The invention relates to an adhesive composition based on polychloroprene dispersions and having improved adhesive properties, a method for the production of said composition, and the use thereof as a contact adhesive for inorganic and organic substrates.
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(54) Title: ADHESIVE COMPOSITION BASED ON POLYCHLOROPRENE DISPERSIONS

(54) Bezeichnung: KLEBSTOFFZUSAMMENSETZUNG AUF BASIS VON POLYCHLOROPREN-DISPERSIONEN

(57) Abstract: The invention relates to an adhesive composition based on polychloroprene dispersions and having improved adhesive properties, a method for the production of said composition, and the use thereof as a contact adhesive for inorganic and organic substrates.

Adhesive composition based on polychloroprene dispersions

The invention relates to adhesive composition based on polychloroprene dispersions having improved pressure-sensitive adhesion properties, to a process for preparation thereof, and to the use thereof as pressure-sensitive contact adhesive for organic or inorganic substrates.


Suitable emulsifiers include in principle all compounds and mixtures thereof which adequately stabilize the emulsion, such as, for example, the water-soluble salts, especially the sodium, potassium and ammonium salts, of long-chain fatty acids, rosin and derivatives of rosin, relatively high molecular mass alcohol sulfates, arylsulfonic acids, formaldehyde condensates of arylsulfonic acids, nonionic emulsifiers based on polyethylene oxide and on polypropylene oxide, and also polymers having an emulsifying action, such as polyvinyl alcohol (DE-A 2 307 811, DE-A 2 426 012, DE-A 2 514 666, DE-A 2 527 320, DE-A 2 755 074, DE-A 3 246 748, DE-A 1 271 405, 1 301 502, US-P 2 234 215, JP-A 60-31 510 (= 58-136 824 of 07.28.1983)).

Polychloroprene either is appropriately compounded and vulcanized and then used to produce industrial rubber articles, or is used as a base material for contact adhesive ("Handbook of Adhesives", Chapter 21, Van Nostrand Reinhold, New York, 2nd Edition 1977).

Contact adhesives based on polychloroprene are predominantly solventborne adhesives, which are applied to both adherends and allowed to dry. By subsequently joining the two parts under pressure, a bond of high strength is obtained. With these
solventborne contact adhesives, the long period within which adhesive bonding is possible at room temperature ("open time") is regarded as particularly advantageous.

On economic and environmental grounds there is a growing demand for suitable aqueous polychloroprene dispersions which can be processed to give corresponding aqueous adhesive formulations. A disadvantage here, however, is that following the evaporation of the water the "open time" — in comparison to solventborne adhesives — is much shorter. Particularly when high-melting resins are added which raise the heat resistance of the bonds, achieving good, reproducible contacting of the substrates to be bonded, particularly in the case of poorly absorbing or nonabsorbent substrates, can be done only by prior thermal activation of the dry adhesive film (H.W. Lucas, in "Adhesives Age", 1992, No. 2, page 28).

"Open time" is defined in the present specification as the chronological distance between the point in time at which the applied adhesive is sufficiently dry to allow the substrates to be bonded and the point in time at which it is no longer possible solely by application of pressure at room temperature to obtain a satisfactory bond.

It was therefore an object to provide an aqueous adhesive composition which is based on an aqueous polychloroprene dispersion and which following evaporation of the water possesses a long "open time" within which bonding is possible at room temperature without thermal activation. By adding a high-melting resin to the adhesive composition, furthermore, it is possible to achieve an improvement in the heat resistance of the pressure-sensitive contact adhesive.

The object has been achieved by the preparation of an aqueous adhesive composition based on polychloroprene dispersions, obtainable by continuous polymerization of chloroprene in aqueous emulsion in the presence of unmodified resin acids as emulsifier. This aqueous dispersion of adhesive base material can then be processed with the prior art adhesives auxiliaries and additives to give an adhesive composition possessing a sufficiently long "open time" within which bonding is possible at room temperature without thermal activation.
The invention accordingly provides an adhesive composition based on a polychloroprene dispersion comprising a tricyclic diterpenecarboxylic acid having at least two conjugated C=C double bonds per molecule.

Thus, in one aspect of the invention, there is provided an adhesive composition comprising: i) a polychloroprene dispersion, ii) at least one adhesive resin, and iii) a thickening agent; wherein the polychloroprene dispersion i) is a reaction product of an emulsion polymerization that comprises a) chloroprene, b) at least one ethylenically unsaturated monomer that is copolymerizable with chloroprene and c) as emulsifier, a tricyclic diterpenecarboxylic acid comprising at least 40% by weight of abietic acid, and wherein the thickening agent comprises one or more thickening agents present in the adhesive composition at from 0.01 to 1 wt. %, based on the adhesive composition.

In another aspect of the invention, there is provided an adhesive composition comprising: i) 100 parts by weight of a polychloroprene dispersion, ii) 15 to 75 parts by weight of at least one adhesive resin, 0.05 to 5 wt. % based on the adhesive composition of a thickening agent; and 1 to 10 parts of zinc oxide or magnesium oxide, wherein the polychloroprene dispersion i) is a reaction product of an emulsion polymerization that comprises a) chloroprene, b) at least one ethylenically unsaturated monomer that is, copolymerizable with chloroprene and c) as emulsifier, a tricyclic diterpenecarboxylic acid comprising at least 40% by weight of abietic acid.
Preferred adhesive compositions are those comprising 100 parts by weight of a polychloroprene dispersion which as an emulsifier comprises a tricyclic diterpenecarboxylic acid having at least two conjugated C=C double bonds per molecule, from 15 to 75 parts by weight of a tackifier resin, from 1 to 10 parts of a metal oxide selected from the group consisting of zinc oxide and magnesium oxide, and also, if desired, further auxiliaries and additives, all present in the form of a dispersion.

The invention further provides a process for preparing an adhesive composition by mixing a polychloroprene dispersion with the customary adhesives auxiliaries and additives, characterized in that the polychloroprene dispersion comprises a tricyclic diterpenecarboxylic acid having at least two conjugated C=C double bonds per molecule.

The polychloroprene dispersion present in the adhesive composition of the invention is obtained by emulsion polymerization of the chloroprene and from 2 to 20 parts by weight of an ethylenically unsaturated monomer which is copolymerizable with chloroprene in an alkaline medium in the presence of from 1 to 10 parts by weight of a tricyclic diterpenecarboxylic acid having at least two conjugated C=C double bonds per molecule, as emulsifier, all figures based on 100 parts by weight of both monomers.

The polychloroprene dispersion present in the adhesive composition of the invention, following evaporation of the water, has an “open time” in the range from 4 to 15 days.

Suitable copolymerizable monomers are described, for example, in “Methoden der Organischen Chemie” (Houben-Weyl) XIV/1; 738 ff. Georg Thieme Verlag Stuttgart 1961. Preferred compounds are those having from 3 to 12 carbon atoms and 1 or 2
copolymerizable C= C double bonds per molecule. Examples of prepared copolymerizable monomers are 2,3-dichlorobutadiene and 1-chlorobutadiene.

The polychloroprene dispersion for use in the process of the invention is prepared by emulsion polymerization at from 0 to 70°C, preferably at from 5 to 50°C, and at pH values of from 10 to 14, preferably from 11 to 13. Activation is accomplished by the customary activators and/or activator systems.

Examples that may be mentioned include the following: formamidinesulfonic acid, potassium peroxodisulfate, redox systems based on potassium peroxodisulfate and, if desired, silver salt (Na salt of anthraquinone-β-sulfonic acid) with, for example, compounds such as formamidinesulfinic acid, Na salt of hydroxymethanesulfinic acid, sodium sulfite and sodium dithionite serving as redox partners. Also suitable are redox systems based on peroxides and hydroperoxides. The polychloroprenes of the invention can be prepared either continuously or batchwise.

To adjust the viscosity of the polychloroprenes of the invention it is possible to use customary chain transfer agents such as mercaptans, as described, for example, in DE-A 3 002 711, GB-P 1 048 235, FR-P 2 073 106, or such as xanthogen disulfides, as described, for example, in DE-A 1 186 215, in DE-A 2 156 453, 2 306 610, and 3 044 811, in EP-A 53 319, in GB-P 512 458 and 952 156, and in US-A 2 321 693 and 2 567 117.

Particularly preferred chain transfer agents are n-dodecyl mercaptan and the xanthogen disulfides used in DE-A 3 044 811, DE-A 2 306 610, and DE-A 2 156 453.

After the polymerization has been carried out up to the desired conversion, which in the case of soluble polychloroprene is normally between 50 and 80% and in the case of polychloroprene gel is more than 80%, it is advantageous to terminate the reaction by adding known stopping agents such as tert-butylpyrocatechol, phenothiazine, and diethylhydroxylamine. Unreacted monomers can be removed with the aid of steam and vacuum.
In one preferred embodiment of the process of the invention, in the case where the polychloroprene dispersion is prepared by emulsion polymerization, chloroprene is reacted with from 5 to 9 parts by weight of 2,3-dichlorobutadiene in the presence of from 2.0 to 6.0 parts by weight of a tricyclic diterpene carboxylic acid having at least two conjugated C=C double bonds per molecule, as emulsifier, all figures being based on polymerizable monomers employed.

The tricyclic diterpene carboxylic acids for use in accordance with the invention can be used in the form of the crude, unmodified resin acids (S.W. Barendrecht, L.T. Lees in Ullmanns Encyclopädie der Technischen Chemie, 4th Ed. Vol. 12. 528-538, Verlag Chemie, Weinheim – New York 1976), which are obtained from tall oil, pine balsam or root resin, provided these are free from distillable constituents of turpentine oil.

If the tricyclic diterpene carboxylic acids themselves are readily available, they may also be employed in pure form.

Suitable tricyclic diterpene carboxylic acids include, for example, abietic acid, palustric acid, neoabietic acid and levopimaric acid.

The tricyclic diterpene carboxylic acids containing conjugated unsaturation may be determined by nature and amount by gas chromatography from a mixture of resin acids; for example, in accordance with or analogy to J. Amer. Oil Chem. Soc. 54, 289 (1977).

Where an unmodified resin acid obtained from tall oil, pine balsam or root resin is used, it naturally contains not only tricyclic diterpene carboxylic acids containing conjugated unsaturation but also further constituents. Without restriction, an example that can be mentioned of suitable, commercially available unmodified resin acids is the resin acid obtained from tall oil that has the following composition:
<table>
<thead>
<tr>
<th>Fraction in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>abietic acid</td>
</tr>
<tr>
<td>neoabietic acid</td>
</tr>
<tr>
<td>palustric acid</td>
</tr>
<tr>
<td>pimaric acid</td>
</tr>
<tr>
<td>isopimaric acid</td>
</tr>
<tr>
<td>dehydroabietic acid</td>
</tr>
<tr>
<td>other resin acids</td>
</tr>
<tr>
<td>sum of all resin acids</td>
</tr>
<tr>
<td>fatty acids</td>
</tr>
<tr>
<td>combined acids</td>
</tr>
<tr>
<td>unsaponifiable fractions</td>
</tr>
</tbody>
</table>

(from the company brochure from Bergvik Kemi AB, Söderhamn, Sweden)

As a further example, mention may be made of the composition of an unmodified resin acid obtained from pine balsam:

<table>
<thead>
<tr>
<th>Fraction in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>abietic acid</td>
</tr>
<tr>
<td>neoabietic acid</td>
</tr>
<tr>
<td>palustric acid</td>
</tr>
<tr>
<td>pimaric acid</td>
</tr>
<tr>
<td>isopimaric acid</td>
</tr>
<tr>
<td>other resin acids</td>
</tr>
</tbody>
</table>

Besides the tricyclic diterpenecarboxylic acids containing conjugated unsaturation it is also possible in addition to use further emulsifying substances, such as the watersoluble salt of the condensation product of naphthalenesulfonic acid and formaldehyde, for example.
The adhesive composition of the invention is free from or low in organic solvents. "Low" in this context denotes an amount of less than 30% by weight (organic solvent), based on the finished adhesive.

Besides the polychloroprene dispersion, the adhesive composition of the invention includes, if desired, further adhesives auxiliaries and additives. By way of example it is possible to add fillers such as quartz flour, quartz sand, highly disperse silica, heavy spar, calcium carbonate, chalk, dolomite or talc, together where appropriate with wetting agents, examples being polyphosphates (such as sodium hexametaphosphate), naphthalenesulfonic acid, ammonium or sodium salts of polyacrylic acids, the fillers being added generally in amounts of from 10 to 60%, preferably from 20 to 50% by weight, based on adhesive, and the wetting agents in general in amounts of from 0.2 to 0.6% by weight, based on filler.

A particularly important additive is zinc oxide, as an acceptor for small amounts of hydrogen chloride which may be given off by the polymers.

Further suitable auxiliaries are, in amounts for example of from 0.01 to 1% by weight, based on adhesive, organic thickeners to be employed, such as cellulose derivatives, alginates, starch, starch derivatives or polyacrylic acid, or, in amounts of from 0.05 to 5% by weight, based on adhesive, inorganic thickeners to be employed, such as bentonites, for example.

For preservation it is also possible to add fungicides to the adhesive composition of the invention. They are generally employed in amounts of from 0.02 to 1.0% by weight, based on adhesive. Examples of suitable fungicides are derivatives of phenol or of cresol, or organotin compounds.

Tackifying resins as well, such as unmodified or modified natural resins, for example, such as rosin esters, hydrocarbon resins or synthetic resins such as phthalate resins, can be added, if desired, to the adhesive composition in dispersed form; cf. "Klebharze" R. Jordan, R. Hinterwaldner, pp. 75-115, Hinterwaldner Verlag Munich 1994. Preference is given to alkylphenolic resin dispersions having
softening points of more than 110°C, and particular preference to a terpene-phenolic resin having a softening point of above 110°C.

Organic solvents such as, for example, toluene, xylene, butyl acetate, methyl ethyl ketone, ethyl acetate, dioxane or mixtures thereof or plasticizers such as, for example, those based on adipate, on phthalate or on phosphate may be added if desired to the polychloroprene dispersions.

The adhesives of the invention can be used for adhesively bonding any desired substrates of identical or different kind, e.g., of wood, paper, plastics, textiles, leather, rubber and inorganic materials, such as ceramic, earthenware or asbestos cement.

The aqueous adhesive composition of the invention additionally allows substrates which are difficult to bond adhesively to be adhesively bonded, such as, for example, thermoplastic olefins (TPOs), or ethylene-vinyl acetate copolymers (EVAs) with high ethylene content, which otherwise cannot be adhesively bonded without the surface being pretreated with a primer. Substrates difficult to bond adhesively are materials having a surface tension of less than 35 mN/m. The determination of this surface tension is described, for example, in “Handbook of adhesives”, Chapter 1, p. 12, Van Nostrand Reinhold, New York, 2nd Edition 1977, or in “Strukturelles Kleben und Dichten”, Schindel-Bidinelli, Vol. 1, p. 191, Hinterwaldner Verlag, Munich 1988.

25 Examples

A) Preparation of the polychloroprene dispersions

Polymerization is carried out by a continuous process as described in EP-A 0 032 977.
Example 1 (comparative example)

Introduced into the first reactor of a polymerization cascade composed of 7 identical reactors each having a volume of 50 liters are the aqueous phase (W) and the monomer phase (M), introduced via a measurement and control apparatus in a continually constant ratio, and also the activator phase (A). The average residence time per reactor is 25 minutes. The reactors correspond to those described in DE-A 2 650 714 (figures in parts by weight per 100 g part by weight of monomers used).

(M) = monomer phase:

- Chloroprene: 93.0 parts by weight
- 2,3-Dichloro-1,3-butadiene: 7.0 parts by weight
- n-Dodecyl mercaptan: 0.22 parts by weight
- Phenothiazine: 0.015 parts by weight

(W) = aqueous phase:

- Deionized water: 115.0 parts by weight
- Sodium salt of a disproportionated abietic acid: 2.6 parts by weight
- Sodium salt of a condensation product of naphthalenesulfonic acid and formaldehyde: 0.7 parts by weight
- Potassium hydroxide: 1.0 parts by weight

(A) = activator phase:

- 1% strength aqueous formamidinesulfonic acid solution: 0.05 parts by weight

At an internal temperature of 40°C there is slight onset of the reaction. Through external cooling, the heat of polymerization produced is removed and the polymerization temperature is held at 45°C. At a monomer conversion of 66% the reaction is terminated by adding phenothiazine. The residual monomer is removed
from the polymer by steam distillation and the polymer latex is thickened by adding alginate, as described in “Neoprene Latices, John C. Carl. E.I. DuPont 1964. p. 13”.

The viscosity of the latex is 100 mPas, the solids content 58%.

After a polymerization time of 120 hours the polymerization line is run out.

**Example 2 (inventive example)**

The procedure of the 1st example is repeated but replacing the disproportionated abietic acid of the aqueous phase with an equal amount of unmodified resin acid based on tall oil.

The viscosity of the latex is 104 mPas, the solids content 58%.

**Example 3 (comparative example)**

The procedure described in Example 1 is repeated but replacing the 7 parts of 2,3-dichlorobutadiene with chloroprene and raising the conversion to 85%. After the thickening operation, a dispersion is obtained which has a solids content of 56% and a viscosity of 105 mPas. The polymer is 60% gelled.

**Example 4 (comparative example)**

Polymerization is carried out as described in Example 1 but at 10°C and without 2,3-dichlorobutadiene.

(M) = monomer phase:

Chloroprene 100.0 parts by weight
n-Dodecyl mercaptan 0.13 parts by weight
Phenothiazine 0.015 parts by weight
(W) = aqueous phase:

Deionized water 115.0 parts by weight
Sodium salt of a disproportionated abietic acid 2.6 parts by weight
Sodium salt of a condensation product of naphthalenesulfonic acid and formaldehyde 0.7 parts by weight
Potassium hydroxide 1.0 parts by weight

(A) = activator phase:

5

1% strength by weight aqueous formamidinesulfinic acid 0.07 parts by weight
Potassium persulfate 0.05 parts by weight
Anthraquinone-2-sulfonic acid Na 0.005 parts by weight

At an internal temperature of 15°C there is onset of the reaction in the first reactor of the cascade. By external cooling the heat of polymerization liberated is removed and the polymerization temperature is lowered to 10°C. At a monomer conversion of 80% the reaction is terminated by adding phenothiazine. The residual monomer is removed from the polymer by steam distillation and the polymer latex is thickened.

After a polymerization time of 4 days, the polymerization line is run out.

A dispersion is obtained which has a solids content of 56% and a viscosity of 98 mPas.

B) Measurement methods

1) Determination of the gel content

The dispersion is applied to a glass plate and dried for three days at room temperature under a nitrogen atmosphere to form a film. 250 mg of sample are dissolved or swollen in 25 ml of THF (to which 1 g of polymerization inhibitor per
liter of THF has been added) for 24 hours at room temperature in a closed vessel. The mixture is ultra centrifuged at 20 000 rpm for 1 hour and the weight fraction of the material removed by centrifugation is determined after drying.

**Determination of the peel strength**

The test is carried out in accordance with EN 1392. A wet film of the dispersion 100 um thick is applied to two test specimens (Nora* rubber, roughened, 100 x 30 mm) and vented at room temperature for 1 hour. The test specimens are then joined for 10 seconds at 4 bar. A tensile test is carried out on a commercially customary tensile test machine at room temperature. The strength values are determined immediately after bonding and after 1 and 9 days.

**Measurement of the contact bonding time on polyester ("open time")**

Polyester film (Hostaphan* RN 75/0, thickness: 0.075 mm.) is presented and the dispersions are applied in a width of 5mm using a film-drawing instrument with a doctor blade aperture of 0.2 mm. The strips of polyester bearing the adhesive dispersion are stored in a climatized chamber at 23°C and 50% relative humidity. At intervals of 12 hours, two strips of cardboard in each case are crossed in relation to one another and loaded with a 50 g weight for 10 seconds. The end of the contact bonding time is exceeded when, in the separation test by hand; it is no longer possible to contact the films.

**C) Inventive preparation of an adhesive based on a polychloroprene dispersion**

For the preparation of the formulation, the polychloroprene dispersion is introduced into a glass beaker. With stirring, the stabilizer, the ageing inhibitor, ZnO, and the resin are added.

* Trade-mark
Table 1  Preparation of the formulation for the comparison tests

<table>
<thead>
<tr>
<th>Product</th>
<th>Function</th>
<th>Added as</th>
<th>Solids content (%)</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polychloroprene dispersion</td>
<td>Polymer</td>
<td>Dispersion</td>
<td>55-58</td>
<td>70</td>
</tr>
<tr>
<td>Rhenofit* DDA-EM 50 (1)</td>
<td>Aging Inhibitor</td>
<td>Dispersion</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Emulvin*W (2)</td>
<td>Stabilizer</td>
<td>Solution</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Akroperse* W-9804 (3)</td>
<td>ZnO</td>
<td>Dispersion</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>Alresen* VPT 1550 (4)</td>
<td>Resin</td>
<td>Dispersion</td>
<td>50</td>
<td>30</td>
</tr>
</tbody>
</table>

Sources: (1), (2) = Bayer AG, (3) = Akrochem, Akron/Ohio USA, (4) = Vianova Resins Mainz-Kastel, Germany

Measurement of the "open time"

Table 2  Measurement of the contact adhesion time on polyester film

<table>
<thead>
<tr>
<th>Contact bonding time</th>
<th>12 h</th>
<th>24 h</th>
<th>32 h</th>
<th>3d</th>
<th>6d</th>
<th>9d</th>
<th>12d</th>
<th>24d</th>
<th>25d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion 4</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion 3</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion 1</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion 2 ***)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

** inventive example

Measurement of the peel strength

*Trade-mark
Table 3  Measurement of the strength of foam/metal bonds depending on the open time (the bonding carried out was of a PU foam to ST37 steel)

<table>
<thead>
<tr>
<th>Dispersion no.</th>
<th>Storage time before bonding, in hours</th>
<th>4 N/mm</th>
<th>3</th>
<th>1</th>
<th>2 **)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N/mm</td>
<td>0.8</td>
<td>1.0</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>12</td>
<td>N/mm</td>
<td>0.4</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>24</td>
<td>N/mm</td>
<td>0</td>
<td>0.8</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>96</td>
<td>N/mm</td>
<td>0</td>
<td>0.2</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>144</td>
<td>N/mm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**) – inventive example

The unusually long “open time” of the polychloroprene dispersion of the invention is demonstrated in Example 2 in Tab. 2. The adhesion to nonabsorbent substrates such as steel (Tab 3, No. 2) is also excellent in comparison to adhesive formulations based on other polychloroprene dispersions, even after a storage time of 6 days.

Assessment of the adhesion to TPO
Following application of the adhesive dispersion, the material was dried at RT for 24 h and the adhesion of the adhesive film to this TPO substrate (DOW Engage* type) was tested.

*Trade-mark
Table 4 Measurement of the adhesion to TPO

<table>
<thead>
<tr>
<th>Dispersion No.</th>
<th>4</th>
<th>3</th>
<th>1</th>
<th>2* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assessment of the adhesion to TPO</td>
<td>Adhesive film dry, easy to remove from the substrate</td>
<td>Adhesive film dry, easy to remove from the substrate</td>
<td>Adhesive film tacky, but low level of adhesion to TPO</td>
<td>Adhesive film tacky, strong adhesion to TPO</td>
</tr>
</tbody>
</table>

In the case of comparative experiments 3 and 4, the dry adhesive film can be removed without problems from the TPO substrate (no adhesion to TPO). In the case of comparative experiment 1, the dry adhesive film exhibits a slight adhesion to the TPO substrate. Only with the adhesive composition of the invention were adhesive films produced which possess an excellent adhesion. In the attempt to remove the dry adhesive film from the TPO the adhesive film tears, since the adhesion to TPO is too strong.
CLAIMS:

1. An adhesive composition comprising i) a polychloroprene dispersion, ii) at least one adhesive resin, and iii) a thickening agent, wherein the poly-chloroprene dispersion i) is a reaction product of an emulsion polymerization that comprises a) chloroprene, b) at least one ethylenically unsaturated monomer that is copolymerizable with chloroprene and c) as emulsifier, an unmodified resin acid comprising at least 40% by weight of abietic acid, and wherein the thickening agent comprises one or more thickening agents present in the adhesive composition at from 0.01 to 1 wt. %, based on the adhesive composition.

2. The adhesive composition of claim 1, wherein the thickening agent is one or more materials selected from the group consisting of cellulose derivatives, alginates, starch, starch derivatives and polyacrylic acid.

3. The adhesive composition of claim 1, wherein the thickening agent comprises one or more inorganic thickening agents.

4. The adhesive composition of claim 1, wherein the inorganic thickening agent comprises bentonite.

5. The adhesive composition of claim 1, wherein the adhesive resin comprises a terpenephenoal resin having softening point above 110°C.

6. The adhesive composition of claim 1, wherein the emulsifier further comprises other tricyclic diterpenecarboxylic acids having at least two conjugated C=C double bonds per molecule.

7. The adhesive composition of claim 1, wherein the adhesive composition has an open time after evaporation of the water of 4 to 15 days.

8. A contact adhesive for bonding inorganic or organic substrates comprising the adhesive composition of claim 1.
9. An adhesive composition comprising 100 parts by weight of a polychloroprene dispersion, 15 to 75 parts by weight of the at least one adhesive resin, 0.05 to 5 wt. % based on the adhesive composition of a thickening agent, and 1 to 10 parts of zinc oxide magnesium oxides, wherein the polychloroprene dispersion i) is a reaction product of an emulsion polymerization that comprises a) chloroprene, b) at least one ethylenically unsaturated monomer that is, copolymerizable with chloroprene and c) as emulsifier, an unmodified resin acid comprising at least 40% by weight of abietic acid.

10. The adhesive composition of claim 9, wherein the adhesive resin comprises a terpene phenol resin having a softening point above 110°C.

11. The adhesive composition of claim 9, wherein the thickening agent is one or more materials selected from the group consisting of cellulose derivatives, alginates, starch, starch derivatives and polyacrylic acid.

12. The adhesive composition of claim 9, wherein the thickening agent comprises one or more inorganic thickening agents.

13. The adhesive composition of claim 12, wherein the inorganic thickening agent comprises bentonite.

14. The adhesive composition of claim 9, wherein the emulsifier further comprises other tricyclic diterpenecarboxylic acids having at least two conjugated C=C double bonds per molecule.

15. The adhesive composition of claim 9, wherein the adhesive composition has an open time after evaporation of water from 4 to 15 days.

16. A contact adhesive for bonding inorganic or organic substrates comprising the adhesive composition of claims 9 to 15.