



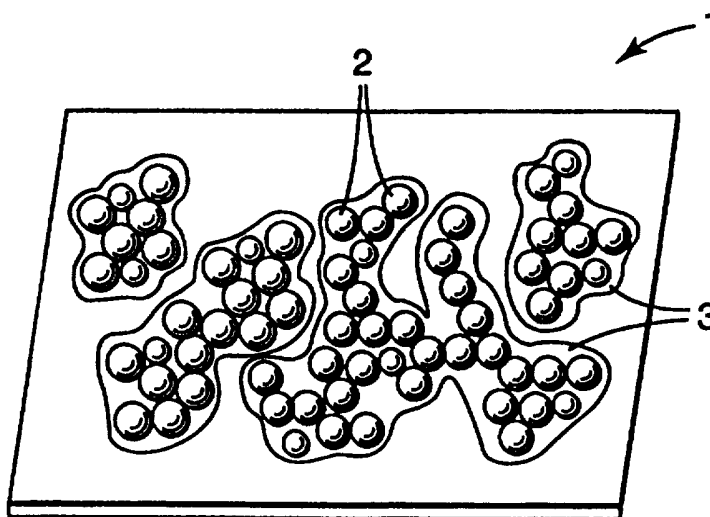
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09J 7/02, E04F 13/08, E04G 23/02	A1	(11) International Publication Number: WO 97/20008 (43) International Publication Date: 5 June 1997 (05.06.97)
(21) International Application Number: PCT/US96/18887 (22) International Filing Date: 25 November 1996 (25.11.96) (30) Priority Data: 7/314043 1 December 1995 (01.12.95) JP (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: ABE, Hidetoshi; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: ADHESIVE SHEET, AND STRUCTURE USING THE SAME**(57) Abstract**

An adhesive sheet comprising a backing layer, and an adhesive layer which is formed on said layer and contain tacky elastic microsphere and an adhesive polymer, wherein a) said adhesive layer has convex adhesive parts containing one or more clusters of at least two said elastic microspheres and said adhesive polymer, and b) a contact area rate between said adhesive layer and a plate surface is from 20 to 90 % when said contact area rate is measured by adhering said adhesive sheet to a flat glass plate surface under pressure of 2 kg/25 cm². A

structure having an adherent adhesive sheet comprising an article of mortar or concrete with rough surface and said adhesive sheet which is adhered to said rough surface, and having passageways which are formed by said surface and an adhesive layer of said adhesive sheet and communicate with an atmosphere.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

ADHESIVE SHEET, AND STRUCTURE USING THE SAME

Field of Invention

5 The present invention relates to an adhesive sheet which comprises elastic microspheres in an adhesive layer and is adhered to a substrate having an uneven surface, a method for producing such adhesive sheet, and a structure having an adhered adhesive sheet. In particular, the present invention relates to an adhesive sheet which has a good adhering property when it is adhered to a substrate
10 exposed outdoors such as an outer wall of a building of mortar or concrete.

Background of Invention

 The following adhesive sheets (a) to (d) are known as adhesive sheets (also known as adhesive films) such as a decorative sheet or a retroreflective
15 sheet, which are adhered to a substrate having an uneven surface such as a wall, for example:

 (a) An adhesive sheet disclosed in Japanese Patent Publication JP-A-2-32180 comprises a backing layer which comprises a nonwoven fabric and a flexible resin, and an adhesive coated on said backing layer. This adhesive sheet intends to
20 improve a follow-up property of the sheet to the uneven surface of the substrate by the use of the above backing layer having good flexibility. When it is adhered to a porous substrate such as mortar or concrete materials and used outdoors, water or vapor containing water which is absorbed by the substrate migrates to an interface between the adhesive layer and the substrate, but cannot escape from the interface,
25 whereby the adhesive layer and in turn the adhesive sheet is blistered by an osmotic pressure. Since the surface of the substrate is very rough, it is difficult to decorate the surface by, for example, printing.

 (b) A repeelable adhesive tape disclosed in Japanese Patent Publication JP-U-572946 comprises a backing layer, a viscoelastic layer formed on the backing
30 layer, and an adhesive layer which contains microspheres and is formed on said viscoelastic layer. This adhesive tape intends to improve the following-up property

to the uneven surface of the substrate by the function of the viscoelastic layer. But, since an average particle size of the microspheres is as small as 1 to 10 μm , the tape has insufficient adhesion force to a substrate surface having relatively large unevenness such as the mortar or concrete material. In addition, since the viscoelastic layer is additionally formed, the production steps may be complicated. Here, a degree of unevenness" is expressed by a surface roughness, and is defined in Japanese Industrial Standards JIS B 0601 (1994). When an arithmetical average surface roughness (Ra) measured at a cut-off value of 8 mm and an evaluated length of 40 mm is about 20 to 100 μm , a surface is ranked as "a surface having a relatively large degree of unevenness" or "a rough surface".

(c) A pressure sensitive adhesive sheet disclosed in Japanese Patent Publication JP-A-7-3222 and Japanese Patent Publication JP-A-7-48549 comprises, in general, a pressure sensitive adhesive layer which is photocured, and microspheres surfaces of which are treated to lower their surface energy and which are contained in said layer. This pressure sensitive sheet intends to improve its following-up property to the uneven surface of the substrate by surface treating nontacky microspheres having an average diameter of 5 to 200 μm to make mobility of the microspheres in the pressure sensitive layer easy when the sheet is adhered. However, since the microspheres are embedded in the adhesive layer and do not form convex parts, the adhesion of the sheet to the uneven surface cannot be improved.

(d) An adhesive tape disclosed in Japanese Patent Publication JP-U-1-70848 comprises a backing layer tape and an adhesive which is formed on the backing layer in a relatively regular uneven pattern such as a net pattern. But, the formation of the regular pattern is difficult, and a contact area is not increased effectively on the substrate the surface unevenness of which is not necessarily regular, such as the mortar or concrete material.

As adhesive sheets having an adhesive layer which contains tacky elastic microspheres, the following adhesive sheets (e) and (f) are known:

(e) An adhesive film disclosed in Japanese Patent Publication JP-A-6-287525 comprises a film backing and an adhesive layer which is formed on said film

and comprises tacky elastic microspheres having a volume average diameter of 100 to 300 μm and an adhesive, whereby an air trapped between the film and a flat surface of a substrate can escape when the adhesive film is adhered to the substrate. The microspheres are contained in the adhesive discretely or in a "cluster state" (which will be defined later) in which the microspheres are dispersed in the form of minute bulks consisting of two or more agglomerated microspheres. When the elastic microspheres are contained discretely, the adhesive film cannot have a sufficient adhesion force on the surface of the substrate which has a relatively large degree of unevenness and irregular patterns and configurations, such as the mortar or concrete material. This Japanese KOKAI Publication suggests that the formation of the clusters of the elastic microspheres is advantageous to escape bubbles, but does not describe or teach limitation in relation to the clusters which provide good adhesion to the uneven surface, and a method for forming advantageous thereto.

(f) A peelable adhesive material disclosed in Japanese Patent Publication JP-A-6172739 contains only tacky microspheres having an average particle size of 1 to 200 μm , or such tacky microspheres and a nontacky binder. This adhesive material does not have a film-form backing, and the formation of clusters of the elastic microspheres is not suggested. Since a production method of this adhesive material does not include any means for coating the adhesive material directly on a backing, formation of clusters of tacky microspheres is very difficult. In addition, noninclusion of a tacky polymer makes the effective formation of the cluster of microspheres difficult.

Summary of Invention

The conventional adhesive sheets do not have sufficient adhesion force on the substrate having a rough surface having a relatively large degree of unevenness, and irregular shape and configuration of the unevenness such as the mortar or concrete material. As the results, the adhesive sheet tends to peel off from the substrate as the time passes.

Since the mortar and concrete materials are water absorbing porous materials, when the adhesive sheet is adhered thereto, vapor containing water which

penetrated in the substrate migrates to the adhesion interface to cause the blister of the adhesive layer. As the result, the adhesive layer tends to peel off from the substrate.

5 In view of the above problems, one aspect of the present invention provides an adhesive sheet which can maintain a sufficient adhesion force on a substrate having a relatively large degree of unevenness and irregular shape and configuration of unevenness and comprising a water-absorbing porous material such as a mortar or concrete material, and can prevent blister of an adhesive layer caused by vapor containing water which migrates from the inside of the substrate to an adhesion
10 interface.

Another aspect of the present invention provides a method for producing an adhesive sheet which can form clusters of elastic microspheres useful in the adhesive sheet.

15 An adhesive sheet of the invention comprises a backing layer, and an adhesive layer which is formed on said backing layer and contain tacky elastic microspheres wherein a) said adhesive layer has convex adhesive parts containing one or more clusters of at least two said elastic microspheres and said, and b) a contact area rate between said adhesive layer and a plate surface is from 20 to 90 % when said contact area rate is measured by adhering said adhesive sheet to a flat
20 glass plate surface under the pressure of 2 kg/25 cm².

Brief Description of the Drawing

Fig. 1 schematically shows the adhesive sheet having the clusters of microspheres according to the present invention.

25

Embodiments of the Invention

An adhesive sheet of the invention is schematically shown in Fig. 1. The adhesive sheet 1 has discrete adhesive parts 3 containing the convex clusters of the microspheres 2. Since the convex adhesive parts contain the cluster or clusters of
30 the elastic microspheres, sufficient adhesive force is attained even on a substrate having a rough surface such as the mortar or concrete material.

"Tacky elastic microsphere" and "microsphere" mean particles having a volume average diameter of less than 500 μm and at least a surface of which has tackiness, and exhibits rubbery elasticity as a whole. The rubbery elasticity of the microspheres is necessary for the increase of the adhesion force of the adhesive layer to the uneven surface and the formation of the passageways which prevent the blister of the adhesive layer. In addition, the microspheres themselves make it easy and sure to form the cluster structure, and improve the adhesion force of the adhesive layer to the uneven surface.

"Cluster of elastic microspheres" means an agglomerate of the elastic microspheres which are dispersed in a bulk form of two or more of the microspheres in a matrix of the tacky polymer to form a convex adhesive part having an irregular shape and irregular configuration. That is, the adhesive layer comprises "island" parts (discrete phases) comprising the cluster(s) and the tacky polymer, and relatively flat "sea" parts (continuous parts) comprising the tacky polymer but no cluster.

"Adhesive layer" means is a layer comprising microspheres and tacky polymer, and having plural convex adhesive parts with the irregular shapes.

"Tacky polymer" means a polymer which has tackiness at room temperature and can be used as a pressure-sensitive adhesive.

Each convex adhesive part comprises an agglomerate of the elastic microspheres which are arranged in a two-dimensional plane, an agglomerate of the elastic microspheres which are three dimensionally arranged, or both. When the adhesive sheet is adhered to a substrate, the agglomerated elastic microspheres in the cluster are shifted to deform the convex adhesive part in a shape which is suitable to be adhered to the uneven surface of the substrate. However, a degree of this deformation should be configured so that passageways which communicate with the atmosphere are formed and maintained between the uneven surface and the adhesive layer. The degree of the deformation can be controlled by the tackiness of the elastic microspheres, and the inclusion of the elastic microspheres and the tacky polymer in a specific ratio.

The irregular shape of the convex adhesive part serves to improve the adhesion of the adhesive layer to the substrate having the irregular uneven surface. The irregular shape of the convex adhesive part is derived from the irregularly shaped and arranged cluster of the elastic microspheres. The cluster of the elastic microspheres can be formed by coating an adhesive coating composition on a coating surface of the backing layer having a specific wetting index to form the adhesive layer. The cluster formation may be accelerated by controlling a viscosity of the adhesive coating composition in a specific range.

When the adhesive sheet of the present invention is adhered to the surface of the substrate, the above described "sea-island" structure (continuous phase/discontinuous phase) serves to provide passageways which are formed by the substrate surface and the adhesive layer and communicate with the atmosphere, whereby the blister of the adhesive layer caused by the vapor containing water which migrates from the substrate is prevented. To form such passageways, a contact area rate between the adhesive layer and a flat glass surface, which specifies a degree of contact between them and will be defined later, is adjusted in the specific range, when it is measured by adhering the adhesive sheet to the flat glass surface.

The contact area rate is easily regulated by maintaining the ratio of the elastic microspheres to the tacky polymer in the specific range, using the elastic microspheres having the specific average particle size, and adjusting a coating weight of the adhesive layer in a specific range.

1. Elastic Microspheres

Preferably, microspheres for the present invention have a volume average diameter from 10 to 300 μm , preferably from 50 to 250 μm . When the volume average diameter is in the range between 50 μm and 250 μm , the adhesive layer follows the uneven surface very well, an apparent contact area rate increases, and consequently the sufficient adhesion force is achieved.

The volume average diameter is obtained by measuring diameters of 1000 microspheres using an optical microscope and an image analyzer, and calculating an average value according to the following equation:

$$\text{Volume average diameter } (\mu\text{m}) = \Sigma(d_i^4 \times n_i) / \Sigma(d_i^3 \times n_i)$$

5 wherein d_i is a diameter (μm) of a microsphere having an i -th largest diameter, and n_i is the number of microspheres having the diameter d_i .

The microsphere may be solid or hollow having at least one void therein. Polyacrylate is preferred as a material for the microspheres, since it is readily available, and its rubbery elasticity and tackiness are easily controlled.

10 A compressive modulus of the microsphere is preferably in the range between 1×10^4 and 1×10^6 dyne/cm². When the compressive modulus is in this range, the microspheres themselves and/or their clusters are effectively deformed, and the adhesive layer is effectively adhered to the uneven surface.

The compressive modulus is measured using a RSA 11 viscoelastic spectrometer (manufactured by RHEOMETRIX) at 20°C. That is, temperature dependency of the modulus is measured by changing temperature from -80°C to 150°C with applying a compression strain having a frequency of 1 rad/sec., and a measured value at 20°C is used as the compressive modulus.

20 2. Method for Producing Elastic Microspheres

The microspheres may be produced by any of known methods such as suspension polymerization, emulsion polymerization, seed polymerization, and so on. As an example, a method for producing the microspheres of polyacrylate by emulsion polymerization will be explained briefly.

25 In a reactor equipped with a mechanical stirrer, deionized water, an acrylic monomer, a radical polymerization initiator, and other optional additives are added, and an interior of the reactor is purged with an inert gas. Then, the reactor is heated to a specific temperature to initiate polymerization of the monomer while stirring. In general, a stirring rate is from 10 to 700 rpm, and a reaction temperature is from 30 to 120°C. A reaction time is usually from several hours to
30 several ten hours.

As the acrylic monomer, a mixture of an alkyl acrylate (e.g. isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, etc.) and an acrylic unsaturated acid (e.g. acrylic acid, methacrylic acid, itaconic acid, maleic acid, etc.) is used. A weight ratio of the alkyl acrylate to the acrylic unsaturated acid is preferably from 99:1 to 90:10. When an amount of the alkyl acrylate is too small, the tackiness is lowered, while it is too large, the rubbery elasticity is decreased. In either case, the adhesion force to the uneven surface tends to decrease. It is possible to crosslink the polyacrylate by the addition of a crosslinking agent comprising a bifunctional acrylate such as divinyl benzene 1,4-dibutyl-2diacrylate to the above mixture.

The production method of the polyacrylate microspheres is disclosed in, for example, US Patent No. 4,994,322.

The produced microspheres are isolated by filtration and used in general, while the as-produced aqueous dispersion containing the microspheres after the reaction can be used, and the tacky polymer is added to the dispersion to obtain the adhesive coating composition.

3. Tacky Polymer

Tacky polymers such as polyacrylates, polyurethanes, polyolefins, polyesters, and so on may be used. As in the case of conventional pressure-sensitive adhesives, a tackifier may be used in combination with the tacky polymer.

A molecular weight of the tacky polymer is in a range in which the desired tackiness is achieved. In general, a weight average molecular weight is from 10,000 to 100,000.

4. Adhesive Layer

The irregular shaped convex adhesive parts achieve the development of good adhesion to the uneven surface, and the formation of the passageways which communicate with the atmosphere and prevents the blister of the adhesive layer.

A mixing ratio of the microspheres to the tacky polymer is preferably from 20 to 500 wt. parts, more preferably from 100 to 400 wt. parts of the former per 100 wt. parts of the latter. When the amount of the former is less than 20 wt. parts,

it is difficult to form the cluster (which will be explained later) having an effective size, while it exceeds 500 wt. parts, it may be difficult to form the passageways which communicate with the atmosphere between the uneven surface and the adhesive layer so that the prevention of the blister of the adhesive layer due to water and so on will be difficult.

5. Backing Layer

Any conventional material can be used as a backing layer. For example, a sheet of paper, a metal film, a plastic film and so on can be used.

As the plastic film, a synthetic polymer such as polyvinyl chloride, polyester, polyurethane, polyacrylate, etc. can be used. A thickness of the film is usually from 10 to 1500 μm .

A surface of the backing layer on which the adhesive layer is formed may be surface treated to increase the bond force of the adhesive layer to the backing layer, or to control the wetting index which will be explained later.

6. Cluster of Elastic Microspheres

In general, the cluster comprises at least two microspheres. The cluster having a size effective to the preferred adhesion property contains 10 to 200 microspheres. A percentage of the clusters having such effective size in the whole adhesive layer is preferably at least 80 % of all the clusters. The formation, shape and size of the clusters of the microspheres in the adhesive layer can be confirmed by the observation by an optical microscopy using reflected light, at a magnification of 10 to 100 times.

One of suitable methods for forming the clusters comprises adjusting the wetting index on the coating surface of the backing layer in the range between 35 and 70 dyne/cm^2 , coating the adhesive coating composition on the coating surface and drying it to form the adhesive layer.

When the wetting index is too low, coating irregularity appears in the adhesive phase so that the adhesion force to the rough surface tends to decrease,

while the too large wetting index may make it difficult to form the effective clusters. From these view points, the preferred wetting index is from 40 to 60 dyne/cm².

The wetting index of the backing layer can be adjusted by the surface treatment of the backing layer such as corona treatment, plasma treatment, chemical treatment, etc. In the case of the plastic film, its wetting index can be adjusted by a kind and an amount of an additive such as a plasticizer which is contained in the plastic film. As a method for adjusting the wetting index, the corona discharge treatment is preferred, since contamination of the adhesive layer by the chemical can be avoided in comparison with the chemical treatment. In the case of the corona discharge treatment, a discharge energy is generally from 0.1 to 3 kW, and a discharge frequency is from 5000 to 35,000 Hz. While the corona discharge can be carried out in the air or an atmosphere of, for example, nitrogen.

In the chemical treatment, (1) a solution of an acid, an alkali or an organic amine, or (2) a solution of a trichloroacetic acid or a phenol compound can be used as a chemical. Such chemical is applied on the coating surface of the backing layer, optionally heated, and dried.

The wetting index is measured by a wetting test method according to JIS 6768 (1977) at 23±2°C, 50±5 %RH.

The control of the viscosity of the adhesive coating composition is also advantageous for the easy formation of the clusters. Preferably, the viscosity of the adhesive coating composition is from 100 to 6000 cps. When the viscosity is lower than 100 cps, the adhesive layer having a sufficient coating weight may not be formed, while it is higher than 6000 cps, the adhesive layer in which the microspheres are uniformly arranged tends to be formed, so that the effective clusters may not be formed.

As explained above, the mixing ratio of the microspheres to the tacky polymer, and the tackiness of the microspheres may be the factors which control the formation of the effective clusters.

A coating weight suitable for the formation of the effective clusters is from 5 to 150 g/m², more preferably from 50 to 100 g/m².

7. Contact Area Rate

It is necessary to maintain a ratio of the real contact area to the apparent contact area between the adhesive layer and the substrate, that is, the contact area rate, in a specific range for achieving both the high adhesion force to the uneven surface, and the prevention of the blister of the adhesive layer when the adhesive sheet is adhered to the substrate having the porous surface. But, it is very difficult to define a degree of contact between the adhesive layer and the substrate by the measurement of the contact area percentage on the uneven surface. Then, the contact area rate is defined by a contact area percentage between the adhesive layer and a flat surface which is measured by adhering the adhesive sheet to a flat surface of a glass plate.

Concretely, the adhesive layer of the adhesive sheet is adhered to a flat surface of a glass plate such as a slide glass and pressed by a roller of 2 kg by reciprocating it over the adhesive sheet one time. When the glass plate is illuminated by a white light from the glass surface on which the adhesive sheet is not adhered, and the reflected light is observed through a polarized light filter, domains in which the convex adhesive parts and the glass surface are contacted are seen dark, while non-contact domains are seen white. A photograph of such observed state is taken, and a total area of the contact domains and the area of the whole observed field (corresponding to the apparent contact area) are measured, and their ratio (the total area of the contact domains/the area of the whole observed field) is expressed in "percentage", which is used as the contact area rate".

The above measurement can be done using an optical microscope equipped with a Polaroid camera. In this case, the area of the observed field is usually 1 cm². A surface roughness Ra of the used glass plate is 0.1 μm or less.

The contact area rate measured as above is preferably from 20 to 90 % more preferably from 40 to 80 %, in particular from 50 to 70 %. The contact area rate in this range can achieve both the adhesive property of the adhesive sheet to the uneven surface and the effective formation of the passageways which escape the vapor containing water trapped between the adhesive sheet and the substrate.

5 The contact area rate increases, as the size of the microspheres decreases or the coating weight of the adhesive layer increases, while it decreases as the content of the microspheres in the tacky polymer increases. Accordingly, the contact area rate can be controlled in the above range by adjusting these parameters in the desired ranges.

8. Production Method of Adhesive Sheet

10 The adhesive sheet of the present invention can be produced by coating the adhesive coating composition on one or both of the surfaces of the backing layer, and drying it to form the adhesive layer. In this method, the clusters are effectively formed by the use of the above described measures.

15 The adhesive coating composition is prepared by mixing the microspheres, the tacky polymer, the solvent, and optional additives in a mixing apparatus such as a homomixer, a planetary mixer, etc. to obtain a mixture in which all the components are homogeneously dispersed. The prepared coating composition is coated on the backing layer, and dried to form the adhesive layer. Any conventional means such as a knife coater, a roll coater, a die coater, a bar coater, and so on can be used. The drying is carried out at a temperature of 60 to 180°C. A drying time is usually from several ten seconds to several minutes.

20 As the solvent, water or an organic solvent may be used. For the formation of the effective clusters, an aqueous coating composition is suitable. In this case, the drying temperature is usually 100°C or higher. In addition, a co-solvent which is partly miscible with water may be added. Examples of useful co-solvent are alkylene glycol monoalkyl ether esters such as 3-methyl-3methoxybutyl acetate.

25 As the additive, any conventionally used additive may be used as long as the effects of the present invention are not impaired. Examples of the additives are a viscosity modifier, an anti-foaming agent, a leveling agent, a UV light absorber, an antioxidant, a pigment, etc.

30 After the formation of the adhesion layer, it may be coated with a silicone-treated liner for the protection of the adhesion layer.

9. Adhesive Sheet

The adhesive sheet of the present invention can be used as a decorative sheet and adhered to a wall, a floor, or a ceiling of a building. In particular, the adhesive sheet of the present invention is useful, when the surface is covered with a mortar, a concrete, or a wall paper, and has a large degree of unevenness the shape and size of which are irregular.

Since the adhering surface of the adhesive layer of the adhesive sheet according to the present invention has many convex adhesive parts containing the clusters of the microspheres, when it is adhered to the substrate, the surface of the substrate and the adhering surface are spot adhered to form continuous passageways. Since the adhesive sheet of the present invention has such structure, it can remove water which migrated in the substrate from outside through the passageways into the atmosphere, when the adhesive sheet is adhered to the porous substrate which absorbs water. Therefore, the blister of the adhesive layer caused by such water can be prevented. If the blister reaches the backing layer, appearance of the adhered sheet is deteriorated, and the blister causes the peeling off of the sheet from the substrate. Therefore, the adhesive sheet of the present invention is very useful when it is used on the substrate which is exposed outdoors such as the outer wall of the building made of the mortar or concrete.

The adhesive sheet of the present invention has the much larger adhesion force to the mortar surface than the conventional adhesive sheets, for example, 2 kg/2.5 cm or larger), and seldom suffers from the generation of the blister of the adhesive layer caused by the exudation of the vapor containing water.

The present invention together with such effects will be illustrated by the following Examples.

EXAMPLES

In Examples 1-14 and Comparative Examples 3 and 4, the following elastic microspheres, tacky polymer, and backing layer film were used:

Elastic Microsphere

As described above, the elastic microspheres were produced by the suspension polymerization in water as a medium. A monomer composition contained IOA (isooctyl acrylate) and AA (acrylic acid) in a weight ratio of 96:4. A
5 volume average diameter in each Example is shown in Table 1.

The compressive modulus was adjusted to 7×10^5 dyne/cm² for all the diameters of the microspheres. The compressive modulus was measured under the above described measuring conditions with a sample which was produced by removing the solvent from the suspension containing the microspheres, molding
10 them in a cylindrical sample with a diameter of 5 mm and a height of 7 mm, and attached to parallel plate jigs.

Tacky Polymer

As a tacky polymer, an aqueous dispersion tackifier E1000 manufactured by SOKEN CHEMICAL Co., Ltd. was used, which had a monomer composition of
15 butyl acrylate and acrylic acid in a weight ratio of 94:6.

Backing Layer Film

A backing layer was a polyvinyl chloride film of 70 μ m in thickness having a polyester carrier of 50 μ m in thickness. This backing layer was produced by casting a solution of a homopolymer of vinyl chloride. Its coating surface was treated by
20 corona discharge to adjust its wetting index to a value in Table 1.

Preparation of Sample Sheet

To the tacky polymer (100 wt. parts), the microspheres of the weight parts shown in Table 1 was added, and mixed by a homomixer, and the mixture was coated on the backing layer film with a knife coater so as to achieve the coating
25 weight of Table 1 after drying. After drying it at 105°C for 5 minutes, a silicone liner (PD 530 BH manufactured by TOKUSHU SEISHI) was laminated to obtain a liner-laminated adhesive sheet.

In Comparative Examples 1 and 2, conventional products were used. That is, SCOTCHCAL film UPF-1 (manufactured by 3M) and FARAON sheet
30 (manufactured by FARAON) were used in Comparative Examples 1 and 2, respectively. Both are commercially sold as concrete masking films.

With each of the adhesive sheets, the following properties were measured:

Contact Area Rate

On a flat surface of a slide glass of 76 mm in length, 26 mm in width and 1 mm in thickness (MICRO SLIDE GLASS HAKUROKUMA No. 1 manufactured by MATSUNAMI GLASS INDUSTRIES, Co., Ltd.), the adhesive layer of the adhesive sheet of about 5 cm x about 2 cm, from which the liner had been removed, was adhered and pressed by reciprocating a roller of 2 kg over the sheet one time to obtain a sample. Then, the contact area rate was measured with the sample according to the above described method. This flat surface of the slide glass had Ra of about 0.001 μm .

Bubble Escapability

After peeling off the liner, the adhesive sheet of 10 cm x 10 cm was placed on a flat acrylate plate, and squeezed by a squeezer towards the center of the adhesive sheet to gather bubbles. A roller of 2 kg was rolled over the bubbles several times, and a degree of the bubble escape was observed. When all the bubbles escaped, the sheet was ranked "Good", while when a part of bubbles remained, the sheet was ranked "Bad".

Adhesion Force

An adhesive sheet of 15 cm x 2.5 cm was adhered to a mortar plate manufactured by Nippon Test Panel which had been degreased with isopropanol at 20°C, 65 %RH (Ra of the rough surface being in the range between 20 and 100 μm) according to JIS Z 0237 (1980), and kept at the same temperature and the same humidity for 48 hours. Then, a 180 degree peel strength was measured at a peeling rate of 30 cm/min.

Blister

An adhesive sheet of 15 cm x 2.5 cm was adhered to a rough surface of the same mortar plate as used in the measurement of adhesion force with a rivet brush, and dipped in water kept at 40°C for one week. When the sheet was not peeled off, it was ranked "No". When the slight blister was formed but the sheet was not peeled off, the sheet was ranked "Slight". When the blister was formed and the sheet was peeled off, it was ranked "Yes".

Viscosity of Coating Composition

A viscosity of each adhesive coating composition before coating was measured by a B-type viscometer (Spindle No. 4) at 23°C at a rotation speed of 60 rpm.

5 The results are shown in Table 1.

Table 1

	Microsphere diameter (μm)	Microspheres (wt. parts)	Cluster	Wetting index (dyne/ cm^2)	Contact area rate (%)	Coating weight (g/m^2)	Viscosity of coating composition (csp)	Adhesion force ($\text{kg}/2.5\text{cm}$)	Blister	Bubble escapability
Ex. 1	135	100	Yes	47	62	62	950	2.9	No	Good
Ex. 2	135	400	Yes	47	67	67	800	2.6	No	Good
Ex. 3	135	160	Yes	47	63	65	700	2.9	No	Good
Ex. 4	135	250	Yes	47	64	62	850	2.5	No	Good
Ex. 5	135	350	Yes	47	60	67	750	2.9	No	Good
Ex. 6	135	100	Yes	54	55	78	800	2.7	No	Good
Ex. 7	135	100	Yes	65	67	72	800	2.5	No	Good
Ex. 8	135	100	Yes	47	77	104	2000	3.3	Slight	Good
Ex. 9	202	100	Yes	47	61	110	150	2.1	No	Good
Ex. 10	86	100	Yes	47	47	44	150	1.2	No	Good
Ex. 11	135	100	Yes	37	52	86	200	1.6	No	Good
Ex. 12	135	25	Yes	47	70	60	1200	3.5	No	Good
Ex. 13	135	25	Yes	47	77	64	1200	3.8	Slight	Good
Ex. 14	135	25	Yes	47	86	64	1200	4.2	Slight	Good

	Microsphere diameter (μm)	Microspheres (wt. parts)	Cluster	Wetting index (dyne/cm ²)	Contact area rate (%)	Coating weight (g/m ²)	Viscosity of coating composition (csp)	Adhesion force (kg/2.5cm)	Blister	Bubble escapability
C. Ex. 1	-	-	No	-	100	133	-	1.2	Yes	Bad
C. Ex. 2	-	-	No	-	100	47	-	0.7	Yes	Bad
C. Ex. 3	135	10	No	47	100	132	1000	5.1	Yes	Bad
C. Ex. 4	135	900	Yes	47	92	127	200	1.1	Yes	Bad
C. Ex. 5	135	100	Yes	37	17	36	200	0.4	No	Good
C. Ex. 6	40	100	No	47	50	19	150	0.1	No	Good

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. An adhesive sheet comprising
 - 5 i) a backing layer, and
 - ii) an adhesive layer which is formed on said backing layerand contain tacky elastic microspheres and an adhesive polymer, wherein a) said adhesive layer has convex adhesive parts containing one or more clusters of at least two said elastic microspheres and said adhesive polymer, and b) a contact area rate
 - 10 between said adhesive layer and a plate surface is from 20 to 90 % when said contact area rate is measured by adhering said adhesive sheet to a flat glass plate surface under the pressure of 2 kg/25 cm².
2. The adhesive sheet according to claim 1, wherein a wetting index on
 - 15 a surface of said backing layer is from 35 to 70 dyne/cm², and said adhesive layer is one formed by coating an adhesive coating composition comprising said elastic microspheres, said tacky polymer and a solvent on said surface of said backing layer.
3. A method for producing an adhesive sheet as claimed in claim 1,
 - 20 comprising steps of:
 - i) preparing an adhesive coating composition comprising 100 wt. parts of a tacky polymer and 20 to 500 wt. parts of elastic microspheres, and
 - ii) coating said coating composition on a coating surface of a backing
 - 25 layer having a wetting index of 35 to 70 dyne/cm² to form clusters of said elastic microspheres, whereby an adhesive layer having convex adhesive parts which contain said clusters and said tacky polymer is formed.
4. The method according to claim 3, wherein said coating composition
 - 30 has a viscosity of 100 to 6000 cps.

5. A structure having an adhered adhesive sheet comprising an article of mortar or concrete with a rough surface and an adhesive sheet as claimed in claim 1 which is adhered to said rough surface, and having passageways which are formed by said surface and an adhesive layer of said adhesive sheet and
- 5 communicate with an atmosphere.

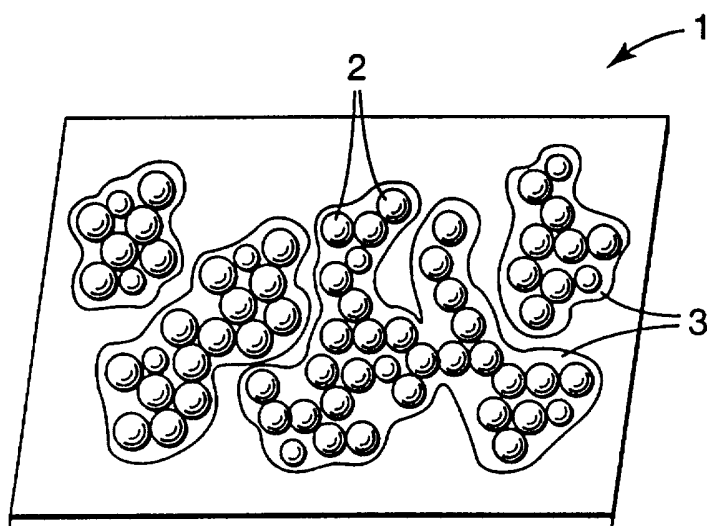


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.

PC 1, US 96/18887

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09J/02 E04F13/08 E04G23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J E04F E04G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 22971 A (MINNESOTA MINING & MFG ;MATSUDA HIROSHI (JP)) 13 October 1994 see claims	1-4
A	& JP 06 287 525 A (3M) 11 October 1994 cited in the application	1-4

A	US 4 054 697 A (REED DAVID ROBERT ET AL) 18 October 1977 see claims	5

A	US 3 085 482 A (YAKUBIK M.) 16 April 1963 see figures 3,4 see claims	5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 March 1997

Date of mailing of the international search report

09. 04. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Oudot, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PC 1/US 96/18887

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9422971 A	13-10-94	JP 6287525 A EP 0693097 A US 5607763 A	11-10-94 24-01-96 04-03-97
US 4054697 A	18-10-77	GB 1493407 A AU 8735575 A CA 1054459 A DE 2556666 A FR 2294837 A	30-11-77 16-06-77 15-05-79 01-07-76 16-07-76
US 3085482 A	16-04-63	NONE	