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(54) Title: ADHESIVE FOR SECURE TOPICAL ATTACHMENT TO THE SKIN AND COMFORTABLE REMOVAL		
(57) Abstract		
<p>The present invention relates to topical adhesives for attachment to the skin. In particular the present invention relates to such topical adhesives which can be employed for attachment to the skin of protective articles, clothing, prosthesis, heat wraps, pads, and/or packs, cold wraps, hearing aids, protective face masks, ornamental articles, or eye wear but excluding absorbent articles. The topical adhesive provides secure attachment and is pleasing to the skin upon application, yet causes no discomfort and a low level of adhesive residues on the skin upon removal. This is achieved by selecting the chemical composition and rheological characteristics of the topical adhesives, in particular with reference to the relationship between the elastic modulus G' and the viscous modulus G'' of the topical adhesive.</p>		

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10 ADHESIVE FOR SECURE TOPICAL ATTACHMENT TO THE SKIN AND COMFORTABLE REMOVAL

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Field of the invention

The present invention relates to topical adhesives for attachment to the skin. In particular the present invention relates to such topical adhesives which can be employed for attachment to the skin, particularly for the adhesion of protective articles such as genital-, knee- or elbow-protectors or bandages; clothing such as bras, surgical gowns, or parts of garments during fitting at a tailor; nasal plasters; prosthesis such as breast replacements or wigs; heat wraps, pads, and/or packs, e.g. for topical relief of pain or simply to provide warmth; cold wraps e.g. to provide pain relieve from bruises and to reduce swelling; hearing aids; protective face masks; ornamental articles such as jewelry, earrings, guises, tattoos; goggles or other eye wear. The topical adhesive provides secure attachment and is pleasing to the skin upon application, yet causes no discomfort and a low level of adhesive residues on the skin upon removal. This is achieved by selecting the chemical composition and rheological characteristics of the topical adhesives, in particular with reference to the relationship between the elastic modulus G' and the viscous modulus G'' of the topical adhesive.

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Background of the invention

35 The general prior art in the field of topical adhesives for attachment to the skin is particularly developed in the field of band-aids, plasters and bandages. These articles are, however, typically applied in an emergency situation where for

example a cut into the skin of the wearer has occurred and absorption of the body liquids emanating from a wound is desired. In this context performance aspects of the absorbent article such as comfortable and easy use and application, painless removal, discreteness are subordinate to criteria such as sterility, healing support, mechanical protection of the wound. Also such wound covering absorbent articles are mostly adhered to skin areas where prior to application of the absorbent article body hair can be removed or where little or no hair grows.

10 The present invention relates to topical adhesives which are particularly useful to protective articles such as genital-, knee- or elbow-protectors or bandages; clothing such as bras, surgical gowns, or parts of garments during fitting at a tailor; nasal plasters; prosthesis such as breast replacements or wigs; heat wraps, pads, and/or packs, e.g. for topical relief of pain or simply to provide warmth; cold wraps e.g. to provide pain relieve from bruises and to reduce swelling; hearing aids; protective face masks; ornamental articles such as jewelry, earrings, guises, tattoos; goggles or other eye wear. Such articles are not used for absorption of body liquids. For example attachment of a wig to the skin on the skull or of elbow and knee protectors to these surfaces of the body which undergo substantial extending and wrinkling can suitably be done by the adhesive of the present invention.

Topical adhesives that are used for absorbent articles such as sanitary napkins or pantliners have generally been disclosed in US statutory invention registration H1602 or WO 96/33683. Some more details of the adhesive have been disclosed in PCT application WO 95/16424. In this document sanitary articles having a topical adhesive which is applied on the wearer facing side of a sanitary napkin along the entire periphery are disclosed. The problem underlying this document is primarily the safe attachment to the skin but mentions also the problems of detachment of such articles after use without causing undue pain to a wearer.

The disclosure of WO 95/16424 includes a detailed analysis of the criteria for the topical adhesive in respect to rheological criteria. However, this document has little regard to the problem of painless removal of such articles since the rheological criteria taught include epilatory, i.e. hair removal, compositions which are commercially available such as STREP MIELE (TM) sold in Italy by

Laboratori Vaj S.p.A. The adhesives for topical attachment mentioned in WO 95/16424 include also today's pressure sensitive adhesives which are used to attach sanitary napkins to undergarments. Further, this document only identifies static rheological characteristics but is silent as to the dynamic rheological behaviour of a topical adhesive.

In WO 96/13238 a frequency dependent topical adhesive model is disclosed. However, all measurements disclosed, e.g. on page 9, were made at temperatures between -60°C and $+120^{\circ}\text{C}$ and at actual frequencies of 0.1 to 100 rad/s. In order to obtain the necessary data at application temperature (about 20°C , typical bath room, i.e. storage temperature) the Williams-Landel-Ferry (hereinafter WLF) equation was used.

This WLF equation is empirical and only valid within certain limits e.g. it cannot be used to extrapolate to temperatures below the glass transition temperature of a polymeric adhesive also the WLF cannot be used on the basis of values obtained below the glass transition temperature. Details about the WLF equation and its applicability can be found in "Principles of Polymer processing" by Z. Tadmor and C.G. Gogos, published by John Wiley & Sons or in "Viscoelastic Properties of Polymers" by J.D. Ferry also published by John Wiley & Son. Since this is already missing from WO 96/13238 the applicability of the disclosed data cannot be assessed.

European Patent Application EP-638 303 discloses the use of a topical adhesive on side cuffs of sanitary napkins in order to keep the cuffs in an upright position. Swiss publication CH-643730 discloses the use of a very long sanitary napkin having chamfered outer edges with a topical adhesive at the four corners of the outer edges in order to provide a topical adhesive area well outside the region of pubic hair growth. Both applications are silent as to the adhesive composition.

Based on the above state of the art it is an objective of the present invention to provide a topical adhesive for secure attachment and painless removal from the skin, combined with a reduced amount of residual adhesive that remains on the skin or on the hairs after removal of the topical adhesive composition, for articles outside the absorbent article field.

It is yet a further objective of the present invention that the adhesive for topical attachment does not cause a cold or otherwise unacceptable temperature sensation upon application despite a temperature difference of the adhesive in respect to the skin temperature.

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In addition to the above objectives of the present invention it is also desirable for topical adhesives to provide additional benefits such as delivery/dispersal of a compound or composition which is beneficial for the skin or for the body in general. Further, topical adhesives which do not affect the natural skin condition, e.g. by being breathable or water vapour transmitting, are preferred.

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Brief description of the invention

15 The present invention relates to topical adhesives which are particularly useful to protective articles such as genital-, knee- or elbow-protectors or bandages; clothing such as bras, surgical gowns, or parts of garments during fitting at a tailor; nasal plasters; prosthesis such as breast replacements or wigs; heat wraps, pads, and/or packs, e.g. for topical relief of pain or simply to provide
20 warmth; cold wraps e.g. to provide pain relieve from bruises and to reduce swelling; hearing aids; protective face masks; ornamental articles such as jewelry, earrings, guises, tattoos; goggles or other eye wear. Such articles are not used for absorption of body liquids. For example attachment of a wig to the skin on the skull or of elbow and knee protectors to these surfaces of the body
25 which undergo substantial extending and wrinkling can suitably be done by the adhesive of the present invention.

Detailed analysis of the sequence of common situations occurring from the application of such articles to the time of removal has shown that specific
30 adhesive characteristics need to be satisfied in order to achieve the desired performance objectives, in particular secure initial attachment, secure attachment during use, painless removal at the end and a reduced level of adhesive residues on the skin after removal. The characteristics which have been considered in this context are the elastic modulus describing the elastic
35 behaviour of the material and the viscous modulus which describes the viscous behaviour of the adhesive material.

The viscous behaviour of the adhesive can be interpreted to represent an indication of the ability of the adhesive to quickly attach and securely adhere. The elastic behaviour can be interpreted as an indication of the "hardness" behaviour of the adhesive. Its value is also critical for good initial attachment.

5 Their combination is believed to be an indicator of the required force upon removal. The relation between elastic and viscous modulus is considered to be an indication on which fraction of the removal energy will be dissipated within the adhesive and which fraction is available to trigger the actual removal. The relation between the elastic and viscous modulus also gives an indication of the
10 internal cohesiveness of the adhesive, which is in turn related to the possible presence of adhesive residues on the skin after removal of the topical adhesive composition.

In order to provide topical adhesives for secure initial and prolonged attachment
15 and easy/painless removal the relation between the elastic modulus and the viscous modulus as well as their dynamic behaviour is of key importance.

The topical adhesive has an elastic modulus at a temperature of 37°C (100° Fahrenheit) abbreviated G'_{37} and a viscous modulus at a temperature of 37°C
20 (100° Fahrenheit) of G''_{37} . The difference $\Delta(G'_{37} - G''_{37})$ between the elastic modulus G'_{37} at a frequency of 1 rad/sec and the viscous modulus G''_{37} at a frequency of 1 rad/sec is also defined for the topical adhesive. This difference gives an indication of the behaviour of the topical adhesive with respect to the level of adhesive residues left on the skin after removal of the topical adhesive.
25 The adhesive further has a dynamic elastic behaviour defined as $\Delta G'_{37}$ which is the difference of G'_{37} at a frequency of 100 rad/sec and G'_{37} at a frequency of 1 rad/sec and a dynamic viscous behaviour $\Delta G''_{37}$ which is the difference of G''_{37} at a frequency of 100 rad/sec and G''_{37} at a frequency of 1 rad/sec.

30 The topical adhesive according to the present invention satisfies the following conditions:

• G'_{37} (1 rad/sec) is in the range 1500 Pa to 20000 Pa,
preferably 1500 Pa to 15000 Pa, most
35 preferably 3000 Pa to 10000 Pa.

• G''_{37} (1 rad/sec) is in the range 100 Pa to 15000 Pa,

preferably 100 Pa to 10000 Pa, most preferably 300 Pa to 5000 Pa.

- 5 • the ratio of G'_{37} (1 rad/sec) / G''_{37} (1 rad/sec) is in the range of 3 to 30.
 - the ratio
$$\frac{G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})}{G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec})}$$
 is not less than 0.5, preferably in the range 0.7 to 3, most preferably in the range 1 to 1.8.
 - 15 • either the ratio of $\Delta G'_{37}/G'_{37}$ (1 rad/sec) is not greater than 1.5, preferably not greater than unity and most preferably not greater than 0.8,
 - or $\Delta G'_{37}$ is not greater than 10000 Pa, preferably less
 - 20 than 5000 Pa, most preferably less than 2000 Pa,
 - or both.
 - the difference $\Delta(G'_{37} - G''_{37})$ (1 rad/sec) is greater than or equal to 1250 Pa, preferably greater than or equal to 2500 Pa, more preferably greater than or
 - 25 equal to 3500 Pa.
- Further preferred conditions are:
- the value of the ratio G'_{37}/G''_{37} at least for the frequency range from above 1 rad/s up to 100 rad/s should preferably be 3.3 or above, more preferably 5 or
 - 30 above, most preferably 10 or above, while not exceeding about 30, preferably 20, anywhere in the frequency interval.
 - the rheological behaviour can also be related to the values of the Glass Transition Temperature T_g . For topical adhesives according to the present
 - 35 invention T_g should preferably be less than -15°C , more preferably less than -20°C and most preferably less than -25°C .

• the rheological behaviour and acceptance of a topical adhesive can also be related to the specific heat capacity. Preferably the specific heat capacity of the topical adhesive is less than 4 J/g/K, more preferably less than 3 J/g/K and most preferably less than 2 J/g/K.

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• the rheological behaviour and acceptance of a topical adhesive can also be related to the specific heat conductivity of the adhesive. Preferably the specific heat conductivity is as low as possible, preferably between 1 and 0.1 W/m/K, most preferably between 0.6 and 0.1 W/m/K . However, even though these ranges allow selection of appropriate adhesives, in the case of heat or cold wraps it is desirable to have a relatively high value of heat conductivity to support the function of such articles.

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Adhesive compositions which satisfy the above criteria can be used as topical adhesives for the above mentioned articles provided they also satisfy the common requirements of being safe for use on human or animal skin during use and generally after disposal of the article.

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Often the criteria of hygienic appearance and pleasant feel upon contact are important such that adhesive composition which are transparent or white, and which prevent a cold, unpleasant feeling upon application are preferred.

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The above rheological criteria and other considerations can be satisfied by adhesive compositions where the composition comprises from 45%, preferably from 51 %, to 99.5 % of a plasticising compound or composition which is liquid at 20°C, from 0.5 to 20 %, preferably 5 % to 15 %, of a polymeric compound or composition which is soluble or swellable in the plasticising compound or composition and with a tackifying resin in an amount in the range from 0% to 50% by weight of the composition, preferably from 0 % to 600 % by weight of the polymeric compound. The plasticising compound or composition is preferably selected from the group consisting of water, alcohols (preferably glycerol), glycols, polyglycols, liquid polybutenes, oil or combinations thereof. The polymeric compound or composition is preferably selected from the group consisting of block-copolymer-thermoplastic-elastomers, styrene-block-copolymers and hydrogenated styrene-block-copolymers, polyacrylics, polyvinyl alcohol, natural gum or gelatines, polyethyleneoxide, polyvinylpyrrolidone (PVP), polyvinylethers, cellulose derivatives, or combinations thereof.

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Detailed description of the invention

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Adhesive for topical attachment

10 The topical adhesive according to the present invention is applied directly to the skin. In a particular application the adhesive can be used on protective articles such as genital-, knee- or elbow-protectors or bandages; clothing such as bras, surgical gowns, or parts of garments during fitting at a tailor; nasal plasters; prosthesis such as breast replacements or wigs; heat wraps, pads, and/or packs,
15 e.g. for topical relief of pain or simply to provide warmth; cold wraps e.g. to provide pain relieve from bruises and to reduce swelling; hearing aids; protective face masks; ornamental articles such as jewelry, earrings, guises, tattoos; goggles or other eye wear. The word "skin" according to the present invention does relate to the outer surface of the derma of humans or animals.

20 In order to provide fixation of an article according to the present invention to the skin it is necessary to provide a certain area on the side of the article which is facing the skin with the topical adhesive.

25 The topical adhesive is provided with the preferred pattern on the wearer facing surface of the article in a layer having a thickness or caliper that is preferably constant. The layer can be preferably continuous or alternatively discontinuous, e.g. in form of dots, spirals, or stripes.

30 Physical, Rheological and Adhesive Characteristics of a Topical Adhesive

Even though topical adhesives are used like pressure sensitive adhesives on human skin hair and mucous tissues, it is understood that the topical adhesive compositions could only with difficulty be considered typical pressure sensitive
35 adhesives (referred to as PSA hereinafter) on the basis of the most characteristic rheological behaviours identifying such materials.

In fact as the person skilled in the art of adhesives knows, the most characteristic feature that distinguishes a PSA from other substances that can temporarily stick things (as e.g. water between two glass plates could) is the fact that their rheological parameters and especially the Elastic Modulus G' vary greatly with the frequency of applied stresses. More in particular, G' of PSA can increase over some orders of magnitude while the frequency of applied stresses varies from typical bonding frequency to typical debonding frequency, i.e. 1 rad/s to 100 rad/s as indicated below.

As a first consequence, it derives that it is inadmissible to define materials intended for use as " topical adhesives" by giving values of rheological parameters and especially of G' at a fixed value of frequency. This can be misleading because in the absence of other characteristics it will include materials which have no practical value. It is hence necessary that rheological characterisation must be on the base of dynamic considerations.

This not only applies to the Elastic Modulus G' but also to the viscous modulus G'' and hence also for $\tan(\delta) = G'' / G'$. It is well known that typical PSA have not only a high variation of G' across the considered frequencies but also there is an even higher variation of G'' which can get close or become even higher than the value of G' , i.e. $\tan(\delta)$ becomes about or even greater than 1, in particular at the frequencies that are typical of the debonding.

Without wishing to be bound by theory this can be interpreted as meaning that a high fraction of the energy applied for the debonding is dissipated within the adhesive (so it is not effective in causing the debonding) while this fact causes macroscopically the recording of a very high level of adhesive force.

As indicated above materials useful as topical adhesives according to the present invention have rheological characteristics which are measured at a reference temperature of 37°C (as usual body temperature of humans) and in a range of frequencies. It has been found that upon application of an article such as a wig with a topical adhesive the adhesive contact is formed at a low frequency, while debonding happens at the speed of removing the article. This speed is expressed as a frequency of 100 rad/s while the low frequency of forming the adhesive bond has been found to be on the order of 1 rad/s.

Therefore, the frequency range for use according to the present invention is between 1 and 100 rad/s.

5 It is believed that the adhesive bonding characteristics are selected most appropriately at human body temperature. Since the topical adhesive according to the present invention is used directly on skin and the person skilled in the art is directed to select the adhesive composition to have a small specific heat capacity (e.g. preferably less than 4 J/g/K) the actual temperature of the topical adhesive will reach 37°C very quickly or even be warmed up by a human prior to
10 application.

In order to provide good conditions of bonding, i.e. at a frequency of about 1 rad/sec, the absolute values of the elastic modulus should not be too high, otherwise the adhesive is too hard and it is not able to intimately join or mold to
15 the surface to which it is expected to adhere. It is also important to have a low absolute value of G'' in order to have good cohesion which is particularly valuable when using articles which are frequently removed and adhered again or replaced, while the material remains soft and capable of gently adhering to skin.

20 The ratio of G'_{37} (1 rad/sec) over G''_{37} (1 rad/sec) is important to ensure that these two values are balanced upon adhesion to the skin. At the same time the absolute changes of G'_{37} need to be limited within the range of frequencies considered. Hence a value for the ratio of $\Delta G'_{37}$ (i.e. G'_{37} (100 rad/sec) - G'_{37} (1 rad/sec)) over G'_{37} (1 rad/sec) has to be kept small in order to maintain the
25 secure attachment of the topical adhesive without causing discomfort over time or at removal/ delamination. This can also be expressed in absolute terms by keeping the $\Delta G'_{37}$ below certain values.

30 Importantly, the ratio of
$$\frac{G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})}{G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec})}$$

35 needs to be large enough to ensure that the dynamic behaviour of both the elastic and the viscous module are maintained in a relationship which provides secure adhesion and painless and easy removal.

Further, when considering particularly the removal phase of a topical adhesive composition for attachment of articles to the skin of a wearer, it is commonly recognized that good conditions of removal of the topical adhesive are achieved when the adhesive can be easily removed from the skin, and particularly from the hairs that may grow on the skin where the article contacts the wearer's body, without causing pain to the wearer, therefore without sticking too hard upon removal to the skin and hairs of the wearer. Particularly, as is apparent to those skilled in the art, a good removal also implies that the topical adhesive does not leave residual remains on the skin or on the hairs. The difference $\Delta(G'_{37} - G''_{37})$ between the elastic modulus G'_{37} (1 rad/sec) and the viscous modulus G''_{37} (1 rad/sec) of the topical adhesive of the present invention is relevant to the scope of providing a reduced level of adhesive residues on the wearer's skin after removal of the topical adhesive. Such a difference gives in fact an indication on the behaviour of the topical adhesive of the present invention as far as the level of adhesive residues on the skin after removal of the topical adhesive from the wearer's skin is concerned.

Without being bound to any theory, it is believed that the difference between the elastic modulus G' and the viscous modulus G'' is a direct measure of the internal cohesiveness of the topical adhesive. Therefore increasing the difference $\Delta(G'_{37} - G''_{37})$, provided the other rheological conditions are satisfied, increases the internal cohesiveness of the topical adhesive, and decreases the possibility that residues of adhesive remain on the skin upon removal of the topical adhesive.

Finally the person skilled in the art will also recognise that the Glass Transition Temperature T_g of the adhesive composition, specific heat capacity, and specific heat conductivity are parameters which are useful to more fully define the group of useful topical adhesives.

The following set of characteristics should be satisfied:

- G'_{37} (1 rad/sec) is in the range 1500 Pa to 20000 Pa, preferably 1500 Pa to 15000 Pa, most preferably 3000 Pa to 10000 Pa.

- G''_{37} (1 rad/sec) is in the range 100 Pa to 15000 Pa,

preferably 100 Pa to 10000 Pa, most preferably 300 Pa to 5000 Pa.

- 5 • the ratio of G'_{37} (1 rad/sec) / G''_{37} (1 rad/sec) is in the range of 3 to 30.
- the ratio
$$\frac{G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})}{G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec})}$$
 is not less than 0.5, preferably in the range 0.7 to 3, most preferably in the range 1 to 1.8.
- 15 • either the ratio of $\Delta G'_{37}/G'_{37}$ (1 rad/sec) is not greater than 1.5, preferably not greater than unity and most preferably not greater than 0.8,
 - or $\Delta G'_{37}$ is not greater than 10000 Pa, preferably less
 - 20 than 5000 Pa, most preferably less than 2000 Pa,
 - or both.
- the difference $\Delta(G'_{37} - G''_{37})$ (1 rad/sec) is greater than or equal to 1250 Pa, preferably greater than or equal to 2500 Pa, more preferably greater than or
- 25 equal to 3500 Pa.

Further preferred conditions are also:

- 30 • the value of the ratio G'_{37}/G''_{37} at least for the frequency range from above 1 rad/s up to 100 rad/s should preferably be 3.3 or above, more preferably 5 or above, most preferably 10 or above, while not exceeding about 30, preferably 20, anywhere in the frequency interval.
- the rheological behaviour can also be related to the values of the Glass
- 35 Transition Temperature T_g . For topical adhesives according to the present invention T_g should preferably be less than -15°C , more preferably less than -20°C and most preferably less than -25°C .

• the rheological behaviour and acceptance of a topical adhesive can also be related to the specific heat capacity. Preferably the specific heat capacity of the topical adhesive is less than 4 J/g/K, more preferably less than 3 J/g/K and most preferably less than 2 J/g/K.

• the rheological behaviour and acceptance of a topical adhesive can also be related to the specific heat conductivity of the adhesive. Preferably the specific heat conductivity is as low as possible (except for energy transmitting articles where high values are more desirable), more preferable between 1 and 0.1 W/m/K, most preferably between 0.6 and 0.1 W/m/K.

Chemical and compositional characteristics of a Topical adhesive

In order to provide topical adhesive compositions which satisfy the requirements of the above rheological and physical characteristics of a topical adhesive the following formulation criteria can be used in addition. It should be noted that the most of the compositions useful as topical adhesive have a substantially gel-like structure and are preferably gels. This derives from the fact that:

- the prevailing component is the plasticiser which is a material liquid at room temperature

- a macromolecular or polymeric component is present in minor quantities vs. the plasticiser. It forms, in the preferred embodiments, a three dimensional network caused by physical or chemical links between the molecules. Particularly useful physical links are the ones present in systems containing Block Thermoplastic Elastomers.

More specifically, the compositions typically comprise:

- from 0.5 to 20 %, preferably 5 % to 15 %, by weight of a macromolecular polymeric substance or a mixture of such substances soluble or swellable in the below mentioned plasticiser(s). As not limiting examples such macromolecular or polymeric substances can be natural and/or synthetic such as natural gums or derivatives such as natural gums and gelatins, their derivatives and alginates; polyacrilics; polyvinyl alcohol; polyethylene oxide; polyvinylpyrrolidon (PVP) or

polyvinylethers, their copolymers and derivatives; cellulose derivatives; Block Copolymer Thermoplastic Elastomers and preferably Styrenic Block Copolymers and more preferably the hydrogenated grades Styrol/Ethylene-Butylene/Styrol (SEBS), Styrene/Isoprene/Styrene (SIS), and Styrol/Ethylene-Propylene/Styrol (SEPS).

- from 45 to 99.5 % by weight, preferably from 51 to 99.5% by weight, of a plasticising substance or a mixture of plasticising substances, which are liquid at room temperature. As non-limiting examples the plasticiser can be water, various alcohols (like in particular glycerol), glycols and their ethers, polyglycols, liquid polybutenes, esters such phthalates, adipates, stearates, palmitates, sebacates, or myristates, natural or synthetic oils such as vegetable oils, mineral oils, or combinations thereof.

- from 0% to 50% by weight of the composition, preferably from 0 to 600 % by weight of the macromolecular polymeric substance of a tackifying resin whose main scope is to tailor the Tg especially in systems based on synthetic polymers.

- from 0 to 10 % and more preferably form 0 to 5 % by weight of substances for facilitating and stabilising the gel and the gel forming process both of hydrophilic or hydrophobic liquid plasticisers. These may be for oily systems, e.g. the fatty acids of C₈ to C₂₂, their metallic salts and their polyoxo-derivatives; lanolin derivatives; silica; bentonite, montmorillonite and their derivatives; polyamides, waxes or mixtures thereof.

Common additives known in the art as preservatives, antioxidants, anti UV, pigments, mineral fillers, rheology modifiers etc. can also be comprised in quantities up to 10 % each.

When chemical crosslinks are formed in the system, a crosslinking agent can be present preferably in quantities up to 5 % by weight. Chemical crosslinking can be formed also by mutual neutralisation of polymers having different functionalities as in the reaction between acid polyacrylics and polysaccharides.

The resulting compositions for topical adhesives can be divided into three families according to the nature of the main component, i.e. usually the liquid plasticiser(s):

1) Hydrophobic compositions in which the plasticiser is typically an oil or blend of oils of vegetable or mineral origin and the polymer is usually a synthetic polymer, preferably an elastomer, soluble or swellable in oil(s).

5 2) Mixed phase compositions in which both hydrophobic and hydrophilic components, possibly in both plasticisers and polymers, form two or more separate phases. In such cases an emulsifier/surfactant is preferably present at a suitable level to form stable emulsions between the incompatible phases. For topical adhesives according to the present invention it is preferably that the hydrophobic components are prevailing vs. the hydrophilic ones.

10 3) Hydrophilic compositions in which typically the plasticiser is water/glycerol/glycols and the like and/or mixtures thereof and the polymeric phase is of synthetic (e.g. polyacrilics) or natural (e.g. natural gums) origin or mixtures thereof.

15 It is to stress that, differently from the medical field and from the cited prior art, the hydrophilic compositions are not preferred while the hydrophobic and mixed phases compositions 1) and 2) are preferred in the applications of the present invention.

20 This depends partially on technical reasons in the sense that many hydrophilic compositions used in the medical field show too low elastic character and cohesion for being useful in the present application.

25 Further hydrophilic topical adhesives also tend to be perceived as cold and wet which upon application to the skin of a human is not in line with typical expectation. Additional problems result from the fact that in particular topical adhesives comprising water as the plasticiser have a tendency to dry out unless they are sealed into an impermeable package.

30 Application of topical adhesive

Articles in which the topical adhesive according to the present invention can be used, can be made by any of the ways usual in the art. The application of the adhesive to the skin facing surface of such an article should not cause major problems to those skilled in the art since it can be provided by any well known techniques commonly used for other adhesives. The total area of the skin or

wearer facing surface of an article which is covered by the topical adhesive depends on the intended use of the article. For conservation of adhesive it should be not more than 80 %, preferably from 30% to 60% of the wearer facing surface of the article.. Preferably, the adhesive extends close to the periphery of the article, but since it is not intended for absorbent articles it can also cover the central area of the articles. Most preferably the adhesive is provided in a pattern of small incremental areas such as dots or similar.

The topical adhesive is applied on at least part of the wearer facing surface of the article in a layer having a thickness or caliper that is preferably constant, or that alternatively can vary over the surface interested by the application of the topical adhesive.

If possible, the article also provides breathability by being at least water vapour permeable, preferably air permeable to prevent stuffiness. Breathability, if not supported by the topical adhesive as such, can be limited to the area of the article where no adhesive is applied.

The topical adhesive on an article is preferably protected prior to use. This protection can be provided by a release liner such as a siliconised or surfactant treated paper, providing easy release for the selected topical adhesive.

In order to evaluate the effect of the difference $\Delta(G'_{37} - G''_{37})$ of topical adhesives according to the present invention on the amount of the adhesive residues that remain on the skin upon removal of the topical adhesive a Residue Test has been developed. In this test the adhesion of a standard substrate, provided with a layer of topical adhesives featuring a given value of $\Delta(G'_{37} - G''_{37})$, is achieved on the skin of the forearm of a wearer, and after successive removal the amount of the adhesive residues that remain on the skin is evaluated.

Residue Test

The Residue Test is utilized to evaluate the amount of adhesive residues that remain on the wearer's skin after removal of a sample provided with a layer of a topical adhesive and previously attached to the wearer's forearm skin. The test specifically evaluates the amount of the adhesive residues as the residual skin

stickiness caused by the adhesive residues, in terms of the peak tensile force (N) necessary to detach a standard steel plate adhered to the skin after removal of the sample with the topical adhesive.

5 Sample preparation.

The test is performed on rectangular samples 50x20 mm made of a polyester film 23 μm thick, such as that sold by Effegidi S.p.A. of Colorno (Parma, Italy), provided on one side with a continuous layer of the selected topical adhesive having a constant thickness of 1.35 mm, applied with an Acumeter Model LH-1 extruder. A release paper is applied to protect the adhesive layer. The samples are prepared individually and tested after one hour from preparation.

Apparatus.

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1) Climatically controlled Lab.

Maintenance of 23°C and 50% Relative Humidity.

2) Instron Limited UK Model 6021 Dynamometer.

20 Load cell = 10 N

Test speed = 1000 mm/min

3) Weight

1 Kg, cylindrical weight with 44 mm diameter and 82 mm height.

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4) Cardboard plate

Square cardboard plate 60x60 mm.

5) Steel plate

30 Rectangular steel plate 50x60 mm with a smooth flat surface and provided with means for connection to the movable clamp of the dynamometer.

Residue measurement.

35 No special treatment of the wearer's skin is required beyond normal cleaning/washing with water and soap and drying at least two hours before the test to allow equilibrium with the room conditions is reached for the skin. A

rectangular area about 10 mm longer and wider than the dimensions of the sample is selected on the inner part of the wearer's forearm skin, e.g. by drawing it on the skin with suitable means, said area being centered between the wrist and the elbow, with the long side of the area aligned with the length of the arm.

5 The sample is then applied on the skin by an operator, being centered with respect to the previously defined selected area, and a pressure is exerted on it by positioning by hand the weight on the sample and leaving it there for 30 seconds, with the cardboard plate interposed between the weight and the sample in order to cover the whole surface of the sample.

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After removal of the weight and of the cardboard plate the sample is worn by the wearer for one hour, and then the sample with the topical adhesive is removed from the wearer's forearm skin by the operator with a slow and smooth pull, without touching the skin where the sample was applied. The steel plate is

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connected to the upper movable clamp of the dynamometer so that its flat surface is positioned horizontally, perpendicular to the direction of movement of the clamp, and facing down. The wearer positions his arm horizontally on a suitable support under the moving clamp of the dynamometer, with the selected area of the skin where the sample had been applied positioned directly under the

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steel plate. The wearer's forearm and the steel plate on the clamp are mutually positioned and oriented in such a way that the steel plate is centered with respect to the selected area on the forearm, with the longer dimensions of the steel plate and of the selected area being parallel, and with the surface of the steel plate and of the forearm skin in the selected area about parallel to each

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other.

The Instron is operated to move the clamp with the steel plate towards the selected area until full contact between the flat surface of the steel plate and the skin is achieved and to apply a compression force of 9.8 N for 30 seconds, then

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the clamp is raised and the peak tensile force measured in Newton (N) necessary to detach the steel plate from the selected area is recorded as a measure of the residue amount.

The measurements are performed and averaged on five samples of the same

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type to ensure a representative residue value to be determined for the sample under investigation.

The amount of adhesive residues left on the skin after removal of the topical adhesive has been evaluated for two different samples A and B provided with two different topical adhesive compositions according to the present invention.

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Sample A and Sample B are provided with a layer of topical adhesive according to Composition 1 and Composition 2, respectively, as described hereinbelow.

Composition 1

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An oil based composition according to the present invention was prepared using 9.9 % by weight of Kraton G-1651, a Styrene/Ethylene-Butylene/Styrene block copolymer containing 33% by weight styrene and available from Shell Co., and 59.3 % by weight of Kaydol, a paraffinic mineral oil available from Witco Co.

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Moreover the composition contained 301 parts of tackifying resin per 100 parts of Kraton polymer. The tackifying resin was Escorez 5300, a hydrogenated resin available from Exxon Co.

20

Magnesium Stearate, available from Carlo Erba S.p.A., was used a co-gelifying agent for oil at a level of 0.7 % by weight.

Irganox 1010, an antioxidant available from Ciba-Geigy, was added at a level of 0.3 % by weight.

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So finally the formulation had the following percent composition:

Kraton G-1651	9.9 % by weight
Kaydol	59.3 % by weight
30 Escorez 5300	29.8 % by weight
Magnesium Stearate	0.7 % by weight
Irganox 1010	0.3 % by weight

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The composition showed the following rheological properties at 37°C.

a) Elastic Modulus at 1 rad/s, $G'_{37} = 6876 \text{ Pa}$

b) Viscous Modulus at 1 rad/s, $G''_{37} = 550,5 \text{ Pa}$

c) Ratio of Elastic and Viscous Modulus at 1 rad/s, $G'_{37} / G''_{37} = 12.49$

d) Ratio of $G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})$

$$\frac{G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec})}{G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})} = 1.22$$

e) The ratio of $\Delta G'_{37}$ over $G'_{37} (1 \text{ rad/s})$ was 0.308,
with $\Delta G'_{37} = 2124 \text{ Pa}$.

Composition 2

The topical adhesive is an oil based composition containing 10% by weight of Kraton G-1651, a Styrene/Ethylene-Butylene/Styrene block copolymer available from Shell Co., 49 % by weight of Kaydol, a paraffinic mineral oil available from Witco Co., 40% by weight of Escorez 5300, a hydrogenated tackifying resin available from Exxon Co., 0.7% by weight of Magnesium Stearate, a co-gelifying agent for oil available from Carlo Erba S.p.A., and 0.3% by weight of Irganox 1010, an antioxidant available from Ciba-Geigy.

So finally the formulation had the following percent composition:

Kraton G-1651	10.0 % by weight
Kaydol	49.0 % by weight
Escorez 5300	40.0 % by weight
Magnesium Stearate	0.7 % by weight
Irganox 1010	0.3 % by weight

The composition has the following rheological properties at 37°C.

a) Elastic Modulus at 1 rad/s, $G'_{37} = 7038 \text{ Pa}$

b) Viscous Modulus at 1 rad/s, $G''_{37} = 487 \text{ Pa}$

c) Ratio of Elastic and Viscous Modulus at 1 rad/s, $G'_{37} / G''_{37} = 14.45$

d) Ratio of $G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})$

$$\begin{aligned} G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec}) \\ = 1.11 \end{aligned}$$

- 5 e) The ratio of $\Delta G'_{37}$ over G'_{37} (1 rad/s) was 0.291,
with $\Delta G'_{37} = 2051$ Pa.

The results of the test are summarized in the following table:

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Sample	$\Delta(G'_{37} - G''_{37})$ (Pa)	Residue (N)
A	6326	0.33
B	6551	0.27

The results show that increasing values of the difference $\Delta(G'_{37} - G''_{37})$ correspond to lower amounts of adhesive residues left on the wearer's skin after removal of topical adhesive compositions according to the present invention.

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Moreover, the above described topical adhesive compositions according to the present invention have been judged as comfortable for initial application and for removal from sensitive, hairy skin without causing pain.

Claims

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1. A topical adhesive for attachment to the skin of protective articles, clothing, prosthesis, heat wraps, pads, and/or packs, cold wraps, hearing aids, protective face masks, ornamental articles or eye wear, but excluding disposable absorbent articles such as wound dressings, sanitary napkins, pantliners, incontinence articles or underarm sweat pads,,

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- said adhesive having an elastic modulus at a temperature of 37°C (100°F), G'_{37} , a viscous modulus at a temperature of 37°C (100°F), G''_{37} , and a difference $\Delta(G'_{37} - G''_{37})$ between said elastic modulus G'_{37} (1 rad/sec) and said viscous modulus G''_{37} (1 rad/sec),

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- said adhesive being selected to have

- G'_{37} (1 rad/sec) in the range 1500 Pa to 20000 Pa, preferably 1500 Pa to 15000 Pa, most preferably 3000 Pa to 10000 Pa;

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- G''_{37} (1 rad/sec) in the range 100 Pa to 15000 Pa, preferably 100 Pa to 10000 Pa, most preferably 300 Pa to 5000 Pa;

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- the ratio G'_{37} (1 rad/sec) / G''_{37} (1 rad/sec) is in the range 3 to 30;

- the ratio

$$\frac{G'_{37} (100 \text{ rad/sec}) - G''_{37} (100 \text{ rad/sec})}{G'_{37} (1 \text{ rad/sec}) - G''_{37} (1 \text{ rad/sec})}$$

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is not less than 0.5, preferably in the range 0.7 to 3, most preferably in the range 1 to 1.8;

- alternatively either

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- G'_{37} (100 rad/sec) - G'_{37} (1 rad/sec) is not greater than 10000 Pa, preferably less than 5000 Pa, preferably less than 2000 Pa;

or

- the ratio $G'_{37} (100 \text{ rad/sec}) - G'_{37} (1 \text{ rad/sec})$

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$$\frac{G'_{37} (100 \text{ rad/sec}) - G'_{37} (1 \text{ rad/sec})}{G'_{37} (1 \text{ rad/sec})}$$

is not greater than 1.5, preferably not greater than 1, most preferably not greater than 0.8,

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or a combination thereof,

• the difference $\Delta(G'_{37} - G''_{37}) (1 \text{ rad/sec})$ is greater than or equal to 1250 Pa, preferably is greater than or equal to 2500 Pa, most preferably is greater than or equal to 3500 Pa.

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2. A topical adhesive according to any preceding claim, characterized in that said adhesive is provided as a continuous layer.

3. A topical adhesive according to any of the preceding claims comprising

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- from 45 % to 99.5 %, preferably 51 % to 99.5 %, by weight of a plasticising compound or composition which is liquid at 20°C;

- from 0.5 % to 20 % by weight of a polymeric compound or composition which is solvable or swellable in said plasticising compound or composition;

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- a tackifying resin in an amount of from 0 % to 50 % by weight, preferably from 0 % to 600 % by weight of said polymeric compound or composition.

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4. A topical adhesive according to claim 3 wherein

- said plasticising compound or composition is selected from the following group: water, alcohols, glycols, oil or combinations thereof; and

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- said polymeric compound or composition is selected from the following group: block-copolymer-thermoplastic-elastomers, styrene-block-copolymers and hydrogenated styrene-block-copolymers.

5. A topical adhesive according to any of the preceding claims wherein 80 % by weight of said adhesive consist of hydrophobic components and most preferably all components of said adhesive are hydrophobic.
- 5
6. An article such as a protective article, clothing, prosthesis, heat wraps, pads, and/or packs, cold wraps, hearing aid, protective face mask, ornamental article or eye wear, but excluding disposable absorbent articles such as wound dressings, sanitary napkins, pant liners, incontinence articles or underarm sweat pads, for topical adhesive attachment to the skin of a wearer, said article having a wearer facing surface and a garment facing surface, said article comprising on at least part of said wearer facing surface a topical adhesive according to claim 1 for said topical adhesive attachment of said article.
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7. Use of a topical adhesive according to claim 1 on protective articles, clothing, prosthesis, heat wraps, pads, and/or packs, cold wraps, hearing aids, protective face masks, ornamental articles, eye wear or make-up.
- 15

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/23460

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 A61L15/58 C09J133/08 C09J129/04 C09J139/06 C09J153/02

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 6 A61L A61K C09J

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 93 10201 A (MINNESOTA MINING & MFG) 27 May 1993 see page 2, line 27 - line 38 see page 4, line 31 - line 41 see page 7, line 1 - page 9, line 27 ---	1,3,4,7
X	FR 2 734 574 A (PACIFIC CORP) 29 November 1996 see page 4, line 21 - page 6, line 26 see page 7, line 15 - page 9, line 9 see claims; examples --- -/--	3-7

Further documents are listed in the continuation of box C. 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. "&" document member of the same patent family
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Date of the actual completion of the international search	Date of mailing of the international search report
29 April 1998	11/05/1998

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Cousins-Van Steen, G</p>
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/23460

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	<p>EP 0 184 470 A (MEDTRONIC INC) 11 June 1986 see page 3, line 10 - line 19 see page 3, line 34 - page 5, line 7</p>	1,3,4,7
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