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(30) Elsőbbségi adatok:
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(72) Feltaláló(k):
Holzner, Armin, 2630 Ternitz (AT)
Kern, Wolfgang, 8055 Seiersberg (AT)
Lenko, Dietmar, 8051 Graz (AT)
Manhart, Jakob Cornelius, 8700 Leoben (AT)
Schaller, Raimund, 2620 Neunkirchen (AT)
SCHLÖGL, Sandra, 8152 Stallhofen (AT)

(73) Jogosult(ak):
Semperit Aktiengesellschaft Holding, 1031 Wien (AT)

(74) Képviselő:
Gödölle, Kékes, Mészáros & Szabó Szabadalmi és Védjegy Iroda, Budapest

(54) **Elasztomer termék kovalensen kötött részecskékkel**

Elastomer product with covalently bonded particles

The invention relates to a method for bonding inorganic or organic solid particles to the surface of an elastomer glove, wherein the elastomer comprises unsaturated carbon-carbon bonds in the molecular structure which are at least partially saturated by epoxidation at least in the region of the surface of the elastomer glove, and to an elastomer glove formed from an elastomer having a surface wherein the elastomer comprises unsaturated carbon-carbon bonds in the molecular structure.

Modifying the surface of natural rubber gloves is already known from the prior art. As an example, the surface is provided with coatings or is roughened in order to improve the lubrication of the gloves. In particular, the intention is to improve the donning capability or the wet donning capability of the gloves. Functionalizations for reducing the allergenic potential associated with natural rubber are also known.

One method for modifying the surface of natural rubber which is known from the prior art is that of epoxidization of the rubber surface.

As an example, US 7 442 746 A discloses a method for synthesizing an epoxidized polymer which comprises the following steps: (1) in a first stage, producing a cationically stabilized polymer latex containing at least one conjugated diolefin monomer, (2) treating the polymer latex from step (1) with formic acid or acetic acid and hydrogen peroxide, and (3) reacting the mixture for a predetermined time and at a predetermined temperature in order to obtain the desired degree of epoxidation.

DE 102 60 219 B discloses epoxidation of the surface layer of a rubber product by immersing the rubber product in or by coating it with a treatment fluid which is produced by adding hydrogen peroxide and other additives such as a surfactant, alcohol, thickening agent, a different (further) agent for reducing surface tension, to an aqueous acetic acid or formic acid solution in order to provide this surface with non-stick or non-tacky properties, lubricant properties and other barrier layer properties without giving rise to toxic gases and without causing contamination due to powder dust during the manufacturing process and without compromising (impairing) the intrinsic properties of the rubber product, such as elasticity, stretch and tensile strength.

GB 1 396 090 A describes a method for manufacturing an article, comprising bringing an alkyl hypohalogenite or halogen-substituted alkyl hypohalogenite into contact with an article moulded from a rubber containing ethylenic double bonds and bonding a coating or another rubber, a metal or wood to the treated surface of the moulded body. Bonding may be obtained with the aid of an epoxy binding agent.

US 5 310 819 A describes elastomeric articles epoxidized at the surface, wherein the ethylenic bonds of the elastomer are saturated by immersing the articles in an epoxidation solution for a sufficient time.

US 5 804 318 A discloses improved lubricating coatings for reducing the coefficient of friction of the surfaces of medical devices. The lubricant hydrogel coatings are covalently bonded to the epoxide-functionalized surfaces.

US 6 797 783 A describes a natural rubber obtained by modifying a deproteinized natural rubber with a nitrogen content of less than 0.10% by weight, wherein the modification comprises epoxidation of the deproteinized natural rubber with trifluoroperacetic acid.

US 2006/074185 A1 describes an ink for inkjet printing. It comprises epoxided latex particles. Dyes and the like are bonded to the latex particles via the epoxide groups.

Amornchaiyapitak C. et al: "Modification of epoxidized natural rubber film surface by polymerisation of methyl methacrylate", European Polymer Journal, Pergamon Press Ltd. Oxford, GB, Vol. 44, No. 6, 1. June 2008, pages 1782-1788 describes the use of methyl methacrylate in the manufacture of natural rubber gloves in reducing friction. Epoxided natural latex rubber is used herein.

Thongnuanchan B. et al: "Epoxidized natural rubber-bonded wood Particleboard", Polymer Engineering & Science, Vol. 47, No. 4, 1. March 2007, pages 421-428, describes the manufacture of particle board from wood particles which are bonded together using an epoxided natural rubber.

DD 296 853 A5 discloses a method for the manufacture of surface-functionalized support materials which can be used as separators, chromatographic materials, ion exchange materials, solid phase synthesis materials or as catalyst supports. They are manufactured by chemically binding mixtures of epoxided polydienes or polydiene copolymers with reactive organic compounds or transformation products formed from epoxided polydienes or polydiene copolymers with reactive organic compounds such as amines, carboxylic acids, amino acids and their derivatives to the surface of inorganic solid bodies such as pulverized amorphous or ceramic glasses, precipitated or fumed silica as well as main group and transition group metal oxides.

The aim of the present invention is to provide the opportunity for modifying the surface of elastomer gloves and of modifying elastomer surfaces.

This aim is achieved on the one hand by using the method disclosed above to covalently bond the solid particles to the epoxide groups after epoxidation, or in the case of the elastomer glove mentioned above, the surface exhibits solid inorganic or organic particles which are at least partially covalently bonded to the elastomer.

The advantage herein is that the solid inorganic or organic particles (hereinafter termed particles) covalently bonded to the elastomer improve the lubrication of the elastomer gloves (hereinafter termed elastomer products). The donning capability, in particular the wet donning capability, of elastomer gloves can therefore be improved. The covalent bonding means that the improvements or changes to the properties as a result of the surface modification last for a longer time. In addition, the particles impart an additional functionality to the elastomer product if the particles are chosen appropriately, for example by using particles loaded with active substances. The advantage of bonding the particles by means of epoxide groups is that the elastomer surface can be epoxidized by a thermal process; in other words, actinic radiation in order to prepare the surface is not necessary. Furthermore, epoxy groups that have not reacted on the surface of the elastomer reduce its tackiness and the at least partial saturation of the ethylenic groups of the elastomer improves resistance to aging.

The particles are preferably formed from inorganic particles. This enables the tackiness to be reduced and/or improves the donning capability, in particular the wet donning capability, of gloves because the contact surface area of the elastomer with a hand is reduced. In general, the adhesion of an elastomer product to a surface can be reduced as a result of this effect. Furthermore, is also possible to impart an additional functionality to the elastomer product via these solid particles, for example if solid particles which absorb moisture are used.

In order to improve bonding of the solid particles to the functionalized surface of the elastomer product, it is advantageous if the surface of the solid particles is also functionalized prior to the reaction.

Thus, the solid particles can be functionalized by generating free mercapto groups and/or free amino groups and/or carboxylic acid groups and/or epoxide groups and/or hydroxyl groups and/or anhydride groups and/or isocyanate groups and/or isothiocyanate groups on the surface of the solid particles. The advantage of using these functional groups is that they provide anchoring groups with a high reactivity for bonding the solid particles to the elastomer surface.

However, the solid particles can also be functionalized by means of at least one chemical compound which is selected from a group comprising or consisting of acrylate groups, anhydride groups, isocyanate groups, isothiocyanate groups, methacrylate groups and vinyl groups. The advantage of using these functional groups is that anchoring groups can be made available for coupling further functional compounds to the solid particles.

In a further variation, in order to produce what are known as "powder-free" elastomer gloves, particles that are purely adhesively bonded are removed from the surface of the elastomer product. This reduces the allergenic potential of the elastomer products. In addition, these particles, which have a less pronounced effect than the covalently bonded particles, can therefore optionally be recycled to the production process. This prevents wounds from being contaminated by particles when the elastomer product is used in the medical field. The elastomer product is also suitable for use in clean rooms.

Epoxidation of the elastomer may be carried out on a solid surface of the elastomer product. This variation of the method is in particular used for the manufacture of single-layered elastomer products, because this enables selected areas of the surface of the elastomer to be modified. Furthermore, by preventing bulk epoxidation, the aging properties of the elastomer can be improved.

In addition to this variation of the method, within the context of the invention it is also possible for epoxidation to be carried out on a latex in the liquid phase. This variation of the method may be used to produce multi-layered elastomer products. The advantage here is that with this variation of the method, not only the region of the surface can be epoxidized, but also the individual latex particles, thereby enabling the potential properties of the elastomer product to be adapted.

It is also possible to carry out the epoxidation only in discrete regions of the elastomer. This means that stronger structuring of the elastomer surface can be obtained, thereby enabling the lubrication of the elastomer to be influenced. In addition, specific properties can be imparted to specific regions of the elastomer. The particles preferably have a particle diameter of between 10 nm and 10 µm. Although an effect will still be observed with particles below 10 nm, with a view to improving the lubrication of the elastomer, this is not in fact satisfactory. With particle sizes of more than 10 µm, however, it has been observed that the improvement in bonding to the elastomer surface diminishes again because of the size of the particles.

In accordance with another embodiment, the particles may be at least partially cross-linked with one another. This may be accomplished, for example, by means of unreacted functional groups on the surface of the particles. This means that a "net-like" structure can be obtained. In addition, the adhesion of the particles to the elastomer surface can be improved because the particles can be more effectively fixed in position as a result of the cross-linking.

The particles may incorporate at least one active substance, meaning that the functionalization spectrum of the elastomer surface can be significantly broadened. The particles may optionally be post-loaded, resulting in a longer service life of the elastomer product.

The invention will now be described in more detail below for the purposes of better comprehension with the aid of the accompanying figure.

In the diagrammatically simplified drawing:

Figure 1 shows the modification of NR latex films by epoxidation and subsequent bonding of amino-functionalized SiO_2 particles.

The term "elastomer product" means a glove, preferably a surgical glove or an examination glove.

For the purpose of completeness, it should be pointed out that the term "elastomer product" as used in the context of the invention is intended to mean a product produced from an elastomer which comprises unsaturated carbon-carbon bonds in the molecular structure, i.e. in particular ethylenic bonds (=diene rubber). The elastomer is preferably a natural rubber or a synthetic isoprene rubber. In addition, the invention is also applicable to using other types of rubber having unsaturated carbon-carbon bonds of this type, in particular homopolymers and copolymers such as nitrile butadiene rubber, carboxylated nitrile butadiene rubber, polybutadiene, polychloroprene, or styrene butadiene rubber.

The dipping process used to manufacture rubber gloves has already been extensively described in the prior art. It usually involves at least the following steps: preparing a dipping mould, coagulant dipping, and latex dipping. In addition, this dipping process also includes various washing and drying steps. The dipping process is usually operated continuously, for example in what is known as a chain dipping unit. For further details on this subject, reference should be made to the relevant prior art.

The element which is common to all the embodiments of the invention is that the unsaturated carbon-carbon bond is saturated by epoxidation at least in the region of the surface of the elastomer product or the elastomer (hereinafter, reference will only be made to an elastomer, this term also being intended to include the elastomer product), preferably by up to at least 2%, in particular between 10% and 80%.

In principle, there are two variations of the method. Firstly, it is possible to carry out epoxidation of a solid surface of the elastomer. Secondly, another possibility is epoxidation in the liquid phase of the latex, after which an appropriate mould is dipped in the latex in order to allow the elastomer article to be produced.

In the variation of the method which is carried out on the solid surface of the elastomer, the elastomer product is not necessarily produced using a dipping process. It is also possible to use any other moulding method known in the art, for example injection moulding processes, extrusion processes, compression moulding, etc., although the dipping process is preferred for manufacturing the elastomer product within the context of the invention.

In order to saturate or react the unsaturated carbon-carbon bonds on a solid surface of an elastomer product, for example an elastomer film, the elastomer surface is brought into contact with the respective reagent, for example by dipping in the epoxidation reagent, or by being sprayed with it. The elastomer is preferably used in a pre-cross-linked form and pre-cross-linking is preferably carried out by a photochemical process with a thiol as described in the publications AT 502 764 A1 and AT 508 099 A1. In general, in the context of the invention, pre-cross-linking is preferably carried out by means of a photochemical process with a thiol. However, it would also be possible within the context of the invention to use any other type of pre-cross-linking, for example sulphur cross-linking or peroxide cross-linking or cross-linking generally by means of actinic radiation,.

Similarly, sulphur cross-linking (at increased temperature) may be used as the pre-cross-linking method, in a manner which is known in the art.

The reagent for epoxidizing the elastomer may, for example, be an aliphatic or aromatic peracid, for example peracetic acid, performic acid, trifluoroperacetic acid, permaleic acid, perbenzoic acid, monoperphthalic acid, o-sulphoperbenzoic acid, p-nitroperbenzoic acid and m-chloroperbenzoic acid, the former being preferable. The concentration of peracid may be between 1% by weight and 41% by weight, in particular between 2% by weight and 4% by weight, the rest being water (with hydrogen peroxide and carboxylic acid(s)). Commercially available peracids are used.

However, it would also be possible to use other epoxidizing agents such as, for example, hydrogen peroxide in an acid or an alkaline medium or tert-butylhydroperoxide in an alkaline medium, or the epoxidation of the elastomer may be carried out as described in one of the prior art documents cited above, to which explicit reference is made. It would also be possible to carry out the epoxidation using catalysts, for example metal-salen complexes + NaOCl (Jacobsen epoxidation) or Shi catalyst + oxone (Shi epoxidation).

Another possibility is to form peracids in situ by reacting a carboxylic acid with H_2O_2, for example by in situ formation of performic acid.

The temperature at which the epoxidation reagent treatment is carried out may be between 30°C and 70°C, in particular between 40°C and 50°C. Furthermore, the duration of "wetting" may be between 1 minute and 400 minutes, in particular between 40 minutes and 100 minutes. The wetted elastomer may then be immersed in water for a period of between 30 seconds and 5 minutes in order to rinse off surplus epoxidation reagent.

Finally, the wetted elastomer is dried at a temperature of between 20°C and 100°C, in particular between 55°C and 70°C. Drying preferably takes place within a period of between 10 minutes and 100 minutes, in particular between 15 minutes and 30 minutes.

It is also possible to wet the elastomer with the epoxidation reagent in several steps, in which case intermediate drying may optionally be carried out between the individual steps.

As a result of epoxidation, the ethylenic double bonds react at least partially to form an oxirane ring on the surface of the elastomer, inter alia. These oxirane rings are consequently available for covalent bonding of the particles to the elastomer as functional groups.

In accordance with another variation of the method, the epoxidation is carried out in the liquid phase on an optionally pre-cross-linked latex. This latex is then moulded in order to produce the elastomer product, for example by dipping. The latex dipping may optionally be onto a pre-cross-linked, preferably photochemically pre-cross-linked, latex film, in particular in order to produce an at least double-layered elastomer product.

In this procedure, a suspension is produced from the latex. To stabilize it, at least one stabilizing agent may be added to this suspension, for example a polyethylene glycol nonyl phenylether, for example Synperonic® NP 30. The stabilizing agent may be dissolved in water and then added to the latex, or it may be added to the latex without adding more water. The total proportion of the at least one stabilizing agent may be between 2 phr and 15 phr (parts per hundred parts of rubber).

The latex may have a solids content of between 20% drc (dry rubber content) and 60% drc.

The latex may be used at a temperature of between 20°C and 60°C.

The suspension may then be rendered acidic, preferably adjusting the pH to a value of between 2 and 5, in particular between 3 and 4. In order to adjust the pH, it is preferable to use a carboxylic acid, in particular acetic acid. However, it would also be possible to use other acids, for example inorganic acids such as HCl. In this regard, it is also possible to use a buffer. Suitable buffer substances are sodium, potassium, calcium or magnesium formate, acetate or butyrate, sodium dihydrogen phosphate, disodium hydrogen phosphate or sodium, potassium, calcium or magnesium carbonate, wherein sodium carbonate is preferable.

The epoxidation reagent may either be added to this suspension or generated in it in situ.

For the first variation, once again a peracid, in particular peracetic acid, is preferably employed, although other acids may also be used, for example those specified above. The peracid may in particular be used as an aqueous solution in a concentration of between 1% by weight and 41% by weight.

Particularly preferably, a quantity of peracid is added such that the ratio of the molar concentration of peracid to the molar concentration of polyisoprene units of the elastomer is between 0.04 and 0.7.

When adding the peracid directly, the concentration may be between 4% mol and 70% mol, expressed with respect to the isoprene units.

If the peracid is produced in situ, the concentration of carboxylic acid may be between 10% mol and 120% mol, with that of H_2O_2 being between 10% mol and 120% mol, in each case with respect to the isoprene units.

When the epoxidation reagent is created in situ as described above, the oxidizing agent, in particular hydrogen peroxide, and a carboxylic acid, in particular formic acid or acetic acid, are added to the suspension. The oxidizing agent and the carboxylic acid may be added in equimolar quantities.

The carboxylic acid may in particular be used in the form of an aqueous solution in a concentration of between 20% by weight and 60% by weight.

The oxidizing agent may in particular be used in the form of an aqueous solution in a concentration of between 25% by weight and 50% by weight.

Particularly preferably, the oxidizing agent and carboxylic acid are added in a quantity such that the ratio of the concentration of peracid produced therefrom, in particular performic acid, to the concentration of polyisoprene units of the elastomer is between 0.1 and 0.3.

Epoxidation in the liquid phase may be carried out at a temperature of between 20°C (room temperature) and 80°C and/or for a period of between 20 minutes and 60 hours. Epoxidation of the latex particles is terminated by neutralization, for example with a 10% by weight potassium hydroxide solution.

The elastomer product is then produced from the suspension prepared in this manner, in particular by dipping a mould.

Moulding may optionally be carried out in several steps, for example in two to eight repetitions.

Before and/or after epoxidation, further process chemicals may be added to the treated latex such as, for example, antioxidants, stabilizers, antiozonants, anti-foaming agents, colorants, or inorganic fillers, for example chalk.

In order to produce an at least two-layered elastomer product, in a first step, a first layer is produced from an elastomer, for example using a known dipping process, and this is pre-cross-linked, in particular photochemically pre-cross-linked. After at least one optional drying and/or at least one optional washing step, the modified latex, functionalized as described above, is used to apply at least one further layer of elastomer to the initially produced elastomer layer, in particular by dipping. This is again followed by at least one drying and/or at least one washing step.

Particles are subsequently applied to the surface of the elastomer which has been epoxidized, i.e. which has been provided with epoxide groups, in particular by one of the two variations of the method, whereupon these particles become covalently bonded to the elastomer surface via the epoxide groups by means of ring opening.

In particular, inorganic solid particles are used, preferably industrially available solid particles. These particles are preferably selected from a group comprising or consisting of sulphides, oxides, hydroxides, carbonates, borates, sulphates, phosphates, silicates, and metal particles, for example gold, silver or copper. In particular, the solid particles are selected from a group comprising or consisting of chalk, diatomaceous earth, silica, kaolinite, quartz, amorphous silicic acid, SiO_2, calcite, TiO_2.

It would also be possible to use particles comprising voids, which are optionally loaded with an active substance, for example zeolites or cyclodextrins. These particles may also optionally be used to adsorb substances such as sweat, for example.

However, it would also be possible to use solid organic particles, for example at least partially consisting of starch or cellulose, covalently bonded to the elastomer surface.

Advantageously, the surface of the solid particles is functionalized prior to bonding to the epoxy groups of the elastomer surface. This functionalization may take place by generating free mercapto groups and/or free amino groups and/or anhydride groups and/or isocyanate groups and/or isothiocyanate groups and/or hydroxyl groups on the surface of the solid particles. In particular, a chemical compound may be used for this purpose which is selected from a group comprising 3-mercaptopropyl trimethoxysilane, 3-mercaptopropyl triethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-isocyanate propyltriethoxysilane, 3-isocyanate propyltrimethoxysilane, and hydroxymethyl triethoxysilane. These compounds may be obtained respectively from ABCR or Sigma Aldrich or Evonik Industries.

In this connection, it should be pointed out that the functionalized solid particles are at least for the most part widely commercially available, for example from Hoffmann Mineral or Sigma Aldrich or Evonik Industries.

However, the solid particles may also be functionalized with at least one chemical compound selected from a group comprising or consisting of silanes, siloxanes and carboxylic acids with functional groups, such as anhydride, epoxy, isocyanate, isothiocyanate or mercapto groups. Examples in this regard are (3-glycidoxypropyl)trimethoxysilane, 3-(triethoxysilyl)propylsuccinic anhydrides, and mercaptopropyltrimethoxysilane. These compounds may be obtained from ABCR or Sigma Aldrich.

The mercapto group is available in particular in the form of a thiol. For this purpose, it is preferable to use thiols selected from a group comprising or consisting of trimethylolpropane tris-3-mercaptopropionate, 16-mercaptohexadecanoic acid, (11-mercaptoundecyl)tetra(ethylene glycol), N-acetyl-L-cysteine, pentaerythritol tetramercaptoacetate, trimethylolpropane trimercaptoacetate, trimethylolpropane tri-3-mercaptopropionate, pentaerythritol tetra-3-mercaptopropionate, propylene glycol-3-mercaptopropionate, ethoxylated trimethylolpropane tri-3-mercaptopropionate, polyol-3-mercaptopropionate, and polyester-3-mercaptopropionate. These compounds are available from Bruno Bock Thiochemicals and/or Sigma Aldrich, for example.

In addition to these preferred chemical compounds containing a mercapto group, it would also be possible within the context of the invention to use other compounds of this type, for example HS-R1R2R3, where R1 is an element from the group comprising or consisting of alkyl, aryl, alkylaryl, arylalkyl, alkylarylalkyl, arylalkylaryl, silyl-groups, R2 is an element from the group comprising or consisting of acryl, amino, amino acid, anhydride, carbonyl (C=O), carboxylic acid, carboxylate, epoxy, hydroxyl, isocyanate, isothiocyanate, methacryl, mercapto, sulphonic acid, vinyl groups, and R3 is an element from the group comprising or consisting of H, alkyl and aryl groups.

In particular, the amino group is used in the form of primary amines. To this end, it is preferable to use amines which are selected from a group comprising or consisting of 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, and N-2-(aminoethyl)-3-aminopropyl triethoxysilane.

However, the scope of the invention also encompasses the use of non-functionalized particles, especially if these are already provided with functional groups due to their chemical structure.

For the purposes of functionalization, the at least one thiol and/or amine and/or anhydride and/or isocyanate and/or isothiocyanate and/or the compound containing the hydroxyl groups is/are dissolved in a solvent, in particular water; it is also possible to use organic solvents. The concentration of the at least one thiol and/or amine and/or anhydride and/or isocyanate and/or isothiocyanate and/or the compound containing the hydroxyl groups and/or of the at least one chemical compound which is selected from the group comprising or consisting of silanes, siloxanes and carboxylic acids containing functional groups, such as anhydride, epoxy, isocyanate, isothiocyanate or mercapto groups, may be between 0.1% by weight and 50% by weight, in particular between 0.5% by weight and 15% by weight, in each case expressed with respect to the total weight with the (inorganic) particles.

The respective particles used for functionalization are then added to this solution.

The solid particles may be functionalized at a temperature of between 0°C and 200°C and/or for a period of between 5 minutes and 720 minutes and/or at a pH between 3 and 6. Functionalization preferably takes place with stirring.

The reaction itself may be carried out in both aqueous media and in liquid organic media, for example ethanol, toluene, cyclohexane, hexane, or isopropanol. One possible process sequence is diagrammatically illustrated in Figure 1, wherein amino-functionalized SiO_2 particles are used as the particles.

The advantage of this strategy is that it means that non-covalently bonded particles can be removed in a quantitative manner because the tackiness of the elastomer surface is substantially reduced in the first step by saturation of the unsaturated carbon-carbon bonds.

The functionalized particles are suspended in water or an organic solvent. The suspension is preferably produced in a concentration of between 0.01% by weight and 10% by weight, in particular between 0.01% by weight and 1% by weight, of particles modified with amino group(s) and/or mercapto group(s) and/or carboxylic acid group(s) and/or epoxide group(s) and/or hydroxyl group(s) and/or anhydride group(s) and/or isocyanate group(s) and/or isothiocyanate group(s) by means of commercially available dispersing equipment. Thereafter, this suspension is placed in contact with the functionalized elastomer surface, for example by immersing the elastomer in the suspension. This may optionally be carried out several times. In this regard, it would also be possible for the elastomer to be only partially immersed. If dipping is carried out multiple times, this partial immersion may be limited to one or more dipping steps, and it is also possible to opt for only partial immersion in all of the dipping steps.

The elastomer which has been treated in this manner may then be dried. To this end, the temperature may be selected to be in the range 40°C to 150°C, in particular in the range 40°C to 100°C. Drying may take place for a period of between 5 minutes and 1000 minutes, in particular for a period of between 10 minutes and 900 minutes.

The solid particles become covalently bonded to the elastomer surface during the drying process.

After bonding, particles which are purely adhesively bonded are preferably removed from the surface of the elastomer product, for example by washing and/or mechanically, for example by means of ultrasound.

The solid particles used for the purposes of the invention preferably have a particle size of between 10 nm and 10 µm, in particular between 20 nm and 50 nm or between 1 µm and 5 µm.

In principle, it is possible to use at least one type of particle for the entire surface of the epoxidized elastomer—it would also be possible to use at least two different types of particles, for example both quartz and zeolite, in order to obtain a different profile of properties for the elastomer.

To this end, in accordance with one variation, however, the particles may be disposed only in discrete regions on the elastomer surface. In order to obtain this, the region of the elastomer surface which does not have to be further functionalized is covered by means of an appropriate mask so that during a subsequent washing step, the non-covalently bonded particles are washed away.

In this respect, in another embodiment, it is also possible to apply the particles to only discrete regions.

The mask may be a mechanical mask or a chemical mask or an optical mask. The term "chemical mask" should be understood to mean a substance which is applied to the regions which are not to be coated, for example by painting, before applying the respective suspensions or emulsions or solutions.

Similarly, it is also possible for the elastomer to be epoxidized only in the regions provided with the particles, in which case appropriate masks may be used for this purpose, as discussed above.

In addition to providing the pure surface structuring, it is also possible, for example, to apply permanent information to the elastomer product, for example the glove size in the case of elastomer gloves.

In accordance with another embodiment, the particles may be at least partially cross-linked with one another following covalent bonding to the elastomer surface.

This cross-linking may be accomplished by means of unreacted functional groups of the functionalized particles described above, in which case an additional reagent may optionally be used which reacts with these functional groups and thus produces a bond between the particles.

However, it is also possible to use multi-functional thiols and/or amines and/or anhydrides and/or isocyanates and/or isothiocyanates, i.e. chemical compounds containing more than one mercapto and/or amino or carboxylic acid group and/or epoxide group and/or hydroxyl group and/or anhydride group and/or isocyanate group and/or isothiocyanate group such as, for example, trimethylolpropane-tris-3-mercaptopropionate, thereby enabling free mercapto groups to be generated at least on the surface of the previously epoxidized elastomer, which will allow another reaction to occur with other chemical compounds in order to further modify the properties of the elastomer product.

In addition to the embodiment in which chemical compounds with multiple homofunctionality are used, i.e. compounds having exclusively mercapto groups as functional groups in the molecule, another possibility is to use multi-functional chemical compounds with heterofunctionality. In the case of these compounds, for example, in addition to at least one mercapto group by means of which the compound is bonded to the particle surface, at least one other functionality is provided, for example an amino group, a carboxylic acid group, an epoxide group, a hydroxyl group, an anhydride group, an isocyanate group, an isothiocyanate group, a vinyl group, and mixed variations are also possible, in which case more than one of these groups is present in addition to the mercapto group or groups, for example a carboxylic acid group and an amino group.

When using multi-functional thiols or multi-functional amines or multi-functional polycarboxylic acids, polyalcohols, polyacetals, therefore, reactive groups may also be generated on the surface of the particles, for example further thiol groups or amino groups or carboxylic acid groups.

It is also possible to use polymers containing functional groups (alkenes, acrylates, anhydrides, epoxides, isocyanates, isothiocyanates, methacrylates, thiols) in order to modify the particles in order to obtain a covalent bond to the elastomer surface. The polymers may be used in dispersion, in solution and as a pure substance.

The functional groups may be present as side groups or end groups.

The reactive groups may be used to provide the functionalized particles with other chemical compounds which are capable of reacting with these groups.

The other chemical compound may be selected from a group comprising acrylates, amines, amino acids (cysteine), acetylated amino acids (N-acetyl cysteine), anhydrides, carboxylic acids, ethers, epoxides, isocyanates, isothiocyanates, methacrylates, silanes, and siloxanes. This therefore provides an additional improvement to the lubrication properties or can introduce another functionality (for subsequent reactions).

Depending on the reaction partner, this reaction may take place at a temperature of between 20°C and 80°C and on the basis of known reaction mechanisms. How long this reaction will take also depends on the respective specific compounds used for the reaction and may be between 1 minute and 100 minutes. The reaction may optionally be carried out under pressure or under vacuum.

In accordance with another embodiment of the invention, the functional groups on the particle surface which are not needed for covalent bonding to the elastomer are covalently bonded to a polymer layer in at least certain regions.

By way of example, the polymer layer may be produced from a polyurethane or a silicone or a mixture of SBR with silicone or an acrylate or a siloxane or a polymer with functional groups.

in particular alkenes, acrylates, anhydrides, epoxides, isocyanates, isothiocyanates, methacrylates, thiols, alcohols, and carboxylic acids. The polymers or monomers used to form the polymer layer may if appropriate be functionalized beforehand, in particular with at least one type of the functional groups mentioned above.

Preferred polymers are silicones, polyurethanes, urethane acrylates, acrylates, polyisocyanates, polyesters, polyols, vinyl polymers, and diene elastomers. Examples of these are Desmophen® 1652, Synthomer VL 11005, Desmolux® XP 2740, Bayhydrol® UV XP 264, Desmolux® VP LS 2299, polyvinyl alcohol, polyacrylic acid, obtainable from Bayer or Synthomer.

Again, suspensions are produced from the optionally functionalized polymers or monomers or oligomers (for functionalization purposes, the respective reagent may be added to this suspension), and at least one emulsifier and/or at least one photoinitiator may be added if the monomers or oligomers are to be photochemically cross-linked.

The particles may also be used to apply and/or incorporate at least one active substance. Examples of possible active substances are antiperspirants, antibacterial active substances, fungicides, odorants, skincare products such as a vitamin or aloe vera, pigments, active substances for modifying water absorption behaviour, stabilizers, etc.

The method proposed by the invention is used to functionalize the functionalization, i.e. the functionalized elastomer surface. The functional groups disposed on the surface as a result of the first functionalization therefore act as anchor groups for the other functionalization.

Using the method proposed by the invention, elastomer products can be manufactured which have a better lubrication and a better resistance to aging compared with an untreated elastomer. Furthermore, it is also possible to influence properties such as a skincare effect, water absorption behaviour, etc., and completely new properties can be imparted to the elastomer product, such as structured elastomer surfaces, smell, colour, "look and feel", for example.

The coefficient of friction of NR surfaces modified with particles was determined using tribological measurement methods employing a linear tribometer as specified by B. Bhushan, Modern tribology handbook, CLC-Press, Boca Raton, London, New York, Washington D.C. 2001, and compared with the properties of commercially available surgical gloves. The results set out in the table below demonstrate that the coefficients of friction of elastomer surfaces modified with particles fall within the range of powdered NR surfaces.

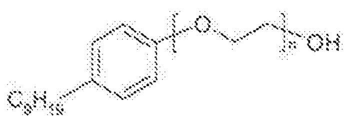
Comparison of the coefficients of friction of selected NR surfaces

Sample description	Coefficient of friction, m
Prior art glove with chlorinated interior	m ~ 0.31
Prior art glove with coated interior	m ~ 0.22
Prior art glove with powdered interior	m ~ 0.50
NR surface modified with functionalized SiO_2 particles	m ~ 0.7

A description will be provided below of a few examples worked through during the development of the invention; they should not be construed as being restrictive.
The chemicals used for these examples are set out in Table 1.

Table 1: Materials and chemicals employed

Chemical	Manufacturer	Structural formula, specifications
Aktisil AM	Hoffmann Mineral	Amino-modified SiO_2 particles (d_{50} = 2.2 µm)
Aktisil MM	Hoffmann Mineral	Mercapto-modified SiO_2 particles (d_{50} = 2.2 µm)
Nanoparticles	Sigma Aldrich	Amino modified SiO_2 particles (d_{50} = 20 nm)
Conc. peracetic acid (39%)	Sigma Aldrich	
Formic acid	Sigma Aldrich	

H_2O_2	Sigma Aldrich	
Synperonic NP 30	Sigma Aldrich	

1. Modification of the dried film surface

1.1 Epoxidation with peracids

During epoxidation of the NR films, the following steps were carried out:

- washing the dried latex film in deionized water (10 min at RT (= room temperature, = 20°C))
- epoxidizing the washed latex film in an aqueous peracetic acid solution (2% by weight) at 40°C for 40 min
- briefly immersing the epoxidized latex film in deionized water (1 min at RT)
- drying at 70°C for 15 min.

1.2 Epoxidation of the liquid phase

1.2.1 Epoxidation with peracids

During epoxidation of the liquid NR latex, the following steps were carried out:

- stabilizing the NR latex with Synperonic NP 30 (10 phr) and adjusting the solid content to 20-60% by weight
- acidifying the latex with acetic acid to a pH of 3-4
- optionally, adding peracetic acid (39% solution); the molar concentration ratio was as follows:

$$\frac{[Peracid]}{[Polyisopreneunit]} = 0.07 - 0.5$$

or 0.07% mol to 0.5% mol peracetic acid with respect to the isoprene units,

or in-situ formation of performic acid using H_2O_2 and formic acid in a molar concentration ratio of:

$$\frac{[H_2O_2]}{[Polyisopreneunit]} = \frac{[HCOOH]}{[Polyisopreneunit]} = 0.2 - 1.0$$

- reaction temperature 21°C - 60°C
- reaction time from 3-48 h
- terminating the reaction by neutralization with a KOH solution (10% by weight).

As an example, 4 g of Synperonic was dissolved in 33.2 g H_2O at 40°C and added to 67 g of NR(60% drc). This mixture was stirred for 15 hours. The pH was then adjusted to approximately 4 and 28.44 g of HCOOH (98-100%) and 33.26 g of H_2O_2 (30-%) were slowly added.

2. Producing films formed by epoxidized NR latex

The corresponding latex films were produced in a two-layer dipping process:

- dipping a porcelain mould in a pre-cross-linked NR latex (20 s at RT)
- drying for 0-15 s at 120°C
- dipping the epoxidized NR latex (30 s at RT)
- drying for 20 min at 120°C
- stripping film.

3. Coupling of inorganic particles

Example 1: Implementation in aqueous systems

During the process of coupling inorganic SiO_2 macroparticles, the following process steps were carried out:

- producing an aqueous suspension with 0.015-0.5% by weight of commercially available amino-or mercapto-modified SiO_2 macroparticles by weighing the particles in deionized H_2O
- dispersing the suspension with a dispersing device (Ultraturax) for 10 min at room temperature and then in the ultrasound bath for 10 min at room temperature
- fixing an epoxidized NR latex film in a Petri dish
- pouring the aqueous suspension over the elastomer film
- removing the film from the Petri dish after 2 min
- drying the sample for 10-900 min at 40-100°C
- washing the film in water at room temperature for 16 h
- drying the film for 10-15 min at 70°C.

Example 2: Implementation in organic solvents

- Preparing a suspension with 0.015-0.2% by weight of amino- or mercapto-modified SiO_2 macroparticles in toluene
- dispersing the suspension in the ultrasound bath for 10 min at room temperature
- pouring the suspension over the elastomer film, preventing the film from floating up with the aid of tweezers
- removing the film from the Petri dish after 2 min
- drying the sample for 10-900 min at 40-100°C
- washing the film in toluene at room temperature for 16 h
- drying the film for 10-15 min at 70°C.

Example 3: Coupling of nanoscale particles

- Preparing a suspension with 0.015-0.05% by weight of amino-modified SiO_2 nanoparticles (suspended in ethanol) in toluene
- dispersing the suspension in the ultrasound bath for 30 min at room temperature
- pouring the suspension over the elastomer film, preventing the film from floating up with the aid of tweezers
- removing the film from the Petri dish after 2 min
- drying the sample for 10-900 min at 40-100°C
- washing the film in toluene at room temperature for 16 h
- drying the film for 10-15 min at 70°C.

On a commercial scale, the transformation of the method may be implemented directly, for example on a chain dipping plant by dipping the gloves on the mould into the particle dispersion. In this regard, it is advantageous if the particles are dispersed in the corresponding dipping tank, at least part of the time, preferably all the time, and consumed particles are topped up. Thermal coupling may take place when drying or optionally vulcanizing (in the case of S-vulcanized gloves) the gloves in the oven. The elastomer products may then be washed with water in order to remove non-bonded particles.

Alternatively, the particles may also be applied by dipping the gloves (on the mould) into a slurry of particles.

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Elasztomer termék kovalensen kötött részecskékkel

Szabadalmi igénypontok:

1. Eljárás szervetlen vagy szerves szilárd részecskék elasztomer kesztyű felületéhez való kötésére, az elasztomer a molekulaszerkezetben tartalmaz olyan telítetlen szén-szén kötéseket, amelyek legalább részben, epoxidálással telítve lettek legalább az elasztomer kesztyű felületi régiójában, azzal jellemezve, hogy a szilárd részecskék kovalensen kötődnek az epoxidcsoportokhoz az elasztomer felület epoxidálása után.

2. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy a szilárd részecskék felülete funkcionalizálva van a reakció előtt.

3. A 2. igénypont szerinti eljárás, azzal jellemezve, hogy a szilárd részecskék funkcionalizálását szabad merkaptocsoportok és/vagy szabad aminocsoportok és/vagy karboxilcsoportok és/vagy epoxidcsoportok és/vagy hidroxicsoportok és/vagy anhidridcsoportok és/vagy izocianátcsoportok és/vagy izotiocianátcsoportok kialakításával valósítjuk meg a szilárd részecskék felületén.

4. A 2. vagy 3. igénypont szerinti eljárás, azzal jellemezve, hogy a szilárd részecskéket legalább egy kémiai vegyület segítségével funkcionalizáljuk, amelyet a 3-aminopropiltrimetoxiszilán, 3-merkaptopropiltrietoxiszilán, hidroximetiltrietoxi-szilán, 3-izocianáto-propiltrimetoxiszilán, 3-glicidoxipropiltrimetoxiszilán, 3-(trietoxiszilil)propilborostyánkősav-anhidrid által alkotott csoportból választunk.

5. Az 1-4. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy a tapadással kötött szilárd részecskéket eltávolítjuk az elasztomer felületéről.

6. Az 1-5. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az elasztomer epoxidálását szilárd felületen végezzük.

7. Az 1-6. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az epoxidálást latexen folyadék fázisban végezzük.

8. Az 1-8. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az epoxidálást az elasztomer diszkrét régióiban végezzük.

9. Elasztomer kesztyű felülettel rendelkező elasztomerből, amelynél az elasztomer a molekulaszerkezetében tartalmaz telítetlen szén-szén kötéseket, azzal jellemezve, hogy a felület tartalmaz olyan szervetlen vagy szerves szilárd részecskéket, amelyek legalább részben kovalensen kötöttek az elasztomerhez.

10. A 9. igénypont szerinti elasztomer kesztyű, amely legalább két réteget tartalmaz.

11. A 9. vagy 10. igénypont szerinti elasztomer kesztyű, azzal jellemezve, hogy a szilárd részecskék csak a felület diszkrét régióiban vannak elrendezve.

12. A 9-11. igénypontok egyike szerinti elasztomer kesztyű, azzal jellemezve, hogy a szilárd részecskék részecskeátmérője 10 nm és 10 μm közötti.

13. A 9-12. igénypontok egyike szerinti elasztomer kesztyű, amelynél a szilárd részecskék legalább részben egymással térhálósítva vannak.

14. A 9-14. igénypontok egyike szerinti elasztomer kesztyű, azzal jellemezve, hogy a szilárd részecskék magukban foglalnak legalább egy hatóanyagot.

Fig.1