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(54) Title: CELLULOSE FIBRE-BASED SUPPORT INTENDED TO BE SILICONIZED

(57) Abstract: A support based on cellulose fibres on which at least one organic molecule provided with an acid halide functional group able to create a covalent bond with the free OH functional groups of the cellulose after the release of the hydrogen halide is grafted, characterised in that the longest chain of the organic molecule has, at the free end thereof, a vinylic functional group. The use of the support for siliconizing.



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CELLULOSE FIBRE -BASED SUPPORT INTENDED TO BE SILICONIZED

The invention relates to a novel support based on cellulose fibres as well as to the manufacturing process thereof. It relates also to the use of the said support for
5 siliconizing.

The siliconized supports are used especially as supports of self-adhesive labels or adhesive tapes, for the feminine hygiene market, of envelope and weight/price label market, this list not being limiting.

10

In practice, the siliconized supports form a structure, on which the self-adhesive labels or products are maintained before the use thereof, thus allowing not only protecting them (especially the adhesive surface thereof), but also favouring the detaching thereof by assuring a perfect adhesive transfer.

15

The silicones intended to be applied on the base support are classified according to their cross-linking mode.

A first category consists of the silicones cross-linking under UV irradiation or electron
20 beams. This first category remains in the minority for economical and technical reasons.

A second category consists of the so-called "thermal cross-linking" silicones i.e. of silicones cross-linking at a surface temperature of the sheet of between 110 and 130 °C. In this case, the support covered with silicone is passed through a kiln, the
25 temperature of which is such that the temperature at the surface of the paper corresponds to the cross-linking temperature of the silicone.

The cost and the reactivity of the silicones require that the support, on which they are applied, fulfils a certain number of criteria.

30

First of all, the chemical structure of the support must not prevent the silicone system from cross-linking, i.e. the polyaddition reaction between the vinylic functional groups of the silicone resin and the hydrogen siloxane functional groups of the cross-linking agent. Next, it is necessary that the support is capable of fixing the silicone to the
35 surface thereof. Furthermore, considering the high cost of silicone, it is important that

the amount of silicone deposited on the support is as small as possible. To do this, the support has to form a barrier and thus limit as much as possible the penetration of the silicone inside the support. Likewise, the surface of the support has to be as regular as possible so as to allow a homogenous application of the silicone.

5

In other words, the first problem set is how to develop a support that allows simultaneously an efficient fixing and an optimal cross-linking of the silicone while still reducing as much as possible the penetration of the said silicone inside the support itself.

10

Moreover, according to the market concerned, the support intended to be siliconized has to be more or less transparent. Thus, for example, when the support is intended for office or large-sized labels, as well as to the hygiene and envelope market, in which the application is done manually, transparency is not an essential quality. On the other hand, transparency is required when the siliconized support is intended for the weight/price market.

15

Different supports have thus been developed, which fulfil more or less the above-mentioned objectives.

20

In general, the supports proposed for siliconizing consist of a cellulose support coated with a layer of water-soluble binder and latex able to comprise also pigments. These supports can be manufactured according to different processes by coating, by a size-press or even by a metering size-press followed by a calendering or a supercalendering step. All these techniques allow obtaining supports of different qualities in terms of mechanical resistance, density, silicone barrier property, dimensional stability and, as previously mentioned, transparency.

25

First of all, the so-called "coated" papers are distinguished, which have a good dimensional stability, but a lower mechanical resistance, transparency and density. In practice, these papers consist of a support based on cellulose fibres covered, by coating, with at least one, even two layers of a mixture common in paper-making, based on pigments (generally kaolin, calcium carbonate), binders (starch, PVA, latex), the coated paper obtained then being calendered. To obtain a satisfactory barrier to silicone, it is necessary to coat the paper in an amount of 5 to 12 g/m² of the pigment-

30
35

based mixture. Due to the above-mentioned characteristics, this support finds a more specific application in the field of office and large-sized labels, as well as on the hygiene and envelope market, in which the application is done essentially manually.

5 A second category of supports corresponds to papers known by the denomination of "glassine". These supports have a high density, mechanical resistance and transparency, but a lower dimensional stability than the above-mentioned coated papers. These papers are obtained by coating of a cellulose support by means of a mixture of water-soluble binders of the starch and/or polyvinyl alcohol type generally in
10 the presence of a viscosifying agent, for example a carboxymethyl cellulose (CMC). Unlike the coated papers, the cellulose support is more refined. Moreover and most of all, the coating step is replaced by a surface application step with a size-press or a metering size-press, before a final step, which is not a calendering step but a supercalendering step. Consequently, glassines of this type are pigment-free. In
15 practice, the weight of the coating is between 2 and 4 g/m². These papers correspond to so-called "standard" glassines and they are used especially for the weight/price market, as well as for the double-faced adhesive tape market. To a person skilled in the art, a surface application by size-press is technically distinguished from a coating. The treatment by size-press allows treating the two sides of the cellulose support at the
20 same time, as only one operation, whereas the coating is carried out on one side of the support and then possibly on the other side, as two separate operations.

A third support category corresponds to supports that could be called "pigmented glassines", the composition of which is very close to that of the previously described
25 glassines, with the difference that the coating mixture contains pigments as well.

The fourth type of support corresponds to supports by the name of "SCK", the structure of which is very close to that of a standard glassine, the essential difference being that the supercalendering operation is replaced, in most cases, by a calendering operation.
30 It follows that, compared to a standard glassine, a less transparent and less dense support is obtained.

A fifth category of cellulose supports is described in the document WO 01/04418. This document describes a glassine-type of paper, the coating layer of which is
35 distinguished from that of a standard glassine in that it consists of an aqueous solution

associating functionalized polyorganosiloxane (POS), grafted with a polymeric material of the acrylic type. As shown in this document, the barrier to silicone is considerably enhanced compared to the one obtained with the standard glassines.

- 5 At the moment, among the thermal cross-linking silicones are developed the so-called "LTC"-silicones (Low Temperature Curing), which correspond to silicones, the polymer and/or cross-linking agent of which has been chemically modified so as to allow the system to cross-link at lower temperatures than the standard systems, i.e. at temperatures lower than 100 °C, in practice of between 60 and 100 °C.

10

Considering these perspectives, there is thus a special interest for developing supports that can be siliconized with the LTC-silicones with the intention of either saving energy or enhancing the productivity.

- 15 The second problem that the invention proposes to solve is thus how to develop supports that can be siliconized with LTC, i.e. supports treated so that an efficient and long-lasting anchorage of LTC-silicones is enabled while still maintaining a perfect functionality of the siliconized paper.

- 20 The applicant has discovered that all the desired properties of a cellulose support intended to be siliconized, i.e. the cross-linking of the silicone and this, whatever the nature of the silicones used may be (thermal cross-linking - high or low temperature - under irradiation), the fixing of the silicone on the support, the ability to the silicone barrier and the transparency were either maintained, or strongly enhanced when
25 organic molecules were grafted on the cellulose support, one of the free ends of the molecules having a functional group capable of reacting with OH functions of the cellulose, whereas the other end has a free vinylic functional group intended for reacting with the cross-linking agent of the silicone system.

- 30 The reactivity of the free end on one hand and of vinylic functional groups on the other, of the organic molecule thus allows generating a covalent bond between the silicone and the cellulose, thus creating a perfect fixing of the silicones. Furthermore, the length of the chain of the organic molecule determines the more or less big barrier with regard to the silicone.

35

One of the technologies allowing the grafting of acid halide on the hydroxyl functional groups of a cellulose material is described particularly in the document WO 99/08784. In fact, this document describes the possibility of grafting acid halides, especially stearic acid chloride (C₁₈) or behenic acid chloride (C₂₂) on a solid support, and especially of paper. The length of the stearic or behenic chains gives barrier properties to the obtained paper. The applications cited in this document are essentially from the field of packaging, especially of food packages having a grease barrier. No reference is made to the possibility to use hydrophobic molecules, the free end of which would have a vinylic functional group.

The document WO97/12917 describes the possibility of utilising cellulose microfibrils having the OH functions esterified by an organic compound comprising possibly a radical vinyl. These microfibrils are used as reinforcement fillers in film type composites, or as structuring filler in paints, glues and inks. Usage as filler has two consequences.

The first one is that individualized and pretreated microfibrils are in the form of a dispersion mixed directly with the constituent or constituents of the final material. The second one is that cellulose fibres are a minority in the support, in practise less than 25 % by weight.

Thus, the invention relates to a support based on cellulose fibres, on at least one side of which is grafted at least one organic molecule provided with a function able to create a covalent bond with the free OH functional groups of the cellulose. It is characteristic to this support that the cellulose fibres represent at least 50 % by weight of the support and that the organic molecule has a vinylic functional group.

Of course, the organic molecule can be grafted alone or as a mixture with organic molecules having the same functional characteristics and/or with the organic molecules devoid of one or the other of these functional groups.

In a known manner, the vinylic functional group is distinguished from a double bond in that it is positioned at the end of the chain.

In an advantageous embodiment, the vinylic functional group is positioned at the end of the longest chain.

In the rest of the description and in the claims, the expression "support based on cellulose fibres" denotes a support comprising cellulose fibres, more or less refined according to the desired characteristics (density, transparency, mechanical characteristics) in practice in proportions of between 80 and 100 % by weight, the balance consisting, if need be, of synthetic fibres, e.g. of the polyester or polyethylene, polypropylene, polyamide, polyvinyl chloride type, and/or of artificial fibres (for example viscose, cellulose acetate), and/or of natural fibres (for example cotton, wool, wood pulp), and/or of carbon fibres (possibly active), and/or of mineral fibres (for example glass fibres, ceramic fibres), of mineral fillers such as starch, kaolin, CaCO₃ etc.

Likewise, the expression "organic molecule" should be understood to mean a molecule containing at least one element from C, H, O, N, nonmetals such as for example Cl, Br, F, I, S, P, metals such as Na, Li, K, Mg, Pb etc.

Of course, the organic molecule may be the result of a mixture of organic molecules corresponding to the definition above.

Finally, as far as the functional group of the organic molecule capable of creating a covalent compound with the free OH functional groups of the cellulose is concerned, it may concern a functional group chosen from a group comprising acid halide functional group, alkyl halide functional group, sulphonyl halide functional group, format halogen functional group, acid anhydride functional group (cyclic or linear), alkyl ketene dimer, alkylene oxide, isocyanate, aldehyde, di alkyl sulphate, the halide functional group being chosen from a group comprising chlorine, fluoride, iodine and brome.

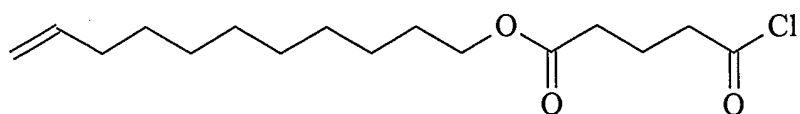
In practice, the organic molecule represents less than 5 %, advantageously between 0.01 and 1.5 %, by weight of the support.

Advantageously, the functional group is an acid chloride functional group.

Thus, and in a first embodiment, the organic molecule is undecylenic acid chloride.

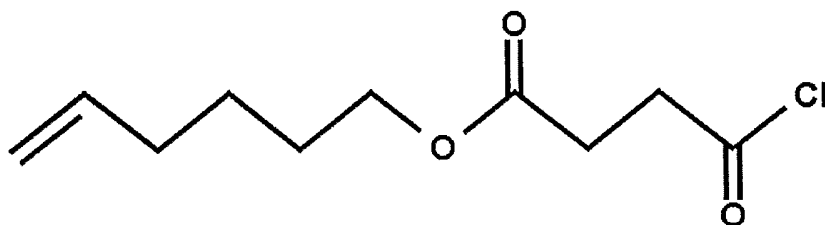
In a second embodiment, the organic molecule is pentanedioic acid, monoundec-10-enyl ester monochloride, which has the following formula:

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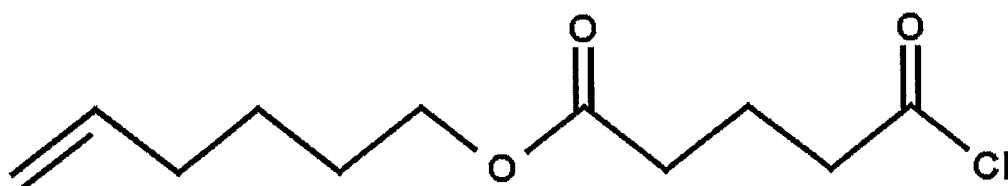
This molecule is obtained by an acylation reaction of ω -undecylenic alcohol on glutaric anhydride at temperatures in the order of 100°C. The generated carboxylic acid is then chlorinated in the presence of carbonyl chloride (COCl₂). The skeleton of the molecule consists of 16 carbon atoms and one oxygen atom coming from the ester bond. The organic chain thus contains 17 atoms, 3 of which are heteroatoms and is functionalized with a double vinylic bond at one of the ends and an acid chloride functional group at the other end. In the rest of the description and in the examples, this molecule is called C₁₇.

In a third embodiment, the organic molecule is butanedioic acid, mono-5-hexenyl ester, monochloride, which has the following formula:



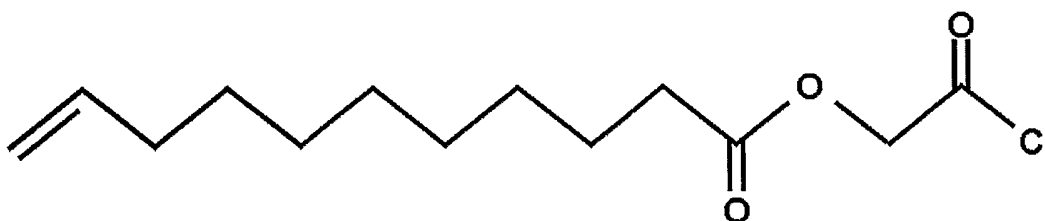
This molecule is obtained by a reaction of 5-hexanol on anhydride succinic and subsequent chlorination of the generated carboxylic acid functional group.

In a fourth embodiment, the organic molecule is pentanedioic acid, mono-5-hexenyl ester, monochloride, which has the following formula:



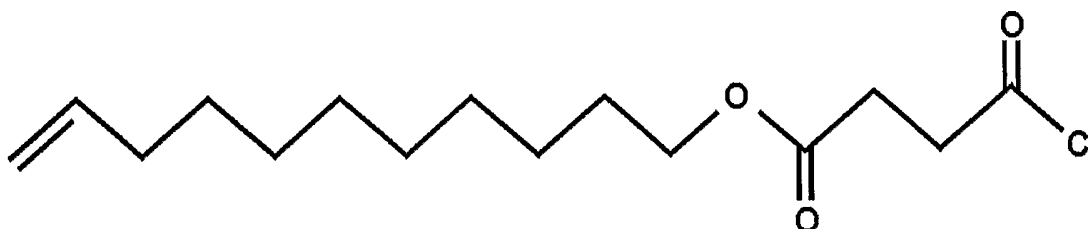
This molecule is obtained by a reaction of 5-hexanol on anhydride glutaric, after which the generated carboxylic acid functional group is chlorinated.

In a fifth embodiment, the organic molecule is glycolic acid, mono-10-undecenyl ester, monochloride, which has the following formula:



This molecule is obtained by reaction of the undecylenic acid on the glycolic acid hydroxyl functional group, after which the generated carboxylic acid functional group is chlorinated.

In a sixth embodiment, the organic molecule is butanedioic acid, monoundec-10-enyl ester, monochloride, which has the following formula:



This molecule is obtained by reaction of 10 undecenol on anhydride succinic, after which the generated carboxylic acid functional group is chlorinated.

As previously indicated, the support based on cellulose fibres may be in several forms.

First of all, the support based on cellulose fibres may correspond to a coated paper. In a first embodiment, the support based on cellulose fibres is covered on one side, by coating at least one, even two, layers of a mixture common in paper-making, the grafting of the organic molecule, on this same side, being carried out either before or after the calendering.

In practice, the cellulose support is covered with a composition based on:

- pigments,
- water-soluble binders,
- 5 - latex,
- common additives,

the composition being deposited in an amount of from 5 to 12 g/m² as dry matter and the support being calendered, either before or after the grafting of the organic molecule.

- 10 In a second embodiment, the coated paper, grafted on one side, is grafted on the other side. The second side can be coated beforehand. In this case, the grafting is carried out before or after the calendering step.

- 15 In a third embodiment, the paper is coated on one side and grafted on the other side, before or after the calendering.

The pigments can be of different nature, such as the kaolin, the aluminium hydroxide, talc etc., even though the calcium carbonate is preferred in practice. Likewise, starch, PVA etc. is advantageously used as a water-soluble binder.

20

In the rest of the description and in the claims, the expression "latex" denotes submicronic particles of polymers, such as for example butadiene styrene, vinyl acetate and acrylic polymers, dispersed into the water and stabilized by the presence of surfactants.

25

Likewise, by "common additives" is denoted the insolubilizing agents, the viscosifying agents, the antifoams and all the compounds necessary for the good rheology of the composition.

- 30 Another type of cellulose support, able to be treated with the organic molecules of the invention, corresponds to the glassines.

In this second case, the cellulose support is coated with a pigment-free composition and contains:

- 35 - between 90 and 100 % by dry weight of water-soluble binders,

- the balance to 100 % consisting, if need be, of common additives, the composition being deposited in an amount of from 2 to 4 g/m² as dry matter, for the two sides.

- 5 In a preferred embodiment, the composition contains, as a water-soluble binder, polyvinyl alcohol and starch. The advantage of using this type of binder is that it increases the number of free OH functional groups at the surface of the cellulose support and thus increases the number of fixing sites of the organic molecule.
- 10 As already said, this type of support is obtained by surface application of the composition with a size-press or a metering size-press on the two sides of the refined support based on cellulose fibres, followed by a supercalendering or a simple calendering step.
- 15 When we proceed to a supercalendering step of the support, the supercalendering operation proper, as well as the low basis weight of the layer, makes this support a paper corresponding to the definition of the glassine, i.e. a high transparency and density support having enhanced mechanical characteristics, as well as an excellent barrier to silicone.
- 20 On the other hand, when we proceed to a simple calendering step, the obtained paper has a lower density and transparency. In practice, these kinds of papers are, as already said, known by the name "SCK" and they are developed almost exclusively for the American market.
- 25 In all cases, one or two sides of the standard glassine or the SCK can be grafted. Furthermore, it is possible, according to the desired quality of the support, not to proceed to the calendering or supercalendering step.
- 30 The cellulose support can also be a support comprising pigments, called also by the name "pigmented glassine". In this case, the support is coated with a composition based on:
- pigments,
 - water-soluble binders,
 - 35 - latex,

- common additives,

the composition being deposited in an amount of from 4 to 8 g/m² and the support being supercalendered before or after the grafting of the organic molecule.

- 5 As previously, the grafting can be carried out on one or two sides of the cellulose support. Moreover, according to the desired quality of the support, it is possible not to proceed to the supercalendering step.

10 In a last embodiment, the grafting is carried out directly on the cellulose support, on one or two sides, in the absence of any preliminary treatment by a size-press, by a metering size-press or by coating, and before or after a possible calendering or supercalendering step.

15 More generally, any solid material having hydroxyl functional groups, on which the organic molecule of the invention is grafted, is also part of the invention. In an advantageous embodiment, the organic molecule is the pentanedioic acid, monoundec-10-enyl ester monochloride.

20 The object of the invention is also the above-described supports covered with silicone in practice in an amount of from 0.3 to 2 g/m², advantageously of between 0.5 and 0.8 g/m², preferably of 0.6 g/m². In practice, the quantity of the silicone applied depends on the characteristics of the base support.

25 The invention relates also to the manufacturing process of the support based on cellulose fibres.

30 More precisely, the invention relates also to a manufacturing process of a support based on cellulose fibres, according to which the previously described organic molecule is grafted on one or two sides before or after a possible calendering or supercalendering, the cellulose support having being or not treated beforehand by coating one or two sides by a size-press or by a metering size-press.

Of course, any grafting technique known by a person skilled in the art can be envisaged, such as for example grafting by solvent.

In a particular embodiment, the grafting is respectively carried out in two steps of:

- applying organic molecule on the support,
- subjecting the support thus treated to a gaseous flow, which is neutral with regard to the grafting reaction, at a temperature below the boiling temperature of the organic molecule.

In practice, the organic molecule is put in solution and then the solution is applied on the support. In a second embodiment, the organic molecule is sprayed directly on the support.

As already said, this advantageous grafting process is more particularly described in the document WO 99/08784.

The invention concerns also the use of the support based on cellulose fibres such as previously described for the siliconizing. It can involve thermal siliconizing at high temperature of between 110 and 130 °C, but also siliconizing with the LTC-silicones cross-linking at temperatures below to 100 °C. In this latter case, the applicant has in fact noticed, that the grafting of the organic molecule allowed fixing the LTC-silicones.

The invention and the advantages which stem therefrom will become more apparent from the following illustrative examples in support of the disclosed figures.

The figures 1 and 2 represent the penetration factors of the reagents Shirlastain and Malachite according to the quantity of the silicone layer applied on the non treated glassines (SiY 2010) and the same glassines treated with a constant concentration of undecylenic acid.

The figures 3 and 4 represent the penetration factors of the reagents Shirlastain and Malachite according to a growing concentration of undecylenic acid for a constant coating of silicone.

The figure 5 represents the penetration factors of the reagent Green Malachite according to the different quantities of the silicone layer applied on the non treated glassines and glassines treated at different concentrations of the pentanedioic acid, monoundec-10-enyl ester monochloride.

The figure 6 represents the penetration factors of the reagent Green Malachite according to the different quantities of the silicone layer applied on the non-treated glassines and glassines treated at a concentration of 0.25% of the pentanedioic acid, monoundec-10-enyl ester monochloride.

The figure 7 represents penetration factors of the reagent Green Malachite according to the different quantities of the silicone layer applied on the non-treated glassines and glassines treated at a concentration of 0.25 % butanedioic acid, mono-5-hexenyl ester monochloride (C11), pentanedioic acid, mono-5-hexenyl ester monochloride (C12) and glycolic acid mono-10-undecylen ester monohloride (C14).

EXAMPLE 1 : Study of the fixing of the silicone and the cross-linking capacity thereof

In this example, the fixing and the cross-linking of the silicone are compared when the cellulose support is treated with four different organic molecules.

Organic molecules:

- an organic molecule free of a vinylic functional group, such as stearic acid chloride (C₁₈): CH₃-(CH₂)₁₆-CO-Cl or behenic acid chloride (C₂₂): CH₃-(CH₂)₂₀-CO-Cl,
- an organic molecule having a double bond integrated in the carbonaceous chain, such as e.g. oleic acid chloride (C₁₈): CH₃(CH₂)₇-CH=CH-(CH₂)₇-CO-Cl,
- an organic molecule of the invention having a vinylic functional group at the free end of the longest chain thereof, such as undecylenic acid chloride (C₁₁) : CH₂=CH-(C-CO-Cl),
- an organic molecule having the same number of carbone, but devoid of vinylic functional group, such as e.g. lauric acid chloride (C₁₂): CH₃-(CH₂)₁₀-CO-Cl.

The grafting of these molecules in the form of chloride is carried out at concentrations of between 0.1 and 1.5 % by weight and this is done on finished cellulose supports, i.e. on calendered cellulose supports. Each of the supports is immersed in a solution of acid chloride into a solvent of petroleum ether solvent for 10 seconds. The amount of solvent absorbed by the support is determined beforehand in order to determine the suitable concentration. The reaction is carried out for 30 minutes at 100°C.

Papers

The paper supports used are the following:

- SILCA 2010 Yellow (64 g/m²) standard glassine: reference 1,
- 5 - Prototype of glassine generating a poor fixing of the silicone: reference 2,
- SILKRAFT 9564 White (62 g/m²) standard glassine: reference 3.

Silicone

The silicone provided by RHODIA is composed of a system consisting of:

- 10 - polydimethylsiloxane Rhodia PDMS 11367, molecular mass 10 000 g/mol, n: 130,
- cross-linking agent (Rhodia XL 12031, molecular mass 3 000 g/mol, n: 50),
- platinum catalyst (Rhodia catalyst 12070).

15 Siliconizing condition

The silicone bath contains:

- 25 g of PDMS 11367,
- 1.45 g of cross-linking agent 12031, and
- 0.78 of platinum catalyst 12070.

20

The association of these 3 products has been voluntarily created by the applicant to provide a silicone system very sensitive to fixing on glassine support.

25 The silicone is applied on the cellulose support by means of a blade coater (Euclid). In all the cases, the pressure of the blade is adapted to the thickness of the silicone, which is about 1 μ m.

After coating the paper with a amount silicone of 1 g/m², the sample is subjected to cross-linking in a ventilated kiln at 150 °C for 30 seconds.

30

Fixing analysis

It is carried out by means of a test called Rub Test. This internal test measures the residual silicone content of the siliconized paper after an abrasion operation of the described siliconized surface according to an internal standard.

35

A low value of the Rub Test means a poor fixing of the silicone film on the support (Rub off). With the silicone formula used in the examples, the fixing of the silicone is estimated to be good if the Rub Test value is higher than 90 %.

5 Cross-linking analysis

It is measured by means of a test called Poly Test. This internal test measures the residual silicone content of a siliconized paper after immersion into an organic solvent. A value < 95 % means a dissatisfactory cross-linking of the silicone film on the support, whatever the used silicone system may be.

10

Results

1. Stearic acid chloride

The results are given in the following table.

15

<i>Paper</i>	<i>Fatty acid chloride</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
Silkraft White Reference 3	No treatment	0 %	98 %	98 %
	Stearic (C ₁₈)	0.1 %	42 %	97 %
	Stearic (C ₁₈)	0.5 %	35 %	97 %
	Stearic (C ₁₈)	1 %	20 %	97 %
	Stearic (C ₁₈)	1.5 %	17 %	98 %

Table 1

20

As can be seen from this table, if the Poly Test is satisfactory and this, whatever the concentration of the stearic acid chloride may be, on the other hand, the Rub Test is very unfavourable, which means that the cellulose supports, on which long molecules denoted of vinylic functional groups are grafted, are unsuitable for siliconizing.

On the other hand, it seems that the cross-linking is satisfactory, even with long carbonaceous chains such as those of stearic acid.

25

2. Behenic acid chloride

Similar results are obtained with the behenic acid chloride because the Rub Test falls, according to the fatty acid concentration, to 18 %. On the other hand, the results of the Poly Test remain satisfactory.

5

<i>Paper</i>	<i>Fatty acid chloride</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
Silkraft White Reference 3	No treatment	0 %	98 %	98 %
	Behenic (C ₂₂)	0.1 %	30 %	96 %
	Behenic (C ₂₂)	0.5 %	29 %	97 %
	Behenic (C ₂₂)	1 %	21 %	96 %
	Behenic (C ₂₂)	1.5 %	18 %	98 %

Table 2

3. Oleic acid chloride

The results are given in table 3.

10

<i>Paper</i>	<i>Fatty acid chloride</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
Silkraft White Reference 3	No treatment	0 %	98 %	98 %
	Oleic (C ₁₈ with=)	0.1 %	37 %	98 %
	Oleic (C ₁₈ with=)	1 %	17 %	97 %

Table 3

As can be seen from this table, with unsaturated oleic acid chloride similar results to those obtained with the saturated fatty acids are obtained, and this for the same length of the carbonaceous chains. Consequently, this means that the presence of one double bond in the body of the carbonaceous chain does not react with the hydrogen-siloxane functional groups of the cross-linking agent.

15

4. Undecylenic and lauric acid chloride

The results are given hereinafter in table 4.

<i>Paper</i>	<i>Fatty acid chloride</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
Silca Yellow Reference 3	No treatment	0 %	98 %	99 %
	Undecylenic (C ₁₁ with =)	0.1 %	98 %	99 %
	Undecylenic (C ₁₁ with =)	0.5 %	99 %	99 %
	Lauric (C ₁₂)	0.1 %	36 %	96 %
	Lauric (C ₁₂)	0.5 %	24 %	95 %

Table 4

5

As can be seen from this table, when the organic molecule is chosen so as to have a vinylic end, then the results of the Rub Test are entirely satisfactory because they are equal to 98 %, even up to 99 % for a concentration of undecylenic acid of 0.5 %. Consequently, this confirms that the undecylenic acid chloride reacts well by the two ends thereof, on the one hand with the hydroxyl bonds of the cellulose or of the size-press slurry, and on the other hand by the vinylic functional group thereof with the hydrogen-siloxane bonds of the cross-linking agent. On the other hand, for a saturated acid of the same type corresponding to a lauric acid, the results in terms of Rub Test are not satisfactory.

15

To confirm the relevance of the use of molecules of the invention, a similar test had been carried out with a glassine prototype (reference 2), the Rub Test of which is of 57 %. The results are given in table 5.

Paper	Fatty acid chloride	%	Rub Test (%)	Poly Test (%)
Prototype Reference 2	No treatment	0 %	57 %	98 %
	Undecylenic (C ₁₁ with =)	0.1 %	90 %	98 %
	Undecylenic (C ₁₁ with =)	0.5 %	96 %	97 %
	Undecylenic (C ₁₁ with =)	1 %	97 %	98 %
	Lauric (C ₁₂)	0.5 %	18 %	97 %

Table 5

5 As can be seen from this table, when the same support is treated with the undecylenic acid chloride, the Rub Test starts from 90 % and goes up to 97 % for an undecylenic acid concentration of 1 %. When the same support is treated with the lauric acid chloride, inverse results are observed. On the other hand, the Poly Test remains satisfactory for all cases of the figure.

10

As a conclusion of this example, the molecules of the invention thus allow enhancing the fixing of the silicone on the cellulose support while still maintaining a perfect cross-linking of the silicone system.

15 EXAMPLE 2 : Silicone barrier ability (organic molecule = undecylenic acid)

The silicon barrier ability is measured with a laboratory siliconizing test.

20 This test compares and analyses the ability of several papers to generate a good silicone covering.

A silicone covering is considered good if the silicone film applied on the paper remains sufficiently at the surface thereof, thus allowing a homogenous protection of the paper surface for the further transformation steps (gluing, die cutting etc.).

25

It is always possible to obtain a good silicone covering by depositing a considerable amount of silicone, but the cost of the silicone requires very low silicone coatings, the range of which is estimated to vary between 1 and 2 g/m². Such being the case, a

paper generating a good silicone barrier ability is a paper allowing obtaining a good silicone covering with a silicone coating in a smaller amount than that of the reference paper.

- 5 The silicone covering is evaluated with the coloured reagents called Green Malachite or Shirlastain A, which, applied at the surface of the siliconized paper, react according to the level of protection given by the silicone film: (respectively + green and – yellow if the silicone covering is insufficient), the obtained tones being analysed with a colorimetry technique and expressed by an IP-value in per cent. As far as the two
10 reagents are concerned, the lower the IP-value, the better the silicone covering.

The comparison of the silicone barrier between two papers is thus made in the following conditions.

- 15 With the blade applicator described in the example 1, different silicone coatings are applied on the papers (a standard range is 0.6 – 0.8 and 1.0 g/m² of silicone), the silicone coatings are analysed with the coloured reagents and the IP-curves=f (silicone coatings) are straightened. The paper allowing obtaining the lowest IP with the thinnest silicone coating has better silicon barrier ability: the curve thereof will be by definition,
20 flatter.

- The curves of the figures 1 and 2 show the penetration factor with the reagents Shirlastain and Green Malachite with different silicone coatings of between 0.6 and 1 g/m² on the non-treated glassines (SiY 2010) and of the same glassines treated with
25 undecylenic acid chloride at a constant concentration.

- For the treated glassine, the IP-curve=f (silicone coating) is, whichever the coloured reagent may be, flatter and always situated below the curve obtained with the non-treated standard glassine.

30

It is clear that the use of undecylenic acid chloride allows enhancing in a very considerable manner the silicone barrier ability of a standard glassine.

- The figures 3 and 4 represent the penetration factor curves with Shirlastain A and
35 Green Malachite when the silicone is applied in an amount of 0.60 g/m² for a growing

- C11 concentrations. As showed by these curves, a small amount of acid chloride allows dividing the IP by two. In other words, if a thin coating in an amount of 0.60 g/m² is deposited at the surface of a non-treated glassine, the IP-value of about 20 % gives evidence of a rather mediocre silicone cover quality (but normal for a standard glassine with such a small amount of coating), whereas the same glassine treated with 0.25 % of undecylenic acid chloride has an IP-value of only 10 % with regard to the IP of Shirlastain and 5 % with regard to the IP of Green Malachite, which testify for an excellent silicone covering level for such a low amount of coating.
- 5
- 10 The conclusion is that even a small amount of undecylenic acid chloride allows enhancing essentially the silicone barrier of a glassine.

EXAMPLE 3 : Support treated with pentanedioic acid monoundec-10-enyl ester monochloride (C₁₇)

15

In all the tests, the support used is a support called SILCA CLASSIC (standard glassine) (60 g/m²) sold by the applicant.

20

The grafting of organic molecule on the support is obtained in the same conditions as those indicated in the example 1.

Likewise, the silicone, the siliconizing conditions, the fixing analysis and the cross-linking analysis are carried out in the same conditions as in example 1.

25

As for the silicone barrier ability, it is evaluated according to the same colorimeter technique (Green MALACHITE) than the one described in the preceding example 2.

1. Poly Test and Rub Test

Paper	Organic molecule	%	Rub Test (%)	Poly Test (%)
SILCA Classic	C ₁₇	Ref.=0 %	93.53 %	97.31 %
	C ₁₇	0.10 %	96.65 %	98 %
	C ₁₇	0.25 %	97.42 %	97 %
	C ₁₇	0.50 %	98.21 %	98 %
	C ₁₇	1.00 %	98.23 %	97.28 %
	C ₁₇	1.50 %	99.21 %	98.36 %

Table 6

5

The results of the table 6 show that the silicone fixing and cross-linking performances are very good (Rub Test and Poly Test > 97 %) and they are identical to the results obtained with the C11 (see example 2).

10 2. Silicone barrier : IP test Green Malachite

The glassine is treated with a C₁₇ quantity of between 0.05 and 0.5 %. The support is first coated with an amount of silicone of between 0.6 g/m² and 1.2 g/m². To study the silicone barrier in even more aggressive conditions than in the example 2, we have explored a considerably lower silicone coating range. As the blade coater Euclid did not allow depositing silicone quantities below 0.6 g/m² in standard conditions, it has been necessary to dilute (50 % in mass with an organic solvent – toluene) the silicone bath. This dilution allows depositing up to 0.3 g/m² of silicone on the tested papers. The results are represented on the figure 5 and 6.

As these figures show, the silicone coatings vary between 0.3 g/m² and 1.2 g/m². The non treated glassine has a very low IP-value (2 %) for a silicone amount of 1.2 g/m². This value can be taken as a reference value. When the amount of silicone on the non-treated support is reduced, the IP value increases from 7 % for 1 g/m² to 47 % for 0.3 g/m². On the other hand, the glassines treated with the C₁₇ have a much flatter curve (except for the case of the figure, in which the support is coated with 0.05 % of the molecule), see figure 5. Considering that the upper limit of the penetration factor is at 2

25

%, figure 6 shows that the IP values of the treated glassines are situated below this limit for a minimum quantity of silicone in the order of 0.5 g/m².

These results show that the IP value is below 2 % when the paper support is treated with the molecule C₁₇ of the invention at a concentration of 0.25 % and coated with a silicone layer of 0.5 g/m². In other words, this example shows that the amount of silicone actually used on the glassines in the trade (1.2 g/m²) could be reduced by 50 % to take place in about 0.6 g/m² with a paper treated with C₁₇.

These results show that while still allowing an excellent fixing and a very good cross-linking of the silicone film, the grafting on a standard glassine of a small amount of the pentanedioic acid monoundec-10-enyl ester monochloride (C₁₇) (0.25%) allows a very considerable reduction of the silicone coating.

EXAMPLE 4 : Study of the fixing of LTC-silicone on a cellulose support treated with undecylenic acid chloride (C₁₁=)

In this example, the fixing and the cross-linking of the LTC-silicone (Low Temperature Curing) are compared when the cellulose support is treated or not treated by an acid chloride having a vinylic functionality (undecylenic acid chloride: C₁₁=) or without it (saturated acid chloride: lauric acid chloride: C₁₂).

Organic molecules:

- an organic molecule of the invention having a vinylic functional group at the free end of the longest chain thereof, as well as an acid chloride functional group, such as undecylenic acid chloride : (C₁₁=:CH₂=CH-(CH₂)₈-CO-Cl),
- an organic molecule having the same number of carbon, but devoid of a vinylic functional group (saturated carbonaceous chain) composed of an acid chloride functional group e.g. lauric acid chloride : (C₁₂: CH₃-(CH₂)₁₀-CO-Cl).

Cellulose support:

SILCA 2010 YELLOW (64 g/m²): standard glassine paper

LTC-silicone:

The LTC-silicone provided by Wacker composed of a system:

- of polydimethylsiloxane PDMS D 920,
- of a cross-linking agent V 525 XL,
- of a platinum catalyst C 05.

5 Siliconizing conditions:

The Wacker LTC-silicone bath contains:

- 18.074 g of PDMS D 920,
- 1.432 g of cross-linking agent V 525 XL,
- 2.14 g of platinum catalyst C 05.

10

The silicone is applied on the cellulose support as in the previous examples by means of a blade coater (Euclid). In all the cases, the pressure of the blade is adapted so that the quantity of the deposited silicone is of 1 g/m². After the deposit on the paper, the sample is subjected to the cross-linking in a ventilated kiln at 80 °C for 30 seconds.

15

The fixing analysis (Rub Test) and the cross-linking analysis (Poly Test) are carried out in the same conditions as in the example 1.

Results:

20 The fixing and cross-linking results are collected in table 7.

<i>Paper</i>	<i>Organic molecule</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
SILCA 2010 Yellow	/ (ref)	0	15.3 %	98.6 %
SILCA 2010 Yellow	Undecylenic (C ₁₁ =)	0.1 %	98.6 %	96.6 %
SILCA 2010 Yellow	Undecylenic (C ₁₁ =)	0.5 %	99.1 %	97 %
SILCA 2010 Yellow	Lauric (C ₁₂)	0.1 %	14.1 %	97.6 %
SILCA 2010 Yellow	Lauric (C ₁₂)	0.5 %	12.3 %	97.2 %

Table 7

25 The results obtained from the Poly Tests are satisfactory, whichever the papers (treated or not) may be. The LTC temperature conditions (80 °C for 30 seconds instead of 150 °C for the conventional system) as well as the different cellulose supports (treated or not) allow a good cross-linking (Poly Test 95 %) of the LTC-silicone.

Moreover and contrary to the standard silicone system provided by Rhodia (cf. example 1), the LTC-silicone system of Wacker adheres only very weakly to the standard glassine (Silca 2010 yellow). In fact, the 15.3 % value of the Rub Test shows that the fixing is almost non-existent, whereas with the Rhodia silicone system it is 98 %.

5 %. A treatment of this cellulose support with undecylenic acid chloride (0.1 and 0.5 %) allows the support, once treated, to fix silicone more than is convenient (98.6 and 99.1 %, respectively).

10 The same support, but treated with the saturated equivalent of undecylenic acid chloride, lauric acid chloride, has also very low rub off-values (14.1 and 12.3 % for the respective treatments of 0.1 and 0.5 % of C12). In this case, the grafted saturated acid chloride does not enhance the fixing of LTC-silicone on the cellulose support.

15 These results of the Rub Test show that the presence of the vinylic functional group grafted on the cellulose support allows generating a strong fixing between the LTC-silicone and the treated glassine contrary to the non-treated glassine or the glassine treated with lauric acid chloride. Consequently, this confirms the double chemical reaction of undecylenic acid chloride in this example. At first, the acid chloride functional groups form covalent bonds with the hydroxyl functional groups of the

20 cellulose support. Subsequently, during the siliconizing operation, the hydrogen – siloxane functional groups of the LTC cross-linking agent react by addition with the double vinylic bonds of the grafted molecule. Thus, the generated chemical bonds between the cellulose support and the cross-linked LTC-silicone allow an acceptable fixing between the two materials (Rub Test 90 %). Previously, this fixing was inexistent

25 (Rub Test before treatment: 15.3 %).

As a conclusion, the molecule of the invention, composed on the other hand of an acid chloride functional group at one of the ends thereof, and on the other hand of a double vinylic bond at the other end thereof, allows strongly enhancing the fixing of the silicone

30 of the LTC-type (Low Temperature Curing) on a cellulose support while still maintaining a perfect cross-linking of the LTC-silicone system.

EXAMPLE 5 : Support treated with butanedioic acid, mono-5-hexenyl ester monochloride (C₁₁), pentanedioic acid mono-5-hexenyl ester monochloride (C₁₂) and

35 glycolic acid mono-10 undecylen ester monochloride (C₁₄)

In all tests, the used support is a support called SILCA CLASSIC (standard glassine) (60 g/m²) sold by the applicant.

- 5 The grafting of the organic molecule on the support is obtained in the same conditions as those indicated in example 1 at a concentration corresponding 0.25 % by weight.

Further, the silicone, siliconizing conditions, fixing analysis and cross-linking analysis are carried out in the same conditions as in example 4 (use of LTC silicone or the sample is subjected to cross-linking in a ventilated kiln at 80°C during 30 seconds).

The ability to silicone barrier is, in its turn, evaluated according to the same colorimetric technique (Green Malachite) as the one described in example 2 earlier.

15 1. Poly Test and Rub Test

<i>Paper</i>	<i>Organic molecule</i>	<i>%</i>	<i>Rub Test (%)</i>	<i>Poly Test (%)</i>
SILCA Classic	/	/	14 %	98 %
	C ₁₁	0.25 %	98 %	98 %
	C ₁₂	0.25 %	98 %	97 %
	C ₁₄	0.25 %	98 %	98 %

Table 8

As can be seen from the table, the tested molecules represent nearly perfect rub test and poly test results, which was not the case with a non-treated support, where the silicone adhesion is relatively weak (rub test of 14 %) (cf. example 4).

2. Silicone barrier: IP Green Malachite test

25 The glassine is treated with a quantity of C₁₁, C₁₂ and C₁₄ equal to 0.25 % during 30 minutes at 100°C. The support is then coated with a quantity of silicone of between 0,3 g/m² and 1 g/m².

The results are represented in figure 7. Reference glassine shows an IP value of 33 % for a silicone quantity of 0.3 g/m². On the contrary, the IP values of treated glassines are systematically below this value for a minimum quantity of silicone of 0.3 g/m² (i.e.: IP malachite = 10 %).

CLAIMS

1. A support based on cellulose fibres on at least one side of which is grafted at least one organic molecule provided with a functional group capable of creating a covalent
5 bond with the free OH functional groups of the cellulose, characterised in that the cellulose fibres represent at least 50 % by weight of the support, and in that the organic molecule has a vinylic functional group.
2. A support according to claim 1, characterised in that the vinylic functional group is
10 positioned on the longest chain.
3. A support according to claim 1, characterised in that the functional group capable of creating a covalent bond is chosen from the group comprising acid halide functional group, alkyl halide functional group, sulphonyl halide functional group, format halogen
15 functional group, acid anhydride functional group (cyclic or linear), alkyl ketene dimer, alkylene oxide, isocyanate, aldehyde, di alkyl sulphate, the halide functional group being chosen from a group comprising chlorine, fluoride, iodine and brome.
4. A support according to claim 1, characterised in that the organic molecule is acid
20 chloride chosen from a group comprising pentanedioic acid, monoundec-10-enyl ester monochloride, butanedioic acid, mono-5-hexenyl ester, monochloride, pentanedioic acid, mono-5-hexenyl ester, monochloride, glycolic acid, mono-10-undecenyl, ester monochloride, butanedioic acid, monoundec-10-enyl ester, monochloride.
- 25 5. A support according to claim 1, characterised in that the organic molecule represents between 0.01 and 1.5 % by weight of the support.
6. A support according to claim 1, characterised in that the side of the cellulose support intended to be grafted is covered beforehand by coating with a composition
30 based on:
 - pigments,
 - water-soluble binders,
 - latex,
 - common additives,

the composition being deposited in an amount of from 5 to 12 g/m² as dry matter, and the support being calendered.

7. A support according to claim 6, characterised in that the non coated side is also grafted.

8. A support according to claim 1, characterised in that the cellulose support is coated with a pigment-free composition and contains:

- between 90 and 100 % by dry weight of water-soluble binders,
- the balance to 100 % consisting, if need be, of common additives, the composition being deposited in an amount of 2 – 4 g/m² as dry matter, for the two sides.

9. A support according to claim 8, characterised in that the cellulose support covered with the composition has been subjected to a supercalendering step.

10. A support according to claim 8, characterised in that the cellulose support covered with the composition has been subjected to a calendering step.

11. A support according to claim 8, characterised in that the two sides of the support are grafted.

12. A support according to claim 1, characterised in that the cellulose support is coated with a composition based on:

- pigments,
- latex,
- water-soluble binders,
- common additives,

the composition being deposited in an amount of from 4 to 8 g/m² and the support thus being supercalendered, before or after the grafting of the molecule.

13. A support according to claim 10, characterised in that the two sides of the support are grafted.

14. A support according to one of claims 1 to 13, characterised in that it is covered with silicone deposited in an amount of from 0.3 to 2 g/m², advantageously of from 0.5 to 0.8 g/m², preferably of 0.6 g/m².
- 5 15. A manufacturing process of a support based on cellulose fibres, according to which, on the free OH functional groups of the support is grafted at least one organic molecule having a vinylic functional group and being provided with an acid halide functional group able to create a covalent bond with the said free OH functional groups after the release of the hydrogen halide, the grafting being carried out on one or two
10 sides before or after a possible calendering or supercalendering, the cellulose support having been treated or not having been treated beforehand by coating the one or two sides, by a size-press or by a metering size-press.
16. The use of the support object of one of the claims 1 to 14 for siliconizing.

1/4

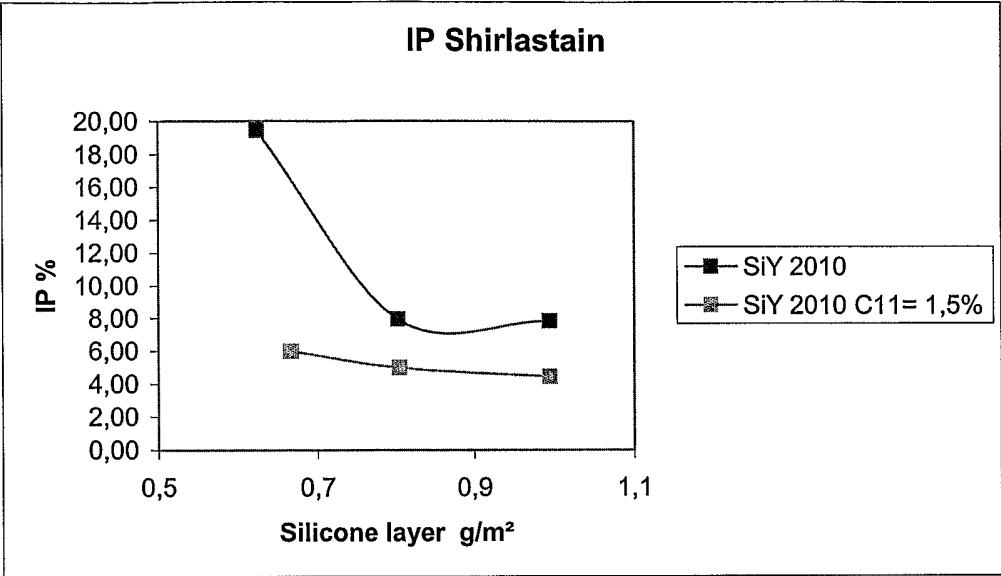


Figure 1

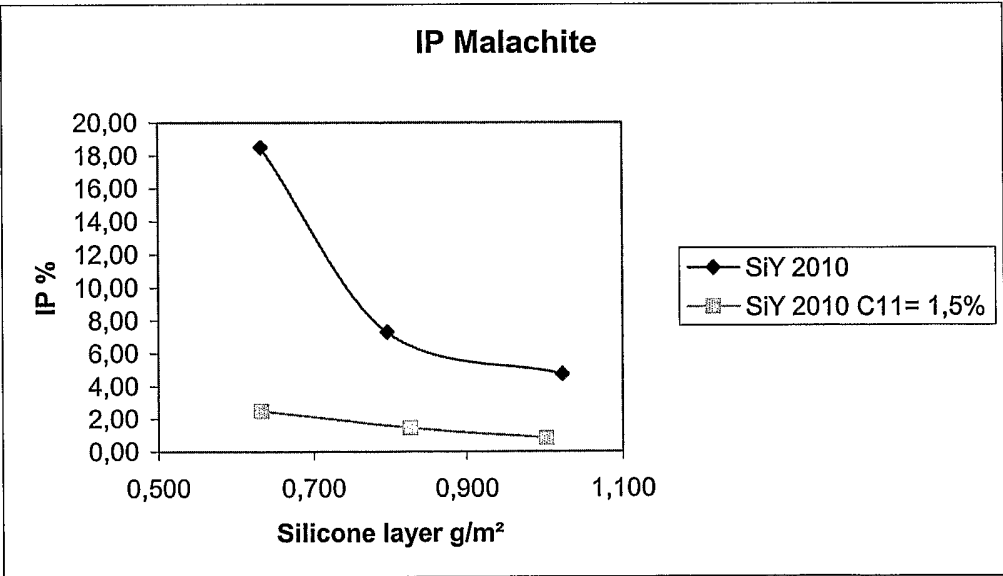


Figure 2

2/4

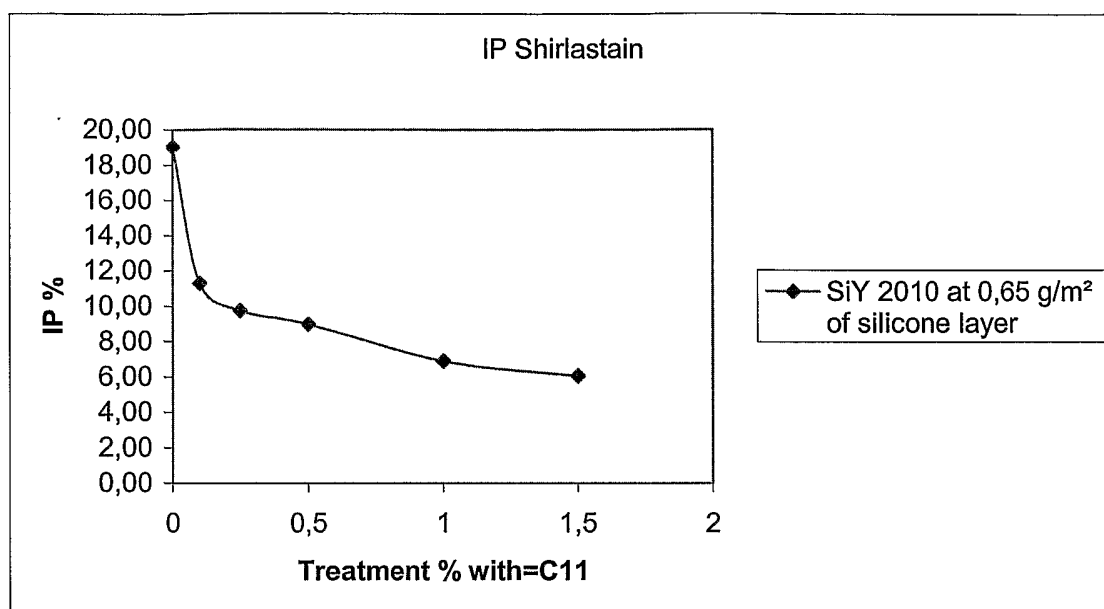


Figure 3

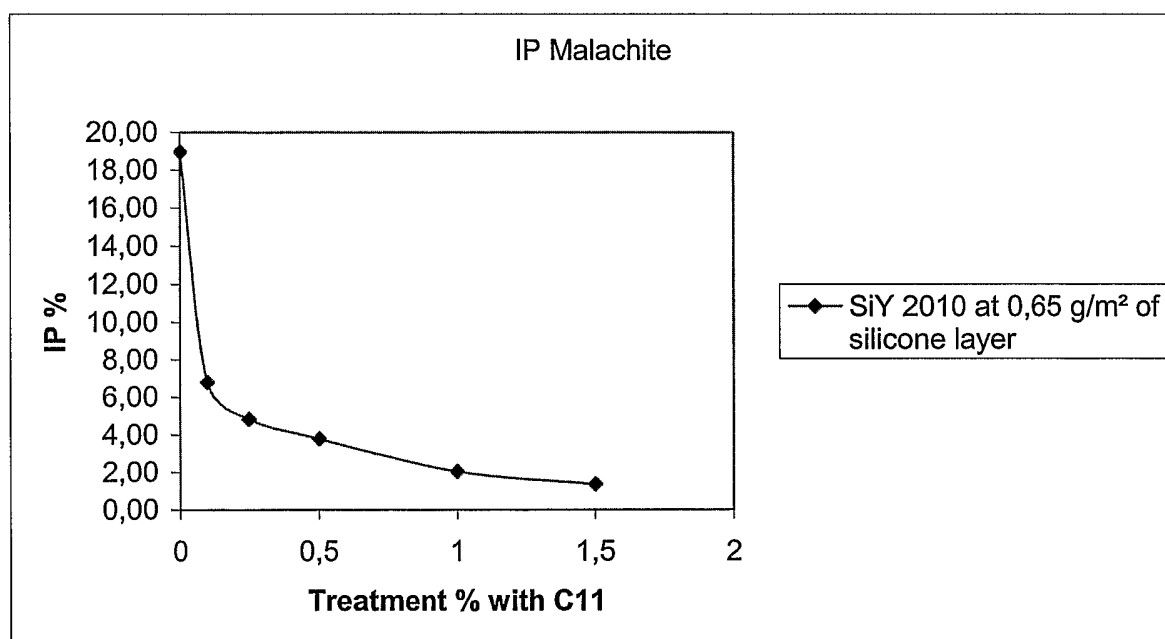


Figure 4

3/4

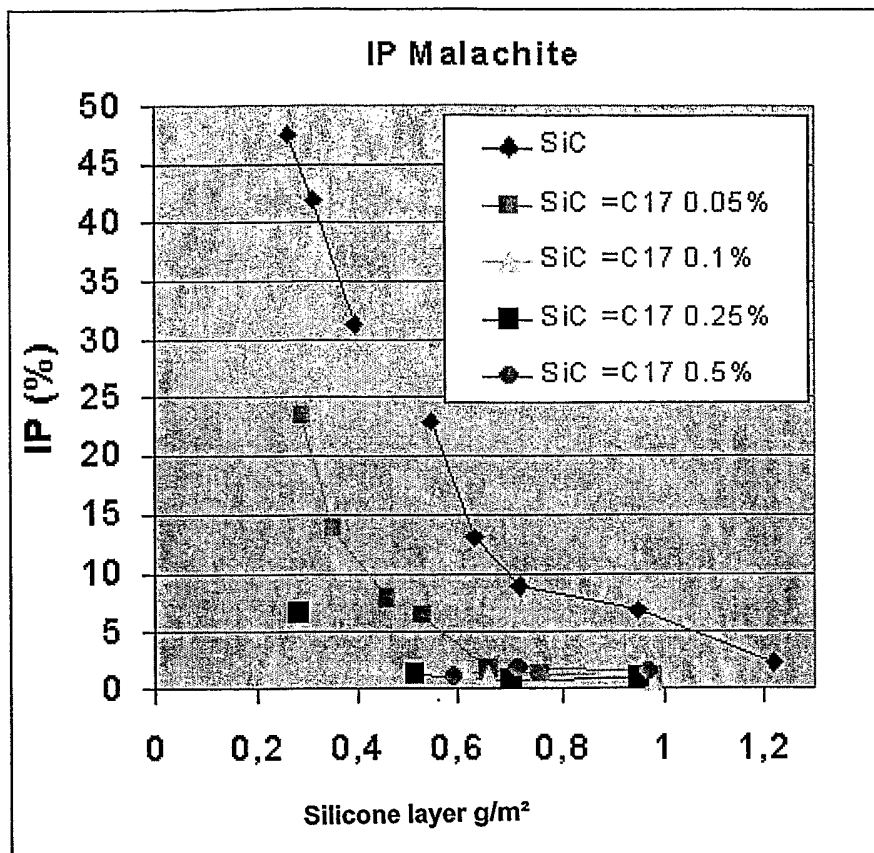


Figure 5

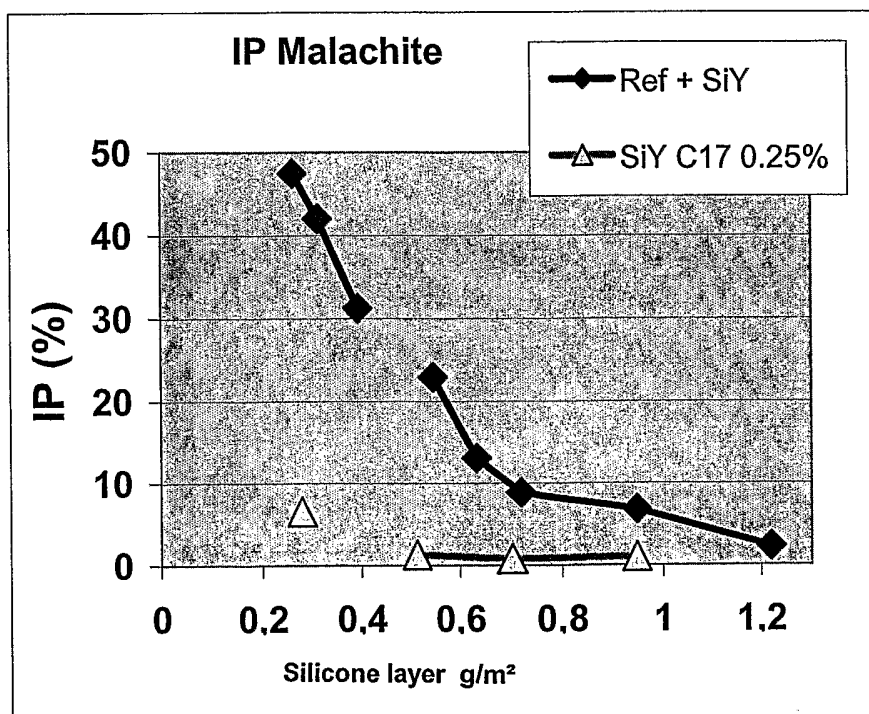
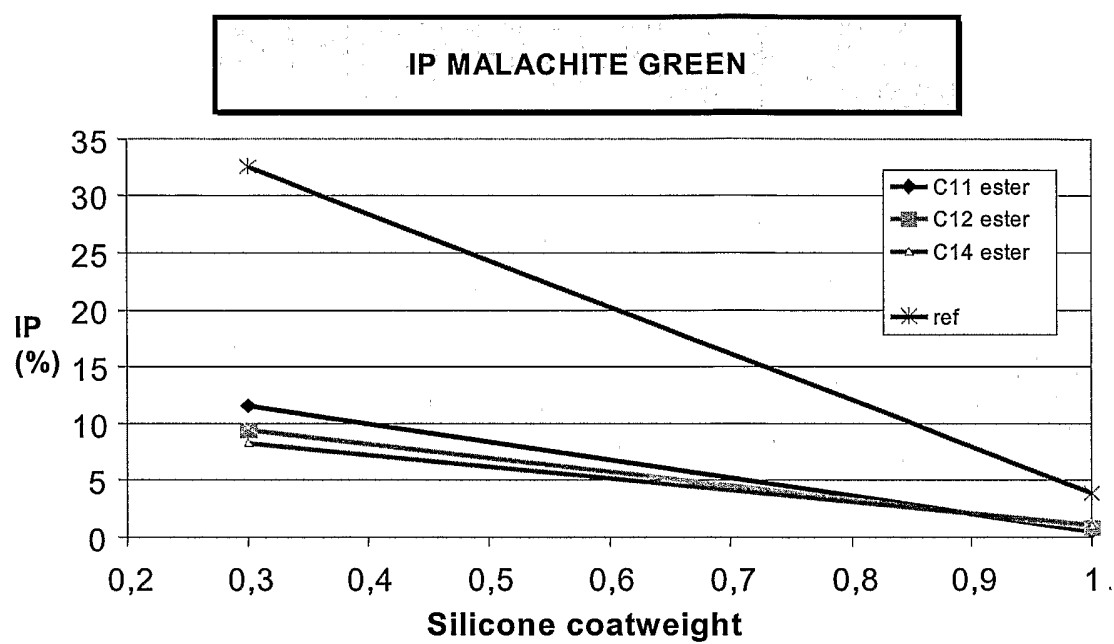


Figure 6

4/4**Figure 7**

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI2005/000041

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 D21H17/03 D21H17/14 D21H25/02 C08B3/14 C08B3/20 D06M13/207 //D06M101:06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08B D06M D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *G* document member of the same patent family		
Date of the actual completion of the international search 12 May 2005		Date of mailing of the international search report 20/05/2005
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Nestby, K

INTERNATIONAL SEARCH REPORT

International Application No
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