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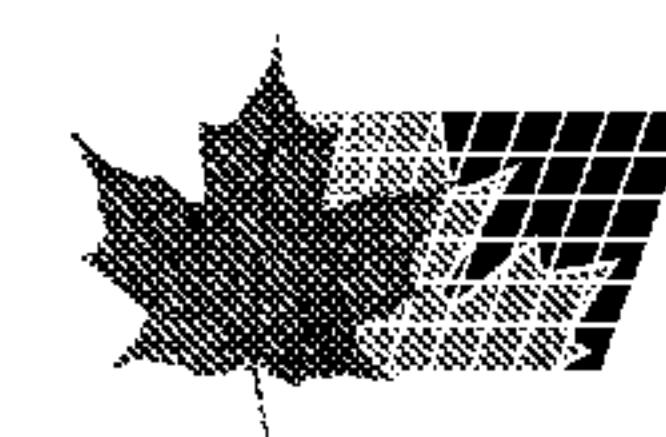
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(54) Titre : PROCEDE DE RENFORCEMENT DES PROPRIETES ADHESIVES DE SUBSTANCES AUTO-ADHESIVES
SUR DES SUBSTRATS AU MOYEN D'UN TRAITEMENT PAR PLASMA

(54) Title: METHOD FOR INCREASING THE ADHESIVE PROPERTIES OF PRESSURE-SENSITIVE ADHESIVE
COMPOUNDS ON SUBSTRATES BY WAY OF PLASMA TREATMENT

(57) Abrégé/Abstract:

Invention for increasing the adhesion between a pressure-sensitive compound layer which has a surface facing away from a substrate and a surface facing the substrate, and the surface of a substrate, the surface of the pressure-sensitive adhesive compound layer facing the substrate and the surface of the substrate that is covered by the pressure-sensitive adhesive compound layer being treated with atmospheric-pressure plasma.



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(54) Title: METHOD FOR INCREASING THE ADHESIVE PROPERTIES OF PRESSURE-SENSITIVE ADHESIVE COMPOUNDS ON SUBSTRATES BY WAY OF PLASMA TREATMENT

(54) Bezeichnung : VERFAHREN ZUR ERHÖHUNG DER ADHÄSIVEN EIGENSCHAFTEN VON HAFTKLEBEMASSEN AUF UNTERGRÜNDEN MITTELS PLASMABEHANDLUNG

(57) Abstract: Invention for increasing the adhesion between a pressure-sensitive compound layer which has a surface facing away from a substrate and a surface facing the substrate, and the surface of a substrate, the surface of the pressure-sensitive adhesive compound layer facing the substrate and the surface of the substrate that is covered by the pressure-sensitive adhesive compound layer being treated with atmospheric-pressure plasma.

(57) Zusammenfassung: Verfahren zur Erhöhung der Adhäsion zwischen einer Haftklebemassenschicht, die eine einem Substrat abgewandte und eine dem Substrat zugewandte Oberfläche aufweist, und der Oberfläche eines Substrats, wobei die dem Substrat zugewandte Oberfläche der Haftklebemassenschicht und die Oberfläche des Substrats, die mit der Haftklebemassenschicht bedeckt ist, jeweils mit Atmosphärendruckplasma behandelt werden.

Description**Method for increasing the adhesive properties of
pressure-sensitive adhesive compounds on substrates by
5 way of plasma treatment**

The invention relates to a process for enhancing the adhesive properties of pressure-sensitive adhesives on substrates by means of plasma treatment.

10

Pressure-sensitive adhesives are in principle subject to the problem of simultaneous requirement for volume optimization and surface optimization, i.e. cohesion and adhesion. In many instances, the weakness of an adhesive bond is found at the surface, i.e. the adhesion.

20 The term "adhesion" usually means the physical effect by which two phases brought into contact with one another are held together at their interface by virtue of intermolecular interactions arising there. The adhesion therefore determines the extent of bonding of the adhesive on the substrate surface, and can be determined in the form of what is known as "tack" and 25 in the form of bond strength. Plasticizers and/or "tackifier" resins are often added to the adhesive in order to exert a controlled effect on its adhesion.

30 Adhesion can be defined in simple terms as "the interaction energy per unit of area" [in mN/m], but this is not measurable because of experimental restrictions, for example lack of knowledge of the actual contact areas. Surface energy (SE) is also often described by using "polar" and "nonpolar" components. 35 This simplified model is now well accepted for practical purposes. This energy and its components are often measured by measuring the static contact angle of

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various test liquids. The surface tensions of these liquids are divided into polar and nonpolar components. The polar and nonpolar components of the surface energy of the test surface are determined from the observed 5 contact angles of the droplets on the test surface. The OWKR approach can by way of example be used here. An alternative method conventionally used in industry is determination by means of test solutions in accordance with DIN ISO 8296.

10

In the context of discussions of this type, the terms "polar" and "high-energy" are often treated as equivalent, as also are the terms "nonpolar" and "low-energy". This derives from the fact that polar dipole 15 forces are large in comparison with what are known as "disperse" or nonpolar interactions, which do not involve permanent molecular dipoles. The basis for this approach to surface energy and surface interactions is the assumption that polar components interact only with 20 polar components and nonpolar components only with nonpolar components.

However, it is also possible that a surface has small or moderate polar surface energy components without 25 "high" surface energy. A guideline that can be used is: as soon as the polar component of the SE is greater than 3 mN/m the surface is to be designated "polar" for the purposes of this invention. This corresponds approximately to the practical detection limit.

30

In principle, there are no specific boundaries for terms such as "high-energy" and "low-energy". For the purposes of discussion, the limit is set at 38 mN/m or 38 dyn/cm. At this and higher values by way of example 35 the printability of a surface is mostly adequate. The surface tension (= surface energy) of pure water can

serve for comparison, and is about 72 mN/m (being inter alia temperature-dependent).

In particular on low-energy substrates such as PE, PP, 5 or EPDM, but also on many coating materials, major problems arise in achieving satisfactory adhesion when pressure-sensitive adhesives or other adhesives or coatings are used.

10 Equally, it is known that polar pressure-sensitive adhesives such as the acrylates class exhibit satisfactory behavior on high-energy substrates, but often fail on very low-energy substrates. There are 15 other compositions for example based on natural or synthetic rubber which provide improved adhesive bonds on both low- and high-energy substrates.

Acrylates in particular moreover also exhibit the typical "delayed maturity" behavior, i.e. a process 20 which often takes some days to establish "flow-contact" with the substrate before the adhesive bond achieves its final strength. In most instances this behavior is undesirable.

25 And even if fewer problems are generally encountered with adhesive bonding on high-energy or polar substrates such as steel, there are still many pressure-sensitive adhesives that fail to achieve a fully satisfactory level of interaction. This is 30 apparent from peel tests where many pressure-sensitive adhesives fail to exhibit cohesive fracture on steel, indicating that adhesion is failing.

In this connection, it is often considered desirable to 35 develop adhesives which exhibit comparable behavior across different substrates.

Adhesive bonding of different substrates to one another (polar to nonpolar), for example in the case of double-sided adhesive tapes, in particular requires optimization specifically on different substrates.

5 Problems of this type could also arise during the adhesive bonding of two substrates with different properties in one plane (for example placed alongside one another or on top of one another) by a single-sided adhesive tape.

10 In particular for the sector covering high-performance adhesive tapes and adhesive assembly tapes, there are carrierless, viscoelastic adhesive tapes. In this context, the term "carrierless" means that there is no

15 layer that is necessary merely for structural integrity, and therefore that the adhesive tape has sufficient intrinsic cohesion for the specified use. There is no need to use a carrier foil or the like, for example nonwoven or textile. These adhesive tapes, too,

20 are mostly based on highly crosslinked acrylate adhesives. These pressure-sensitive adhesive tapes are moreover mostly relatively thick, typically thicker than 300 μm .

25 Such a "viscoelastic" polymer layer can be regarded as a very high-viscosity liquid which when subjected to pressure exhibits flow behavior (also termed "creep"). When these viscoelastic polymers are exposed to a slow-acting force they have a particular ability to provide

30 relaxation of the forces to which they are exposed, and the same applies to a polymer layer of this type: they are able to dissipate the forces into vibration phenomena and/or deformation phenomena (which can also in particular - at least to some extent - be

35 reversible), thus providing a "protective buffer" against the forces to which they are exposed and preferably avoiding any mechanical destruction by said

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forces, but advantageously at least mitigating same, or else at least delaying the occurrence of the destruction. When exposed to a very fast-acting force, viscoelastic polymers usually exhibit elastic behavior, 5 i.e. fully reversible deformation, and forces which extend beyond the elastic capability of the polymers here can cause fracture. Contrasting with this are elastic materials, which exhibit the elastic behavior described even on exposure to slow-acting forces. The 10 properties of these viscoelastic adhesives can also be varied greatly by using admixtures, fillers, foaming or the like.

In particular, it is often advantageous to produce a 15 syntactic foam. If this is achieved by way of example by adding expandable microballoons which expand only after addition, the term used for the purposes of this disclosure is "foaming". If, instead of this, preexpanded or non-expandable hollow fillers such as 20 hollow glass beads are added, the term used for the purposes of this disclosure is "foaming" or "filling". Both "foaming" and "filling" produce a syntactic foam.

By virtue of the elastic properties of the viscoelastic 25 polymer layer which in turn make a substantial contribution to the adhesive properties of adhesive tapes using this type of viscoelastic carrier layer, it is not possible to achieve complete dissipation of the stress caused by way of example by exposure to tension 30 or to shear. This is expressed via the relaxation capacity, which is defined as $((\text{stress}(t = 0) - \text{stress}(t) / \text{stress}(t = 0)) * 100\%$. The relaxation capacity of viscoelastic carrier layers is typically more than 50%.

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To the extent that any adhesive is viscoelastic, for high-performance carrierless adhesive tapes it is

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preferable to use adhesives which exhibit these particular relaxation properties.

A problem that is particularly difficult to solve is
5 the simultaneous optimization of adhesion and cohesion for single-layer carrierless self-adhesive tapes, there is no possibility here of specific coating of the sides of the adhesive tape for the respective substrates.

10 However, it is not then possible to proceed simply changing the chemical formulation of a pressure-sensitive adhesive in a desired manner in order to optimize adhesion, since many volume-related properties are influenced concomitantly. By way of example, these
15 can be viscosity, resistance to dynamic shocks, solvents, or temperature change, or the problem can simply be limitations of the production/polymerization process. In practice there is therefore often restriction to a particular underlying chemistry which
20 then has to be used to ensure, *inter alia*, adhesion.

It is moreover possible that a pressure-sensitive adhesive, for example a viscoelastic thick-layer product, fails both at high and at low temperatures. A
25 typical reason for failure at low temperatures is that the glass transition point has been reached and that resultant hardening occurs. In that case, fracture is often caused by adhesive failure. At the same time, the product can also soften at high temperatures with
30 resultant inadequate strength or durability in shear tests again with fracture caused by adhesive failure.

The physical pretreatment of substrates (for example by flame, corona, or plasma) to improve adhesive bond
35 strengths is especially customary with liquid reactive adhesives. One function of this physical pretreatment can also be cleaning of the substrate, for example to

remove oils, or roughening to enlarge the effective area.

The term mostly used for physical pretreatment is "activation" of the surface. This mostly implies a non-specific interaction, contrasting by way of example with a chemical reaction using the key-in-lock principle. Activation mostly implies an improvement in wettability, printability, or anchoring of a coating.

10 In the case of self-adhesive tapes, it is customary to apply an adhesion promoter to the substrate. However, this is often a complicated manual step that is susceptible to error.

15 Use of physical pretreatment of the substrate (flame, corona, or plasma) to improve the adhesion of pressure-sensitive adhesives has not achieved universal success, since nonpolar adhesives such as natural or synthetic rubber typically do not profit from that process.

20 DE 10 2007 063 021 A1 describes activation of adhesives by means of filamental corona treatment. The effect of the corona treatment was in essence restricted to increased values for holding power (HP). No improvement 25 of other adhesive properties was achieved. This is probably attributable to the formation of degradation products through electron bombardment in a corona discharge. In particular bond strength observed was unaltered or indeed reduced. In fact it is also clear 30 to the person skilled in the art that any assumption that increased values for holding power of a pressure-sensitive adhesive mean that bond strength has also been increased would be an over-simplification. Nor is it likely that the oxidative-polar modification that is 35 taught for the adhesive can provide any improvement on nonpolar substrates. Corona treatment is moreover

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associated with a large number of other restrictions, as will be described hereinafter.

The solutions available hitherto in the teaching of the prior art for increasing the bond strength of a shaped layer of viscoelastic pressure-sensitive adhesive relate to addition of one or more layers of an adhesive by lamination, thus giving a multilayer structure. The obvious disadvantages of a multilayer structure are the increased manufacturing cost and the number of steps in the process. This type of solution is in principle susceptible to problems of delamination between the layers, since interlaminate adhesion is not based on strong covalent chemical interactions but instead on nonspecific interactions of general polar type. In this context, corona treatments on interior interfaces of adhesive tapes are described in order to improve interlaminate adhesion, for example in WO 2006/027389 A1, DE 10 2006 057 800 A1, or EP 2 062 951 A1.

Chemico-physical modifications of substrates are also in principle known, with subsequent application of adhesive tapes, where the adhesive tapes themselves are not modified. DE 695 31 394 T2 describes by way of example how chemico-physical oxidation of a polymer surface can be used in combination with application of a coupling agent in an electrical field in order to improve adhesion of a surface. The application of an unmodified adhesive tape to the surface thus modified is also claimed.

A process for improving the adhesion of pressure-sensitive adhesives is therefore desirable, where the process:

- should ideally have a favorable effect on all aspects of adhesion such as bond strength, shear resistance, and flow-contact,
- should not be restricted to particular classes of substrates or pressure-sensitive adhesives, and
- should have good technical suitability for achieving the object.

10 It is an object of the invention to find the stated favorable effects on physical surface modification of pressure-sensitive adhesives and substrates, in order to achieve high-strength bonds. The main object is to achieve a high level of anchoring between the pressure-
15 sensitive adhesive layer and the substrate.

Said objects are achieved via a process as described in the main claim. The dependent claims here provide advantageous embodiments of the subject matter of the
20 invention.

Accordingly, the invention provides a process for increasing the adhesion between a layer of pressure-sensitive adhesive which has a surface facing away from the substrate and which has a surface facing toward the substrate and the surface of a substrate, where that surface of the layer of pressure-sensitive adhesive that faces toward the substrate and the substrate surface covered with the layer of pressure-sensitive
25 adhesive are respectively treated with atmospheric-pressure plasma.

A surprising feature of the process of the invention is that a significant increase both of bond strength and
30 of shear resistance and of other adhesion properties is observed for very many adhesive-tape-substrate combinations. In particular, this is also true for low-

energy substrates. This improvement is obtained irrespective of whether the substrate is very smooth or rough, or even structured/textured.

5 Surprisingly, the process of the invention is robust and easy to use.

The plasma is preferably applied by means of one or more nozzles, preferably operating with compressed air 10 or N₂.

It is particularly preferable that the plasma is applied by means of a rotary nozzle, particularly preferably operating with compressed air.

15 Modern indirect plasma techniques are often based on a nozzle system. These nozzles can be of round or linear design and, without any intention of introducing a restriction here, rotary nozzles are sometimes used. This type of nozzle system is advantageous because it 20 is flexible and inherently suitable for single-side treatment. Nozzles of this type, for example from Plasmatreat, are widely used in industry for the pretreatment of substrates prior to adhesive bonding. Disadvantages are the indirect treatment, which is less 25 efficient because it is discharge-free, and the resultant reduced web speeds. However, the customary design of a round nozzle is especially suitable for treating narrow webs of product, for example an adhesive tape which is a few cm in width.

30 Various plasma generators are available in the market, and differ in the method of plasma generation, in nozzle geometry, and in the gas atmosphere used. Although the treatments differ inter alia in their 35 efficiency, the fundamental effects are mostly similar and are determined especially via the gas atmosphere used. Plasma treatment can take place in a variety of

atmospheres, and this atmosphere can also comprise air. The treatment atmosphere can be a mixture of various gases selected inter alia from N₂, O₂, H₂, CO₂, Ar, He, and ammonia, where water vapor or other constituents 5 may also have been admixed. This list of examples does not constitute any restriction.

In one advantageous embodiment of the invention, the following pure, or mixtures of, process gases form a treatment atmosphere: N₂, compressed air, O₂, H₂, CO₂, 10 Ar, He, ammonia, ethylene, where water vapor or other volatile constituents may also have been added. Preference is given to N₂ and compressed air.

In principle, it is also possible to admix coating 15 constituents or polymerizing constituents in the form of gas (for example ethylene) or liquids (atomized in the form of aerosol) with the atmosphere. There is almost no restriction on the aerosols that can be used. Plasma techniques involving indirect operation are 20 particularly suitable for the use of aerosols, since there is no risk here of contamination of the electrodes.

Since the effects of plasma treatment are chemical in 25 nature, and alteration of surface chemistry is of prime importance, the methods described above can also be described as chemico-physical treatment methods. Although there can be differences in the detail, there is no intention to emphasize any particular technique 30 for the purposes of this invention, either in terms of the method of plasma generation or in terms of engineering.

Preference is further given to the application of plasma jet by means of rotation of the nozzle tip. The 35 plasma jet then passes in a circle across the substrate at a predetermined angle and advantageously provides a good treatment width for adhesive tapes. Given an

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appropriate advance rate, the rotation causes the treatment jet to pass repeatedly across the same locations, and therefore implicitly to achieve repeated treatment.

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In an equally preferred variant of the plasma treatment, a fixed plasma jet is used without any rotary nozzle.

10 In an equally preferred plasma treatment, a lateral arrangement of a plurality of nozzles, offset if necessary, is used to provide treatment over an adequate width with no gaps and with some overlaps. A disadvantage here is the necessary number of nozzles, 15 and typically it is necessary to use from two to four non-rotating round nozzles instead of one rotary nozzle.

20 The design of a round nozzle is generally preferred for adhesive bonding of narrow adhesive tapes. However, linear nozzles are also suitable.

25 In another advantageous embodiment of the invention, the treatment distance is from 1 to 100 mm, preferably from 3 to 50 mm, particularly preferably from 4 to 20 mm.

It is further preferable that the treatment velocity is from 0. to 200 m/min, preferably from 1 to 50 m/min, particularly preferably from 2 to 20 m/min.

30

Particular preference is given to universal treatment by means of a rotary nozzle with from 9 to 12 mm of distance between nozzle and the surface requiring treatment with a relative lateral movement of from 4 to 35 6 m/min between nozzle and substrate.

The treatment must, of course, take place within a range within which the gas is reactive or, respectively, within a distance (for example from a nozzle) within which the gas remains reactive. In the 5 case of a nozzle, said range comprises the effective range of the plasma jet.

The plasma treatment of the surfaces can also be repeated.

10 A treatment can be repeated in order to achieve the desired intensity. This always occurs in the case of the preferred rotary treatment or in the case of nozzle arrangements which overlap to some extent.

15 The required treatment intensity can by way of example be achieved via a plurality of passes under a nozzle or via arrangement of a plurality of nozzles in series.

The repeated treatment can also be utilized in order to refresh the treatment.

20 Division of at least one of the treatments into a plurality of individual treatments is another possibility.

25 In principle, both surfaces are treated, i.e. adhesive tape and substrate. In the case of double-sided adhesive tapes this can be true for both sides.

There is no prescribed juncture, but a juncture briefly prior to adhesive bonding is preferred.

30 In the case of treatment directly prior to the adhesive bonding the chronological separation from the adhesive bonding can be <1 s, in the case of in-line treatment prior to the adhesive bonding it can be in the range from seconds to minutes, in the case of off-line treatment it can be in the range from hours to days, 35 and in the case of treatment in the production process of the adhesive tape it can be in the range from days to many months.

Plasma treatment can, like most physical treatments, become less effective over the course of time. However, this phenomenon can be greatly dependent on the details 5 of the treatment and of the substrate and of the adhesive tape. During any possible decrease of effectiveness, adhesion obviously remains improved in comparison with the untreated condition. The improved adhesion during said period is in principle also part 10 of this teaching.

A repeated treatment can in principle be used to supplement or refresh a treatment.

The chronological separation between the multiple treatments can therefore vary from about 0.1 s (during 15 the rotation of the nozzle) up to about 1 year (when a product is treated before delivery and there is a refreshment treatment prior to use).

The treatments of the two surfaces are in principle independent of one another, spatially and 20 chronologically.

By way of example, it is possible that one treatment takes place in a first step and that the second treatment takes place in a second step.

One or both of said treatments can take place in-line 25 with the adhesive bonding.

There is no restriction on the number of individual nozzles or other plasma generators used for a single treatment or for all of the treatments.

There is no restriction on the number of individual 30 treatments carried out with the plasma generator(s).

By way of example, it would be conceivable to use a particular plasma generator for the pretreatment of one of the relevant surfaces, and at a subsequent juncture to use a different plasma generator to supplement or 35 refresh this treatment.

By way of example, the surface could also have been flame- or corona-pretreated before it is treated with

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the process taught here. By way of example, foils or plastics parts are sometimes provided with a physical pretreatment by the producer.

5 In one variant of the invention, the plasma is applied by a plasma nozzle unit with additional introduction of a precursor material into the operating gas stream or into the plasma jet. In this case, contact can take place at different times or simultaneously.

10

An atmospheric-pressure plasma (and surface treatment by means of same) differs substantially from a corona discharge (and surface treatment by means of same).

15 Corona treatment is defined as a surface treatment which uses filamental discharges and which is generated via high alternating voltage between two electrodes, whereupon the discrete discharge channels come into contact with the surface requiring treatment, in which 20 connection see also Wagner et al., Vacuum, 71 (2003), pp. 417 to 436. The process gas can be assumed to be ambient air unless otherwise stated.

25 The substrate is almost always placed within or passed through the discharge space between an electrode and an opposing electrode, this being defined as "direct" physical treatment. Substrates in the form of webs here are typically passed between an electrode and a grounded roll.

30

In particular, the term "corona" mostly means a "dielectric barrier discharge" (DBD). At least one of the electrodes here is composed of a dielectric, i.e. of an insulator, or has a coating or covering of same.

35

The treatment intensity of a corona treatment is stated as "dose" in $[\text{Wmin}/\text{m}^2]$, where the dose $D = P/b \cdot v$, where

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P = electrical power [W], b = electrode width [m], and v = web speed [m/min].

The substrate is almost always placed within, or passed
5 through the discharge space between an electrode and an
opposing electrode, this being defined as "direct"
physical treatment. Substrates in web form here are
typically passed between an electrode and a grounded
roll. Another term that is also sometimes used is
10 "ejected corona" or "single-side corona". This is not
comparable with an atmospheric-pressure plasma, since
very irregular discharge filaments are "ejected"
together with a process gas, and it is impossible to
achieve stable, well-defined, efficient treatment.

15

"Atmospheric-pressure plasma" is defined as an
electrically activated, homogeneous, reactive gas which
is not in thermal equilibrium, with a pressure close to
ambient pressure. Electrical discharges and ionizing
20 processes in the electrical field activate the gas and
generate highly excited states in the gas constituents.
The gas used or the gas mixture is termed process gas.
In principle, it is also possible to admix coating
constituents or polymerizing constituents in the form
25 of gas or aerosol with the plasma atmosphere.

The term "homogeneous" indicates that there are no
discrete, inhomogeneous discharge channels encountering
the surface of the substrate requiring treatment (even
30 though these may be present in the generation space).

The "not in thermal equilibrium" restriction means that
the ion temperature can differ from the electron
temperature. In a thermally generated plasma these
35 would be in equilibrium (in which connection see also
by way of example Akishev et al., *Plasmas and Polymers*,
Vol. 7, No. 3, Sept. 2002).

When atmospheric-pressure plasma is used for the physical treatment of a surface, the electrical discharge mostly takes place in a space separate from 5 the surface. The process gas is then passed through said space and electrically activated, and then in the form of plasma mostly passed through a nozzle onto the surface. The reactivity of the plasma jet mostly decreases rapidly with time after discharge: in spatial 10 terms typically after millimeters to centimeters. An English term often used for the decreasing reactivity of the plasma as it is discharged is "afterglow". The lifetime of the plasma discharged, and the distance over which it remains effective, depend on molecular 15 details and on the precise method of plasma generation.

This type of physical treatment is termed "indirect" when the treatment is not undertaken at the location of 20 generation of the electrical discharges. The treatment of the surface takes place at or in the vicinity of atmospheric pressure, but there may be increased pressure in the electrical discharge space.

However, there are also by way of example known 25 generation systems for carrying out indirect plasma treatments in which electrical discharges take place in the gas stream outside of a nozzle and likewise provide a plasma-jet treatment.

30 Equally, there are known homogeneous atmospheric-pressure plasmas in which the treatment takes place in the discharge space at atmospheric pressure, the term used being "glow discharge plasma", see for example T. Yokoyama et al., 1990 J. Phys. D: Appl. Phys. 23 1125.

35

Constituents of the atmospheric-pressure plasma can be:

- highly excited atomic states

- highly excited molecular states
- ions
- electrons
- unaltered constituents of the process gas.

5

It is preferable to use commercially available systems for the generation of atmospheric-pressure plasma. The electrical discharges can take place between metal electrodes, or else between metal dielectric, or else 10 are generated via piezoelectric discharge or other methods. Some examples of commercial systems are Plasma-Jet (Plasmatreat GmbH, Germany), Plasma-Blaster (Tigres GmbH, Germany), Plasmabrush and Piezobrush (Reinhausen, Germany), Plasmaline (VITO, Belgium), or 15 ApJet (ApJet, Inc., USA). The systems mentioned operate with different process gases, for example air, nitrogen or helium, and different resultant gas temperatures.

Preference is given to the process from Plasmatreat 20 GmbH (Steinhagen, Germany) described by way of example in the following quotation from WO 2005/117507 A2:

"The prior art of EP 0 761 415 A1 and EP 1 335 641 A1 discloses a plasma source in which by means of a with application of a high-frequency high voltage in a 25 nozzle tube between a pin electrode and an annular electrode by means of a nonthermal discharge from the operating gas a plasma jet is generated, which is discharged from the nozzle aperture. At a suitably adjusted flow rate, said nonthermal plasma jet 30 comprises no electrical streamers, and it is therefore possible to direct only the high-energy, but low-temperature plasma jet onto the surface of a component. Streamers here are the discharge channels along which the electrical discharge energy proceeds during the 35 discharge.

The plasma jet can also be characterized via the high electron temperature, the low ion temperature, and the high gas velocity."

5 In the case of a corona discharge as defined above, the high voltage applied causes formation of filamental discharge channels with accelerated electrons and ions. The low-mass electrons in particular encounter the surface at high velocity with energies that are
10 sufficient to break most of the molecular bonds. The reactivity of the other reactive gas constituents produced is mostly a subordinate effect. The broken bond sites then react further with constituents of the air or of the process gas. An effect of decisive
15 importance is the formation of short-chain degradation products via electron bombardment. Treatments of higher intensity also cause significant ablation of material.

The reaction of a plasma with the substrate surface
20 promotes the direct "incorporation" of the plasma constituents. Alternatively, it is possible that an excited state or an open bond site is produced on the surface and that these then undergo secondary further reaction, for example with atmospheric oxygen. In the
25 case of some gases, such as noble gases, no chemical bonding of the process gas atoms or process gas molecules to the substrate is to be expected. The activation of the substrate here takes place exclusively by way of secondary reactions.

30 The significant difference is therefore that in the case of the plasma treatment there is no direct exposure of the surface to discrete discharge channels. The effect therefore takes place homogeneously and non-
35 aggressively primarily by way of reactive gas constituents. Free electrons are possibly present during indirect plasma treatment, but these are not

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accelerated electrons, since the treatment takes place outside of the generating electrical field.

The plasma treatment is therefore less destructive than
5 a corona treatment, since no discrete discharge channels encounter the surfaces. Amounts produced of short-chain degradation products are smaller, where these can form a layer with adverse effect on the surface. Better wettability values can therefore often
10 be achieved after plasma treatment than after corona treatment, with longer-lasting effect.

The reduced extent of chain degradation and the homogeneous treatment via use of a plasma treatment
15 make a substantial contribution to the robustness and effectiveness of the process taught.

The adhesive of the invention is a pressure-sensitive adhesive, i.e. an adhesive which can give a durable
20 bond with almost all adhesion substrates even when the pressure applied is relatively weak, and after use can in essence in turn be peeled from the adhesion substrate to leave no residue. A pressure-sensitive adhesive has a permanent pressure-sensitive adhesive
25 effect at room temperature, i.e. because its viscosity is sufficiently low and its tack is high it wets the surface of the respective adhesion substrate even when the pressure applied is low. The adhesive bonding capability of the adhesive derives from its adhesive
30 properties, and the peelability derives from its cohesive properties.

It is preferable that the layer of pressure-sensitive adhesive is based on natural rubber, synthetic rubber,
35 or polyurethanes, and the layer of pressure-sensitive adhesive here is preferably composed exclusively of acrylate or mostly of acrylate (hotmelt or UV), in

particular being viscoelastic, or else blends and copolymers.

The pressure-sensitive adhesive can have been blended 5 with tackifiers in order to improve adhesive properties.

Suitable tackifiers, also termed tackifier resins, are in principle any of the known classes of substance. Examples of tackifiers are hydrocarbon resins (for 10 example polymers based on unsaturated C₅- or C₉-monomers), terpene-phenolic resins, polyterpene resins based on raw materials such as α- or β-pinene, aromatic resins such as coumarone-indene resins or resins based on styrene or α-methylstyrene, for example colophony 15 and its downstream products, e.g. disproportionated, dimerized or esterified colophony, e.g. reaction products with glycol, glycerol, or pentaerythritol, to mention just a few. Preference is given to resins without readily oxidizable double bonds, for example 20 terpene-phenolic resins, aromatic resins, and particularly preferably resins produced via hydrogenation, for example hydrogenated aromatic resins, hydrogenated polycyclopentadiene resins, hydrogenated colophony derivatives, or hydrogenated 25 polyterpene resins. Preference is given to resins based on terpene-phenolics and on colophony esters. Equally, preference is given to tackifier resins with softening point above 80 °C in accordance with ASTM E28-99 (2009). Particular preference is given to resins based on 30 terpene-phenolics and on colophony esters with softening point above 90 °C in accordance with ASTM E28-99 (2009). Typical amounts used are from 10 to 100 parts by weight, based on polymers of the adhesive.

35 In order to achieve a further improvement in cable compatibility, the adhesive formulation can optionally

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have been blended with light stabilizers or primary and/or secondary antioxidants.

Antioxidants that can be used are UV absorbers, sterically hindered amines, thiosynergists, phosphites, 5 or products based on sterically hindered phenols.

It is preferable to use primary antioxidants such as Irganox 1010 (tetrakis(methylene (3,5-di(tert)butyl-4-hydrocinnamate))methane; CAS No. 6683-19-8 (sterically hindered phenol), BASF) or Irganox 254, alone or in 10 combination with secondary antioxidants such as Irgafos TNPP or Irgafos 168.

The antioxidants here can be used in any desired combination with one another, and mixtures that exhibit 15 particularly good antioxidant effect here are those of primary and secondary antioxidants in combination with light stabilizers such as Tinuvin 213.

Antioxidants that have proven very particularly advantageous are those in which a primary antioxidant 20 has been combined with a secondary antioxidant in one molecule. These antioxidants involve cresol derivatives whose aromatic ring has substitution by thioalkyl chains at any desired two different sites, preferably in ortho- and meta-position with respect to the OH 25 group, where the bonding of the sulfur atom on the aromatic ring of the cresol unit can also be by way of one or more alkyl chains. The number of carbon atoms between the aromatic system and the sulfur atom can be from 1 to 10, preferably from 1 to 4. The number of 30 carbon atoms in the alkyl side chain can be from 1 to 25, preferably from 6 to 16. Particular preference is given here to compounds of the following type: 4,6-bis(dodecylthiomethyl)-o-cresol, 4,6-bis(undecylthio- 35 methyl)-o-cresol, 4,6-bis(decylthiomethyl)-o-cresol, 4,6-bis(nonylthiomethyl)-o-cresol, or 4,6-bis(octylthiomethyl)-o-cresol. Antioxidants of this type are

supplied for example by Ciba Geigy as Irganox 1726 or Irganox 1520.

The amount of the antioxidant or antioxidant package
5 added should be in the range from 0.1 to 10% by weight, preferably in the range from 0.2 to 5% by weight, particularly preferably in the range from 0.5 to 3% by weight, based on total solids content.

10 In order to improve processing properties, the adhesive formulation can moreover have been blended with conventional processing aids such as antifoams, deaerators, wetting agents, or flow control agents. Suitable concentrations are in the range from 0.1 up to
15 5 parts by weight, based on solids.

Fillers (reinforcing or nonreinforcing) such as silicon dioxides (spherical, acicular, lamellar, or irregular, for example the fumed silicas), glass in the form of
20 solid or hollow beads, non-expandable, organic microspheres made of in particular phenolic resins, chalk, calcium carbonates, zinc oxides, titanium dioxides, aluminum oxides, or aluminum oxide hydroxides, carbon blacks, fibers, carbon nanotubes
25 (CNTs), can serve to improve processability or adhesion properties. Suitable concentrations are in the range from 0.1 to 70 parts by weight, based on solids, in particular up to 40 parts by weight, particularly preferably from 1 to 20 parts by weight.

30 Fibers that can be used are (chemically derived) fibers (staple fibers or continuous filaments made of synthetic polymers, also known as synthetic fibers, made of polyester, polyamide, polyimide, aramid, polyolefin, polyacrylonitrile, or glass, (chemically derived) fibers made of natural polymers, for example
35 cellulosic fibers (viscose, modal, lyocell, cupro, acetate, triacetate, Cellulon), or for example rubber

fibers, or for example vegetable-protein fibers and/or for example animal-protein fibers and/or natural fibers made of cotton, sisal, flax, silk, hemp, linen, coconut, or wool. Yarns manufactured from the stated 5 fibers are moreover equally suitable. Staple fibers are individual fibers of restricted length. Filaments (continuous fibers) are the opposite of staple fibers. Preference is given to stable pressure-resistant hollow microspheres of which the shell is not based on 10 polymers.

In particular, particular preference is also given to the combination of filling and resin addition. As can be seen from the data sets in the examples, addition of resin and of a filler can permit high maximal force in 15 peel tests, at the same time as high shear resistance in terms of good holding power and a small value for shear under static load.

It is moreover possible to add the following, or to 20 incorporate them by compounding: low-flammability fillers, such as ammonium polyphosphates, and also electrically conductive fillers, such as conductive carbon black, carbon fibers and/or silver-coated beads, and also ferromagnetic additives, such as iron(III) 25 oxides, antioxidants, light stabilizers, antiozonants, before or after increasing the concentration of the polyacrylate.

Particular preference is given to expandable 30 microballoons, because these permit foaming of the adhesive.

Microballoons involve resilient hollow spheres which have a thermoplastic polymer shell. Said spheres have a filling of low-boiling-point liquids or liquefied gas. 35 Shell material used is in particular polyacrylonitrile, PVDC, PVC or polyacrylates. Particularly suitable as low-boiling-point liquid are hydrocarbons of the lower

alkanes, such as isobutane or isopentane, enclosed in the form of liquefied gas under pressure within the polymer shell. Exposure of the microballoons, in particular exposure to heat, firstly softens the 5 exterior polymer shell. At the same time, the liquid blowing gas present in the shell is converted to its gaseous state. During this process, the microballoons expand irreversibly and three-dimensionally. The expansion ends when the internal and external pressures 10 are equal. The polymeric shell is retained, and the result here is therefore a closed-cell foam.

A wide variety of types of microballoon is available commercially, for example the Expancel DU products (dry 15 unexpanded) from Akzo Nobel, which differ in essence in their size (from 6 to 45 μm diameter in the unexpanded state) and in the temperature at which they begin to expand (from 75 to 220°C). If the type of microballoon and, respectively, the foaming temperature have been 20 adjusted appropriately for the temperature profile required for the compounding of the material and the machine parameters, compounding of the material and foaming can also take place simultaneously in a single step.

25

Unexpanded types of microballoon are moreover also available in the form of aqueous dispersion with about 40 to 45% by weight content of solids or of 30 microballoons, and also moreover in the form of polymer-bound microballoons (masterbatches), for example in ethyl-vinyl acetate with about 65% by weight microballoon concentration. The microballoon dispersions and the masterbatches are as suitable as the DU products for the foaming of adhesives in 35 accordance with the process of the invention.

In particular for "foam-in-place" applications, it can be advantageous to use expandable microballoons, in preexpanded form (expanded by the producer, and sometimes also further expandable subsequently, for 5 example the DE products from Expancel), in incipiently expanded form (partially expanded in the process of production of the adhesive tape), or in unexpanded form. In the case of "foam-in-place" applications, the foaming of the adhesive tape is initiated or continued 10 after adhesive bonding.

Other possible variants for the foaming of the adhesive can be chemical foaming with substances that cleave to give a gas, or the physical foaming that is known from 15 the literature, via mechanical incorporation of gases such as air or nitrogen.

If the hollow bodies (in particular microballoons) introduced to form the foam are destroyed subsequently, 20 it is nevertheless possible to obtain a non-syntactic foam of high quality.

In relation to the preferred adhesives, it must be noted that not every arbitrarily selected test can 25 demonstrate the improvement of adhesion via the invention. If by way of example the fracture in a bond strength test was 100% cohesive fracture without the treatment taught, the increased adhesion cannot provide any measurable gain, since the weakest bond is provided 30 by the bulk properties of the adhesive tape. The increased adhesion can thus be hidden.

In particular cases, a complex mixed fracture with components of adhesive and cohesive failure can 35 generate a high force in the peel test. If adhesion is improved by the treatment taught, the force measured in the peel test can fall, because by way of example the

type of fracture changes to pure cohesive fracture. The improved adhesion could be demonstrated in such cases by way of example via the increased amount of residues of the composition on the substrate.

5

In principle, the decisive factor for ability to increase the practical performance capability of the adhesive tape via increased adhesion is the combined effect of pressure-sensitive adhesive and carrier.

10

The preferred properties mentioned below lead to a particularly large improvement in adhesion (tested for example via bond strength measurement) through the process taught, since the bulk properties of the adhesive tape then permit this. However, this particular increase is surprising, since the good bulk properties are not so clearly discernible when adhesion is weak.

20

A suitable filler, for example using hollow glass beads, can markedly increase the pressure- and shear-resistance of a pressure-sensitive adhesive. However, this favorable bulk property cannot be utilized until adhesion is sufficiently high. Very many different ideas have been disclosed and described for the filling of pressure-sensitive adhesives. Most of them improve aspects of cohesion, but not of adhesion. Because of the poor adhesion, the maximal performance capability of the products is often not fully utilized (or even known). The invention is therefore particularly suitable for these filled pressure-sensitive adhesives, in particular highly filled pressure-sensitive adhesives, in particular syntactic foams.

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The adhesive treated in the invention can have been applied on a carrier material, in particular a foil carrier (made of PE, PP, PS, or polyester, such as

PET), foam carrier, textile carrier, nonwoven carrier, or paper carrier, or a composite carrier.

The carrier can comprise one or more layers of foils or of foam carriers.

5

The adhesive tape formed from carrier and adhesive can moreover comprise one or more functional layers such as barrier layers, layers of material that can form a hotmelt, or other functional layers.

10 The carrier preferably has viscoelastic properties.

On that side of the carrier that faces away from the substrate there can moreover be a second adhesive present, which does not have to be identical with the 15 first, and which can have been treated but has not necessarily been treated by the process of the invention.

The uncovered side of the second adhesive layer can 20 have been treated with atmospheric-pressure plasma. This also applies to the "second" substrate on which the second adhesive is adhesive-bonded.

Preference is given to double-sided self-adhesive 25 tapes, preferably on a foil carrier or foam carrier.

Advantageous embodiments of the invention comprise the adhesive tapes K1 to K8 described in the examples.

30 Preference is moreover given to double-sided carrierless adhesive transfer tapes.

It is particularly preferable that the thickness of the layer of pressure-sensitive adhesive or of the adhesive 35 tape formed thereby is $\geq 20 \mu\text{m}$, preferably $\geq 100 \mu\text{m}$, very particularly preferably $\geq 300 \mu\text{m}$, and/or at most $\leq 1500 \mu\text{m}$, preferably $\leq 1000 \mu\text{m}$.

Preference is in particular given to a single-layer structure made of a viscoelastic layer. No weaknesses can arise here at the inner interfaces, and the product 5 is simple and inexpensive. The greatest compromises between adhesion and cohesion in the design of the product are typically involved here, since no specific external layers are used to ensure adhesion. These products therefore profit particularly from 10 subsequently increased adhesion.

In particular, preference is given to a single-layer structure of a filled and resin-blended viscoelastic pressure-sensitive adhesive tape, and particular 15 preference is given here to a syntactic foam.

Preference is equally given to a multilayer structure of viscoelastic layers.

20 In principle, a suitable substrate is any of the substrates that can actually be treated with the selected plasma. The substantial exceptions in the case of most atmospheric plasma treatments are fluoropolymer-based plastics, and among these primarily 25 the fully fluorinated plastics. However, even these materials can be treated with suitable intensive plasmas.

In particular, the concept underlying the invention 30 includes not only high-energy materials but also low-energy materials, or polar and nonpolar materials.

Particular preference is given to the substrates mentioned in the examples.

35

Particular preference is given to steel, aluminum, polyesters such as PET, PVC, PC, PMMA, PE, PP, EPDM,

glass, ABS, coating materials and coatings (inter alia acrylate- or PU-based), CEC, composite materials such as CFC, wood-composite products, coated paperboard packaging materials, foils, bottles, plastics 5 containers, but this list is not to be interpreted as exclusive.

Treatment with atmospheric-pressure plasma therefore differs - as already mentioned - essentially from 10 corona treatment. Indirect treatment with atmospheric-pressure plasma by means of nozzles is particularly suitable here for the process taught.

A plasma nozzle with a stable plasma jet can still 15 achieve a homogeneous effect from a distance of some cm. In contrast, a typical traditional corona gap has a maximal aperture of from 2 to 3 mm, and at greater distances either discharge becomes impossible or the discharges become very inhomogeneous. Treatment giving 20 good results from thick irregularly shaped substrates or components is therefore possible only by using a plasma nozzle.

A plasma nozzle is particularly suitable for treatments of narrow materials with the width of an adhesive tape. 25 Plasma nozzles are available with various geometries: round, linear, etc. The design of a round nozzle is generally suitable for treatment of narrow adhesive tapes. However, linear nozzles are also suitable.

The plasma has low potential and can be rendered 30 practically potential free by taking an appropriate measure. It is therefore also possible to treat sensitive electronic components by the process taught.

Plasma treatment in air can be ozone-free (TÜV Nord, Report No. 34 268 8, for a plasma generator from 35 Plasmatreat GmbH). Another price advantage is obtained when no ozone destructor is required.

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Indirect plasma treatment by means of nozzles does not damage the reverse side of the substrate or adhesive tape, because no reverse opposing electrode is used. Self-adhesive tapes typically have a release liner or 5 release coating (e.g. siliconized) which would be damaged by unintended corona discharges on the reverse side. A potential-free plasma-nozzle treatment is very particularly suitable for preventing reverse-side discharges.

10

The process of the invention provides a wide variety of advantages.

The process can achieve an increase not only in bond strength but also in shear strength, over a wide range 15 of pressure-sensitive adhesives and substrates. The surface energy of the substrate prior to treatment is of no significance.

The process is robust and not dependent on optimized 20 treatment for each composition and/or on optimized treatment for each substrate.

In many cases, the process can generate a comparable final bond strength with a given adhesive tape across a 25 plurality of classes of substrate, frequently via cohesive fracture. This "universal tape" provides particular advantages, for example in the design of adhesive bond with different adhesive-bonding partners.

30 The effect of the process taught is synergistic, i.e. more than the sum of the individual effects of treatment of substrate or adhesive.

In particular, the frequent lack of success with 35 treatment of one side alone renders the treatment of both sides non-obvious.

The invention can combine the following desirable properties in a single adhesive tape (with the precondition of suitable bulk properties):

- 5 ° high peel strength
- ° high initial adhesion
- ° high shear resistance
- ° high temperature resistance
- ° suitability for substrates with low surface energy (LSE).

10

The process is so robust and simple that it can achieve maximization of adhesion with a single parameter set (for example in accordance with the process PV1 explained in the examples) for most of the adhesive 15 tapes and substrates studied. "Maximization" is defined here as an increase up to the measurable limit. Either the material encounters its cohesion limit or the measured time in holding-power tests is too long. A further increase in adhesion cannot then provide any 20 further gain in terms of strength of adhesive bond. However, measurable differentiation when other analytical methods are used is not excluded.

The process taught can therefore be a "universal 25 treatment". This is a particular feature of the invention.

An adhesive tape thus treated and adhesive-bonded exhibited the same or at least comparable performance 30 on all substrates. By virtue of the process taught, the adhesive bonds became independent of the substrate. In this sense, the adhesive tapes described therefore assumed the character of "universal adhesive tapes". This is equally a particular feature of the invention. 35 This is particularly surprising when acrylate adhesives are used.

In particular because the invention permits equivalent adhesive bonding on different substrates: it is particularly desirable to avoid any necessity of developing a specific pretreatment method for each 5 substrate and each adhesive in order to obtain an adequate adhesive bond.

The process also generates good resistance to nonpolar solvents.

10

Test methodsBond strength, steel, 90°

The bond strength tests were carried out by methods 15 based on PSTC-101 by peeling the adhesive tapes from the substrates at 300 mm/min at an angle of 90° between peel direction and substrate. For the test, the substrates were inserted into a specific holder which permits perpendicular upward peeling of the sample at 20 an angle of 90°. A Zwick tensile tester was used to measure the bond strength. The test results have been averaged over a peel distance of at least 75 mm, are stated in N/cm after standardization for the width of 25 the adhesive tape, and have been averaged from three tests.

The double-sided carrierless adhesive tapes were laminated to a 36 µm etched PET foil, which gives a very good bond to the surface of the adhesive. The 30 other adhesive tapes have a carrier with good tensile strength.

Shortly after adhesive bonding, a 2 kg roller was used 5 times to apply pressure to the test samples, the 35 velocity of roller application being 10 m/min. Unless otherwise stated, this was followed by three days of aging at 23°C and 50% +/- 5% rel. humidity prior to the

test. The test conditions used for bond strength determination were 23°C +/- 1°C temperature and 50% +/- 5% rel. humidity. The bond strength test applied tension either to the laminated PET foil or to the 5 carrier of the adhesive tape.

Unless otherwise stated, the expression "bond strength" in this invention is used for the parameters mentioned here, in particular peel angle 90° and peel velocity 10 300 mm/min. In particular, the aging time of three days at 23°C and 50% +/- 5% rel. humidity after adhesive bonding and prior to the test is also included here.

Holding power

15 Holding power gives the strength of the adhesive bond for a loading force acting parallel to the adhesive-bonded tape. It is the time required for shear load to remove an adhesive tape completely from a steel plate.

20 To determine the values for holding power, a double-sided adhesive tape is adhesive-bonded between two polished steel plates with an adhesive-bonding area of 25 mm x 20 mm. The steel plates have holes suitable for the suspension of the test sample and for attachment of 25 a suspended weight. After adhesive bonding, pressure is applied for one minute to the test samples by using a force of 600 N. Unless otherwise stated, the test samples are aged for 14 days at 23°C and 50% +/- 5% rel. humidity after adhesive bonding and prior to 30 testing. Unless otherwise stated, the test samples are tested at constant 70°C in a temperature-controlled chamber and with static loading with a weight of 1 kg. The time to failure in minutes [min] is stated as result.

35

Static glass transition temperature

Static glass transition temperature was determined by dynamic scanning calorimetry in accordance with DIN 53765. Unless otherwise stated in any individual case, the glass transition temperature T_g information relates 5 to the glass transition temperature T_g in accordance with DIN 53765:1994-03.

Molecular weights

Average molecular weight M_w and polydispersity D were 10 determined by means of gel permeation chromatography (GPC). THF was used as eluent with 0.1% by volume of trifluoroacetic acid. The measurement was made at 25°C. The precolumn used was PSS-SDV, 5 μm , 103 Å (10-7 m), ID 8.0 mm \times 50 mm. The separation columns used were 15 PSS-SDV, 5 μm , 103 Å (10-7 m), 105 Å (10-5 m) and 106 Å (10-4 m) with in each case ID 8.0 mm \times 300 mm. Sample concentration was 4 g/l, and flow rate was 1.0 ml per minute. Measurements were made against PMMA standards.

20 Solids content

Solids content is a measure of the proportion of constituents that cannot be vaporized in a polymer solution. It is determined gravimetrically by weighing the solution, then removing the vaporizable fractions 25 in a drying oven at 120°C for 2 hours, and weighing the residue.

K value (FIKENTSCHER method):

The K value is a measure of the average molecular size 30 of highly polymeric substances. It is measured by producing one percent (1 g/100 ml) polymer solutions in toluene and determining their kinematic viscosities with the aid of a VOGEL-OSSAG viscometer. After standardization to the viscosity of toluene, the 35 relative viscosity is obtained, and the K value can be calculated from this by the method of Fikentscher (Polymer 8/1967, 381 ff.).

Density determination by means of pyknometer:

The principle of measurement is based on the displacement of the liquid present in the pyknometer.

5 The empty pyknometer and the liquid-filled pyknometer are first weighed, and then the body on which the measurement is to be made is placed in the vessel.

The density of the body is calculated from the weight differences:

10 If

- m_0 is the mass of the empty pyknometer,
- m_1 is the mass of the water-filled pyknometer,
- m_2 is the mass of the pyknometer with the solid,
- m_3 is the mass of the pyknometer with the solid,

15 with water added until it is full,

- ρ_w is the density of water at the appropriate temperature,
- ρ_F is the density of the solid.

The density of the solid is then given by:

20

$$\rho_F = \frac{(m_2 - m_0)}{(m_1 - m_0) - (m_3 - m_2)} \cdot \rho_w$$

Three determinations are carried out for each sample.

It should be noted that this method gives the envelope

25 density (in the case of porous solids, here a foam, the density based on the volume inclusive of the pore spaces).

A number of examples will be used below for further

30 explanation of the invention, without any intention of resultant restriction of any type.

Plasma process PV1

Plasma process PV1 used a RD1004 plasma generator with

35 an FG5001 plasma generator from Plasmatreat GmbH

(Steinhagen, Germany). The plasma jet generated was passed out at a slightly oblique angle through a nozzle tip rotating at 2800/min, so that the treatment describes a circle. The nozzle here had been attached 5 fixedly and vertically at an angle of 90° to the substrate, and a moving table on which the samples (substrates) had been placed was passed under the nozzle.

10 With uniform movement of the nozzle relative to the substrate at constant distance from the substrate, the treatment is carried out over a width corresponding to the diameter of the plasma cone at the given distance. In particular, this diameter is greater than the 15 diameter of the plasma jet itself. In the case of the distance selected here between nozzle and substrate, this corresponds to a treatment width of about 25 mm.

In process PV1 (unless otherwise stated):

20 - both the substrate and the adhesive were treated
- treatment of substrate and treatment of adhesive to be adhesive-bonded thereto took place in direct succession
25 - treatment velocity was 5 m/min
- treatment used compressed air as process gas
- the distance from the moving table during treatment was 12 mm.

30 The distance of 12 mm from the moving table gives a different distance between nozzle and treated surface, depending on substrate thickness. The distance of nozzle from the substrate surface can be calculated from the stated data for the substrates (substrates and 35 adhesive tapes). If the distance between nozzle and substrate surface was adjusted to a particular value, this has been explicitly noted.

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The capability of achieving treatment with the same effect at varying distances is one of the main features of the invention.

5

Adhesives and self-adhesive tapes used

Table 1: Adhesive tapes used

Adhesive tape	Pressure-sensitive adhesive	Structure	Thickness of adhesive tape
K1	acrylate (hotmelt), syntactic foam with microballoons	viscoelastic single-layer product	905 µm
K2	acrylate (hotmelt), pure acrylate	viscoelastic single-layer product	900 µm
K3	acrylate (hotmelt), syntactic foam with microballoons and with added resin	viscoelastic single-layer product	1105 µm
K4	acrylate (hotmelt), syntactic foam with hollow glass microbeads and with added resin	viscoelastic single-layer product	990 µm
K5	acrylate (UV technology), syntactic foam with hollow glass microbeads	viscoelastic single-layer product	800 µm
K6	natural rubber	adhesive on textile carrier	280 µm
K7	synthetic rubber	adhesive on foil carrier	100 µm
K8	polyurethane, syntactic foam with microballoons	viscoelastic single-layer product	1000 µm

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The following descriptions provide details and precise data.

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Table 2: Raw materials used

Chemical compound	Trade name	Producer	CAS No.
bis(4-tert-butylcyclohexyl) peroxydicarbonate	Perkadox 16	Akzo Nobel	15520-11-3
2,2'-azobis(2-methylpropionitrile), AlBN	Vazo 64	DuPont	78-67-1
2,2'-azobis(2-methylbutyronitrile)	Vazo 67	DuPont	13472-08-7
pentaerythritol tetraglycidyl ether	Polypox R16 ----- Denacol EX-411	UPPC AG ----- Nagase Chemtex Corp.	3126-63-4
3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate	Uvacure 1500	Cytec Industries Inc.	2386-87-0
N'-(3-(dimethylamino)propyl)-N,N-dimethyl-1,3-propanediamine	Jeffcat® Z-130	Huntsman	6711-48-4
triethylenetetramine	Epikure 925	Hexion Specialty Chemicals	112-24-3
microballoons (MB) (dry-unexpanded microspheres, diameter from 9 to 15 μm , temperature for start of expansion from 106 to 111°C, TMA density $\leq 25 \text{ kg/m}^3$)	Expancel 051 DU 40	Expancel Nobel Industries	
hollow glass microbeads (HGM) (borosilicate glass, effective density 0.7 g/cm ³ , size distribution from 10 to 100 μm with $d_{50} = 35 \mu\text{m}$, compressive strength 24.1 MPa)	Q-CEL 5070S	OMEGA MINERALS	
terpene-phenolic resin (softening point 110°C; $M_w = 500$ to 800 g/mol; $D = 1.50$)	Dertophene T110	DRT resins	25359-84-6
resorcinol bis(diphenyl phosphate)	Reofos RDP	Chemtura	57583-54-7
aqueous carbon black dispersion (aqueous, solvent-free, organic pigment preparation)	Levanyl Black N-LF	Lanxess	

n-butyl acrylate	n-butyl acrylate	Rohm & Haas	141-32-2
acrylic acid	pure acrylic acid	BASF	79-10-7
2-ethylhexyl acrylate		Brenntag	103-11-7
methyl acrylate		BASF	96-33-3
SIS/SI block copolymer	Vector 4113	Dexco Polymers	
hydrocarbon resin	Escorez 1310LC	Exxon	
technical white mineral oil	Tufflo 6056	Citco	8042-47-5
antioxidant	Irganox 1010	BASF	

The expansion capability of the microballoons can be described via determination of TMA density [kg/m³]
 5 (Stare Thermal Analysis System from Mettler Toledo; heating rate 20°C/min). TMA density here is the minimal achievable density at a certain temperature T_{max} under atmospheric pressure prior to collapse of the microballoons.

10

Adhesive M1 and adhesive tape K1

Production of main polymer for M1
 30.0 kg of 2-ethylhexyl acrylate, 67.0 kg of butyl
 15 acrylate, 3.0 kg of acrylic acid, and 66.7 kg of acetone/isopropanol (96:4) are charged to a reactor conventionally used for free-radical polymerization processes. After nitrogen gas had been passed through the system for 45 minutes, with stirring, the reactor
 20 is heated to 58°C, and 50 g of Vazo® 67, dissolved in 500 g of acetone, were added. The exterior heating bath was then heated to 70°C, and the reaction was carried out at this constant external temperature. After 1 h, a further 50 g of Vazo® 67, dissolved in 500 g of acetone, were added, and after 2 h the mixture was
 25 diluted with 10 kg of acetone/isopropanol mixture

(96:4). After 5.5 h, 150 g of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, dissolved in 500 g of acetone, were added; after 6 h 30 min, a further 10 kg of acetone/isopropanol mixture (96:4) were used for 5 dilution. After 7 h, a further 150 g of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, dissolved in 500 g of acetone, were added, and the heating bath was controlled to a temperature of 60°C.

10 After 22 h of reaction time, the polymerization was terminated and the system was cooled to room temperature. The solids content of the product was 50.2%, and this was dried. The K value of the resultant polyacrylate was 75.2, its average molar mass was $M_w = 1\ 370\ 000$ g/mol, its polydispersity D (M_w/M_n) was 15 17.13, and its static glass transition temperature T_g was -38.0°C.

Process 1: Concentration increase/production of polyacrylate hotmelts

20 The acrylate copolymers (main polymers M1 and M2) are very substantially freed from the solvent by means of single-screw extruders (vented extruders, BERSTORFF GmbH, Germany) (residual solvent content $\leq 0.3\%$ by weight; cf. the individual examples). The parameters 25 for concentration-increase of main polymer M1 are shown here by way of example. The rotation rate of the screw was 150 rpm, the motor current was 15 A and the liquid output achieved was 60.0 kg/h. Concentration was increased by applying a vacuum at three domes. The 30 reduced pressures were in each case from 20 mbar to 300 mbar. The discharge temperature of the concentrated hotmelt is about 115°C. Solids content after this step to increase concentration was 99.8%.

35 **Process 2: Production of foamed composition**

Foaming is carried out in an experimental system corresponding to the depiction in figure 2.

The appropriate main polymer K (M1 to M5) is melted in a feed extruder 1 (single-screw conveying extruder from Troester GmbH & Co KG, Germany) and conveyed thereby in the form of polymer melt by way of a heatable hose 11 5 into a planetary-gear extruder 2 (PGE) from ENTEX (Bochum); (in particular, a PGE with four modules T_1 , T_2 , T_3 , T_4 that could be heated independently of one another was used). By way of the feed aperture 22, the molten resin is then added. There is moreover the 10 possibility of introducing additional additives or fillers, for example color pastes, by way of other feed locations that are present. At point 23 the crosslinking agent is introduced. All of the components are mixed to give a homogeneous polymer melt.

15

By means of a melt pump 24a and a heatable hose 24b, the polymer melt is transferred into a twin-screw extruder 3 (BERSTORFF) (input position 33). At position 34 the accelerator component is added. The entire 20 mixture is then freed from all gas inclusions in a vacuum dome V at a pressure of 175 mbar; (see above for criterion for freedom from gas). On the screw, the vacuum zone is followed by a blister B, permitting pressure increase in the subsequent segment S. By 25 suitable control of extruder rotation rate and of the melt pump 37a, a pressure greater than 8 bar is generated in the segment S between blister B and melt pump 37a, and the microballoon mixture (microballoons embedded into the dispersion aid in accordance with the 30 data in the series of experiments) is added at the feed point 35 and incorporated homogeneously into the premix by means of a mixing element. The resultant melt mixture is transferred into a die 5.

35 The incorporated microballoons expand after leaving the die 5, i.e. after pressure reduction, and by virtue of the pressure reduction here the polymer composition is

cooled under low-shear conditions, in particular without shear. This gives a foamed self-adhesive composition S, which is then formed into a layer between two release materials, in particular between a 5 release material which can be reused after removal (process liner), the composition then being shaped by means of a calender 4 into the form of a web.

An alternate process can be found in 10 DE 10 2009 015 233 A1.

Production of K1

Table 3: Components for K1

15

Components	main polymer M1 Expancel 051 DU 40 Levanyl N-LF Polypox R16 Jeffcat Z-130 Reofos RDP	[% by weight]	94.85 1.93 2.15 0.22 0.19 0.66
Structure	Thickness Density	[μm] [kg/m^3]	905 650

The components mentioned were blended in accordance with process 2 and extruded to produce the foamed adhesive tape K1.

20

Adhesive M2 and adhesive tape K2

Production of main polymer M2:

54.4 kg of 2-ethylhexyl acrylate, 20.0 kg of methyl acrylate, 5.6 kg of acrylic acid, and 53.3 kg of acetone/isopropanol (94:6) are charged to a reactor conventionally used for free-radical polymerization processes. After nitrogen gas had been passed through the system for 45 minutes, with stirring, the reactor

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was heated to 58°C, and 40 g of Vazo® 67, dissolved in 400 g of acetone, were added. The exterior heating bath was then heated to 75°C, and the reaction was carried out at this constant external temperature. After 1 h, 5 another 40 g of Vazo® 67, dissolved in 400 g of acetone, were added, and after 4 h the mixture was diluted with 10 kg of acetone/isopropanol mixture (94:6).

After each of 5 h and 7 h, 120 g of bis(4-*tert*-butyl-cyclohexyl) peroxydicarbonate, in each case dissolved in 400 g of acetone, were used for post-initiation. After 22 h of reaction time, the polymerization was terminated and the system was cooled to room temperature. The solids content of the product was 15 55.9%, and this was dried. The K value of the resultant polyacrylate was 58.8, its average molar mass was $M_w = 746\ 000$ g/mol, its polydispersity D (M_w/M_n) was 8.9, and its static glass transition temperature T_g was -35.6°C.

20

Concentration increase/production of polyacrylate hotmelts in accordance with process 1 (see above)

Production of K2

25 Table 4: Components for K2

Components	main polymer M2 Polypox R16 Jeffcat Z-130	[% by weight]	99.45 0.4 0.15
Structure	Thickness Density	[μm] [kg/m³]	900 1015

The components mentioned were blended in accordance with process 2 and extruded to produce the adhesive tape K2.

30

Adhesive tape K3

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Production of K3

Table 5: Components for K3

5

Components	Main polymer M2 Dertophene T110 Expancel 051 DU 40 Levanyl N-LF Polypox R16 Epikure 925		[% by wt]	69.6 28.3 0.7 0.5 0.14 0.14
Structure	Thickness Density	[μm] [kg/m ³]	[μm] [kg/m ³]	1105 780

The components mentioned were blended in accordance with process 2 and extruded to produce the foamed
5 adhesive tape K3.

Adhesive tape K4

Production of K4

10 Table 6: Components for K4

Components	Main polymer M2 Dertophene T110 Q-Cel 5070S Polypox R16 Jeffcat Z-130		[% by wt]	48.7 19.8 31.0 0.21 0.28
Structure	Thickness Density		[μm] [kg/m ³]	990 1010

The components mentioned were blended in accordance with process 2 and extruded to produce the filled adhesive tape K4.

15

Adhesive tape K5

Adhesive tape K5 is GT6008, which is a filled single-layer acrylate foam without resin addition from 3M with density 700 kg/m³ and thickness 800 μm. It comprises
20 hollow glass microbeads (HGM) as filler in order to provide a syntactic foam. The adhesive tape is produced

by UV-polymerization, the process being based by way of example on DE 40 02 834 A1.

Adhesive M6 and adhesive tape K6

5 Adhesive M6 is a natural rubber composition:

Constitution	
	Weight of solids [% by wt.]
Raw material	
V145 natural rubber	41.90
HIKO RES	41.40
MS 40 chalk filler	12.70
Powder premix 3 for NR	4.00

10 Powder premix 3 is composed of 50% by weight of chalk, 25% by weight of TiO_2 , and 25% by weight of antioxidants.

HIKO RES involves a C_5 -based hydrocarbon resin.

15 This natural rubber composition is applied at 50 g/m² to a textile carrier equipped with a reverse-side release system.

Adhesive M7 and adhesive tape K7

20 **Content of adhesive M7**

Table 7: Components for M7

Quantity	Component
100 g	Vector 4113
125 g	Escorez 1310LC
25 10 g	Tufflo 6056

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1.5 g Irganox 1010

Adhesive M7 in accordance with this formulation was applied at a layer thickness of 50 g/m² to an MOPP foil 5 (thickness 85 µm) (adhesive tape K7).

Adhesive M8 and adhesive tape K8

10 The polyurethane-based polymer M8 and the adhesive tape K8 were produced in accordance with WO 2009/138402 A1, and specifically in accordance with example 4 in that document. Furthermore, reference may also be made to EP 2 325 220 A1 in connection with the production process. It is a viscoelastic syntactic foam using 15 preexpanded microballoons as filler. The product was produced with a thickness of 1000 µm.

Substrates used

20 **For bond strength testing:**

Table 8: Substrates used in bond strength testing

Substrate	Description	Thickness
EPDM	LyondellBasell (HX TRC 135X/4 Black), smooth	3.5 mm
PE, PP, ABS,	Standard plastics sheets made of polyethylene,	3 mm
PET	polypropylene, acrylonitrile-butadiene-styrene, polyethylene terephthalate	
ASTM steel	Standard steel test plates in accordance with ASTM standard	1 mm
Coating material 1	BASF FF79-0020 (based on polyurethane) coated onto metal sheet with basecoat	1 mm
Coating material 2	BASF FF99-0778 (based on acrylate resin) coated on thin metal sheet, mounted onto plastics sheet	3.5 mm
CFC	Carbon fiber composite	2.3 mm
CEC	Cathodic electrocoat on metal sheet	0.8 mm

Data, examples**5 Demonstration of the advantageous nature of the process of the invention for acrylate-based adhesives**

(Plasma treatment in accordance with process PV1 or based on PV1 on the stated surfaces, adhesive bonding immediately after treatment)

10

Table 9

Adhe- sive tape	Treatment	Bond strength					
		[N/cm]					
		EPDM	PE	ABS	ASTM steel	Coating material	Coating material
K1	PV1	42.16	42.98	42.55	44.41	39.99	40.54
	No treatment	1.93	0.62	13.70	5.38	3.21	4.87
	Only substrate treated	5.78	5.78	3.90	5.30	4.44	4.25
	Only adhesive treated	1.10	0.71	11.47	43.22	2.85	4.00
K2	PV1	35.69	17.05	33.97	33.26	26.71	30.82
	No treatment	1.95	1.78	11.90	12.39	6.34	10.70
	Only substrate treated	18.61	14.16	13.66	13.19	12.61	12.19
	Only adhesive treated	0.96	1.93	8.75	19.54	6.35	8.11
K3	PV1	87.53	76.85	84.87	84.65	81.76	83.81
	No treatment	3.11	2.38	38.11	49.67	11.91	30.21
	Only substrate treated	61.65	64.85	43.25	73.14	37.47	39.20
	Only adhesive treated	3.63	2.80	65.86	83.01	5.57	26.45
K4	PV1	68.61	62.80	71.62	71.53	74.18	73.36
	No treatment	1.62	2.07	12.52	25.74	8.66	17.27
	Only substrate						

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	treated	30.42	28.05	30.63	32.55	33.2	33.17
Only adhesive							
	treated	3.36	2.02	10.27	69.17	9.63	17.57
K5	PV1	39.25	30.17	37.80	39.38	38.20	38.10
	No treatment	0.69	0.63	9.95	28.25	2.15	17.17
	Only substrate	24.04	22.69	25.70	30.90	24.69	27.37
treated							
	Only adhesive	0.60	0.56	1.51	38.74	2.15	2.76
treated							

This demonstrates, for various acrylate compositions, that the bond strength increased by this invention can be rendered substantially independent of the substrate, 5 in particular also on substrates with low surface energy.

In individual cases, bond strength on a substrate with high surface energy, for example steel, can also be in 10 the vicinity of the maximum for the adhesive provided, even without this invention. This is not inimical to the invention.

A possibility that cannot be excluded in individual 15 cases is that the adhesive bond on a substrate does not achieve the maximum possible bond strength with every treatment setting after aging for three days at 23°C. This can be compensated by adjusting treatment parameters appropriately or by using a longer maturing 20 time.

A particularly important discovery is that in almost all cases revealed here the sum of the bond strength increases from individual treatment of substrate OR 25 adhesive does not reach the value achieved from treatment of substrate AND adhesive. (The "bond strength increase" is defined here as the difference between the value "after treatment" and "prior to

treatment".) The effect due to the process taught is in most cases synergistic, i.e. more than the sum of the individual effects.

5 In particular, the often unsatisfactory effect of treatment of one side alone renders the treatment of both sides non-obvious. Adhesive bonding of K1 on PE can be taken as an example:

- Bond strength without treatment was 0.62 N/cm.
- 10 - After treatment only of the substrate, bond strength was 5.78 N/cm, i.e. the increase achieved was disappointing: 5.16 N/cm.
- After treatment only of the adhesive, bond strength was 0.71 N/cm, i.e. the increase achieved was negligible: 0.09 N/cm.
- 15 - The sum of these increases is therefore low: 5.25 N/cm.
- In contrast, the increase due to the process taught is remarkable: 42.36 N/cm.

20

Relative increase and maximal bond strength

(due to process PV1)

Table 10

Average values on 6 substrates (EPDM, PE, ABS, ASTM steel, coating material 1, coating material 2)						
Adhesive tape	Particular feature of adhesive	Average of bond strength	improvement	Average bond	maximal	strength
						[N/cm]
K1	Foam	2055%		42.11		
K2	Pure acrylate	675%		29.58		
K3	Foam with resin	1233%		82.97		
K4	Foam with resin	1567%		70.35		
K5	Foam	2166%		37.15		

25

This shows that particularly high relative increases in bond strength are obtained by using a filler or by foaming. In particular, the combination with resin addition leads not only to a large relative increase 5 but also to high absolute bond strength.

Demonstration on other substrates

with adhesive tape K1

(Plasma treatment in accordance with process PV1,
10 adhesive bonding immediately after treatment)

Table 11

Adhesive	Bond	strength		
tape K1	[N/cm]			
Treatment:	PP	PET	CFC	CEC
PV1	45.53	47.10	38.16	37.58
Without				
treatment	3.95	9.61	7.16	3.97
Only				
substrate	17.71	12.11	12.47	14.81
treated				
Only				
adhesive	2.98	25.85	37.16	36.98
treated				

The effect is demonstrated here for other substrates.
15 In particular, the effect is revealed for a carbon fiber composite (CFC) and cathodic electrocoat (CEC).

These substrates and the substrates in the preceding examples are particularly relevant for automobile 20 construction. EPDM is a typical material for seals, and CEC and coating materials 1 and 2 are used for coatings on bodywork. CFC is a material with future relevance for lightweight construction.

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Demonstration of the advantageous nature for other adhesives

(Plasma treatment in accordance with process PV1, adhesive bonding immediately after treatment)

5

Table 12

Adhesive tape	Underlying chemistry of pressure-sensitive adhesive	Treatment	Bond strength [N/cm]	
			PE	ASTM steel
K6	Natural Rubber	PV 1	9.40	8.80
		no treatment	5.56	8.22
K7	Synthetic rubber	PV 1	8.80	7.96
		no treatment	4.04	6.72
K8	Polyurethane	PV 1	18.98	17.01
		no treatment	3.51	3.61

The effect is demonstrated here for adhesives based on 5 different chemistry. In principle, the favorable effect can be seen, but, by virtue of the restricted maximal bond strength of the adhesives, the increase of bond strength is less significant. This demonstrates the restricted performance capability of these self-10 adhesive tapes, despite increased adhesion due to the process corresponding to the present teaching.

Demonstration of improved shear resistance

(Plasma treatment in accordance with process PV1,
15 adhesive bonding immediately after treatment)

Table 13

Adhesive tape	Without plasma	PV1	PV1	(Average max. bond strength in accordance with table 10 [N/cm])	
				Max. [mm]	shear bond strength
K2	100	10 000	1 mm		29.58
K3	200	10 000	10 mm		82.97

K4 150 10 000 1 mm 70.35

Here, the improvement of adhesion for the adhesive tapes based on the polymer M2 is demonstrated by improved holding power (HP) at 70°C. The adhesive tapes K2 to K4 used are based on the main polymer M2 and differ in resin addition and filler addition. Without the plasma treatment taught, the values for HP at 70°C are unsatisfactory, but after treatment they are fully satisfactory. In particular, the combination of use of hollow microspheres as filler and addition of resin (adhesive tape K4) exhibits good holding power with a small value for shear under load, and also with high bond strength (see table above).

Demonstration of high bond strengths after short time

15 (Plasma treatment in accordance with process PV1, adhesive bonding immediately after treatment)

Table 14

Adhesive tape	Treatment	Aging time after adhesive bonding	Bond strength [N/cm]						
			EPDM	PE	ABS	ASTM steel	Coating 2		
prior to									
measurement as									
stated, at									
23°C/50% rh									
K1	none	3 days	1.93	0.62	13.70	5.38	4.87		
	PV1	5 min	45.99	37.27	25.65	32.32	29.17		
	PV1	3 days	42.16	42.98	42.55	44.41	40.54		
K2	none	3 days	1.95	1.78	11.90	12.39	10.70		
	PV1	5 min	19.09	25.10	17.72	14.37	23.07		
	PV1	3 days	35.69	17.05	33.97	33.26	30.82		
K3)	none	3 days	3.11	2.38	38.11	49.67	30.21		
	PV1	5 min	51.63	47.82	86.45	90.37	84.82		
	PV1	3 days	87.53	76.85	84.87	83.01	83.81		
K5	none	3 days	0.69	0.63	9.95	28.25	17.17		

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PV1	5 min	21.09	34.47	42.90	43.74	42.59
PV1	3 days	39.25	30.17	37.80	39.38	38.10

Here, it is demonstrated that this process does not require long maturing times. In the examples, the bond strengths always reach at least 14 N/cm after 5 min.

5

Remarkably, the values reached by the bond strengths due to treatment by PV1 in the examples are already higher after 5 min than those after three days of maturing time without treatment. Particularly suitable adhesives reach >40 N/cm after 5 min.

The bond strength achieved after 5 min. on steel by the adhesive tape K3 by virtue of our invention was 90 N/cm, an exceptionally high value.

15

Demonstration of alternate treatment parameters

(Plasma treatment based on process PV1, changes from PV1 as stated, adhesive bonding immediately after treatment)

20

Table 15

Substrate	Adhesive tape	Process gas	Distance from surface of adhesive [mm]	Distance from surface of substrate [mm]	F [N/cm]
ASTM steel	K2	no treatment	-	-	10.70
ASTM steel	K2	air	5	8	33.14
ASTM steel	K2	air	8	8	35.85
ASTM steel	K2	air	11	8	33.69
ASTM steel	K2	air	14	8	32.87
ASTM steel	K2	air	17	8	32.67
PP	K3	no treatment	-	-	4.48
PP	K3	N2	5	6	83.55

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PP	K3	N2	11	12	82.63
PP	K3	N2	17	18	82.86

PP	K3	air	5	6	79.85
PP	K3	air	8	9	83.90
PP	K3	air	11	12	83.21
PP	K3	air	17	18	57.52

Here, it is demonstrated that the process is robust in respect of variation of distances and operating gas.

5 Process latitude is surprisingly great.

Remarkably, the treatment distance available when operating with N₂ is greater than that when operating with air.

What is claimed is:

1. A process for increasing the adhesion between a layer of pressure-sensitive adhesive which has a surface facing away from the substrate and which has a surface facing toward the substrate and the surface of a substrate, where that surface of the layer of pressure-sensitive adhesive that faces toward the substrate and the substrate surface covered with the layer of pressure-sensitive adhesive are respectively treated with atmospheric-pressure plasma.
5
2. The process as claimed in claim 1,
15 characterized in that the following pure, or mixtures of, process gases form a treatment atmosphere: N₂, compressed air, O₂, H₂, CO₂, Ar, He, ammonia, ethylene, where water vapor or other volatile constituents may also have
20 been added, preferably N₂ and compressed air.
3. The process as claimed in claim 1 or 2,
25 characterized in that the treatments take place at or in the vicinity of atmospheric pressure.
4. The process as claimed in at least one of claims 1 to 3,
30 characterized in that reactive aerosols are present in the treatment atmosphere or are added.
5. The process as claimed in at least one of the preceding claims,
35 characterized in that the plasma is applied by means of one or more nozzles.

6. The process as claimed in at least one of the preceding claims,
characterized in that
5 the plasma is applied by means of a rotary nozzle,
particularly preferably in the case of an operation using compressed air.

7. The process as claimed in at least one of the preceding claims,
10 characterized in that
the treatments take place immediately prior to the adhesive bonding of the layer of adhesive to the substrate.
15

8. The process as claimed in at least one of the preceding claims,
characterized in that
in the case of treatment directly prior to the adhesive bonding the chronological separation from
20 the adhesive bonding is <1 s, in the case of in-line treatment prior to the adhesive bonding it is in the range from seconds to minutes, in the case of off-line treatment it is in the range from hours to days, and in the case of treatment in the production process of the adhesive tape it is in
25 the range from days to many months.

9. The process as claimed in at least one of the preceding claims,
30 characterized in that
initially one treatment takes place and the second treatment takes place with chronological separation from the first immediately prior to the adhesive bonding of the layer of adhesive to the substrate.
35

10. The process as claimed in at least one of the preceding claims,
characterized in that
one or both treatments is/are composed of a
5 plurality of individual treatment steps.
11. The process as claimed in at least one of the preceding claims,
characterized in that
10 the chronological separation between multiple treatments varies from about 0.1 s (during the rotation of the nozzle) up to 1 year (when a product is treated before delivery and there is a refreshment treatment prior to use).
- 15 12. The process as claimed in at least one of the preceding claims,
characterized in that
the pretreatment of one of the relevant surfaces
20 uses a particular plasma generator, and at a subsequent juncture a different plasma generator is used to supplement or refresh the treatment.
- 25 13. The process as claimed in at least one of the preceding claims,
characterized in that
the treatments of the surface of the layer of adhesive and of the surface of the substrate are identical.
- 30 14. The process as claimed in at least one of the preceding claims,
characterized in that
the layer of pressure-sensitive adhesive is based
35 on natural rubber, synthetic rubber, or polyurethanes, and the layer of pressure-sensitive adhesive is preferably composed exclusively of

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acrylate or mostly of acrylate (with a thermal crosslinker system and/or hotmelt and/or UV-crosslinked and/or UV-polymerized).

5 15. The process as claimed in at least one of the preceding claims,

characterized in that

the layer of pressure-sensitive adhesive forms a carrierless, single-layer, double-sided adhesive

10 tape.

16. The process as claimed in at least one of the preceding claims,

characterized in that

15 the layer of pressure-sensitive adhesive has been applied on a carrier, preferably on a foil, a foam, a nonwoven, and/or a textile, very particularly advantageously on a viscoelastic carrier.

20

17. The process as claimed in at least one of the preceding claims,

characterized in that

the thickness of the layer of pressure-sensitive adhesive or of the adhesive tape formed thereby is
25 $\geq 20 \mu\text{m}$, preferably $\geq 100 \mu\text{m}$, very particularly preferably $\geq 300 \mu\text{m}$ and/or at most $\leq 1500 \mu\text{m}$, preferably $\leq 1000 \mu\text{m}$.

30 18. The process as claimed in at least one of the preceding claims,

characterized in that

substrates used are polar and nonpolar substrates, in particular steel, aluminum, plastics/polymers
35 such as polyester (for example PET), PVC, PC, PE, PP, EPDM, ABS, rubber, and also glass, ceramic, coating materials and coatings, CEC, composite

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materials such as CFC, wood-composite products, coated paperboard packaging materials, foils, bottles, plastics containers, packaging, and housing parts.

5

19. An adhesive bond between a layer of pressure-sensitive adhesive and a substrate, obtained as claimed in at least one of the preceding claims.
- 10 20. A composite made of two substrates between which there is a layer of pressure-sensitive adhesive, as claimed in any of the preceding claims, where at least one of the surfaces of the substrate and at least one surface of the adhesive tape are subjected to a plasma treatment, and at least one plasma-treated surface of the adhesive tape is laminated to the plasma-treated surface of one of the substrates.

Application number / Numéro de demande: EP20120 58286

Figures: 1

Pages:

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