



(43) International Publication Date
7 April 2016 (07.04.2016)

(10) International Publication Number
WO 2016/050697 A2

- (51) International Patent Classification:
C09J 163/00 (2006.01)
- (21) International Application Number:
PCT/EP2015/072274
- (22) International Filing Date:
28 September 2015 (28.09.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
1417502.0 3 October 2014 (03.10.2014) GB
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: POWDERED HEAT ACTIVATABLE ADHESIVES

(57) Abstract: The invention relates to the deposition of a powdered heat activatable adhesive onto a surface of a substrate by spraying. In particular, the invention relates to a powdered heat activatable adhesive and its use as well as to a process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form an adhesive layer that is preferably still heat activatable.



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POWDERED HEAT ACTIVATABLE ADHESIVES

[0001] This application claims priority of British patent application no. GB 1417502.0, filed on October 3, 2014.

[0002] The invention relates to the deposition of a powdered heat activatable adhesive onto a surface of a substrate by spraying. In particular, the invention relates to a powdered heat activatable adhesive and its use as well as to a process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form an adhesive layer that is preferably still heat activatable.

[0003] Heat activatable adhesives are useful in many technical fields including automotive industry and aviation industry. When the heat activatable adhesives are structural adhesives, they contribute substantially to the structural integrity of the component or product being manufactured. In many instances, structural adhesives are much stronger than conventional non-structural adhesives, often even stronger than the substrates being bonded. Structural adhesives are used to make structures, especially load-bearing structures, and may be based on e.g. epoxies, urethanes or structural acrylics.

[0004] Some structural adhesives are provided as multicomponent systems, typically two-component systems, because the final mixture of all ingredients is too reactive and hence, not storage stable. These structural adhesives require that the components are mixed at the site and subsequently applied to the substrates within a narrow time window.

[0005] In conventional techniques, structural adhesives are applied to substrates in form of solutions, suspensions or melts. In form of their solutions, suspensions or melts, the structural adhesives may either already have developed their adhesive properties, or they may be provided in a form that is dry to the touch but that is capable of developing adhesive properties upon subsequent activation, typically by heat and/or irradiation.

[0006] Applying structural adhesives in form of solutions or suspensions is detrimental, as the solvents need to be evaporated after application. This may cause additional costs and can be hazardous to the environment and the workers using these adhesives.

[0007] Applying structural adhesives in form of melts overcomes the drawbacks of solvents. However, this technique often involves methods such as hot melt extrusion, injection molding and the like. It is not always economic to integrate the step of applying an adhesive melt to a substrate in a complex process at an assembly line, e.g. by means of a robot. Rather, the adhesive melt is usually applied to the substrate in a preceding step providing an intermediate part that is allowed to cool down thereafter. The application of the intermediate part may then be integrated into the overall process of manufacture, e.g. by means of a robot.

[0008] The application of a structural adhesive in form of a melt is particularly challenging when the structural adhesive should not yet develop its final adhesive properties in the course of this application to the substrate. For various applications it is desirable to apply a structural adhesive, which is provided in form of a non-activated melt, to a substrate, whereas the adhesive melt remains non-activated after it has been applied to the substrate but nevertheless has sufficient adherence towards the substrate such that the layer of the adhesive material and the substrate do not fall apart. For these applications it is desirable that the non-activated adhesive that has already been applied to the substrate is still activatable in a subsequent step in order to develop its final adhesive strength.

[0009] A particular problem arises because on the one hand, thermoforming requires heating at least to the softening temperature of the adhesive material, and on the other hand, activation of the final adhesive strength is usually also induced by heat. Accordingly, structural adhesives of this type need to have specific properties at different temperatures: (i) under ambient conditions, the adhesive material should be dry to the touch; (ii) at elevated, intermediate temperature, the adhesive material should be processable in form of a melt, should have sufficient adherence towards the substrate, but should not yet develop its final adhesive strength; and (iii) at elevated, higher temperature, the adhesive material should develop its final adhesive strength.

[0010] There is a demand for structural adhesives that can be applied to a substrate at the site of manufacture without requiring preparation of intermediate parts by preceding steps such as hot melt extrusion and injection molding, and without using solvents.

[0011] US 6,475,316 relates to a method of enhancing adhesion between at least two surfaces including: thermal spraying a powdered surface preparation composition onto at least a portion of a first surface; and subsequently contacting at least a portion of a second surface of a non-powdered material with a portion of the first surface having the powdered surface preparation composition thereon. The thermal spraying preferably includes flame spraying, and more preferably, reactive thermal spraying.

[0012] JP 2009-226329 discloses a method for forming a resin coated film including: a process (1) of treating the surface of powders which bonds a triazine thiol derivative onto the surface of the resin powders; a process (2) of treating a solid surface which bonds the same triazine thiol derivative as the above onto the surface of the solid substrate; a process (3) of bonding which bonds the resin onto the surface of the solid substrate by spraying, at a subsonic or ultrasonic speed, a gas, charged with the treated resin powders after being heated at a temperature lower than the melting point of the resin powders by using a cold spray process, to the treated substrate; and a process (4) of heat treating which heats the resin bonded to the solid substrate.

[0013] JPS 602 35 877 discloses an adhesive which has coatability with an electrodeposit and a rust-inhibiting effect after coating, by blending a specified glycidyl ether type epoxy resin, a modified epoxy resin, a latent curving agent and an electrically conductive material.

[0014] GB-A 1 223 413 relates to a method of bonding two surfaces together with a hot-melt adhesive which comprises heating a first surface, depositing a thermoplastic hot melt adhesive in free-flowing particulate form

onto the heated surface, said surface being heated to a temperature which is sufficient to cause partial melting of said adhesive but insufficient to cause fusion of said adhesive to form a homogeneous layer whereby the adhesive adheres to said surface, thereafter heating said adhesive to produce a homogeneous tacky coating and applying said first surface to a second surface.

[0015] EP-A 2 505 627 discloses an adhering method which comprises spray-coating an adherend with a powder adhesive and then using the adherend, thereby enabling the formation of an automobile interior part having heat tolerance and adhesion strength. The adhering method to be used for forming an automobile interior part involves a step for spray-coating an adherend with a powder adhesive with the use of an electrostatic powder spray gun.

[0016] WO 2014/022182 discloses an approach toward the electrostatic deposition of activatable adhesive formulations.

[0017] It is proposed in US 2014/0027039 that adhesives may be deposited on surfaces such as metal surfaces by spraying a powder of the adhesive material. It has been proposed that the adhesive material can be a material that is softened to adhere to a surface such as a metal surface by heating to a temperature below the temperature at which the adhesive properties are activated.

[0018] Additionally, it has been proposed that the surface may be heated to the appropriate temperature to ensure adhesion of the powdered heat activatable adhesive to the metal surface to provide a coating of the activatable adhesive on the surface. It has also been proposed that the powder may be applied by electrostatic spraying. In the electrostatic process the surface may be provided with an electric charge and the powdered heat activatable adhesive also provided with a charge so that the powder is attracted to the surface which may be heated.

[0019] These processes suffer from the disadvantage that it is difficult to focus the application of the powdered heat activatable adhesive on the surface resulting in the provision of adhesive in areas in which it is not required which is wasteful and can cause problems with subsequent processing.

[0020] The previous proposals have also suggested that where the adhesive is to be used for bonding components in automobile manufacture it should be such that it is activated at the temperatures to which it is exposed in the paint bake or anticorrosion bake ovens employed in automobile assembly.

[0021] It is an object of the invention to provide adhesives and methods for applying such adhesives to substrates which have advantages compared to the prior art.

[0022] This object has been achieved by the subject-matter of the patent claims.

[0023] The invention provides a more versatile and more accurate method for the application of activatable adhesive particles to a substrate by spraying wherein the particles adhere to the surface of the substrate.

[0024] The invention relates to the deposition of a powdered heat activatable adhesive onto a surface of a substrate by spraying. In particular, the invention relates to a powdered heat activatable adhesive and its use as well as to a process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form an adhesive layer that is preferably still heat activatable.

[0025] The invention provides a powdered heat activatable adhesive having an average particle size in the range of from about 20 μm to about 1000 μm and comprising an epoxy based material and a curing agent. Further, the invention provides a process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form the adhesive layer. Preferably, the process comprising supplying a powdered heat activatable adhesive into a preferably heated gas stream flowing under pressure heating the powdered heat activatable adhesive with the gas to a temperature at which it will soften to adhere to the substrate and directing the flowing gas stream containing the heated powdered heat activatable adhesive onto the surface of the substrate.

[0026] A first aspect of the invention relates to a powdered heat activatable adhesive having an average particle size in the range of from about 20 μm to about 1000 μm and comprising an epoxy based material and a curing agent.

[0027] The adhesive according to the invention is powdered. A powder is a dry, bulk solid composed of a large number of very fine particles that may flow when shaken or tilted. In particular, powders refer to those granular materials that have the finer grain sizes, and that therefore have a greater tendency to form clumps when flowing. The powder is characterized by an average particle size in the range of from about 20 μm to about 1000 μm .

[0028] Preferably, under ambient conditions, the powdered heat activatable adhesive according to the invention is a dry powder, and/or is dry to the touch, and/or is a free-flowing powder ($10 < \text{ff}_c$).

[0029] The flow properties of a powder depend on several parameters, e.g., particle size distribution, particle shape, chemical composition of the particles, moisture, and temperature. Flowability of a bulk solid is characterized mainly by its unconfined yield strength, σ_c , in dependence on consolidation stress, σ_1 , and storage period, t . Usually the ratio ff_c of consolidation stress, σ_1 , to unconfined yield strength, σ_c , is used to characterize flowability numerically: $\text{ff}_c = \sigma_1 / \sigma_c$. The larger ff_c is, i.e., the smaller the ratio of the unconfined yield strength, σ_c , to the consolidation stress, σ_1 , the better a bulk solid flows. For the purpose of the specification, flow behavior is preferably defined as follows:

$\text{ff}_c < 1$	not flowing
$1 < \text{ff}_c < 2$	very cohesive
$2 < \text{ff}_c < 4$	cohesive
$4 < \text{ff}_c < 10$	easy flowing
$10 < \text{ff}_c$	free flowing.

[0030] The flowability of a bulk solid depends on the adhesive forces between individual particles. Different mechanisms create adhesive forces. With fine-grained, dry bulk solids, adhesive forces due to van der Waals interactions play an essential role. With moist bulk solids, liquid bridges between the particles are essential.

[0031] Preferably, the powdered heat activatable adhesive according to the invention has a bulk density within the range of about 0.50 ± 0.10 g/mL, or about 0.55 ± 0.10 g/mL, or about 0.60 ± 0.10 g/mL, or about 0.65 ± 0.10 g/mL, or about 0.70 ± 0.10 g/mL, or about 0.75 ± 0.10 g/mL, or about 0.80 ± 0.10 g/mL, or about 0.85 ± 0.10 g/mL, or about 0.90 ± 0.10 g/mL, or about 0.95 ± 0.10 g/mL, or about 1.00 ± 0.10 g/mL, or about 1.05 ± 0.10 g/mL, or about 1.10 ± 0.10 g/mL.

[0032] In a preferred embodiment, all particles of the powdered heat activatable adhesive according to the invention have substantially the same chemical composition. Preferably, the powdered heat activatable adhesive according to the invention is composed of a substantially homogeneous material.

[0033] In another preferred embodiment, the powdered heat activatable adhesive according to the invention comprises different particles that differ from one in their chemical composition. Under these circumstances, the powdered heat activatable adhesive can be regarded as a mixture of powders of different types, preferably of at least two different types, at least three different types, or at least four different types.

[0034] Preferably, the powdered heat activatable adhesive according to the invention is ready to use. Preferably, the powdered heat activatable adhesive according to the invention is a one-component formulation.

[0035] Preferably, the powdered heat activatable adhesive according to the invention is a structural adhesive. Preferably, the structural adhesive is selected from foamable structural adhesives and unfoamable structural adhesives.

[0036] Preferably, the powdered heat activatable adhesive according to the invention comprises substantially no electrically conductive material, e.g. graphite, carbon, charcoal, and the like.

[0037] The adhesive according to the invention is heat activatable, i.e. undergoes activation upon heating. Thus, before the material (powder) is heated, it preferably does not exhibit any significant adhesive properties. Once it is heated to its activation temperature, however, the material develops its adhesive properties.

[0038] It has been surprisingly found that a powder can be manufactured from a heat activatable adhesive material which powder

- (i) is not adhesive at room temperature such that the individual particles do not agglutinate or clump together, i.e. do not adhere to one another (free flowing); under these conditions the material is heat activatable;
- (ii) is slightly adhesive when being applied to the surface of a substrate by means of a gas stream (spraying) whereby the particles form a coherent film on the surface of the substrate, which film adheres to the surface of the substrate due to comparatively weak adhesive properties of the material after having hit the surface of the substrate, but which film still remains heat activatable, i.e. has not yet developed its final adhesive

strength under these conditions; under these conditions the material can fuse to form a film layer but is still heat activatable; and

- (iii) is strongly adhesive after heat treatment (above the activation temperature) of the coherent film that is applied to the surface of the substrate; under these conditions the material is heat activated.

[0039] Therefore, different properties of the powdered heat activatable adhesive according to the invention can be distinguished that are relevant under different conditions, especially at different temperatures. Under ambient conditions, especially at room temperature, the adhesive is a powder that is sprayable and heat activatable. Under the conditions of application by means of a gas stream, e.g. at elevated temperature and/or after acceleration to a sufficient velocity, the adhesive is capable of forming a coherent film adhered to the surface of the substrate due to comparatively weak adhesive properties of the material that remains still heat activatable. Under the conditions of post-curing, especially at higher temperature above the activation temperature, e.g. of above about 140 °C, the adhesive is heat activated thereby exhibiting its full final adhesive strength.

[0040] The powder can be curable and/or foamable and the particles of the powder preferably have a narrow particle size distribution. For example, it is preferred to use a powder having an average particle size in the range of from about 20 µm to about 750 µm, preferably about 30 µm to about 200 µm, and a narrow particle size distribution. Preferably, the powdered heat activatable adhesive has an average particle size in the range of from about 20 µm to about 500 µm, more preferably about 20 µm to about 300 µm or about 50 µm to about 300 µm, still preferably about 100 µm to about 200 µm.

[0041] Preferred average particle sizes of the powdered heat activatable adhesive are about 50±25 µm, about 75±50 µm, about 100±50 µm, about 125±50 µm, about 150±50 µm, about 175±50 µm, about 200±50 µm, about 225±50 µm, about 250±50 µm, about 300±50 µm, about 50±25 µm, about 75±25 µm, about 100±25 µm, about 125±25 µm, about 150±25 µm, about 175±25 µm, about 200±25 µm, about 225±25 µm, about 250±25 µm, or about 300±25 µm.

[0042] Suitable methods to measure the average particle size of a powder are known to the skilled artisan and include laser diffraction and image analysis. Preferably, for the purpose of the specification, the "average particle size" is expressed in terms of the geometric mean value D[4,3] with the volume as the basis for the distribution calculation (volume distribution) in accordance with ASTM E 799. In a preferred embodiment, the particle size is measured using a laser particle size meter, preferably with the powder dispersed in deionized water.

[0043] The average particle size is one parameter that may be adjusted by routine experimentation in order to optimize the properties of the powdered heat activatable adhesive, particularly its utility to be applied to the surface of a substrate by means of a gas stream and to adhere to said surface.

[0044] Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that at most about 20 wt.-%, more preferably at most about 10 wt.-% of the particles have a diameter of less than about 10 µm.

[0045] Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that at most about 20 wt.-%, more preferably at most about 10 wt.-% of the particles have a diameter of more than about 600 μm . Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that at most about 20 wt.-%, more preferably at most about 10 wt.-% of the particles have a diameter of more than about 300 μm . Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that at most about 20 wt.-%, more preferably at most about 10 wt.-% of the particles have a diameter of more than about 250 μm .

[0046] Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that the D_{50} value (median) is within the range of from about 20 μm to about 300 μm , more preferably about 50 μm to about 200 μm , still more preferably about 100 μm to about 150 μm .

[0047] Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that the D_{10} value is within the range of from about 1 μm to about 100 μm , more preferably about 5 μm to about 70 μm , still more preferably about 10 μm to about 50 μm .

[0048] Preferably, the powdered heat activatable adhesive according to the invention has a particle size distribution such that the D_{90} value is within the range of from about 100 μm to about 500 μm , more preferably about 200 μm to about 400 μm , still more preferably about 250 μm to about 350 μm .

[0049] Methods for determining the D_{10} ($D(v, 0.1)$), D_{50} value ($D(v, 0.5)$), D_{90} ($D(v, 0.9)$) and $D[4,3]$ are known to the skilled artisan. Preferably, the D_{10} , D_{50} , D_{90} and $D[4,3]$ values are determined over volume by the Malvern method in dry mode.

[0050] Preferably, the powdered heat activatable adhesive according to the invention is characterized by specific viscoelastic properties. Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain when stretched and quickly return to their original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain. The viscosity of a viscoelastic material gives the substance a strain rate dependence on time. A viscoelastic material loses energy when a load is applied, then removed. Hysteresis is observed in the stress-strain curve, with the area of the loop being equal to the energy lost during the loading cycle. Since viscosity is the resistance to thermally activated plastic deformation, a viscous material will lose energy through a loading cycle. Plastic deformation results in lost energy, which is uncharacteristic of a purely elastic material's reaction to a loading cycle.

[0051] Viscoelasticity is studied using dynamic mechanical analysis, applying a small oscillatory stress and measuring the resulting strain. The principle of the viscosity measurement is to apply a shear force to a material in an oscillation mode or rotational mode and to record the torque resistance. This torque translates into a viscosity value ($\text{Pa}\cdot\text{s}$) for a given shear rate and at a given temperature. Purely elastic materials have stress and strain in phase, so that the response of one caused by the other is immediate. In purely viscous materials, strain

lags stress by a 90 degree phase lag. Viscoelastic materials exhibit behavior somewhere in the middle of these two types of material, exhibiting some lag in strain.

[0052] The complex dynamic modulus G can be used to represent the relations between the oscillating stress and strain. It has two components, the storage modulus G' (elastic component) and the loss modulus G'' (viscous component). The temperature at which the maximum for the loss modulus G'' is observed is also used in polymer science to define the softening point (softening temperature) of the viscoelastic material and its glass transition temperature.

[0053] Preferably, the powdered heat activatable adhesive has a complex viscosity such that the temperature at which the maximum for the loss tangent ($\tan \delta$) is observed [$= T(\tan \delta_{\max})$] is at least about 43 °C. Preferably, $T(\tan \delta_{\max})$ of the powdered heat activatable adhesive is at least about 44 °C, more preferably at least about 45 °C, still more preferably at least about 46 °C, yet more preferably at least about 47 °C, even more preferably at least about 48 °C, most preferably at least about 49 °C, and in particular at least about 50 °C.

[0054] Preferably, the powdered heat activatable adhesive has a complex viscosity such that the temperature at which the maximum for the loss tangent ($\tan \delta$) is observed [$T(\tan \delta_{\max})$] is at most about 100 °C. Preferably, $T(\tan \delta_{\max})$ of the powdered heat activatable adhesive is at most about 95 °C, more preferably at most about 90 °C, still more preferably at most about 88 °C, yet more preferably at most about 86 °C, even more preferably at most about 84 °C, most preferably at most about 82 °C, and in particular at most about 80 °C.

[0055] In preferred embodiments, the powdered heat activatable adhesive has a complex viscosity such that the temperature at which the maximum for the loss tangent ($\tan \delta$) is observed [$T(\tan \delta_{\max})$] is within the range of about 60±10 °C, or about 65±10 °C, or about 70±10 °C, or about 40±5 °C, or about 42±5 °C, or about 44±5 °C, or about 46±5 °C, or about 48±5 °C, or about 50±5 °C, or about 52±5 °C, or about 54±5 °C, or about 56±5 °C, or about 58±5 °C, or about 60±5 °C, or about 62±5 °C, or about 64±5 °C, or about 66±5 °C, or about 68±5 °C, or about 70±5 °C.

[0056] A skilled person knows how to measure these properties of a material including $T(\tan \delta_{\max})$. Preferably, measurements are in accordance with ASTM D 4092 and ASTM D 4065. An Anton Paar rheometer device is preferably used for this viscosity measurement. A sample specimen is a disc of 24 mm diameter and 1 mm height. Viscosity measurements are made at 1 Hz frequency, with a decreasing strain from 1% to 0.1% with a temperature ramp 3°C/min between 120 °C to 40 °C. Strain range has been chosen to fit inside the linear viscoelastic domain.

[0057] These properties of a powdered heat activatable adhesive may be altered or modified in a particular direction. For example, $T(\tan \delta_{\max})$ can be altered or modified by adjusting the epoxy equivalent weight (EEW) of an epoxy based material, or when the powdered heat activatable adhesive comprises a combination of a liquid epoxy based material with a solid epoxy based material, by adjusting the relative content of the two epoxy based materials. This is subject to routine preliminary testing.

[0058] The viscoelasticity is one parameter that may be adjusted by routine experimentation in order to optimize the properties of the powdered heat activatable adhesive, particularly its utility to be applied to the surface of a substrate by means of a gas stream and to adhere to said surface.

[0059] The formulations employed to produce the powdered heat activatable adhesive of the invention will depend upon the use to which the adhesive is to be put. The invention may be used to provide structural adhesives, including foamable structural adhesives. It may also be used to provide soft highly expandable adhesives such as those used to produce automotive sealants and baffles.

[0060] A preferred adhesive formulation for the production of structural adhesives comprises

- i) an epoxy based material;
- ii) a curing agent; and additionally
- iii) an elastomer/epoxy adduct; and/or
- iv) a core/shell material.

[0061] Preferably, the formulation additionally contains a phenoxy resin.

[0062] It is important that the final layers obtained from the powdered heat activatable adhesive of this invention are not brittle and also that they have fracture toughness which is the ability to resist propagation of a flaw once one exists within a layer of the adhesive. It has been unexpectedly found that the use of a phenoxy resin improves the flexibility of the layer and reduces the brittleness. It has also been unexpectedly found that the use of the elastomer/epoxy adduct and/or the core/shell material provide fracture toughness as well as contributing to the flexibility of the layers obtained from the powdered heat activatable adhesive.

[0063] The powdered heat activatable adhesive according to the invention comprises one or more curing agents and/or curing agent accelerators. Amounts of curing agents and curing agent accelerators may vary within the adhesive formulations depending upon the type of cure required and cross link density desired and the desired structural properties of cured adhesive. Preferably, the curing agent is a latent curing agent, i.e. is not reactive under ambient conditions but is heat activatable. Preferably, the curing agent contains functional groups that are capable of reacting with the epoxy groups of the epoxy based material at an elevated activation temperature. Preferably, the curing agent has an activation temperature above about 110 °C, more preferably in the range of from about 130 °C to about 220 °C, preferably about 150 °C to about 220 °C.

[0064] Exemplary ranges for the curing agents or curing agent accelerators present range from about 0.001 wt.-% to about 7 wt.-%. Preferably, the content of the curing agent is at most about 25 wt.-%, more preferably at most about 15 wt.-%, still more preferably at most about 7 wt.-%, relative to the total weight of the powdered heat activatable adhesive. Preferably, the content of the curing agent is at least about 0.001 wt.-%, more preferably at least about 0.01 wt.-%, still more preferably at least about 0.1 wt.-%, relative to the total weight of the powdered heat activatable adhesive.

[0065] The curing agents assist the adhesive in curing by crosslinking of the polymers, epoxy based materials or both. The curing agents may also assist in thermosetting the adhesive.

[0066] Useful classes of curing agents are materials selected from aliphatic or aromatic amines or their respective adducts, amidoamines, polyamides, cycloaliphatic amines, anhydrides, polycarboxylic polyesters, isocyanates, phenol-based resins (e.g., phenol or cresol novolac resins, copolymers such as those of phenol terpene, polyvinyl phenol, or bisphenol-A formaldehyde copolymers, bishydroxyphenyl alkanes or the like), or mixtures thereof. The curing agents may include modified and unmodified polyamines or polyamides such as triethylenetetramine, diethylenetriamine tetraethylenepentamine, cyanoguanidine, dicyandiamides and the like.

[0067] In a particularly preferred embodiment, the curing agent is or comprises dicyandiamide.

[0068] An accelerator for the curing agents (e.g., a modified or unmodified urea such as methylene diphenyl bis urea, an imidazole or a combination thereof) may also be provided. The curing agent should be activated at a temperature at which the formulation will flow and is preferably activated at temperatures above about 110 °C, more preferably at temperatures of at least about 165 °C, most preferably at a temperature in the range of from about 130 °C to about 220 °C, preferably from about 150 °C to about 220 °C such as the temperatures experienced in the automotive anticorrosion coat (known as e-coat) bake oven.

[0069] In a preferred embodiment at least two cross linking agents are included one that is activated at the temperature at which the deposited powder is fused to provide a layer of uncured adhesive on the substrate and this cross linking can control the viscosity of the molten powder so that the particles coalesce into a film and do not sag. The second cross linking agent being activated at a higher temperature to cross link the adhesive and create the final adhesive bond.

[0070] The powdered heat activatable adhesive according to the invention comprises an epoxy based material, i.e. a material that comprises reactive epoxy functional groups. The adhesive includes the epoxy based material in order to form a desirable adhesive that exists first in powder form, can then fuse to form a film layer, and later be activated to cure (for the purpose of the specification also abbreviated as "epoxy").

[0071] The powdered heat activatable adhesive according to the invention comprises an elastomer/epoxy adduct, the epoxy based material is then a component separate from the elastomer/epoxy adduct, i.e. the epoxy based material does not encompass the elastomer/epoxy adduct and vice versa. Thus, all quantities of the epoxy based material on the one hand and of the elastomer/epoxy adduct on the other hand are separate of one another. The same applies to the epoxy equivalent weight of the epoxy based material which, for the purpose of the specification, is not altered by the presence of the elastomer/epoxy adduct, if any. Thus, the elastomer/epoxy adduct is to be disregarded with respect to the properties of the epoxy based material. Analogous considerations apply to the phenoxy resin in case that it should contain residual reactive epoxy functional groups: under these circumstances, the phenoxy resin is to be disregarded with respect to the properties of the epoxy based material.

[0072] The epoxy based material may be any dimeric, oligomeric or polymeric epoxy materials containing at least one epoxy functional group, i.e. a reactive oxirane moiety. Moreover, the term epoxy based material can be used to denote one epoxy based material or a combination of multiple epoxy based materials. The epoxy-based materials may be epoxy-containing materials having one or more oxirane rings polymerizable by a ring opening reaction.

[0073] The powdered heat activatable adhesive may include up to about 80 wt.-% or more of an epoxy based material, preferably between about 2 wt.-% and about 70 wt.-% epoxy based material, between about 4 wt.-% and about 30 wt.-% epoxy based material, or even between about 7 wt.-% and about 18 wt.-% epoxy based material. Preferably, the content of the epoxy based material is at most about 80 wt.-%, relative to the total weight of the powdered heat activatable adhesive. Preferably, the content of the epoxy based material is at least about 2 wt.-%, relative to the total weight of the powdered heat activatable adhesive.

[0074] In preferred embodiments, the content of epoxy based material in the powdered heat activatable adhesive according to the invention is within the range of about 15 ± 13 wt.-%, more preferably about 15 ± 12 wt.-%, still more preferably about 15 ± 11 wt.-%, yet more preferably about 15 ± 10 wt.-%, even more preferably about 15 ± 9 wt.-%, most preferably about 15 ± 8 wt.-%, and in particular about 15 ± 7 wt.-%, relative to the total weight of the powdered heat activatable adhesive.

[0075] In another preferred embodiments, the content of epoxy based material in the powdered heat activatable adhesive according to the invention is within the range of about 25 ± 22 wt.-%, more preferably about 25 ± 20 wt.-%, still more preferably about 25 ± 18 wt.-%, yet more preferably about 25 ± 16 wt.-%, even more preferably about 25 ± 14 wt.-%, most preferably about 25 ± 12 wt.-%, and in particular about 25 ± 10 wt.-%, relative to the total weight of the powdered heat activatable adhesive.

[0076] In still another preferred embodiments, the content of epoxy based material in the powdered heat activatable adhesive according to the invention is within the range of about 35 ± 30 wt.-%, more preferably about 35 ± 27 wt.-%, still more preferably about 35 ± 24 wt.-%, yet more preferably about 35 ± 21 wt.-%, even more preferably about 35 ± 18 wt.-%, most preferably about 35 ± 15 wt.-%, and in particular about 35 ± 12 wt.-%, relative to the total weight of the powdered heat activatable adhesive.

[0077] When the powdered heat activatable adhesive according to the invention comprises more than a single epoxy based material, e.g. a combination of a liquid epoxy based material with a solid epoxy based material, the above contents preferably apply to the overall (total) content of epoxy based materials, relative to the total weight of the powdered heat activatable adhesive.

[0078] The epoxy based material may be aliphatic, cycloaliphatic, aromatic or the like.

[0079] The epoxy based material may be supplied as a solid (e.g., as pellets, chunks, pieces or the like), or a liquid, or a combination of both.

[0080] The epoxy based material may include an ethylene copolymer or terpolymer that may possess an alpha olefin. The epoxy may include a phenolic resin, which may be a novolac type (e.g., an epoxy phenol novolac, an epoxy cresol novolac, combinations thereof, or the like) or other type resin. Other preferred epoxy based materials includes a bisphenol-A epichlorohydrin ether polymer, or a bisphenol-A epoxy based material which may be modified with butadiene or another polymeric additive. Moreover, various mixtures of several different epoxy based materials may be employed as well. Examples of suitable epoxy based materials are sold under the trade name DER® (e.g., DER 331, DER 661, DER 662), commercially available from the Dow Chemical Company, Midland, Michigan.

[0081] The epoxy based material may be combined with a thermoplastic component, which may include styrenics, acrylonitriles, acrylates, acetates, polyamides, polyethylenes, phenoxy resins or the like. The thermoplastic component may be present in an amount of at least about 5 wt.-% of the adhesive formulation. The thermoplastic component may be present in an amount of from about 20 wt.-% to about 60 wt.-% of the adhesive formulation.

[0082] Preferably, the epoxy based material has an epoxy equivalent weight of at least about 200 g/eq, or at least about 210 g/eq, or at least about 220 g/eq, or at least about 230 g/eq, or at least about 240 g/eq; more preferably at least about 250 g/eq, or at least about 260 g/eq, or at least about 270 g/eq, or at least about 280 g/eq, or at least about 290 g/eq; still more preferably at least about 300 g/eq, or at least about 310 g/eq, or at least about 320 g/eq, or at least about 330 g/eq, or at least about 340 g/eq; yet more preferably at least about 350 g/eq, or at least about 360 g/eq, or at least about 370 g/eq, or at least about 380 g/eq, or at least about 390 g/eq; even more preferably at least about 400 g/eq, or at least about 425 g/eq, or at least about 450 g/eq, or at least about 475 g/eq, or at least about 500 g/eq; and most preferably at least about 525 g/eq, or at least about 550 g/eq, or at least about 575 g/eq, or at least about 600 g/eq.

[0083] Preferably, the epoxy based material has an epoxy equivalent weight of at most about 2000 g/eq, or most about 1900 g/eq, or most about 1800 g/eq; more preferably at most about 1700 g/eq, or most about 1600 g/eq, or most about 1500 g/eq; still more preferably at most about 1400 g/eq, or most about 1300 g/eq, or most about 1200 g/eq; yet more preferably at most about 1100 g/eq, or most about 1000 g/eq, or most about 950 g/eq; even more preferably at most about 900 g/eq, or most about 850 g/eq, or most about 800 g/eq; and most preferably at most about 750 g/eq, or most about 700 g/eq, or most about 650 g/eq.

[0084] In preferred embodiments, the epoxy based material has an epoxy equivalent weight within the range of about 550±300 g/eq, or about 600±300 g/eq, or about 650±300 g/eq, or about 700±300 g/eq, or about 750±300 g/eq, or about 800±300 g/eq, or about 850±300 g/eq, or about 900±300 g/eq, or about 950±300 g/eq, or about 1000±300 g/eq, or about 1050±300 g/eq, or about 1100±300 g/eq, or about 1150±300 g/eq; or about 450±200 g/eq, or about 500±200 g/eq, or about 550±200 g/eq, or about 600±200 g/eq, or about 650±200 g/eq, or about 700±200 g/eq, or about 750±200 g/eq, or about 800±200 g/eq, or about 850±200 g/eq, or about 900±200 g/eq, or about 950±200 g/eq, or about 1000±200 g/eq, or about 1050±200 g/eq, or about 1100±200 g/eq, or about 1150±200 g/eq; or about 350±100 g/eq, or about 400±100 g/eq, or about 450±100 g/eq, or about 500±100 g/eq, or about 550±100 g/eq, or about 600±100 g/eq, or about 650±100 g/eq, or about 700±100 g/eq, or about

750±100 g/eq, or about 800±100 g/eq, or about 850±100 g/eq, or about 900±100 g/eq, or about 950±100 g/eq, or about 1000±100 g/eq, or about 1050±100 g/eq, or about 1100±100 g/eq, or about 1150±100 g/eq.

[0085] The epoxy based material may comprise a mixture of two or more epoxy based materials. Under these circumstances, unless expressly stated otherwise, according to a preferred embodiment, the above epoxy equivalent weight applies to the overall epoxy equivalent weight of the mixture. Thus, in this regard the epoxy equivalent weight is to be regarded as an average over all epoxy based materials contained in the powdered heat activatable adhesive according to the invention. The epoxide equivalent weight (EEW) of the mixture comprising epoxy based material A and an epoxy based material B may then simply be calculated according to the following formula:

$$\text{EEW}(A + B) = \frac{\text{total weight of epoxy based materials A + B}}{\frac{\text{weight of epoxy based material A}}{\text{EEW of epoxy based material A}} + \frac{\text{weight of epoxy based material B}}{\text{EEW of epoxy based material B}}}$$

[0086] Thus, for a composition comprising e.g. 22 wt.-% of an epoxy based material A having an EEW(A) of 200 g/eq and 4.25 wt.-% of an epoxy based material B having an EEW(B) of 490 g/eq, the EEW(A+B) amounts to $(22+4.25)/[(22/200)+(4.25/490)] = 221$ g/eq.

[0087] In another preferred embodiment, however, the above epoxy equivalent weight applies to a distinct epoxy based material contained in said mixture of said two or more epoxy based materials.

[0088] A skilled person knows how to determine the epoxy equivalent weight of the individual components of such mixture. For example, a binary mixture of two epoxy based materials having different epoxy equivalent weight provides a bimodal weight distribution that can be analyzed e.g. by gel permeation chromatography and liquid chromatography and the epoxy equivalent weight may be derived from this analysis, preferably in accordance with ASTM-D. 1652.

[0089] Particularly preferred embodiments A¹ to A⁵⁶ of the powdered heat activatable adhesive according to the invention comprising epoxy based material (content relative to the total weight of the powdered heat activatable adhesive, and EEW as average over all epoxy based materials) are summarized in the table here below:

	content [wt.-%]	EEW [g/eq]		content [wt.-%]	EEW [g/eq]
A ¹	2-47	250-730	A ²⁹	2-47	630-930
A ²	7-42	250-730	A ³⁰	7-42	630-930
A ³	12-37	250-730	A ³¹	12-37	630-930
A ⁴	17-32	250-730	A ³²	17-32	630-930
A ⁵	2-47	250-590	A ³³	2-47	630-820
A ⁶	7-42	250-590	A ³⁴	7-42	630-820
A ⁷	12-37	250-590	A ³⁵	12-37	630-820
A ⁸	17-32	250-590	A ³⁶	17-32	630-820
A ⁹	2-47	350-730	A ³⁷	2-47	730-930
A ¹⁰	7-42	350-730	A ³⁸	7-42	730-930
A ¹¹	12-37	350-730	A ³⁹	12-37	730-930
A ¹²	17-32	350-730	A ⁴⁰	17-32	730-930
A ¹³	2-47	350-590	A ⁴¹	2-47	730-860

A ¹⁴	7-42	350-590	A ⁴²	7-42	730-860
A ¹⁵	12-37	350-590	A ⁴³	12-37	730-860
A ¹⁶	17-32	350-590	A ⁴⁴	17-32	730-860
A ¹⁷	2-47	590-930	A ⁴⁵	2-47	730-820
A ¹⁸	7-42	590-930	A ⁴⁶	7-42	730-820
A ¹⁹	12-37	590-930	A ⁴⁷	12-37	730-820
A ²⁰	17-32	590-930	A ⁴⁸	17-32	730-820
A ²¹	2-47	590-730	A ⁴⁹	2-47	820-930
A ²²	7-42	590-730	A ⁵⁰	7-42	820-930
A ²³	12-37	590-730	A ⁵¹	12-37	820-930
A ²⁴	17-32	590-730	A ⁵²	17-32	820-930
A ²⁵	2-47	590-630	A ⁵³	2-47	860-930
A ²⁶	7-42	590-630	A ⁵⁴	7-42	860-930
A ²⁷	12-37	590-630	A ⁵⁵	12-37	860-930
A ²⁸	17-32	590-630	A ⁵⁶	17-32	860-930

[0090] It has been surprisingly found that the epoxy equivalent weight of the epoxy based material has an important influence on the properties of the powdered heat activatable adhesive according to the invention. When the epoxy equivalent weight of the epoxy based material is too low, the powder is not sufficiently dry to the touch but adhesive so that the powder cannot be properly sprayed by means of a gas stream. In this regard, the requirements that need to be satisfied in order to render the powdered heat activatable adhesive according to the invention dry to the touch are stricter and do not correspond to the requirements for non-powdered solid masses. Due to the higher surface area and the powder nature of the powdered heat activatable adhesive according to the invention, adherence and stickiness of the powder particles must be suppressed to a high degree in order to obtain a free-flowing, sprayable powder. It has been found that when the epoxy equivalent weight of the epoxy based material is too high, the powder does not exhibit sufficient adhesiveness when it hits the surface of the substrate so that it either does not adhere to the surface at all or does not fuse to a layer. It has been surprisingly found that an epoxy equivalent weight within the range of from about 450 g/eq to about 1300 g/eq, more preferably from about 600 g/eq to about 1300 g/eq can be optimal.

[0091] Preferably, the powdered heat activatable adhesive according to the invention comprises one or two epoxy based materials, e.g. a first epoxy based material in combination with a second epoxy based material, preferably in combination with a phenoxy resin. Preferably, the powdered heat activatable adhesive according to the invention comprises an epoxy based material that is solid under ambient conditions (solid epoxy based material, first epoxy based material) and an epoxy based material that is liquid under ambient conditions (liquid epoxy based material, second epoxy based material), optionally in combination with a phenoxy resin.

[0092] Preferably, the liquid epoxy based material (as such) has an epoxy equivalent weight of at least about 100 g/eq, more preferably at least about 125 g/eq, still more preferably at least about 150 g/eq, most preferably at least about 175 g/eq.

[0093] Preferably, the liquid epoxy based material (as such) has an epoxy equivalent weight of at most about 500 g/eq, more preferably at most about 450 g/eq, still more preferably at most about 400 g/eq, yet more preferably at most about 350 g/eq, even more preferably at most about 300 g/eq, most preferably at most about 250 g/eq, and in particular at most about 200 g/eq.

[0094] In preferred embodiments, the liquid epoxy based material has an epoxy equivalent weight within the range of about 200 ± 150 g/eq, or about 150 ± 100 g/eq, or about 200 ± 100 g/eq, or about 250 ± 100 g/eq, or about 150 ± 50 g/eq, or about 175 ± 50 g/eq, or about 200 ± 50 g/eq, or about 225 ± 50 g/eq, or about 250 ± 50 g/eq.

[0095] Preferably, the relative difference of the epoxy equivalent weight of the solid epoxy based material (first epoxy based material) to the epoxy equivalent weight of the liquid epoxy based material (second epoxy based material) is within the range of from about 200 to about 1000 g/eq. In preferred embodiments, said relative difference is within the range of about 400 ± 200 g/eq, or 500 ± 200 g/eq, or 600 ± 200 g/eq, or 700 ± 200 g/eq, or 800 ± 200 g/eq.

[0096] Preferably,

- the first epoxy based material is solid under ambient conditions and/or has an epoxy equivalent weight of
 - (i) at least about 400 g/eq, or at least about 410 g/eq, or at least about 420 g/eq, or at least about 430 g/eq, or at least about 440 g/eq, or at least about 450 g/eq, or at least about 475 g/eq, or at least about 500 g/eq, or at least about 525 g/eq, or at least about 550 g/eq, or at least about 575 g/eq; and/or
 - (ii) at most about 1200 g/eq, or at most about 1150 g/eq, or at most about 1100 g/eq, or at most about 1050 g/eq, or at most about 1000 g/eq, or at most about 990 g/eq, or at most about 980 g/eq, or at most about 970 g/eq, or at most about 960 g/eq, or at most about 950 g/eq, or at most about 940 g/eq; and
- the second epoxy based material is liquid under ambient conditions and/or has an epoxy equivalent weight of at most about 300 g/eq, or at most about 290 g/eq, or at most about 280 g/eq, or at most about 270 g/eq, or at most about 260 g/eq, or at most about 250 g/eq, or at most about 240 g/eq, or at most about 230 g/eq, or at most about 220 g/eq, or at most about 210 g/eq, or at most about 200 g/eq;

wherein the above values for the epoxy equivalent weight (EEW) refer to the first epoxy based material as such and the second epoxy based material as such, respectively, i.e. do not refer to an average over the first epoxy based material and the second epoxy based material.

[0097] Preferably, the powdered heat activatable adhesive according to the invention comprises an epoxy based material that is solid under ambient conditions (solid epoxy based material) in combination with an epoxy based material that is liquid under ambient conditions (liquid epoxy based material). The relative weight ratio of the solid epoxy based material to the liquid epoxy based material is not particularly limited. Preferably, said relative weight ratio is within the range of from about 10:1 to about 1:10, more preferably about 1:4 to about 8:1, still more preferably about 1:3 to about 7:1, yet more preferably about 1:2 to about 6:1, even more preferably about 1:1 to about 5:1, most preferably about 2:1 to about 4:1, in particular from about 2.5:1 to about 3:1.

[0098] Preferably, the content of the solid epoxy based material (first epoxy based material) is greater than the content of the liquid epoxy based material (second epoxy based material).

[0099] Preferably, the relative weight ratio of the solid epoxy based material (first epoxy based material) to the liquid epoxy based material (second epoxy based material) is within the range of from about 10:1 to about 1.1:1; more preferably from about 8:1 to about 1.5:1; most preferably from about 5:1 to about 2:1.

[0100] In preferred embodiments, the values for the content of the first epoxy based material [in wt.-% relative to the total weight of the powdered heat activatable adhesive] C_1 , the epoxy equivalent weight of the first epoxy based material as such EEW_1 [in g/eq], the content of the second epoxy based material [in wt.-% relative to the total weight of the powdered heat activatable adhesive] C_2 , and the epoxy equivalent weight of the second epoxy based material as such EEW_2 [in g/eq], satisfy the following requirement:

$$C_1 \cdot EEW_1 + C_2 \cdot EEW_2 \geq X$$

wherein X is about 6000, or about 6200, or about 6400, or about 6600, or about 6800; more preferably about 7000, or about 7200, or about 7400, or about 7600, or about 7800; still more preferably about 8000, or about 8200, or about 8400, or about 8600, or about 8800; yet more preferably about 9000, or about 9200, or about 9400, or about 9600, or about 9800; even more preferably about 10000, or about 10200, or about 10400, or about 10600, or about 10800; most preferably about 11000, or about 11200, or about 11400, or about 11600, or about 11800; and in particular about 12000, or about 12200, or about 12400, or about 12600, or about 12800; and

wherein $EEW_1 > EEW_2$ and preferably also $C_1 > C_2$.

[0101] Particularly preferred embodiments B^1 to B^{16} of the powdered heat activatable adhesive according to the invention comprising a combination of a solid epoxy based material with a liquid epoxy based material (content relative to the total weight of the powdered heat activatable adhesive, and EEW) are summarized in the table here below (here the values for EEW relate to the individual components, liquid vs. solid, but are not to be regarded as average values over the mixture):

	solid epoxy based material		liquid epoxy based material	
	content [wt.-%]	EEW [g/eq]	content [wt.-%]	EEW [g/eq]
B^1	2-34	590-930	1-15	< 590
B^2	6-30	590-930	2-14	< 590
B^3	10-26	590-930	4-12	120-280
B^4	14-22	590-930	6-10	120-280
B^5	2-34	590-630	1-15	< 590
B^6	6-30	590-630	2-14	< 590
B^7	10-26	590-630	4-12	120-280
B^8	14-22	590-630	6-10	120-280
B^9	2-34	730-820	1-15	< 590
B^{10}	6-30	730-820	2-14	< 590
B^{11}	10-26	730-820	4-12	120-280
B^{12}	14-22	730-820	6-10	120-280
B^{13}	2-34	860-930	1-15	< 590
B^{14}	6-30	860-930	2-14	< 590
B^{15}	10-26	860-930	4-12	120-280
B^{16}	14-22	860-930	6-10	120-280

[0102] Preferably the epoxy based material is derived from a bisphenol, preferably being selected from the group consisting of bisphenol A, bisphenol B, bisphenol E, bisphenol F, bisphenol G, bisphenol M, bisphenol P, bisphenol S, bisphenol Z, bisphenol AF, bisphenol AP, bisphenol BP, bisphenol FL, and bisphenol TMC.

[0103] In a preferred embodiment, besides the above epoxy based material, the powdered heat activatable adhesive according to the invention comprises a phenoxy resin. The phenoxy resin typically has a substantially higher molecular weight than the epoxy based material and does not comprise reactive epoxy functional groups. Thus, the phenoxy resin according to the invention is distinct from the epoxy based material according to the invention.

[0104] It is preferred to use a formulation that contains at least about 15 wt.-% of a phenoxy resin, preferably from about 15 wt.-% to about 40 wt.-% of a phenoxy resin. Preferably, the formulation contains at least about 5 wt.-% of an elastomer/epoxy adduct, preferably from about 5 wt.-% to about 40 wt.-% (the elastomer/epoxy adduct is then to be regarded as being separate from the epoxy based material, i.e. the epoxy based material does not encompass the elastomer/epoxy adduct). Additionally the preferred formulation contains at least 5 wt.-% of a core shell polymer, preferably from about 5 wt.-% to about 25 wt.-%. The percentages relate to the entire formulation including other ingredients that may be present.

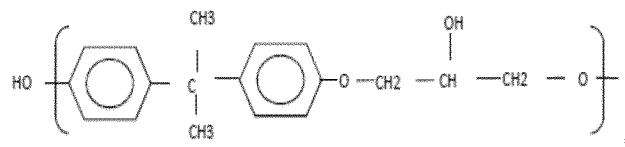
[0105] Preferably, the phenoxy resin can be regarded as the condensation products of

- a bisphenol, preferably being selected from the group consisting of bisphenol A, bisphenol B, bisphenol E, bisphenol F, bisphenol G, bisphenol M, bisphenol P, bisphenol S, bisphenol Z, bisphenol AF, bisphenol AP, bisphenol BP, bisphenol FL, and bisphenol TMC; and
- epichlorohydrin;

or a blend of various resins of this type and/or their derivatives.

[0106] Preferred phenoxy resins include low molecular weight, medium molecular weight, or high molecular weight materials which typically have a melting point around about 150 °C or higher. As one important use of the powders of this invention is in the production of adhesive bonds by the curing of the layers obtained on the surface of the substrate from the powders at temperatures experienced in the automobile e-coat process, it is preferred to formulate the formulation from which the powder is made at temperatures below the melting point of the phenoxy resin. Accordingly it is preferred that the phenoxy resin be provided to the formulating activity as a solution. It has been unexpectedly found that a liquid epoxy based material is a particularly good solvent for the phenoxy resin.

[0107] Preferred phenoxy resins are low molecular weight, medium molecular weight, or high molecular weight thermoplastic condensation products of bisphenol, preferably bisphenol A, and epichlorohydrin and their derivatives. Typically the phenoxy resins that may be employed are of the formula



where n is typically

from about 2 to about 12, preferably 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12; or

from about 13 to about 29; or

from about 30 to about 100, preferably from about 50 to about 90.

[0108] Modified phenoxy resins may also be used. Examples of phenoxy resins that may be used are the products marketed by Inchem Corp. Examples of suitable materials are the PKHB, PKHC, PKHH, PKHJ, PKHP pellets and powder. Alternatively phenoxy/polyester hybrids and epoxy/phenoxy hybrids may be used. In order to enhance the production of the structural adhesive the phenoxy resin may be supplied to the other components as a solution. While any solvent may be used it is particularly preferred to use a liquid epoxy based material as the solvent as this can also contribute to the adhesive properties upon activation.

[0109] Typical other ingredients which may be used in the formulation hardeners (curing agents), tougheners and flexibilizers.

[0110] The adhesive formulation may also include one or more additional polymer and/or copolymer materials, such as thermoplastics, elastomers, plastomers, combinations thereof or the like. Preferably, the powdered heat activatable adhesive according to the invention, which comprises a thermoplastic component.

[0111] Polymers that might be appropriately incorporated into the adhesive include without limitation, polyolefin (e.g., polyethylene, polypropylene) polystyrene, polyacrylate, poly(ethylene oxide), poly(ethyleneimine), polyester, polyurethane, polysiloxane, polyether, polyphosphazine, polyamide, polyimide, polyisobutylene, polyacrylonitrile, poly(vinyl chloride), poly(methyl methacrylate), poly(vinyl acetate), poly(vinylidene chloride), polytetrafluoroethylene, polyisoprene, polyacrylamide, polyacrylic acid, or polymethacrylate.

[0112] Preferably, the powdered heat activatable adhesive according to the invention comprises an impact modifier. The adhesive formulation may include at least one impact modifier. Various impact modifiers may be employed in the practice of the invention and often include one or more elastomers. The impact modifier may be at least about 4 wt.-%, at least about 7 wt.-%, at least about 10 wt.-%, at least about 13 wt.-% and even still more typically at least about 16 wt.-% of the adhesive formulation. The impact modifier may be less than about 90 wt.-%, less than about 40 wt.-% or even less than about 30 wt.-% of the adhesive formulation.

[0113] Preferably, the impact modifier is selected from elastomer/epoxy adducts, core/shell materials, and combinations thereof.

[0114] While it is contemplated that various polymer/elastomer adducts may be employed in the adhesive formulation used in the invention, one preferred adduct is an epoxy/elastomer adduct. The epoxy/elastomer hybrid or adduct may be included in an amount of from about 5 wt.-% to about 80 wt.-% of formulation, typically about 10 wt.-% to about 60 wt.-%, more preferably is about 10 wt.-% to about 30 wt.-% of the formulation (the elastomer/epoxy adduct is then to be regarded as being separate from the epoxy based material, i.e. the epoxy based material does not encompass the elastomer/epoxy adduct). The elastomer-containing adduct may be a combination of two or more particular adducts and the adducts may be solid adducts or liquid adducts

at a temperature of about 23 °C or may also be combinations thereof. The adduct is preferably one or more adducts that are solid at a temperature of about 23°C.

[0115] The adduct itself generally includes about 1:8 to 3:1 parts of epoxy or other polymer to elastomer, and more preferably about 1:5 to 1:6 parts of epoxy to elastomer. More typically, the adduct includes at least about 5 wt.-%, more typically at least about 12 wt.-% and even more typically at least about 18 wt.-% elastomer and also typically includes not greater than about 50 wt.-%, even more typically no greater than about 40 wt.-% and still more typically no greater than about 35 wt.-% elastomer, although higher or lower percentages are possible. The elastomer compound may be a thermosetting elastomer. Exemplary elastomers include, without limitation, natural rubber, styrene-butadiene rubber, polyisoprene, polyisobutylene, polybutadiene, isoprene-butadiene copolymer, neoprene, nitrile rubber (e.g., a butyl nitrile, such as carboxy-terminated butyl nitrile), butyl rubber, polysulfide elastomer, acrylic elastomer, acrylonitrile elastomers, silicone rubber, polysiloxanes, polyester rubber, diisocyanate-linked condensation elastomer, EPDM (ethylene-propylene diene rubbers), chlorosulphonated polyethylene, fluorinated hydrocarbons and the like. An example of a preferred epoxy/elastomer adduct is sold under the trade name HYPOX commercially available from CVC Chemical. Examples of additional or alternative epoxy/elastomer or other adducts suitable for use in the invention are disclosed in US 2004/0204551.

[0116] The elastomer-containing adduct, when added to the adhesive material, may modify structural properties of the adhesive formulation such as strength, toughness, stiffness, flexural modulus, or the like.

[0117] The impact modifier may include at least one core/shell impact modifier. The impact modifier may comprise at least about 60 wt.-%, at least about 80 wt.-% or even at least about 95 wt.-% core/shell impact modifier.

[0118] As used herein, the term core/shell impact modifier denotes an impact modifier wherein a substantial portion (e.g., greater than about 30 wt.-%, about 50 wt.-%, about 70 wt.-% or more) thereof is comprised of a first polymeric material (i.e., the first or core material) that is substantially entirely encapsulated by a second polymeric material (i.e., the second or shell material).

[0119] The first and second polymeric materials, as used herein, can be comprised of one, two, three or more polymers that are combined and/or reacted together (e.g., sequentially polymerized) or may be part of separate or same core/shell systems.

[0120] The first and second polymeric materials of the core/shell impact modifier can include elastomers, polymers, thermoplastics, copolymers, other components, combinations thereof or the like. The first polymeric material, the second polymeric material or both of the core/shell impact modifier may include or may be substantially entirely composed of (e.g., at least about 70 wt.-%, about 80 wt.-%, about 90 wt.-% or more) one or more thermoplastics. Exemplary thermoplastics include, without limitation, styrenics, acrylonitriles, acrylates, acetates, polyamides, polyethylenes or the like.

[0121] Examples of useful core-shell graft copolymers are those where hard containing compounds, such as styrene, acrylonitrile or methyl methacrylate, are grafted onto a core made from polymers of soft or elastomeric containing compounds such as butadiene or butyl acrylate.

[0122] The core polymer may also include other copolymerizable containing compounds, such as styrene, vinyl acetate, methyl methacrylate, butadiene, isoprene, or the like. The core polymer material may also include a cross linking monomer having two or more nonconjugated double bonds of approximately equal reactivity such as ethylene glycol diacrylate, butylene glycol dimethacrylate, and the like. The core polymer material may also include a graft linking monomer having two or more nonconjugated double bonds of unequal reactivity such as, for example, diallyl maleate and allyl methacrylate. The shell portion may be polymerized from methyl methacrylate and optionally other alkyl methacrylates, such as ethyl, butyl, or mixtures thereof methacrylates. Additional core-shell graft copolymers useful in embodiments of the invention are described in US 3,984,497; US 4,096,202; US 4,034,013; US 3,944,631; US 4,306,040; US 4,495,324; US 4,304,709; US 4,536,436; and US 7,892,396, the entireties of which are herein incorporated by reference herein. Examples of suitable core-shell graft copolymers include, but are not limited to, "MBS" (methacrylatebutadiene-styrene) polymers, which are made by polymerizing methyl methacrylate in the presence of polybutadiene or a polybutadiene copolymer rubber. The MBS graft copolymer resin generally has a styrene butadiene rubber core and a shell of acrylic polymer or copolymer. Examples of other useful core-shell graft copolymer resins include, ABS (acrylonitrile-butadiene-styrene), MABS (methacrylate-acrylonitrile-butadiene-styrene), ASA (acrylate-styrene-acrylonitrile), all acrylics, SA EPDM (styrene-acrylonitrile grafted onto elastomeric backbones of ethylene-propylene diene monomer), MAS (methacrylic-acrylic rubber styrene), and the like and mixtures thereof.

[0123] The adhesive formulation may also include one or more fillers, including but not limited to particulated materials (e.g., powder), beads, microspheres, or the like. The precursor layer may also be substantially free of any filler material. Fillers can be useful to reduce any blocking tendency of the uncured powdered heat activatable adhesive, reduce cost, and reduce the coefficient of thermal expansion of the cured material. The precursor layer may include a filler that comprises less than about 25 wt.-% of the precursor material. Ideally, the filler may comprise less than about 2.5 wt.-% of the precursor layer. Any filler present may include a material that is generally non-reactive with the other components present in the precursor layer. Certain fillers can also reduce the tendency of the particles to agglomerate as well as reducing the blocking tendency.

[0124] Examples of suitable fillers include silica, diatomaceous earth, glass, clay (e.g., including nanoclay), talc, pigments, colorants, glass beads or bubbles, glass, carbon or ceramic fibers, nylon aramid or polyamide fibers (e.g., Kevlar), antioxidants, and the like. Such fillers, particularly clays, can assist the activatable material in leveling itself during flow of the material. The clays that may be used as fillers may include clays from the kaolinite, illite, chloritem, smectite or sepiolite groups, which may be calcined. Examples of suitable fillers include, without limitation, talc, vermiculite, pyrophyllite, saunonite, saponite, nontronite, montmorillonite or mixtures thereof. The clays may also include minor amounts of other ingredients such as carbonates, feldspars, micas and quartz. The fillers may also include ammonium chlorides such as dimethyl ammonium chloride and dimethyl benzyl ammonium chloride. Titanium dioxide might also be employed.

[0125] In one embodiment it is preferred to include a thixotropic filler such as aramid fibre or certain clays in the adhesive formulation. The inclusion of such a thixotropic filler can reduce the tendency of the adhesive formulation to flow and sag when it is a fluid state such as when the powder particles coalesce to form a film after application or when it is heated to the activation temperature.

[0126] The adhesive formulation may be foamable and it may contain a heat activatable blowing agent for example one that decomposes to produce gas at temperatures experienced in the automotive anticorrosion coating bake oven. Typically, temperatures are in the range of from about 150 °C to about 220 °C. The blowing agent may be selected to generate gasses for foaming at around the activation temperature of the cross linking agent. Examples of suitable blowing agents include chemical blowing agents (e.g., those agents that provide for material expansion via a chemical reaction) including but not limited to azodicarbonamide, dinitrosopentamethylenetetramine, hydrazides such as 4,4-oxy-bis-(benzenesulphonylhydrazide), trihydrazinotriazine and N,N'-dimethyl-N,N'-dinitrosoterephthalamide. The blowing agent may also be a physical blowing agent, such that material expansion occurs via a phase change mechanism. Physical blowing agents can comprise a volatile gas trapped in a thermoplastic shell which softens and lets the gas expand at the foaming temperature. An example of such a blowing agent is sold under the trade name Expancel, sold by Akzo Nobel, Sundsvall, Sweden. An accelerator for the blowing agents may also be provided in the activatable material. Various accelerators may be used to increase the rate at which the blowing agents form inert gasses. One preferred blowing agent accelerator is a metal salt, or is an oxide, e.g. a metal oxide, such as zinc oxide. Other preferred accelerators include modified and unmodified thiazoles or imidazoles. In addition, the material may include a flame retardant. It is preferred that the crosslinking agent will cure the adhesive during foam formation so that the molten formulation is sufficiently viscous to entrap the gas produced by the decomposition of the blowing agent. Where the adhesive is a structural adhesive typically the degree of expansion is from about 80 % to about 200 %. However, the foams according to the invention may have a higher degree of expansion than foamed structural adhesives, e.g. greater than about 1000 %, more typically greater than about 1500 % and more typically greater than about 2000 %.

[0127] Preferably, the powdered heat activatable adhesive according to the invention comprises an anticaking agent.

[0128] Preferably, the anticaking agent is selected from the group consisting of talcum, earth alkali salts of fatty acids, tricalcium phosphate, powdered cellulose, calcium stearate, magnesium stearate, stearic acid, sodium bicarbonate, sodium ferrocyanide, potassium ferrocyanide, calcium ferrocyanide, silicon dioxide, sodium silicate, calcium silicate, magnesium trisilicate, talcum powder, sodium aluminosilicate, calcium aluminosilicate, potassium aluminium silicate, bentonite, aluminium silicate, and polydimethylsiloxane.

[0129] In another preferred embodiment, the powdered heat activatable adhesive according to the invention comprises substantially no anticaking agent.

[0130] Preferably, the powdered heat activatable adhesive according to the invention comprises particles of type EC, wherein each individual particle of type EC comprises both the epoxy based material as well as the

curing agent. It is preferred that the epoxy based material and the curing agent are intimately mixed with one another so that they can react with one another when the adhesiveness of the material is activated by heating.

[0131] In a preferred embodiment, the powdered heat activatable adhesive according to the invention comprises particles of type E, wherein each individual particle of type E comprises the epoxy based material, but substantially no curing agent. In another preferred embodiment, the powdered heat activatable adhesive according to the invention does not comprise particles of type E, i.e. under these circumstances the total amount of the epoxy based material is contained in particles of type EC.

[0132] In a preferred embodiment, the powdered heat activatable adhesive according to the invention comprises particles of type C, wherein each individual particle of type C comprises the curing agent, but substantially no epoxy based material. In another preferred embodiment, the powdered heat activatable adhesive according to the invention does not comprise particles of type C, i.e. under these circumstances the total amount of the curing agent is contained in particles of type EC.

[0133] Preferably, at least about 50 wt.-% of the particles comprising epoxy based material are particles of type EC and/or at least about 50 wt.-% of the particles comprising curing agent are particles of type EC. Preferably, at least about 90 wt.-% of the particles comprising epoxy based material are particles of type EC and/or at least about 90 wt.-% of the particles comprising curing agent are particles of type EC.

[0134] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises an anticaking agent, at least a portion, preferably the total amount of the anticaking agent is contained

- in particles of type A, wherein each particle of type A comprises neither epoxy based material nor curing agent; and/or
- in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
- in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
- in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.

[0135] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises a blowing agent and/or blowing accelerator, at least a portion, preferably the total amount of the blowing agent and/or at least a portion, preferably the total amount of the blowing accelerator is contained

- in particles of type B, wherein each particle of type B comprises neither epoxy based material nor curing agent; and/or
- in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or

- in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
- in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.

[0136] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises an impact modifier, at least a portion, preferably the total amount of the impact modifier is contained

- in particles of type I, wherein each particle of type I comprises neither epoxy based material nor curing agent; and/or
- in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
- in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
- in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.

[0137] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises a first epoxy based material and a second epoxy based material, e.g. a solid epoxy based material in combination with a liquid epoxy based material, at least a portion, preferably the total amount of the second epoxy based material is contained

- in particles of type EC each individually comprising both the first epoxy based material as well as the curing agent; and/or
- in particles of type E each individually comprising the first epoxy based material, but substantially no curing agent.

[0138] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises a thermoplastic component, at least a portion, preferably the total amount of the thermoplastic component is contained

- in particles of type T, wherein each particle of type T comprises neither epoxy based material nor curing agent; and/or
- in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
- in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
- in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.

[0139] In preferred embodiments, when the powdered heat activatable adhesive according to the invention comprises a filler, at least a portion, preferably the total amount of the filler is contained

- in particles of type F, wherein each particle of type F comprises neither epoxy based material nor curing agent; and/or
- in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
- in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
- in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.

[0140] The powders are preferably prepared by comminuting preferably by grinding pellets of the appropriate adhesive formulation under a cold inert atmosphere such as a stream of liquid nitrogen. Once prepared the powders are preferably stored and transported in a sealed container. In a preferred embodiment the powder are prepared at a temperature no higher than about -20 °C.

[0141] Another aspect of the invention relates to a process for the preparation of a powdered heat activatable adhesive according to the invention comprising the step of milling a composition comprising the epoxy based material and the curing agent.

[0142] All preferred embodiments that have been described above with respect to the powdered heat activatable adhesive according to the invention also apply to the process for the preparation of the powdered heat activatable adhesive and are therefore not repeated hereinafter.

[0143] Preferably, besides the epoxy based material and the curing agent, the composition comprises one or more of the following ingredients:

- anticaking agent; and/or
- blowing agent and/or blowing accelerator; and/or
- impact modifier; and/or
- filler; and/or
- thermoplastic polymer; and/or
- phenoxy resin.

[0144] Preferably, the composition is mixed prior to milling, optionally at elevated temperature below the activation temperature.

[0145] Preferably, milling is performed at reduced temperature, more preferably below about -10 °C, most preferably below about -20 °C.

[0146] Preferably, milling involves cryo-milling.

[0147] Preferably, milling is performed by means of a hammer mill or an air jet mill or a rotor mill.

[0148] Another aspect of the invention relates to a process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form the adhesive layer.

[0149] All preferred embodiments that have been described above with respect to the powdered heat activatable adhesive according to the invention also apply to the process according to the invention wherein said powdered heat activatable adhesive is sprayed on the surface of a substrate to form an adhesive layer. Thus, these preferred embodiments are not repeated hereinafter.

[0150] Preferably, the process according to the invention comprises

- supplying a powdered heat activatable adhesive into a preferably heated gas stream flowing under pressure, and
- directing the flowing gas stream containing the powdered heat activatable adhesive onto the surface of the substrate.

[0151] Preferably, the gas stream is mixed with the powdered heat activatable adhesive in a De Laval nozzle (after Carl G.P. De Laval). A De Laval nozzle (or "convergent-divergent nozzle", "CD nozzle" or "con-di nozzle") is a tube that is pinched in the middle, assuming a well balanced, asymmetric hourglass-shape. It is useful to accelerate a hot, pressurized gas passing through it to a higher speed in the axial (thrust) direction, by converting the heat energy of the flow into kinetic energy.

[0152] In a preferred embodiment of the process according to the invention, the gas stream is heated. Preferably, the powdered heat activatable adhesive is heated with the gas stream and/or is accelerated to a velocity such that upon impact on the surface of the substrate it is heated to a temperature so that it softens and adheres to the substrate. Preferably, the temperature of the gas stream is within the range of from about 25 °C to about 80 °C. Preferably, the temperature of the gas stream prior to mixing with the powdered heat activatable adhesive is at least about 100 °C, or at least about 200 °C, more preferably at least about 250 °C, or at least about 350 °C, still more preferably at least about 400 °C or at least about 500 °C. Preferably, the temperature of the gas stream prior to mixing with the powdered heat activatable adhesive is at most about 900 °C, or at most about 800 °C, more preferably at most about 750 °C, or at most about 650 °C, still more preferably at most about 600 °C, or at most about 500 °C.

[0153] The temperature of the gas stream is one parameter that may be adjusted by routine experimentation in order to optimize the process according to the invention, particularly the adhesion of the powdered heat activatable adhesive and other properties thereof when it is applied to the surface of a substrate.

[0154] In another preferred embodiment of the process according to the invention, the gas stream is not heated.

[0155] Preferably, the adhesive is sprayed at a distance of from about 10 mm to about 100 mm, more preferably about 20 mm to about 60 mm from the surface of the substrate.

[0156] As the time of flight is a function of the distance of spraying, this is also one parameter that may be adjusted by routine experimentation in order to optimize the process according to the invention, particularly the adhesion of the powdered heat activatable adhesive and other properties thereof when it is applied to the surface of a substrate.

[0157] Preferably, the powdered heat activatable adhesive is accelerated so that when it hits the surface of the substrate it has a velocity within the range of from about 50 m/s to about 1000 m/s, more preferably from about 100 m/s to about 1000 m/s. In preferred embodiments, the velocity is within the range of from about 50 m/s to about 400 m/s, more preferably from about 50 m/s to about 300 m/s. Preferred velocities are within the range of about 100 ± 50 m/s, or about 150 ± 50 m/s, or about 200 ± 50 m/s, or about 250 ± 50 m/s, or about 300 ± 50 m/s, or about 350 ± 50 m/s, or about 400 ± 50 m/s, or about 450 ± 50 m/s, or about 500 ± 50 m/s, or about 550 ± 50 m/s, or about 600 ± 50 m/s, or about 650 ± 50 m/s, or about 700 ± 50 m/s, or about 750 ± 50 m/s, or about 800 ± 50 m/s, or about 850 ± 50 m/s, or about 900 ± 50 m/s, or about 950 ± 50 m/s, or about 1000 ± 50 m/s.

[0158] The velocity of the powdered heat activatable adhesive that is accelerated by gas stream is one parameter that may be adjusted by routine experimentation in order to optimize the process according to the invention, particularly the adhesion of the powdered heat activatable adhesive and other properties thereof when it is applied to the surface of a substrate.

[0159] Preferably, the gas stream is or comprises an inert gas. Preferably, the inert gas is nitrogen, argon or a mixture thereof.

[0160] Preferably, the pressure of the gas stream prior to mixing with the powdered heat activatable adhesive is at least about 1.5 bar, more preferably at least about 2.8 bar (40 psi). Preferably, the pressure of the gas stream prior to mixing with the powdered heat activatable adhesive is at most about 10 bar, more preferably at most about 4.1 bar (60 psi).

[0161] The pressure of the gas stream is one parameter that may be adjusted by routine experimentation in order to optimize the process according to the invention, particularly the adhesion of the powdered heat activatable adhesive and other properties thereof when it is applied to the surface of a substrate.

[0162] In a preferred embodiment of the process according to the invention, the substrate is heated. In another preferred embodiment of the process according to the invention, the substrate is not heated.

[0163] In a preferred embodiment of the process according to the invention, the adhesive adheres to the surface of the substrate but remains at a temperature at which it remains activatable by subsequent heating.

[0164] In a preferred embodiment of the process according to the invention the adhesive layer that has formed on the surface of the substrate but that remains activatable by subsequent heating, optionally after cooling, is subsequently heated in order to develop its full adhesive properties. Preferably, the adhesive layer that has formed on the surface of the substrate but that remains activatable by subsequent heating, is subsequently heated to a temperature in the range of from about 130 °C to about 220 °Cm, preferably from about 150 °C to about 220 °C; preferably in the course of applying an automotive anticorrosion coat (known as e-coat) in a suitable bake oven.

[0165] In a preferred embodiment of the process according to the invention, it does not involve any technique selected from the group consisting of electrodeposition, electrostatic deposition, electrostatic spraying, electrostatic brush coating, electric arc spraying, plasma arc spraying, flame spraying, high-velocity oxygen fuel spraying, and detonation gun spraying.

[0166] The adhesive is preferably applied to the substrate by a De Laval nozzle in which a stream of powdered heat activatable adhesive in a gas is supplied from a container into a preferably heated gas stream that has been accelerated and is then ejected from the nozzle onto the surface of a substrate. The ejector of the nozzle is preferably located close to the surface. Preferably, the particles are accelerated, preferably by means of the De Laval nozzle.

[0167] The nozzle and the substrate may be moveable relative to each other and the movement can be programmed to deliver the adhesive precisely in any desired pattern on the surface of the substrate. The apparatus should be set up so that the particles of the activatable adhesive are at the temperature and/or velocity at which they will adhere to the surface of the substrate when they reach the surface and impact on the surface, respectively.

[0168] The adhesive is preferably a heat activated adhesive and the temperature at which the adhesive is activated will depend upon the nature of the adhesive and the nature of the activation and when the activation is to take place. Preferably, the adhesive adheres to the surface of the substrate but remains at a temperature at which it remains activatable by subsequent heating (such as by thermal cross linking and/or thermal expansion).

[0169] The method of the invention is versatile in that it allows for selection of the temperature to which the powdered heat activatable adhesive is subjected and it also allows the length of time to which the powdered heat activatable adhesive is subjected to the temperature to be varied. For example, the length of the ejector of the nozzle, the distance from the tip of the injection nozzle to the surface of the substrate and the temperature of the gaseous stream can be selected as required. This may also allow the material to be subjected to temperatures higher than its activation temperature for sufficiently short times that little or no activation occurs. This can be useful if a higher temperature than the activation temperature is required for adequate adhesion to the surface of the substrate.

[0170] The gas that is used to propel the powder from the nozzle onto the surface of the substrate should be inert to the powder material. It has been unexpectedly found that for many applications air or nitrogen is suitable.

Typical gas pressures are in the range of about 2.8 bar (40 psi) to about 4.1 bar (60 psi) and gas temperatures in the range of about 400 °C to about 600 °C prior to the venturi have been found sufficient to raise a typical automotive activatable adhesive formulation to temperatures of from about 80 °C to about 110 °C at the surface of the substrate if they are sprayed at a distance of from about 20 mm to about 60 mm from the surface of the substrate. Although the surface of the substrate may be heated, it has been found that under these conditions it is not necessary in order to achieve adhesion of a typical automotive formulation.

[0171] The powdered heat activatable adhesive of the invention may be used in various applications including but not limited to automotive industry, aircraft industry, building and construction industry.

[0172] The powdered heat activatable adhesive of the invention may be used with any substrate and may be used for the bonding together of a range of substrates. For example the adhesive may be used to bond together metal substrates such as in automobile manufacture. It may be used in the bonding of different substrates such as the bonding of metal to fiber reinforced composites. It may be used for the bonding of glass such as in windows and automobile windscreens. The powder may also be used to provide a curable fibrous matt in which the powder acts as a curable matrix within the matt, in which instance the powder may be sprayed onto the matt which is vibrated to distribute the powder particles to the interstices of the fibrous malt.

[0173] Another aspect of the invention relates to a substrate provided with a coating of an adhesive provided by the process according to the invention.

[0174] All preferred embodiments that have been described above with respect to the powdered heat activatable adhesive according to the invention and the process according to the invention also analogously apply to the substrate according to the invention and therefore are not repeated hereinafter.

[0175] Preferably, the substrate according to the invention comprises metal and/or polymers. The substrate may also be an organo sheet material or a composite material. Preferably, the substrate according to the invention comprises an automobile component.

[0176] The thickness of the substrate is not particularly limited. Preferably, the substrate has a thickness of from about 50 µm to about 2000 µm, preferably from about 300 µm to about 600 µm, more preferably from about 300 µm to about 500 µm.

[0177] Cured structural adhesive layers formed from powder according to the invention can exhibit relatively high impact resistance particularly for certain combinations and amounts of ingredients (e.g., combination of certain amounts of adduct, amounts of impact modifier or both) as disclosed herein, can exhibit desirable toughness and/or T-peel strengths. As an example, the adhesive material of the invention has been unexpectedly found to exhibit, according to ASTM D 1876-01, T-peel strengths of at least about 2 N/mm, at least about 3.7 N/mm or even at least about 5.5 N/mm.

[0178] The lap shear strengths of the cured structural adhesive layers are determinable according to ASTM D1002-01. Lap shear strength of the adhesive at 23 °C (73.4 °F) may be greater than about 68.9 bar (1000 psi), often greater than about 137.9 bar (2000 psi), can be greater than about 206.8 bar (3000 psi) and can even be greater than about 241.3 bar (3500 psi). Lap shear strength of the adhesive material at -55 °C (-67 °F) is often greater than about 68.9 bar (1000 psi), often greater than about 137.9 bar (2000 psi), can be greater than about 151.7 bar (2200 psi) and can even be greater than about 206.8 bar (3000 psi).

[0179] The invention can be used to deposit powder of a heat activatable adhesive on larger surface areas than has hitherto been possible by extrusion deposition and by pumpable liquid adhesives. It has been unexpectedly found useful in the provision of substantially uniform films of thickness ranging from about 50 µm to about 500 µm on three dimensional structures including those of complex shape. The adhesive may be applied without contact between the applicator and the surface. Additionally, it has been unexpectedly found that sufficient adhesion between the powdered heat activatable adhesive and an oily metal surface can be achieved so avoiding the need for cleaning the surface. It has also been unexpectedly found that adhesive materials such as the products L-5236 and L-5810 as described in EP-A 2569384 and obtainable from L & L Products Europe can be powdered and applied according to the invention without any significant degradation of their adhesive properties particularly when an anticaking agent is included in the formulation.

[0180] It has been unexpectedly found that the powdered heat activatable adhesives of the invention are easy to handle and apply. Their use can be directed and controlled to the areas where adhesion is required so producing very little if any scrap. It has also been unexpectedly found that the powder can be readily coalesced to form a coherent layer in the substrate and the thickness of the layer is easy to control again making efficient use of material. Standard techniques for curing the adhesive such as automotive e-coat baking can be used so that in many instances there is no need for special curing ovens or the like.

[0181] In another embodiment the powder may be of materials used for the production of seals and baffles in automobiles.

[0182] Another aspect of the invention relates to the use of a powdered heat activatable adhesive, preferably of the powdered heat activatable adhesive according to the invention, in the process according to the invention.

[0183] All preferred embodiments that have been described above with respect to the powdered heat activatable adhesive according to the invention and the process according to the invention also analogously apply to the use according to the invention and therefore are not repeated hereinafter.

[0184] The invention may be used to create foams that assist in the reduction of vibration and noise after activation. In this regard, reinforced and vibrationally damped components can have increased stiffness which will reduce natural frequencies that resonate through the automotive chassis thereby reducing transmission, blocking or absorbing noise through the use of the conjunctive acoustic product. By increasing the stiffness and rigidity of the components of a vehicle, the amplitude and frequency of the overall noise, vibration or both that occurs from the operation of the vehicle and is transmitted through the vehicle can be reduced. These foams

usually have a higher degree of expansion than foamed structural adhesives, typically greater than about 1000 %, more typically greater than about 1500 % and more typically greater than about 2000 %.

[0185] In general some desired characteristics of the resulting material include relatively low glass transition point, and good corrosion resistance properties. In this manner, the material does not generally interfere with the materials systems employed by automobile manufacturers.

[0186] Moreover, it will withstand the processing conditions typically encountered in the manufacture of a vehicle, such as the e-coat priming, cleaning and degreasing and other coating processes as well as the painting operations encountered in final vehicle assembly.

[0187] Preferred embodiments of the invention are summarized as embodiments emb-1 to emb-15 hereinafter:

- Emb-1. A process for the provision of an adhesive layer on the surface of a substrate comprising supplying a powdered heat activatable adhesive into a heated gas stream flowing under pressure heating the powdered heat activatable adhesive with the gas to a temperature at which it will soften to adhere to the substrate and directing the flowing gas stream containing the heated powdered heat activatable adhesive onto the surface of the substrate.
- Emb-2. A process according to Emb-1 in which the powdered heat activatable adhesive has a particle size, preferably an average particle size, in the range of 20 to 300 μm preferably 100 to 200 microns.
- Emb-3. A process according to Emb-1 or Emb-2 in which the adhesive is applied to the substrate by a nozzle wherein a stream of powdered heat activatable adhesive in a gas is supplied from a container into a heated gas stream that has been accelerated by passage through a venturi and is then ejected from the nozzle onto the surface of a substrate.
- Emb-4. A process according to Emb-3 in which the nozzle and the substrate are moveable relative to each other.
- Emb-5. A process according to any of Emb-1 to Emb-4 in which the adhesive is a heat activated adhesive.
- Emb-6. A process according to Emb-5 in which the adhesive adheres to the surface of the substrate but remains at a temperature at which it remains activatable by subsequent heating.
- Emb-7. A process according to Emb-5 in which the heating during spraying raises the temperature of the adhesive to a temperature at which it will adhere to the surface of the substrate and will also be heat activated.
- Emb-8. A process according to any of Emb-1 to Emb-7 in which the gas that is used to propel the powder from the nozzle onto the surface of the substrate is air or nitrogen.
- Emb-9. A process according to Emb-8 in which the gas pressure is in the range of 40 to 60 psi and the gas temperature is in the range of 400 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ prior to the venturi.
- Emb-10. A process according to any of Emb-1 to Emb-9 in which the materials are sprayed at a distance of from 20 to 60 mm from the surface of the substrate.

- Emb-11. A process according to any of Emb-1 to Emb-10 in which the adhesives is a structural adhesive, selected from foamable structural adhesives and unfoamable structural adhesives.
- Emb-12. A process according to Emb-11 in which the formulation of the powdered heat activatable adhesive comprises i) a phenoxy resin ii) an elastomer/epoxy adduct iii) a core shell material and iv) a curing agent.
- Emb-13. A process according to Emb-12 in which the formulation additionally contains an epoxy resin.
- Emb-14. A process according to any of Emb-1 to Emb-10 in which the powdered heat activatable adhesive is of materials used for the production of seals and baffles in automobiles.
- Emb-15. A substrate provided with a coating of an adhesive provided by a method according to any of the preceding claims.
- Emb-16. A substrate according to Emb-15 comprising metal.
- Emb-17. A substrate according to Emb-15 or Emb-16 comprising an automobile component.

[0188] The invention is illustrated by the accompanying Figures. Figure 1 shows an apparatus for operation of the method of the invention. Figure 2 shows the substrate shown in Figure 1 coated with the activatable adhesive. Figure 3 shows preferred embodiments of powders and powder mixtures according to the invention.

[0189] Figure 1 shows a heated container (1) containing powdered heat activatable adhesive material (2), the container is provided with a plunger (3) which presses the powder through a duct (4) heated by a coil (5) into a stream of hot inert gas provided in the delivery tube (6) by a fan (7) which delivers the heated gas through a venturi (8) into tube (6) where it is mixed with the powdered heat activatable adhesive. The mixture is ejected from the nozzle of the tube (9) across a space (10) into contact with the surface (11) of a substrate (12). The nozzle can be moved relative to the substrate (13) to deliver the hot powdered heat activatable adhesive to the desired bonding area (13).

[0190] Figure 2 is an enlarged view of the substrate (12) provided with a layer of adhesive (14) built up on the desired bonding area (13).

[0191] The invention is further illustrated by the following Examples which are not to be construed as limiting its scope.

[0192] Example 1:

[0193] An adhesive formulation comprising the following ingredients was comminuted to an average particle size of about 100 µm (as measure used a Beckman Coulter LS 13320 laser scattering particle size analyzer):

Lotader [®] AX-8900 ¹	Polymer backbone	15.50 wt.-%
Evatane [®] 2805 ² /Escorene [®] UL 7760 ³		16.16 wt.-%
Elvax [®] 420 ⁴		10.00 wt.-%
Norsolene [®] S105 ⁵		12.20 wt.-%
	Wax and oil	6.7 wt.-%

	Peroxide curing agent	1.4 wt.-%
	Curing agent	2.50 wt.-%
	Blowing agent	1.60 wt.-%
	Pigment	0.01 wt.-%
	Thixotropic agent	1.00 wt.-%
	Calcium carbonate filler	32.93 wt.-%

¹ Lotader® AX-8900 is a random terpolymer of ethylene, acrylic ester and glycidyl methacrylate;

² Evatane® 2805 is a random copolymer of Ethylene and Vinyl Acetate

³ Escorene® UL 7760 is a high viscosity, 26.7% VA copolymer

⁴ Elvax® 420 0 is an ethylene-vinyl acetate copolymer

⁵ Norsolene® S105 is a light colored, low odor aromatic resin

[0194] The powder was sprayed onto a steel panel employing an apparatus as illustrated in Figure 1. Nitrogen was used as the propelling gas and the pressure in the gas chamber was 50 psi and the temperature of the gas prior to the venturi was 580 °C. The tube (4) for delivery of the powder was at a temperature in the range 80-90 °C. The speed of ejection of the mixture of the powdered heat activatable adhesive and the heated gas from the nozzle was 300 mm/sec and the distance from the nozzle to the surface of the substrate was 30 mm. The substrate was a steel sheet held at room temperature and the nozzle was moved relative to the substrate to provide a coating of the powdered heat activatable adhesive over the desired bonding area (13).

[0195] A uniform coating 0.25 mm thick was provided on the desired bonding area and it could be subsequently activated to produce an automotive adhesive.

[0196] Example 2:

[0197] A series of powdered heat activatable adhesives was prepared only differing in the relative content of two different types of epoxy based material contained therein. The overall content of epoxy based material was kept constant (26 wt.-%), like all other ingredients, their content and the other overall properties of the powder material:

Sample/Ingredients	2-1	2-2	2-3	2-4
Solid epoxy based material (A):				
- type I (EEW 450-530 g/eq)	4.00	-	-	-
- type II (EEW 590-630 g/eq)	-	18.00	-	-
- type III (EEW 730-820 g/eq)	-	-	18.00	-
- type IV (EEW 860-930 g/eq)	-	-	-	18.00
Liquid epoxy based material (B) (EEW ~200 g/eq)	22.00	8.00	8.00	8.00
EEW(A+B)	~220	~374	~411	~433
MBS based core shell impact modifier	13.40	13.40	13.40	13.40
Polyvinylbutyral	4.85	4.85	4.85	4.85
Phenoxy resin derived from Bisphenol A	16.95	16.95	16.95	16.95
Epoxy terminated CTBN adduct	20.00	20.00	20.00	20.00
Micronized Polyamide 6/12 (particle size 20 µm)	8.00	8.00	8.00	8.00
Talc	1.01	1.01	1.01	1.01
Calcium oxide	5.00	5.00	5.00	5.00
Thixotropic agent (Organo clay)	0.76	0.76	0.76	0.76
Pigment	0.05	0.05	0.05	0.05
Disubstituted urea	0.35	0.35	0.35	0.35
Dicyandiamide	3.00	3.00	3.00	3.00
Chemical blowing agent ADCA	0.63	0.63	0.63	0.63
TOTAL	100.00	100.00	100.00	100.00

[0198] Complex viscosity measurements were performed by means of an Anton Paar rheometer device. The sample specimen was a disc of 24 mm diameter and 1 mm height. Viscosity measurements were made at 1 Hz frequency, with a decreasing strain from 1% to 0.1% with a temperature ramp 3°C/min between 120 °C to 40 °C.

[0199] The temperature was determined at which the loss tangent (tan delta) reached its maximum [T(tan delta_{max})]. The results as well as the suitability of the respective materials for being applied in a dry powder spray application are summarized in the table here below:

	Solid epoxy based material (A)	Liquid epoxy based material (B)	EEW A+B	Max tan delta [T(tan delta _{max})]	performance
2-1	4 wt.-% type I (EEW 450-530 g/eq)	22 wt.-% (EEW ~200 g/eq)	~220	40 °C	cakes spontaneously
2-2	18 wt.-% type II (EEW 590-630 g/eq)	8 wt.-% (EEW ~200 g/eq)	~374	58 °C	good
2-3	18 wt.-% type III (EEW 730-820 g/eq)	8 wt.-% (EEW ~200 g/eq)	~411	60 °C	good
2-4	18 wt.-% type IV (EEW 860-930 g/eq)	8 wt.-% (EEW ~200 g/eq)	~433	62 °C	good

[0200] It becomes clear from the above experimental data that the performance of the powdered heat activatable adhesives depends upon T(tan delta_{max}) and that this property (temperature) can be adjusted by altering the composition of the powdered heat activatable adhesives, especially by altering the EEW and by altering the relative ratio of liquid epoxy based material and solid epoxy based material, respectively.

[0201] Example 3:

[0202] In accordance with Example 2, a series of powdered heat activatable adhesives was prepared only differing in the relative content of different types of epoxy based material contained therein:

Sample/Ingredients [wt.-]	3-1	3-2	3-3	3-4	3-5	3-6	3-7
Solid epoxy based material (A)							
- type I (EEW 450-530 g/eq)	4.25	-	-	-	-	4.25	18.00
- type II (EEW 590-630 g/eq)	-	-	18.00	9.00	-	-	-
- type III (EEW 730-820 g/eq)	-	-	-	-	18.00	-	-
- type IV (EEW 860-930 g/eq)	-	18.00	-	9.00	-	13.75	-
Liquid epoxy based material (B) (EEW ~200 g/eq)	22.00	8.00	8.00	8.00	8.00	8.00	8.00
EEW(A+B)	~221	~433	~374	~401	~411	~406	~339

[0203] Selected properties of samples 3-1 to 3-7 were tested and the results are summarized in the tables here below:

[0204] Impact Peel ISO11343 (HDG w/ RP4107S) 23 °C:

	3-1	3-2	3-3	3-4
DRC [N/mm]	14.42	10.57	10.33	10.87
Cleavage Energy [J]	3.71	2.27	2.31	2.71
Failure Mode (%CF)	100% CF	100% CF	100% CF	100% CF

[0205] RTC on 0.77 mm (12.5 x 25 x 0.3 mm) RP4107S:

	3-1	3-2	3-3	3-4
Maximum Stress. lap shear [MPa]	14.80	10.30	11.30	10.20
Rupture	100% CF	100% CF	100% CF	100% CF

[0206] T-Peel on 0.77 mm G10-10 RP4107S @ 0.3 mm:

	3-1	3-2	3-3	3-4
Average Peel [N/mm]	6.32	4.86	5.23	5.27
Cohesive Failure (CF)	100% CF	100% CF	100% CF	100% CF

[0207] T_g cured Anton Paar:

[°C]	3-1	3-2	3-3	3-4	3-5	3-6	3-7
	102.0	99.9	99.9	99.5	n.d.	100.9	103.0

[0208] As demonstrated by the above experimental data, it has been unexpectedly found that the glass transition temperature (T_g) of the cured formulation is not significantly affected by a relative variation of content of solid epoxy based material and liquid epoxy based material. Solid epoxy based material has a higher epoxy equivalent weight (EEW) than liquid epoxy based material, i.e. a decreased specific content of epoxy reactive functional groups. Thus, one would usually expect that T_g of the cured material decreases when the epoxy equivalent weight increases. However, as demonstrated by the above data, this is not the case.

[0209] DSC Enthalpy (J/g):

	3-1	3-2	3-3	3-4	3-5	3-6	3-7
Initial	135.00	n.d.	65.76	80.93	73.68	71.78	73.75

Patent claims:

1. A powdered heat activatable adhesive having an average particle size in the range of from about 20 μm to about 1000 μm and comprising an epoxy based material and a curing agent.
2. The powdered heat activatable adhesive according to claim 1, wherein the epoxy based material has an epoxy equivalent weight of at least about 200 g/eq.
3. The powdered heat activatable adhesive according to claim 2, wherein the epoxy based material has an epoxy equivalent weight of at least about 250 g/eq.
4. The powdered heat activatable adhesive according to claim 3, wherein the epoxy based material has an epoxy equivalent weight of at least about 300 g/eq.
5. The powdered heat activatable adhesive according to claim 4, wherein the epoxy based material has an epoxy equivalent weight of at least about 350 g/eq.
6. The powdered heat activatable adhesive according to claim 5, wherein the epoxy based material has an epoxy equivalent weight of at least about 400 g/eq.
7. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material has an epoxy equivalent weight of at most about 1900 g/eq.
8. The powdered heat activatable adhesive according to claim 7, wherein the epoxy based material has an epoxy equivalent weight of at most about 1300 g/eq.
9. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material has an epoxy equivalent weight within the range of about 550 ± 300 g/eq, or about 600 ± 300 g/eq, or about 650 ± 300 g/eq, or about 700 ± 300 g/eq, or about 750 ± 300 g/eq, or about 800 ± 300 g/eq, or about 850 ± 300 g/eq, or about 900 ± 300 g/eq, or about 950 ± 300 g/eq, or about 1000 ± 300 g/eq, or about 1050 ± 300 g/eq, or about 1100 ± 300 g/eq, or about 1150 ± 300 g/eq.
10. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material has an epoxy equivalent weight within the range of about 450 ± 200 g/eq, or about 500 ± 200 g/eq, or about 550 ± 200 g/eq, or about 600 ± 200 g/eq, or about 650 ± 200 g/eq, or about 700 ± 200 g/eq, or about 750 ± 200 g/eq, or about 800 ± 200 g/eq, or about 850 ± 200 g/eq, or about 900 ± 200 g/eq, or about 950 ± 200 g/eq, or about 1000 ± 200 g/eq, or about 1050 ± 200 g/eq, or about 1100 ± 200 g/eq, or about 1150 ± 200 g/eq.
11. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material has an epoxy equivalent weight within the range of or about 350 ± 100 g/eq, or about 400 ± 100 g/eq, or about 450 ± 100 g/eq, or about 500 ± 100 g/eq, or about 550 ± 100 g/eq, or about 600 ± 100 g/eq, or about

650±100 g/eq, or about 700±100 g/eq, or about 750±100 g/eq, or about 800±100 g/eq, or about 850±100 g/eq, or about 900±100 g/eq, or about 950±100 g/eq, or about 1000±100 g/eq, or about 1050±100 g/eq, or about 1100±100 g/eq, or about 1150±100 g/eq.

12. The powdered heat activatable adhesive according to any of the preceding claims, which additionally comprises a phenoxy resin.
13. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material is the condensation product of a bisphenol and epichlorohydrin or a derivative of such a condensation product.
14. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material is solid under ambient conditions.
15. The powdered heat activatable adhesive according to any of the preceding claims, which is a dry powder.
16. The powdered heat activatable adhesive according to any of the preceding claims, which is dry to the touch.
17. The powdered heat activatable adhesive according to any of the preceding claims, which is a free-flowing powder.
18. The powdered heat activatable adhesive according to any of the preceding claims, wherein all particles have substantially the same chemical composition.
19. The powdered heat activatable adhesive according to any of the preceding claims, which is composed of a substantially homogeneous material.
20. The powdered heat activatable adhesive according to any of the preceding claims, which comprises particles of type EC, wherein each individual particle of type EC comprises both the epoxy based material as well as the curing agent.
21. The powdered heat activatable adhesive according to any of the preceding claims, which comprises particles of type E, wherein each individual particle of type E comprises the epoxy based material, but substantially no curing agent.
22. The powdered heat activatable adhesive according to any of the preceding claims, which comprises particles of type C, wherein each individual particle of type C comprises the curing agent, but substantially no epoxy based material.

23. The powdered heat activatable adhesive according to any of claims 20 to 22, wherein at least about 50 wt.-% of the particles comprising epoxy based material are particles of type EC and/or wherein at least about 50 wt.-% of the particles comprising curing agent are particles of type EC.
24. The powdered heat activatable adhesive according to claim 23, wherein at least about 90 wt.-% of the particles comprising epoxy based material are particles of type EC and/or wherein at least about 90 wt.-% of the particles comprising curing agent are particles of type EC.
25. The powdered heat activatable adhesive according to any of the preceding claims, which comprises an anticaking agent.
26. The powdered heat activatable adhesive according to claim 25, wherein the anticaking agent is selected from the group consisting of talcum, earth alkali salts of fatty acids, tricalcium phosphate, powdered cellulose, calcium stearate, magnesium stearate, stearic acid, sodium bicarbonate, sodium ferrocyanide, potassium ferrocyanide, calcium ferrocyanide, silicon dioxide, sodium silicate, calcium silicate, magnesium trisilicate, talcum powder, sodium aluminosilicate, calcium aluminosilicate, potassium aluminium silicate, bentonite, aluminium silicate, and polydimethylsiloxane.
27. The powdered heat activatable adhesive according to claim 25 or 26, wherein at least a portion of the anticaking agent is contained
 - in particles of type A, wherein each particle of type A comprises neither epoxy based material nor curing agent; and/or
 - in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
 - in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.
28. The powdered heat activatable adhesive according to any of claims 1 to 24, which comprises substantially no anticaking agent.
29. The powdered heat activatable adhesive according to any of the preceding claims, which has a maximum of the loss tangent at a temperature of at least about 43 °C.
30. The powdered heat activatable adhesive according to claim 29, which has a maximum of the loss tangent at a temperature of at least about 46 °C.
31. The powdered heat activatable adhesive according to claim 29 or 30, which has a maximum of the loss tangent at a temperature of at least about 48 °C.

32. The powdered heat activatable adhesive according to any of claims 29 to 31, which has a maximum of the loss tangent at a temperature of at least about 50 °C.
33. The powdered heat activatable adhesive according to any of claims 29 to 32, which has a maximum of the loss tangent at a temperature of at most about 100 °C.
34. The powdered heat activatable adhesive according to any of claims 29 to 33, which has a maximum of the loss tangent at a temperature of at most about 90 °C.
35. The powdered heat activatable adhesive according to any of the preceding claims, wherein the content of the epoxy based material is at most about 80 wt.-%, relative to the total weight of the powdered heat activatable adhesive.
36. The powdered heat activatable adhesive according to any of the preceding claims, wherein the content of the epoxy based material is at least about 2 wt.-%, relative to the total weight of the powdered heat activatable adhesive.
37. The powdered heat activatable adhesive according to any of the preceding claims, wherein the content of the epoxy based material is within the range of about 25±20 wt.-%, relative to the total weight of the powdered heat activatable adhesive.
38. The powdered heat activatable adhesive according to any of the preceding claims, wherein the content of the curing agent is at most about 7 wt.-%, relative to the total weight of the powdered heat activatable adhesive.
39. The powdered heat activatable adhesive according to any of the preceding claims, wherein the content of the curing agent is at least about 0.001 wt.-%, relative to the total weight of the powdered heat activatable adhesive.
40. The powdered heat activatable adhesive according to any of the preceding claims, wherein the curing agent contains functional groups that are capable of reacting with the epoxy groups of the epoxy based material at an elevated activation temperature.
41. The powdered heat activatable adhesive according to any of the preceding claims, wherein the curing agent has an activation temperature above about 110 °C.
42. The powdered heat activatable adhesive according to claim 41, wherein the curing agent has an activation temperature in the range of from about 130 °C to about 220 °C.

43. The powdered heat activatable adhesive according to any of the preceding claims, wherein the curing agent is selected from aliphatic or aromatic amines or their respective adducts, modified and unmodified polyamines or polyamides, amidoamines, polyamides, cycloaliphatic amines, anhydrides, polycarboxylic polyesters, isocyanates, phenol-based resins, or mixtures thereof.
44. The powdered heat activatable adhesive according to any of the preceding claims, wherein the curing agent is or comprises dicyandiamide.
45. The powdered heat activatable adhesive according to any of the preceding claims, wherein the curing agent comprises at least two cross linking agents, wherein one cross linking agent has an activation temperature at which the powdered heat activatable adhesive can be fused to provide a layer of uncured adhesive on a substrate, and wherein the other cross linking agent has a higher activation temperature to cross link the adhesive and create the final adhesive bond.
46. The powdered heat activatable adhesive according to any of the preceding claims, wherein the average particle size is within the range of from about 20 μm to about 500 μm .
47. The powdered heat activatable adhesive according to claim 46, wherein the average particle size is within the range of from about 20 μm to about 300 μm .
48. The powdered heat activatable adhesive according to claim 47, wherein the average particle size is within the range of from about 50 μm to about 200 μm .
49. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution such that at most about 20 wt.-% of the particles have a diameter of less than about 10 μm .
50. The powdered heat activatable adhesive according to claim 49, which has a particle size distribution such that at most 10 wt.-% of the particles have a diameter of less than 10 μm .
51. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution such that at most about 20 wt.-% of the particles have a diameter of more than about 600 μm .
52. The powdered heat activatable adhesive according to claim 51, which has a particle size distribution such that at most about 10 wt.-% of the particles have a diameter of more than about 600 μm .
53. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution such that at most about 20 wt.-% of the particles have a diameter of more than about 300 μm .
54. The powdered heat activatable adhesive according to claim 53, which has a particle size distribution such that at most about 10 wt.-% of the particles have a diameter of more than about 300 μm .

55. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution such that at most about 20 wt.-% of the particles have a diameter of more than about 250 μm .
56. The powdered heat activatable adhesive according to claim 55, which has a particle size distribution such that at most about 10 wt.-% of the particles have a diameter of more than about 250 μm .
57. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution characterized by a D_{50} value within the range of from about 20 μm to about 300 μm .
58. The powdered heat activatable adhesive according to claim 57, wherein the D_{50} value is within the range of from about 50 μm to about 200 μm .
59. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution characterized by a D_{10} value within the range of from about 1 μm to about 100 μm .
60. The powdered heat activatable adhesive according to claim 59, wherein the D_{10} value is within the range of from about 5 μm to about 70 μm .
61. The powdered heat activatable adhesive according to any of the preceding claims, which has a particle size distribution characterized by a D_{90} value within the range of from about 100 μm to about 500 μm .
62. The powdered heat activatable adhesive according to claim 61, wherein the D_{90} value is within the range of from about 200 μm to about 400 μm .
63. The powdered heat activatable adhesive according to any of the preceding claims, which is ready to use.
64. The powdered heat activatable adhesive according to any of the preceding claims, which is a one-component formulation.
65. The powdered heat activatable adhesive according to any of the preceding claims, which comprises a blowing agent and/or a blowing accelerator.
66. The powdered heat activatable adhesive according to claim 65, wherein the blowing agent is selected from chemical blowing agents and physical blowing agents.
67. The powdered heat activatable adhesive according to claim 66, wherein the blowing agent is a chemical blowing agent selected from the group consisting of azodicarbonamide, dinitrosopentamethylenetetramine, hydrazides such as 4,4-oxy-bis-(benzenesulphonylhydrazide), trihydrazinotriazine and N,N'-dimethyl-N,N'-dinitrosoterephthalamide

68. The powdered heat activatable adhesive according to any of claims 65 to 67, wherein at least a portion of the blowing agent and/or at least a portion of the blowing accelerator is contained
- in particles of type B, wherein each particle of type B comprises neither epoxy based material nor curing agent; and/or
 - in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
 - in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.
69. The powdered heat activatable adhesive according to any of claims 1 to 64, which comprises substantially neither blowing agent nor blowing accelerator.
70. The powdered heat activatable adhesive according to any of the preceding claims, which comprises an impact modifier.
71. The powdered heat activatable adhesive according to claim 70, wherein the impact modifier is selected from elastomer/epoxy adducts and core/shell materials.
72. The powdered heat activatable adhesive according to claim 70 or 71, wherein at least a portion of the impact modifier is contained
- in particles of type I, wherein each particle of type I comprises neither epoxy based material nor curing agent; and/or
 - in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
 - in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.
73. The powdered heat activatable adhesive according to any of the preceding claims, wherein the epoxy based material comprises a first epoxy based material and a second epoxy based material.
74. The powdered heat activatable adhesive according to claim 73, wherein the second epoxy based material is liquid under ambient conditions.

75. The powdered heat activatable adhesive according to claim 73 or 74, wherein the content of the first epoxy based material is greater than the content of the second epoxy based material.
76. The powdered heat activatable adhesive according to any of claims 73 to 75, wherein the relative weight ratio of the first epoxy based material to the second epoxy based material is within the range of from about 10:1 to about 1:10.
77. The powdered heat activatable adhesive according to any of claims 73 to 76, wherein the relative weight ratio of the first epoxy based material to the second epoxy based material is within the range of from about 10:1 to about 1.1:1.
78. The powdered heat activatable adhesive according to any of claims 73 to 77, wherein the relative weight ratio of the first epoxy based material to the second epoxy based material is within the range of from about 8:1 to about 1.5:1.
79. The powdered heat activatable adhesive according to any of claims 73 to 78, wherein the relative weight ratio of the first epoxy based material to the second epoxy based material is within the range of from about 5:1 to about 2:1.
80. The powdered heat activatable adhesive according to any of claims 73 to 79, wherein the relative difference of the epoxy equivalent weight of the first epoxy based material to the epoxy equivalent weight of the second epoxy based material is within the range of from about 200 to about 1000 g/eq.
81. The powdered heat activatable adhesive according to any of claims 73 to 80, wherein
- the first epoxy based material is solid under ambient conditions and/or has an epoxy equivalent weight of at least about 450 g/eq; and
 - the second epoxy based material is liquid under ambient conditions and/or has an epoxy equivalent weight of at most about 300 g/eq.
82. The powdered heat activatable adhesive according to any of claims 73 to 81, wherein at least a portion of the second epoxy based material is contained
- in particles of type EC each individually comprising both the first epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the first epoxy based material, but substantially no curing agent.
83. The powdered heat activatable adhesive according to any of the preceding claims, which comprises a thermoplastic component.

84. The powdered heat activatable adhesive according to claim 83, wherein the thermoplastic component is selected from polyamides, styrenics, acrylonitriles, acrylates, acetates, polyethylenes, and phenoxy resins.
85. The powdered heat activatable adhesive according to claim 83 or 84, wherein at least a portion of the thermoplastic component is contained
- in particles of type T, wherein each particle of type T comprises neither epoxy based material nor curing agent; and/or
 - in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
 - in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.
86. The powdered heat activatable adhesive according to any of the preceding claims, which comprises a filler.
87. The powdered heat activatable adhesive according to claim 86, wherein the filler is selected from the group consisting of silica, diatomaceous earth, glass, clay, talc, pigments, colorants, glass beads, glass bubbles, glass, carbon fibers, ceramic fibers, nylon aramid fibers, polyamide fibers, antioxidants, and ammonium chlorides.
88. The powdered heat activatable adhesive according to claim 86 or 87, wherein at least a portion of the filler is contained
- in particles of type F, wherein each particle of type F comprises neither epoxy based material nor curing agent; and/or
 - in particles of type EC each individually comprising both the epoxy based material as well as the curing agent; and/or
 - in particles of type E each individually comprising the epoxy based material, but substantially no curing agent; and/or
 - in particles of type C each individually comprising the curing agent, but substantially no epoxy based material.
89. The powdered heat activatable adhesive according to any of the preceding claims, which is a structural adhesive.
90. The powdered heat activatable adhesive according to claim 89, wherein the structural adhesive is selected from foamable structural adhesives and unfoamable structural adhesives.

91. The powdered heat activatable adhesive according to any of the preceding claims, which comprises substantially no electrically conductive material.
92. A process for the provision of an adhesive layer on the surface of a substrate, wherein a powdered heat activatable adhesive is mixed with a gas stream and sprayed on the surface of a substrate to form the adhesive layer.
93. The process according to claim 92, comprising
 - supplying a powdered heat activatable adhesive into a gas stream flowing under pressure, and
 - directing the flowing gas stream containing the powdered heat activatable adhesive onto the surface of the substrate.
94. The process according to claim 92 or 93, wherein the gas stream is mixed with the powdered heat activatable adhesive in a De Laval nozzle.
95. The process according to any of claims 92 to 94, wherein the particles are accelerated.
96. The process according to any of claims 92 to 95, wherein the gas stream is heated.
97. The process according to claim 96, wherein the powdered heat activatable adhesive is heated with the gas stream and/or is accelerated to a velocity such that upon impact on the surface of the substrate it will soften to adhere to the substrate.
98. The process according to claim 97, wherein the powdered heat activatable adhesive is heated to a temperature within the range of from about 25 °C to about 80 °C.
99. The process according to any of claims 92 to 98, wherein the temperature of the gas stream prior to mixing with the powdered heat activatable adhesive is at least about 100 °C.
100. The process according to claim 99, wherein the temperature is at least about 200 °C.
101. The process according to claim 100, wherein the temperature is at least about 400 °C.
102. The process according to any of claims 92 to 101, wherein the temperature of the gas stream prior to mixing with the powdered heat activatable adhesive is at most about 900 °C.
103. The process according to claim 102, wherein the temperature is at most about 750 °C.
104. The process according to claim 103, wherein the temperature is at most about 600 °C.
105. The process according to any of claims 92 to 95, wherein the gas stream is not heated.

106. The process according to any of claims 92 to 105, wherein the adhesive is sprayed at a distance of from about 20 mm to about 60 mm from the surface of the substrate.
107. The process according to any of claims 92 to 106, wherein the powdered heat activatable adhesive is accelerated so that when it hits the surface of the substrate it has a velocity within the range of from about 50 m/s to about 1000 m/s.
108. The process according to claim 107, wherein the velocity is within the range of from about 50 m/s to about 400 m/s.
109. The process according to claim 108, wherein the velocity is within the range of from about 50 m/s to about 300 m/s.
110. The process according to any of claims 92 to 109, wherein the gas stream is or comprises an inert gas.
111. The process according to claim 110, wherein the inert gas is nitrogen, argon or a mixture thereof.
112. The process according to any of claims 92 to 111, wherein the pressure of the gas stream prior to mixing with the powdered heat activatable adhesive is at least about 1.5 bar.
113. The process according to claim 112, wherein the pressure is at least about 2.8 bar.
114. The process according to any of claims 92 to 113, wherein the pressure of the gas stream prior to mixing with the powdered heat activatable adhesive is at most about 10 bar.
115. The process according to claim 114, wherein the pressure is at most about 4.1 bar.
116. The process according to any of claims 92 to 115, wherein the substrate is heated.
117. The process according to any of claims 92 to 116, wherein the powdered heat activatable adhesive is a powdered heat activatable adhesive according to any of claims 1 to 91.
118. The process according to any of claims 92 to 117, wherein the adhesive adheres to the surface of the substrate but remains at a temperature at which it remains activatable by subsequent heating.
119. The process according to claim 118, wherein the adhesive layer that has formed on the surface of the substrate, optionally after cooling, is subsequently heated in order to develop its full adhesive properties.
120. The process according to claim 119, wherein the adhesive layer that has formed on the surface of the substrate is subsequently heated to a temperature in the range of from about 130 °C to about 220 °C.

121. The process according to any of claims 92 to 120, which does not involve any technique selected from the group consisting of electrodeposition, electrostatic deposition, electrostatic spraying, electrostatic brush coating, electric arc spraying, plasma arc spraying, flame spraying, high-velocity oxygen fuel spraying, and detonation gun spraying.
122. A substrate provided with a coating of an adhesive provided by the process according to any of claims 92 to 121.
123. The substrate according to claim 122 comprising metal and/or polymers.
124. The substrate according to claim 122 or 123, wherein the substrate is an organo sheet or a composite material.
125. The substrate according to any of claims 122 to 124 comprising an automobile component.
126. The substrate according to any of claims 122 to 125, which has a thickness within the range of from about 50 μm to about 2000 μm .
127. Use of a powdered heat activatable adhesive in the process according to any of claims 92 to 121.
128. The use according to claim 127, wherein the powdered heat activatable adhesive is a powdered heat activatable adhesive according to any of claims 1 to 91.
129. A process for the preparation of a powdered heat activatable adhesive according to any of claims 1 to 81 comprising the step of milling a composition comprising the epoxy based material and the curing agent.
130. The process according to claim 129, wherein milling is performed at reduced temperature.
131. The process according to claim 130, wherein the reduced temperature is below about -10 $^{\circ}\text{C}$.
132. The process according to any of claims 129 to 131, wherein milling involves cryo-milling.
133. The process according to any of claims 129 to 132, wherein milling is performed by means of a hammer mill or an air jet mill or a rotor mill.

