 1.36 grams of di-tert-butyl peroxide was added, and the mixture was refluxed at boiling point for 16 hours. The product was purified by evaporating the solvent, yielding a viscous liquid. The number average molecular weight of the product was determined by NMR as 780 g/mol.

EXAMPLE 3

Grafting of a high vinyl content compound based on oligomeric vinyl alcohol

[0093] In an experimental study, 100 grams of dry oligomeric vinyl alcohol was dissolved into hot water having a temperature of 90°C, such that an aqueous solution containing dissolved oligomeric vinyl alcohol (18% dry matter content)

and viscosity of 75 mPa·s, when measured at 25°C, was obtained. The pH value of the aqueous solution was adjusted to 2 with sulfuric acid. Subsequently, an amount of 9.1 grams of 10-undecenal (corresponding to a vinyl group molality of 0.5 mmol/g) was added dropwise into the solution as a reactant while agitating the solution vigorously. The agitation was continued for 2 hours at the temperature of 90°C, thereby reacting the reactant with the dissolved oligomeric vinyl alcohol in a water-based acetalization reaction such that compound based on the oligomeric vinyl alcohol was formed. The pH of the reaction mixture was then adjusted to a pH value 7 with sodium hydroxide and cooled down to 25°C. The formed compound had a Brookfield viscosity of 450 mPa·s, when measured at 100 rpm.

[0094] The experimental study was then repeated, but this time using 17.6 grams of 10-undecenal as reactant (corresponding to a vinyl group molality of 0.9 mmol/g). With this amount of 10-undecenal, the formed compound had a Brookfield viscosity of 3200 mPa·s, when measured at 100 rpm.

[0095] The experimental studies performed with polyvinyl alcohol and oligomeric vinyl alcohol evidence that the viscosities of solutions containing modified polyvinyl alcohol increase as a function of the degree of modification. However, solutions containing oligomeric vinyl alcohol having a very low $\overline{M}_w$ of less than 1000 g/mol, such as in the range of 440-880 g/mol, may be used to suppress the rise of viscosity during an acetalization reaction with organic molecule.

[0096] This enables efficient grafting of the organic molecules into the oligomeric vinyl alcohol, such that a compound which contains a catenated carbon structure and terminates into a functional vinyl group at the other end of the chain may be obtained. Thereby a very high vinyl group molality of the compound may be obtained, which may still be applied on a substrate surface as a coating composition. The limit to the amount of organic molecule, which may be grafted onto an oligomeric vinyl alcohol is considerably higher than with a polyvinyl alcohol such as in sample A, which represents the feasible degree of modification disclosed in the prior art. Table 3 (below) illustrates the viscosity behavior of the modified oligomeric vinyl alcohol in the experimental study as a function of vinyl group molality b_{vin} (mmol/g).

Table 3. The correlation between the vinyl group molality b_{vin} (mmol/g) and the viscosity (mPa·s) of modified oligomeric vinyl alcohol obtained in a water-based acetalization reaction with 10-undecenal.

b_{vin}	viscosity
(mmol/g)	(mPa·s)
0.00	75
0.34	90
0.44	112
0.50	450
0.83	2750
0.90	3200

EXAMPLE 4

Effect of increased vinyl content to the relative rub-off value of a paper substrate

[0097] In order to study the effect of vinyl group molality to silicone adhesion, a comparative experimental study was performed on samples containing either polyvinyl alcohol grafted with 10-undecenal or a compound based on oligomeric vinyl alcohol. The samples containing a compound based on oligomeric vinyl alcohol had been prepared according to Example 3 above. Unmodified polyvinyl alcohol (POVAL® 10-98 grade) served as a reference sample, which could be used as a negative control to determine the effect of the unmodified polyvinyl alcohol on the silicone adhesion. Anchorage is a term used in the field to describe the attachment of the release coating to the paper substrate. Anchorage may be measured as relative rub-off of the silicone from the paper substrate. A relative rub-off value of 100% refers to a perfect anchorage of the silicone, such that the release coating is fully anchored to the substrate. A relative rub-off value of less than 90% means that the release coating could not hold on to the paper substrate sufficiently.

[0098] In the experimental study, aqueous solutions were thus prepared, which contained either

- unmodified polyvinyl alcohol (the reference sample)
- the same polyvinyl alcohol, but grafted with 10-undecenal to a vinyl group molality b_{vin} of 0.09 mmol/g, or
- compound based on oligomeric vinyl alcohol, wherein the compound had been prepared according to Example 3 above to a vinyl group molality b_{vin} of (0.5 mmol/g and 0.9 mmol/g, respectively).

[0099] Glassine paper sheets (UPM Golden) were coated with the aqueous PVA solutions using a laboratory blade coater, thereby obtaining paper substrates with a primer layer that contained either unmodified polyvinyl alcohol, polyvinyl alcohol grafted with 10-undecenal or a compound based on oligomeric vinyl alcohol. The amount of coating applied on each glassine paper sheet was 2 g/m^2. After coating, the paper substrates thus prepared were dried at 105°C for 1 minute. All paper substrates were subsequently subjected to siliconization, which refers to coating of a paper substrate with silicone resin prepared of Wacker Dehesive SFX 251 and V525 cross-linker, using C05 catalyst (all components provided by Wacker). The silicone resin applied on the paper substrate was prepared by stirring 100 parts per weight of the Dehesive SFX 251 with 14.4 parts of the V525 cross-linker for 2 minutes, then adding 1 part of the C05 platinum catalyst and stirring for 5 minutes. Thus the amount of platinum in the formed silicone resin was 10 ppm. The silicone resin thus prepared was then applied on top of the paper substrate by blade coater and cured for 30 seconds at 105°C, thereby curing the silicone resin into a release layer and forming a release liner. Each paper substrate was coated with an amount of 1.2 g/m^2 of the silicone resin thus prepared. The silicone adhesion was tested immediately after the siliconization from the formed release liner. This is referred to as the initial rub off level. To further observe the combined effect of tropical conditions and label adhesive as a function of time to the silicone adhesion level, an adhesive label was attached on each formed release liner immediately after siliconization and the laminates thus formed were stored at 50°C and 70% RH for a period of 2 and 7 days before determining the silicone adhesion level again.

[0100] The level of silicone adhesion in each release liner sample was determined with a semi-automatized method, wherein the amount of silicone was measured using an x-ray fluorescence spectrometer (Oxford Lab-X-3000) before and after a defined amount of rubbing of the release liner sample. The release liner sample was placed on top of a felt, such that the siliconized surface of the release liner sample was facing the felt. The rubbing was performed by pressing the sample with constant pressure against a felt and rotating the sample 10 times around its axis, to increase reliability and comparability of the result. In the case of 2- and 7-day measurements, the release liner was tested after removing the label from the laminate. Thus the 2- and 7-day measurements were performed on surfaces that had been in contact with an adhesive. For each sample, 3 parallel rub-off measurements were performed, of which the arithmetic average was calculated. The results of the rub-off tests are shown in Table 4 (below), wherein the values are the calculated arithmetic average values, given in units of relative rub-off value in percent (%). A relative rub-off value of 90% represents a minimum level which is considered to be acceptable and a relative rub-off value of 95% or above is considered as a good result. An example of a device suitable for producing rub-off on a release liner surface is a Satra rub tester, which has a rotating head holding a circular felt pad under a standard load, which enables semi-automated testing of abrasion resistance of a release layer.

Table 4. Silicone rub-off test results of release liner samples formed of paper substrates containing either unmodified polyvinyl alcohol without vinyl groups, modified polyvinyl alcohol with a vinyl group molality of 0.09 mmol/g or a modified oligomeric vinyl alcohol (i.e. a compound based on oligomeric vinyl alcohol), with a vinyl group molality of either 0.5 mmol/g or 0.9 mmol/g. The release coating applied on the paper substrate was a fast curing silicone system (SFX251 dehesive, V525 cross-linker) wherein the amount of platinum was 10 ppm.

sample type	**vinyl group molality (mmol/g)**	**relative rub-off value (%)**		
		0 d	**2 d**	**7 d**
unmodified polyvinyl alcohol	0	10	9	10
modified polyvinyl alcohol	0.09	15	7	9
modified oligomeric vinyl alcohol	0.5	98	97	95
modified oligomeric vinyl alcohol	0.9	99	99	100

[0101] The results of the experimental study demonstrated that unmodified polyvinyl alcohol (Poval® 10-98) could be grafted in a water-based acetalization reaction to a vinyl group molality of 0.09 mmol/g. This amount of vinyl groups grafted onto a polymer, however, was not sufficient to provide reliable anchorage for fast-curing silicones, which may be used at low levels of platinum catalyst. The oligomeric vinyl alcohol, on the other hand, enables a much higher vinyl group molality to be obtained on a grafted compound. The test results further demonstrate that a primer layer based on modified oligomeric vinyl alcohol worked much better with the fast curing silicone. The release liner samples containing compound based on oligomeric vinyl alcohol presented good relative rub-off values, which remained relatively consistent over time, unlike the samples containing either unmodified or modified polyvinyl alcohol. In view of the test results, the

paper substrates containing compound based on oligomeric vinyl alcohol demonstrated a surprisingly large difference in silicone adhesion levels, when relative rub-off was measured, and thus provided better anchorage capability for the silicone system. A compound based on oligomeric vinyl alcohol thus enabled the use of a fast curing silicone resin with a very low platinum level.

[0102] For the person skilled in the art, it will be clear that modifications and variations of the paper substrate and the method according to the present invention are perceivable. The figures 1-5 are illustrative and have not been drawn into any particular scale. 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) which is suitable for binding silicone in a catalytic hydrosilation reaction, the paper substrate (SUBST1) comprising

    - a cellulose fiber-based support layer (PAP1) and
    - a primer layer (PRIM1) that contains a compound (CMP1) based on oligomeric vinyl alcohol (OLG1),

    wherein the compound (CMP1) contains a catenated carbon structure grafted onto oligomeric vinyl alcohol (OLG1), and wherein the catenated carbon structure

    - contains a chain of at least 4 carbon atoms,
    - terminates into an acetal at the first end of the chain, and
    - terminates into a functional vinyl group at the other end of the chain, and wherein the vinyl group molality (b_{vin}) of the compound (CMP1) is equal to or higher than 0.2 millimoles per gram of the compound (CMP1).

2. A method for manufacturing a paper substrate (SUBST1) which is suitable for binding silicone in a catalytic hydrosilation reaction, the method comprising steps of

    - providing a water-based solution containing dissolved oligomeric vinyl alcohol (OLG1),
    - adding reactant which is an organic molecule (MOL1) that contains at least 4 carbon atoms and comprises both an aldehyde group and a functional vinyl group into the water-based solution containing the dissolved oligomeric vinyl alcohol (OLG1),
    - reacting the reactant with the dissolved oligomeric vinyl alcohol (OLG1) in a water-based acetalization reaction such that a compound (CMP1) based on the oligomeric vinyl alcohol (OLG1) is formed, wherein the compound (CMP1) contains a catenated carbon structure grafted onto oligomeric vinyl alcohol (OLG1), and wherein the catenated carbon structure

        ◦ contains a chain of at least 4 carbon atoms,
        ◦ terminates into an acetal at the first end of the chain, and
        ◦ terminates into a functional vinyl group at the other end of the chain, and

    - coating the compound (CMP1) on a cellulose fiber-based support layer (PAP1) as a primer layer (PRIM1), thereby forming the paper substrate (SUBST1) suitable for binding silicone in a catalytic hydrosilation reaction, wherein the vinyl group molality (b_{vin}) of the compound (CMP1) is equal to or higher than 0.2 millimoles per gram of the compound (CMP1).

3. The method according to claim 2, wherein the viscosity (η) of the reaction solution containing the compound (CMP1) based on the oligomeric vinyl alcohol is less than 8000 mPa·s after the water-based acetalization reaction.

4. The method according to claim 2 or 3, wherein the compound (CMP1) is based on oligomeric vinyl alcohol (OLG1) having a weight average molecular weight of less than 1000 g/mol.

5. The method according to any of the claims 2 to 4, wherein the oligomeric vinyl alcohol (OLG1) contains an average amount of repeat units in the range of 4 to 22.

6. The method according to any of the claims 2 to 5, wherein the dry matter content of the oligomeric vinyl alcohol (OLG1) in the water-based solution is equal to or higher than 18 wt.-%.

7. The paper substrate (SUBST1) according to claim 1 or the method for manufacturing a paper substrate (SUBST1) according to any of the claims 2 to 6, wherein

    - the primer layer (PRIM1) further contains a polymer (POL1), such as unmodified polyvinyl alcohol, starch, and/or carboxymethyl cellulose.

8. The paper substrate (SUBST1) or the method for manufacturing a paper substrate (SUBST1) according to any of the previous claims, wherein the vinyl group molality (b_{vin}) of the compound (CMP1) is equal to or higher than 0.2 millimoles per gram, preferably equal to or higher than 0.3 millimoles per gram, most preferably equal to or higher than 0.5 millimoles per gram of the compound (CMP1).

9. The paper substrate (SUBST1) or the method for manufacturing a paper substrate (SUBST1) according to any of the previous claims, wherein the vinyl group molality (b_{vin}) of the compound (CMP1) is in the range of 0.20 to 1.41, preferably in the range of 0.23 to 1.21, most preferably in the range of 0.28 to 1.01 millimoles per gram of the compound (CMP1).

10. The paper substrate (SUBST1) or the method for manufacturing a paper substrate (SUBST1) according to any of the previous claims, wherein the catenated carbon structure contains a chain of at least 5 carbon atoms, preferably in the range of 5 to 15 carbon atoms.

11. The method for manufacturing a paper substrate (SUBST1) according to any of the previous claims 2-10, wherein the organic molecule (MOL1) is 10-undecenal or 2,2'-dimethyl-4-pentenal.

12. The paper substrate (SUBST1) or the method for manufacturing a paper substrate (SUBST1) according to any of the previous claims, wherein the catenated carbon structure is a linear hydrocarbon that terminates into a functional vinyl group at the other end of the chain.

13. The paper substrate (SUBST1) or the method for manufacturing a paper substrate (SUBST1) according to any of the previous claims, wherein the cellulose fiber-based support layer (PAP1) is made of bleached chemical pulp.

14. Use of oligomeric vinyl alcohol (OLG1) having a weight average molecular weight of less than 1000 g/mol in a method for manufacturing a paper substrate (SUBST1).

15. A release liner (REL1) which comprises a paper substrate (SUBST1) according to any of the claims 1 or 7 to 13 and a release layer (SIL1) based on a silicone compound that has been applied on the paper substrate (SUBST1).

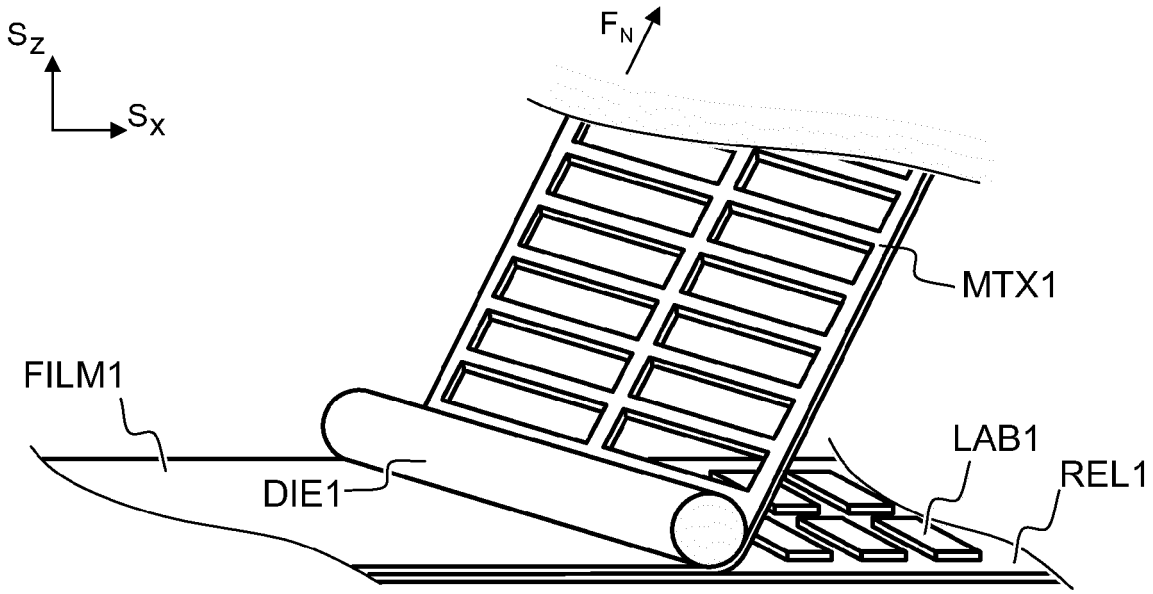

S_Z
S_X
F_N
MTX1
FILM1
LAB1
REL1
DIE1

Fig. 1

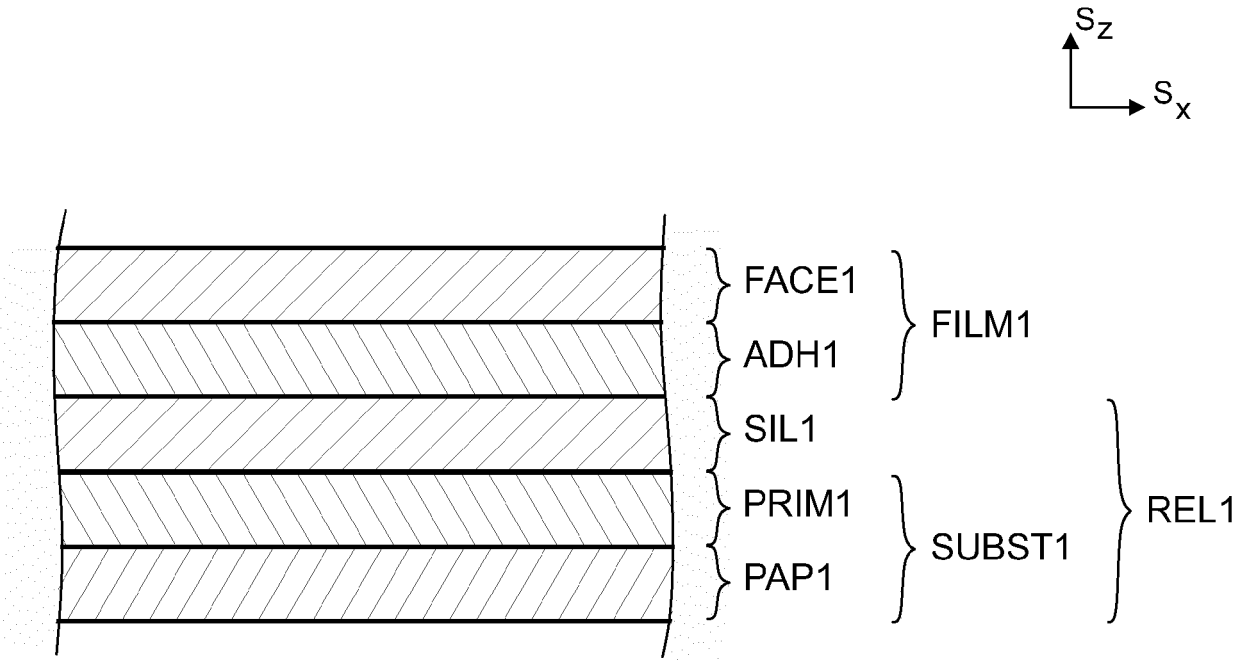

S_Z
S_X
FACE1
ADH1
FILM1
SIL1
PRIM1
PAP1
SUBST1
REL1

Fig. 2

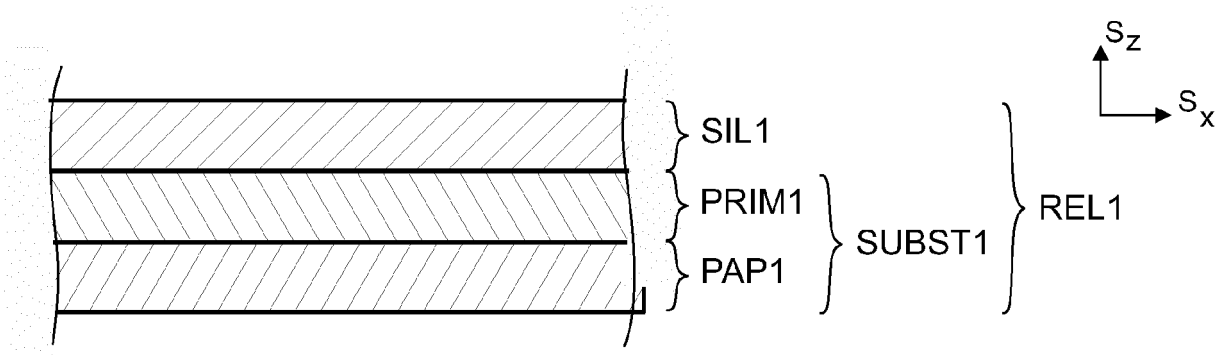

Sz
Sx
SIL1
PRIM1
PAP1
SUBST1
REL1

Fig. 3

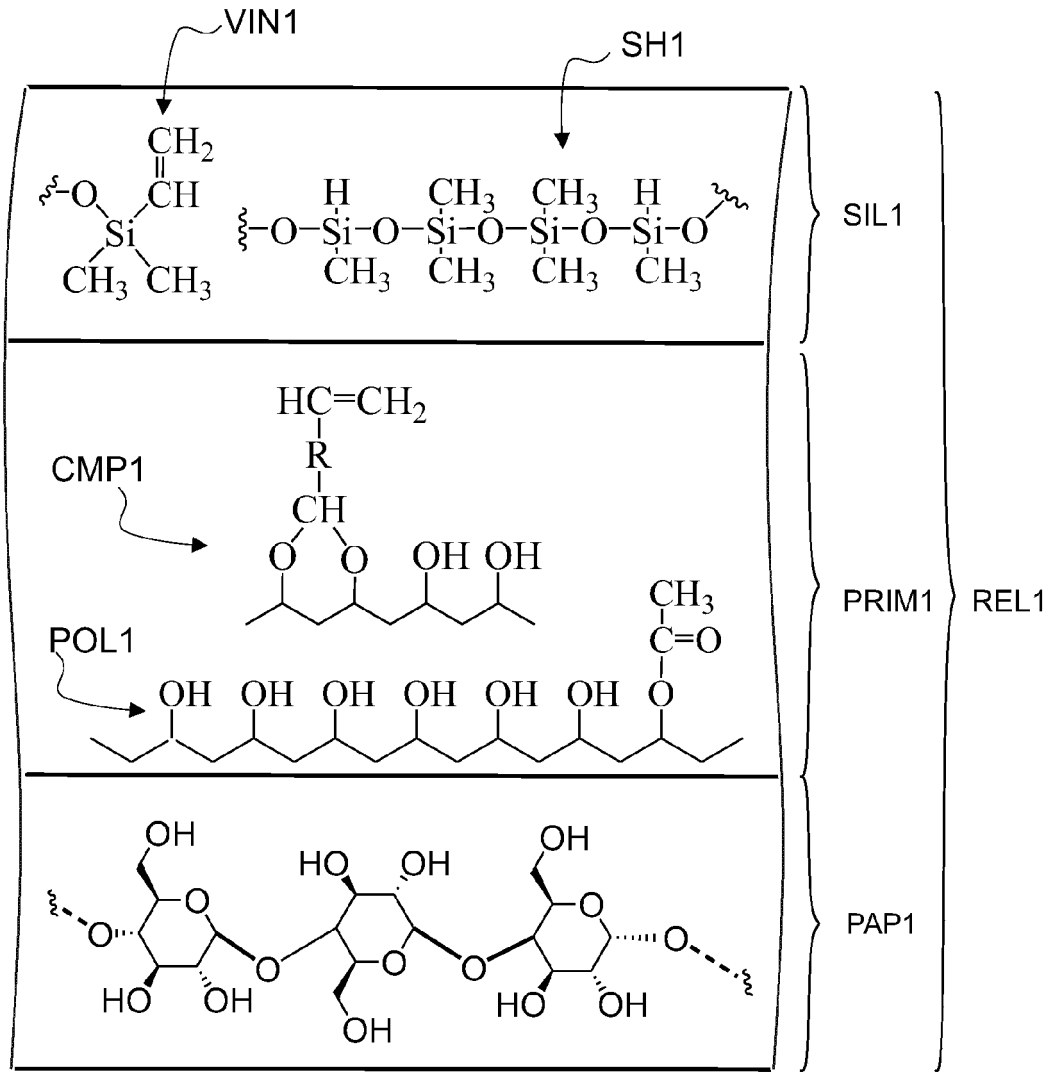

VIN1
SH1
SIL1
CMP1
POL1
PRIM1
REL1
PAP1

Fig. 4

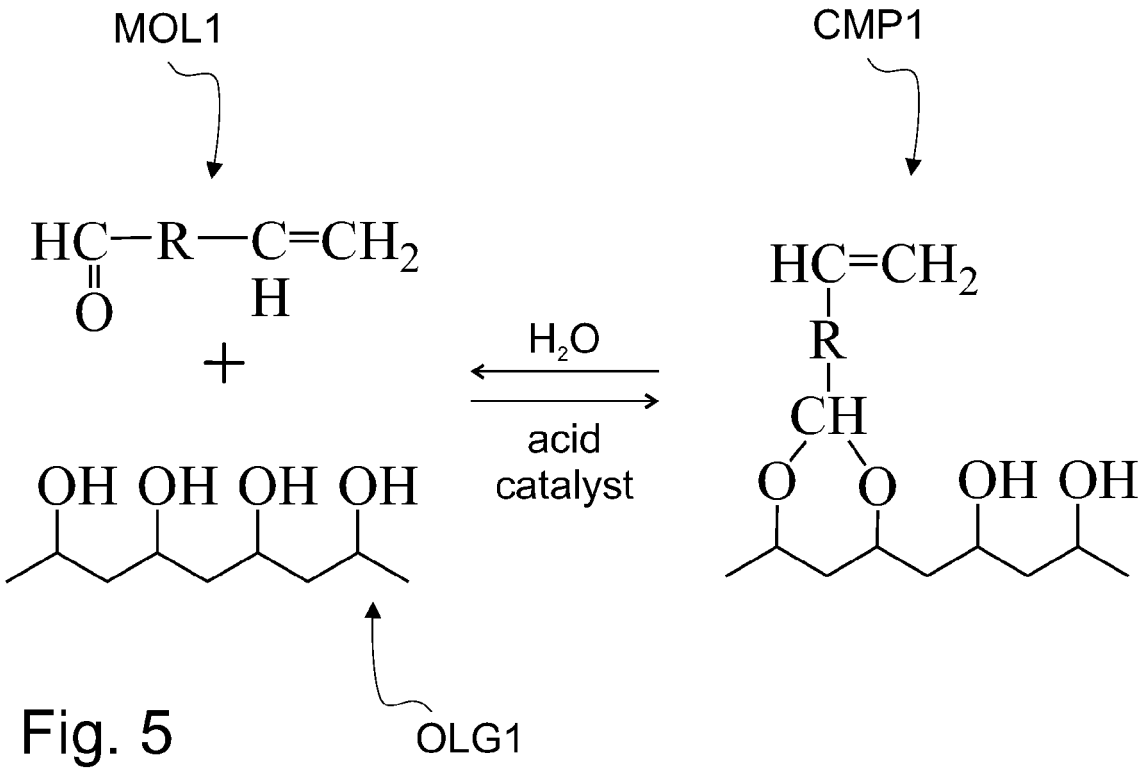

MOL1
CMP1
HC—R—C=CH2
O
H
+
H2O
acid
catalyst
HC=CH2
R
CH
O
O
OH OH
OH OH OH OH
OLG1

Fig. 5

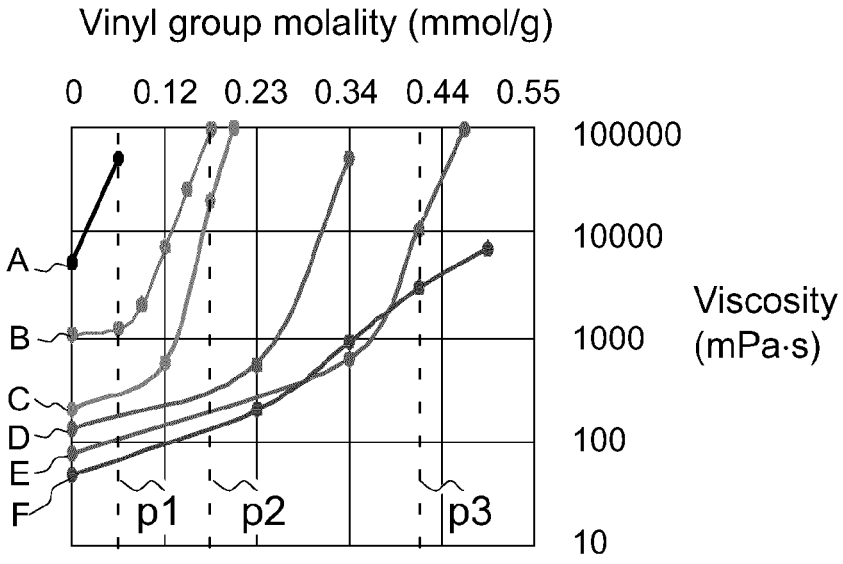

Vinyl group molality (mmol/g)
0
0.12
0.23
0.34
0.44
0.55
100000
10000
1000
100
10
Viscosity
(mPa·s)
A
B
C
D
E
F
p1
p2
p3

Fig. 6

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 19 9296

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2013/040134 A1 (DUFOUR MENNO [FR] ET AL) 14 February 2013 (2013-02-14)	1-4,6-15	INV.
A	* claims 1-16 *	5	D21H27/00
	* paragraph [0001] - paragraph [0012] *		D21H27/06
	* paragraph [0026] - paragraph [0030] *		D21H19/20
	* paragraph [0036] - paragraph [0045] *		D21H19/32
	-----		D21H19/60
X	US 3 859 269 A (MAURER HANS W) 7 January 1975 (1975-01-07)	14	
	* column 1, line 5 - line 62 *		
	* claims 1-3; example I *		

A	US 2012/094101 A1 (TANI PETRI [FI] ET AL) 19 April 2012 (2012-04-19)	1-15	
	* paragraph [0026] - paragraph [0033] *		
	* claims 1-17; figure 2 *		

A	EP 3 208 286 A1 (KURARAY CO [JP]) 23 August 2017 (2017-08-23)	1-15	
	* claims 1-8; table 1 *		
	-----		TECHNICAL FIELDS SEARCHED (IPC)
A	EP 2 574 643 A1 (UPM KYMMENE CORP [FI]) 3 April 2013 (2013-04-03)	1-15	D21H
	* claims 1-9; figure 2 *		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	17 January 2019	Billet, Aina

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 19 9296

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-01-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013040134 A1	14-02-2013	AR 080231 A1	21-03-2012
		AT 14079 U1	15-04-2015
		AU 2011219669 A1	02-08-2012
		BR MU9100104 U2	19-02-2013
		CA 2786827 A1	01-09-2011
		CL 2012002316 A1	30-11-2012
		CN 102762793 A	31-10-2012
		CN 202412832 U	05-09-2012
		CO 6630094 A2	01-03-2013
		DE 11706857 T1	16-01-2014
		DE 202011003029 U1	22-09-2011
		DK 2539505 T3	10-11-2014
		EP 2539505 A1	02-01-2013
		ES 2449314 T1	19-03-2014
		FI 9393 U1	20-09-2011
		FR 2956671 A1	26-08-2011
		HR P20150034 T1	27-02-2015
		HU 4052 U	30-01-2012
		IT MI20110062 U1	24-08-2011
		JP 5815567 B2	17-11-2015
		JP 6130879 B2	17-05-2017
		JP 2013531136 A	01-08-2013
		JP 2015180792 A	15-10-2015
		KR 20120120338 A	01-11-2012
		KR 20150119824 A	26-10-2015
		MX 349553 B	02-08-2017
		MY 156937 A	15-04-2016
		PT 2539505 E	12-12-2014
		RU 2012140499 A	27-03-2014
		RU 2015113583 A	27-10-2015
		SI 2539505 T1	30-01-2015
		TW M424241 U	11-03-2012
		TW 201137012 A	01-11-2011
		US 2013040134 A1	14-02-2013
		WO 2011104427 A1	01-09-2011
US 3859269 A	07-01-1975	NONE	
US 2012094101 A1	19-04-2012	CN 102388180 A	21-03-2012
		EP 2417296 A1	15-02-2012
		ES 2602090 T3	17-02-2017
		HU E030687 T2	29-05-2017
		US 2012094101 A1	19-04-2012
		WO 2010116045 A1	14-10-2010
EP 3208286 A1	23-08-2017	CN 107001510 A	01-08-2017

EPO FORM P0459

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

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 19 9296

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-01-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 3208286 A1	23-08-2017
		JP WO2016060241 A1	07-09-2017
		KR 20170069279 A	20-06-2017
		TW 201619217 A	01-06-2016
		US 2017226247 A1	10-08-2017
		WO 2016060241 A1	21-04-2016
EP 2574643 A1	03-04-2013	CN 102056994 A	11-05-2011
		CN 103741547 A	23-04-2014
		CN 103774494 A	07-05-2014
		DE 09757661 T1	28-03-2013
		DE 12191608 T1	01-08-2013
		DE 12191610 T1	01-08-2013
		DE 202009018749 U1	14-01-2013
		DE 202009018764 U1	02-04-2013
		DK 2300544 T3	22-05-2017
		DK 2574643 T3	21-03-2016
		DK 2574644 T3	02-05-2016
		EP 2300544 A1	30-03-2011
		EP 2574643 A1	03-04-2013
		EP 2574644 A1	03-04-2013
		EP 3009483 A1	20-04-2016
		ES 2564968 T3	30-03-2016
		ES 2570160 T3	17-05-2016
		ES 2594457 T3	20-12-2016
		FI 10176 U1	31-07-2013
		FI 10177 U1	31-07-2013
		FI 20085543 A	04-12-2009
		HK 1197281 A1	09-01-2015
		HU E027117 T2	29-08-2016
		HU E028923 T2	30-01-2017
		HU E029757 T2	28-03-2017
		WO 2009147283 A1	10-12-2009

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2011104427 A **[0008] [0010]**
- US 20030050394 A1 **[0059]**

Non-patent literature cited in the description

- **DVOŘÁČKOVÁ ; DUNG.** Degradation of polyvinyl alcohol (PVA) by Fenton process'', 13th International Research/Expert Conference ''Trends in the Development of Machinery and Associated Technology. *TMT,* 2009 **[0056]**
- **SEMSARZADEH ; MIRZAEI.** *Iranian Polymer Journal,* 2003, vol. 12 (1), 67-75 **[0060]**