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(54) **Eljárás térhálós elasztomer előállítására**

Description

Process for making a crosslinked elastomer

The invention relates to a method for producing a crosslinked elastomer by radiating a polymer dispersion consisting of at least one crosslinkable polymer with electromagnetic irradiation in the ultraviolet (UV light) and/or visible spectral region, wherein crosslinking is carried out in at least two stages as pre-crosslinking and post-crosslinking, and at least one photoinitiator is added to the polymer dispersion to initiate the crosslinking reaction prior to pre-crosslinking, to a method for producing a dipped article produced from at least a latex, in particular a glove or a condom, in which a former with an external contour which corresponds to the dipped article to be produced is immersed for a predefinable period in a dipping tank containing the at least one latex, and thereafter the dipped article is solidified and/or dried, to a device for producing a dipped article produced from a latex, comprising a reactor, at least one dipping former and at least one dipping tank, wherein at least a first irradiation source is associated with the reactor for emitting electromagnetic irradiation in the ultraviolet (UV light) and/or visible spectral region, as well as to a glove produced from a crosslinked elastomer.

In order to provide elastomers with specific elastic properties, the polymer chains of the elastomer have to be at least partially cross-linked with each other. Usually, crosslinking is carried out via double bonds which are located either in the main chain of the elastomer such as, for example, with polyisoprene, polybutadiene, styrene-butadiene rubber, chloroprene or nitrile-butadiene rubber, or in a side chain such as with EPDM, for example. Until now, commercial crosslinking of elastomers, including rubber latex, has been carried out in three different manners, namely by sulphur crosslinking, peroxide crosslinking or by irradiation crosslinking methods.

Further, a method for producing gloves by UV crosslinking of a rubber is known from the Applicant's document EP 1 762 586 A2. In that document, latex is exposed to UV irradiation in a falling film reactor and thereafter the gloves are dipped in the usual manner. Here again, the option of post-crosslinking is discussed, but not gone into in detail. Advantageously in that case, conventional process chemicals such as, for example, the organosulphur compounds that are discussed do not have to be used, and so the risk of contact allergies from gloves of this type can be reduced.

The aim of the present invention is to further improve this UV crosslinking method.

This aim of the invention is accomplished by the following – taken independently: - by the method according to the invention, at least one photoinitiator is also added to the pre-crosslinked polymer dispersion prior to and/or during post-crosslinking and in addition, post-crosslinking is carried out with electromagnetic irradiation in the ultraviolet (UV light) and/or visible spectral region; - and by the method for producing a dipped article wherein the latex is cross-linked in accordance with this method, - by a device wherein an additional irradiation source is disposed after the at least one dipping tank for emitting electromagnetic irradiation in the ultraviolet (UV light) and/or visible spectral region, and – by a glove which is produced in accordance with this method and has a tear strength of at least 14 N/mm^2, in particular at least 20 N/mm^2, preferably at least 25 N/mm^2.

Surprisingly, it has been found that by dividing UV crosslinking into two individual cross-linking stages, namely pre-crosslinking and post-crosslinking, wherein both partial crosslinking stages are carried out by means of irradiation in the UV and/or visible range, the mechanical strength of the elastomer films, in particular the tear strength, can be improved over one-off irradiation with UV light. In addition, this division can improve process control during the production of gloves, because film formation can be improved at the pre-crosslinking stage. As before, the products produced thereby, for example examination gloves, surgical gloves, condoms, catheters, infusion tubes, anaesthesia masks, etc., have a low or zero type IV allergy potential. In addition, the aging resistance of the elastomer can be improved. Additionally, the elastomer products exhibit improved stability to high energy radiation. This is important, in particular with regard to sterilization of medical products with gamma radiation. In addition, the total energy consumption, which is already lower because UV crosslinking can be carried out at room temperature, can be significantly reduced compared with alternative cross-linking methods because the crosslinking is divided up in this manner. Furthermore, by means of post-crosslinking, any concentrations of residual chemicals which might be present can be reduced by covalently binding the residual chemicals to the latex. Because of the higher tear strengths of the films, they can be produced with a smaller wall thickness, whereupon the operating efficiency of the method can be improved.

According to one variational embodiment, the amount of the at least one photoinitiator added for pre-crosslinking is a maximum of the same, preferably less than the amount of the at least one photoinitiator which is used for post-crosslinking. In this manner, formation of a film, for example on the glove former during the dipping process, may be improved, since during pre-crosslinking an intermediate product is produced the mechanical strength of which is still much lower than that of the end product, in particular because of the smaller number of crosslinking sites, and thus the flow behaviour of the latex or gel has a positive effect on the particularly uniform film formation.

However, it should be noted that the added amount of photoinitiator or photoinitiators for pre-crosslinking is greater than for post-crosslinking, although the aforementioned variational embodiment is preferred.

Particularly when producing medical latex products, in particular gloves, it has been shown to be advantageous if, with a view to obtaining balanced mechanical properties, in particular a desired strength with corresponding relaxation of the glove, i.e. reduction of the pressure or force on the hand after extension brought about by donning the glove, thus preventing the wearer from having a "feeling of constriction" or in order to ensure a suitable level of tactility for the glove wearer, in the reaction for crosslinking the latex or the latex mixture, the proportion of the at least one photoinitiator in the polymer dispersion for pre-crosslinking is between 0.2 phr and 5.0 phr or if, in a further variational embodiment, the proportion of the at least one photoinitiator in the polymer dispersion for post-crosslinking is between 0.5 phr and 5.0 phr. Below the lower limit, not enough crosslinking occurs for the desired mechanical properties to be obtained. Concentrations of more than 5.0 phr for pre- or post-crosslinking have a negative effect on the efficiency of the method and further, the crosslinking site density is too great.

To improve the tear strength and also for reasons of efficiency, it is also advantageous if the proportion of the at least one photoinitiator at the polymer dispersion for pre-crosslinking is between 0.5 phr and 3.5 phr, in particular between 0.75 phr and 1.2 phr or if, according to a further variational embodiment, the proportion of the at least one photoinitiator at the polymer dispersion for post-crosslinking is between 0.8 phr and 3.75 phr, in particular between 1 phr and 1.5 phr.

Preferably, the polymer dispersion for pre-crosslinking is irradiated at least twice. Surprisingly, after being irradiated twice or three times, the finished elastomer has more homogenous properties such as mechanical tear strength, for example. In addition, the device of the invention may comprise two or three reactors in the flow direction of the latex disposed one behind the other, in order to allow continuous production. In experiments with four or more exposure cycles, it was discovered that the tear strength of the finished product does not change to an extent such that the efficiency of the method is reduced. In addition, over-crosslinking during the pre-crosslinking phase might also be observed. In the case of a one-off irradiation step, the tear strength may be lower because of less pre-crosslinking.

Preferably, a photoinitiator is used which is selected from a group comprising 2-hydroxy-2-methyl-1-phenylpropanone (trade name: Genocure DMHA; Rahn AG), phenylglyoxylic acid methyl ester, 2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester (trade name: Lucirin TPO L; BASF), methylbenzoylformate (trade name: Genocure MBF; Rahn AG), 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-methyl-1-propanone-1-one (trade name: Irgacure 2959; Rahn AG), 2-dimethylamino-2-(4-methylbenzyl)-1-(4-morpholin-4-ylphenyl)-butane-1-one (trade name: Irgacure 379; CIBA), 2 methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one (trade name: Irgacure 907; CIBA), 2,4,6-trimethylbenzoyldiphenylphosphine oxide (trade name: Lucirin TPO; BASF). On the one hand, good skin tolerance is advantageous, as well as it being harmless as regards food, so that no problems arise if small amounts remain in the finished elastomer, which means that the process, i.e. the washing steps, can be simplified. In addition, said photoinitiators have a high reactivity, so that efficient crosslinking may be carried out with a lower irradiation power or lower photoinitiator concentration; the process costs can also be reduced. In addition, these photoinitiators have high thermal stability. Lucirin TPO (L) and Genocure DMHA also have the advantage that they are available in liquid form and thus can be emulsified more easily in aqueous systems with additional process chemicals such as stabilizers, for example. Furthermore, the absorption range of Lucirin TPO L extends to over 400 nm, so that longer wavelength light may be used for irradiation. This has the further advantage that the irradiation can also penetrate into lower layers. In this manner, thicker-walled or heavily pigmented elastomer films or products may be produced.

According to one variational embodiment of the invention, pre-crosslinking is carried out on a film, in particular if natural rubber is crosslinked. Preferably, the layer is between 0.1 mm and 2 mm thick. In this manner, types of latex which have a high or higher absorption can also be processed continuously. Thin layers during pre-crosslinking mean that the layer to be irradiated can be penetrated almost homogenously.

In particular, the layer thickness of the film during pre-crosslinking is between 0.3 mm and 0.6 mm.

Using at least two irradiation sources for post-crosslinking means that more homogenous dose distributions may be obtained with three-dimensionally shaped products such as gloves, for example, even on a commercial scale. As an example, between three and eight, in particular six emitters are disposed in the device in the process direction one behind the other. Clearly, however, more than eight emitters may be provided.

Carrying out post-crosslinking with a higher irradiation dose than pre-crosslinking is also advantageous. In this manner, lower degrees of crosslinking are made possible during pre-crosslinking, whereby film formation on a dipping former can be improved; the latex particles flow better into one another and can fuse together, and higher tear strengths may subsequently be obtained because of the higher irradiation dose during post-crosslinking.

In this case it is of particular advantage, for example when crosslinking IR latex, for post-crosslinking to be carried out with an irradiation dose which is between 150% and 500% of the irradiation dose for pre-crosslinking.

Preferably, post-crosslinking is carried out with an irradiation dose which is between 200% and 300% of the irradiation dose for pre-crosslinking.

For pre-crosslinking and/or post-crosslinking, at least one co-crosslinking agent with at least one thiol group is added to the latex or the pre-crosslinked latex. In this manner, crosslinking is possible via a (radical) thiol-ene reaction, whereby oxygen inhibition of crosslinking can be reduced, so that crosslinking can be carried out in air. In addition, the gel point is delayed,

whereupon more crosslinking and therefore a higher mechanical tear strength may be obtained.

For the aforementioned reasons regarding the ratios of the amount of photoinitiator for pre-crosslinking and post-crosslinking, it is advantageous for the added amount of the at least one co-crosslinking agent for pre-crosslinking to be a maximum of the same, preferably less than the amount of the at least one co-crosslinking agent which is used for post-crosslinking, wherein the proportion of the at least one co-crosslinking agent for the polymer dispersion for pre-crosslinking is preferably between 0.5 phr and 2.0 phr and the proportion of the at least one co-crosslinking agent for the polymer dispersion for post-crosslinking is between 0.5 phr and 2.5 phr.

In order to improve the tear strength and for economic reasons as well, it is also advantageous for the proportion of the at least one co-crosslinking agent for the polymer dispersion for pre-crosslinking to be between 0.1 phr and 1.5 phr or between 0.2 phr and 1.2 phr and, in a further variational embodiment, for the proportion of the at least one co-crosslinking agent on the polymer dispersion for post-crosslinking to be between 0.9 phr and 2 phr or between 1.2 phr and 1.5 phr.

Preferably, trimethylolpropane-tris-3-mercaptopropionate or pentaerythritol tetrakis-3-mercaptopropionate is used as the co-crosslinking agent, as they have a relatively high reactivity; trimethylolpropane-tris-3-mercaptopropionate has a higher reactivity than pentaerythritol tetrakis-3-mercaptopropionate, but pentaerythritol tetrakis-3-mercaptopropionate has the advantage that it is approved for coming into contact with foodstuffs. In addition, pentaerythritol tetrakis-3-mercaptopropionate has the advantage that the risk of over-crosslinking is lower, so that in this manner, a third exposure cycle during pre-crosslinking is possible. When employing two exposure cycles, however, trimethylolpropane-tris-3-mercaptopropionate has advantages over the use of pentaerythritol tetrakis-3-mercaptopropionate, but in principle, using both co-crosslinking agents is possible, even both at the same time.

Surprisingly, at least one antioxidant may be added to the pre-crosslinked polymer dispersion prior to post-crosslinking, whereby not only can the resistance to aging per se be improved,

but in this manner it is also possible to improve the resistance of the elastomer to high-energy irradiation, such as for sterilization, for example.

Particular antioxidants which may be used are vitamin E and/or sterically hindered phenolic compounds such as, for example, butylated reaction products of p-cresol and dicyclopentadiene (RALOX® LC, Fa. Solvadis). Vitamin E (α-tocopherol) is a known radical scavenger. In addition, it has the advantage that it is harmless to humans, and so the user of the finished elastomer articles, for example gloves, can enjoy additional benefits. Moreover, vitamin E also has the advantage that it only slightly inhibits the thiol-ene reaction.

In order to increase the efficiency of post-crosslinking, it is advantageous if, between pre-crosslinking and post-crosslinking, the pre-crosslinked elastomer is dried to a maximum residual moisture content of 6%. In this manner, light scattering of the latex film is reduced, so that the excitation light can penetrate into deeper layers.

To improve this effect further and thus to increase the tear strength further, it is advantageous if drying is carried out to a maximum residual moisture content of 4% with respect to the film.

Prior to pre-crosslinking, at least one surfactant with at least one photochemical active centre can be added to the polymer dispersion, in particular with a double bond, for example linoleic acid, in order to improve film formation of the latex.

For crosslinking, in particular post-crosslinking, a mercury high pressure vapour lamp doped with gallium may be used for irradiation. Doping with gallium displaces the emission range of the lamp to longer wavelengths which may extend into the visible range. In this manner, deeper-lying layers of the latex can be cross-linked more effectively, in particular when using Lucirin TPO L. It has also been shown that the surface of the latex film is damaged less by an ozone attack, so that the resistance to aging can be further improved.

It is also possible for post-crosslinking to be carried out in an inert gas atmosphere, for example argon or nitrogen, in order to avoid deterioration of the surface properties by the influence of oxygen.

In the method for producing a dipped article, shaping of the latex by immersing the former into the dipping tank may be carried out between pre-crosslinking and post-crosslinking of the latex, whereupon better film qualities are obtained.

It is advantageous in this case if post-crosslinking is carried out on the former, i.e. the film is located on the former during post-crosslinking. Although homogenous irradiation is more difficult in this case, this procedure has the advantage that the films do not have to be removed from the formers, so that on the one hand the efficiency of the method can be improved, and on the other hand problems with handling sticky films can be avoided. It has proved to be advantageous if the former is aligned at different angles to the irradiation source during post-crosslinking. In this manner, the homogeneity of the irradiation can be improved; in particular, shadowing effects due to the three-dimensional nature of the product can be avoided more effectively.

According to one variational embodiment of the device, a rolling unit is disposed after the at least one dipping tank, by means of which the dipped articles can be rolled at least partially, in particular with gloves on the open end of the shaft, and in that the additional irradiation source is assigned to the rolling unit. In this manner, the dipping former and the elastomer film located thereon are not only irradiated during the translational advance movement, but also, a rotational movement is superimposed over the translational movement, whereupon the elastomer film can be irradiated more homogenously over the glove surface, in particular as regards the dose distribution. In this case, the speed of the translational advance movement may be between 1 m/min and 25 m/min; that of the rotational movement may be between a 25 U/m feed rate and 50 U/m feed rate.

For the aforementioned reasons, for pre-crosslinking, at least two reactors each with at least a first irradiation source are preferably disposed one behind the other in the process direction in the device.

At least one container which possibly comprises an agitator may be disposed between the two reactors of the device. It is thus possible to dose or add process chemicals subsequently or simultaneously and in a simple manner between the two exposure cycles.

It should be noted at this point that additional reactors may also be used, for example a third reactor, in order to be able to carry out cleaning of one of the two other reactors in a continuous reaction procedure.

It is possible to use a spectral region for crosslinking with wavelengths selected from a range with a lower limit of 150 nm, in particular 250 nm, preferably 275 nm, and an upper limit of 600 nm, in particular 475 nm, preferably 400 nm.

In addition to the aforementioned photoinitiators, other photoinitiators may also in principle be used which react appropriately in the ultraviolet and/or visible spectral region, in particular in the blue region of the visible spectral region adjoining the UV range. Examples of this are included in EP 1 762 586 A2 cited above.

In addition to the preferred co-crosslinking agents mentioned above, other co-crosslinking agents may also be used in order to improve crosslinking. As an example, at least one selenol may be used as the co-crosslinking agent such as, for example, 1,6 hexane diselenol, or other thiols, in particular multifunctional compounds or derivatives thereof such as, for example, bis-thiols, for example 1,6-hexane dithiol, tristhiols, bis-selenols, tris-selenols, as well as mixtures thereof.

In the method according to the invention, at least one additional auxiliary agent may be used, selected from a group comprising acrylates, in particular multifunctional acrylates such as, for example, hexane diol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), compounds with vinyl or allyl groups such as, for example, triallyl cyanurate, triallyl isocyanurate, as well as mixtures thereof such as, for example, at least one said acrylate, in particular a multifunctional acrylate, with at least one said compound with vinyl or allyl groups, in order to improve the crosslinking behaviour thereby; again, multifunctional compounds are preferred. Such crosslinking (auxiliary) agents may be included in a proportion of up to 10 phr in the polymer dispersion for pre-crosslinking and/or in the polymer dispersion for post-crosslinking.

It is also possible to add at least one sensitizer in order to transfer the light energy more effectively to the photoinitiator and thus accelerate the crosslinking reaction as a whole, or to have

a positive influence on the process, or to make it possible thereby to use photoinitiators which absorb in a different absorption range than would be advantageous for the desired reaction.

The at least one sensitizer may be selected from a group comprising organic dyes such as eosin, aromatic ketones such as benzophenone or thioxanthone for example, condensed aromatic compounds such as anthracene or chrysene for example, inorganic pigments such as zinc phthalocyanine or titanium oxide, as well as mixtures thereof, since these compounds, in particular with the photoinitiator(s) used, interact in a suitable manner.

The proportion of sensitizers is preferably within a range with a lower limit of 0.1% and with an upper limit of 50% of the amount of photoinitiator, or within a range with a lower limit of 10% and with an upper limit of 40% of the amount of photoinitiator, or a range with a lower limit of 15% and an upper limit of 25% of the amount.

The at least one photoinitiator and/or the at least one co-crosslinking agent and/or the at least one sensitizer may be pre-emulsified or predispersed prior to addition to the at least one latex to form a pre-emulsion or pre-dispersion; for this purpose, in order to improve the dispersing or emulsion behaviour of these components, at least one emulsifier or at least one dispersing agent may be added, wherein particularly preferably, a surfactant is used as the emulsifier or dispersing agent, in particular polyethylene glycol sorbitan monolaurate. In this manner, introduction of said components into the, in particular liquid, latex phase is simplified and in this manner too, "equal distribution" of these components through the whole of the liquid phase may be obtained, whereupon higher reaction speeds, i.e. higher conversions per time unit, and thereby shortening of the method may be obtained.

This pre-emulsion or pre-dispersion may be added to the latex or latex mixture at least in part prior to the crosslinking reaction. Similarly, it is possible to add at least a portion of it during the crosslinking reaction or between the exposure cycles of pre-crosslinking. In this manner, the crosslinking behaviour, in particular the start of the crosslinking reaction, of various latex types may be reacted appropriately and the consumption of auxiliary components or starter components may be adapted more effectively to the respectively desired degree of crosslinking. In particular, the degree of crosslinking of the latex or the latex mixture can also be adjusted more effectively thereby.

The at least one latex to be cross-linked according to the invention may be selected from a group comprising natural rubber (NR), polyisoprene-latex (IR), nitrile butadiene rubber latex (NBR), chloroprene-latex (CR), styrene-butadiene latex (SBR), latices of ethyl acrylate copolymers (ACM), latices of elastomers which are produced by re-emulsification, latices of functional copolymers such as, for example, photoinitiator-containing and/or carboxylated latices, latices produced from polymer blends, as well as mixtures thereof, wherein these latices - although the application of the method of the invention does not exclude other types of latex with unsaturated C—C bonds – can result in surprisingly good mechanical properties or appropriately good properties.

In this case it is advantageous when a latex is cross-linked with a solids content which is selected from a range with a lower limit of 20% and an upper limit of 60%, in particular when a latex is crosslinked with a solids content which is selected from a range with a lower limit of 30% and an upper limit of 50%, preferably when a latex is crosslinked with a solids content which is selected from a range with a lower limit of 35% and an upper limit of 45%, since with said solids content(s), appropriately good mixing of the individual educts and thus a rapid reaction process is possible. In addition, this makes it possible to prevent the layer thickness in the pre-crosslinking reactor from varying over the length of the irradiation, in particular if a falling film reactor is used. Above a solids content of the latex of 60%, the latex becomes too viscous and already has a tendency to coagulate. Below 20%, the solids content is too low to form a desired layer thickness during the coagulation - dipping process.

Preferably, the crosslinking reaction is carried out in a falling film reactor or in a dipping reactor, to enable the energy to be applied as far into the core regions of the mixture as possible for a predefinable layer thicknesses of the reaction mixture.

In addition to the aforementioned preferred doped mercury vapour lamp, other mercury lamps, (pulsed) xenon lamps, an excimer lamp, a laser such as, for example, an excimer laser or a laser for at least partial crosslinking in the visible blue range, or an LED light source may be used as the energy source for the electromagnetic radiation. Similarly, microwave-excited UV emitters may be used.

In order to further increase the conversion or to increase the specificity of the reaction, monochromatic radiation may be used; in particular, lasers may be used for this purpose.

As already mentioned, the crosslinking method is particularly preferably employed for producing a medical glove or a surgical glove. In particular, a nitrosamine-free glove may particularly advantageously be produced, in particular from natural rubber.

The photoinitiator and/or fission products from the reaction may be covalently bonded to the elastomer molecules, whereby the effect of a possible migration of these molecules from the glove may be further reduced.

It is also possible that at least one crosslinking auxiliary agent, in particular a multifunctional thiol, might be immobilized on the elastomer molecules, in particular by covalent bonding, in order to further minimize the risk of skin irritation when using a glove.

The glove according to the invention may be produced so as to be free of nitrosamine and/or free of accelerators and/or free of sulphur; "free of sulphur" means that no free sulphur used for vulcanisation is present.

The invention will now be explained in more detail with reference to the following figures.

In a diagrammatic, highly simplified representation:

Fig. 1 shows a process flowchart for the production of powdered surgical gloves;

Fig. 2 shows a device according to the invention for pre-crosslinking with a double exposure cycle;

Fig. 3 shows the arrangement of several irradiation units for post-crosslinking of the latex on the former;

Fig. 4 shows a variational embodiment of the arrangement of the irradiation units for post-crosslinking;

Fig. 5 shows a variational embodiment of the arrangement of the irradiation units for post-crosslinking;

Fig. 6 shows a variational embodiment of the arrangement of the irradiation units for post-crosslinking;

Fig. 7 shows a graph of the tear strength of the elastomer as a function of the number of exposure cycles prior to hot air aging;

Fig. 8 shows a graph of the tear strength of the elastomer as a function of the number of exposure cycles after hot air aging.

It should be noted that in the various embodiments which have been described, identical parts have been given identical reference numerals and/or identical component names, whereupon the disclosures throughout the entire description may be applied to the same parts with the same reference numerals and/or same component names. In addition, positional details used in the description such as, for example, top, bottom, side etc. relate to the figure currently being described and represented, and if the position changes, they should be applied to the new position. Furthermore, individual features or combinations of features from the various exemplary embodiments shown and described may in themselves represent independent inventive or invention-related solutions.

All of the details relating to ranges of values in the present description should be understood to include any and all part-ranges: as an example, a range of 1 to 10 should be understood to mean that all part-ranges starting from the lower limit of 1 to the upper limit 10 are included, i.e. all part-ranges beginning with a lower limit of 1 or above and ending with an upper limit of 10 or below, for example 1 to 1.7, or 3.2 to 8.1 or 5.5 to 10.

Figure 1 shows a variational embodiment of a schematic process flowchart for producing surgical gloves made from latex by dipping in an installation 1.
It should be noted that the invention is not limited to the production of surgical gloves, but rather is aimed at cross-linked elastomers in general, in particular the aforementioned prod-

ucts. In addition to gloves, other latex products may also be produced in accordance with the invention, such as condoms, for example, various medical latex products such as catheters, diaphragms, infusion bags, medical tubes, tissue culture vessels, etc., for example, or even latex products in the consumer goods field such as flippers, pacifiers, etc., for example.

In a mixing step 2, the chemicals necessary for a pre-vulcanization step 3 are mixed into the latex, followed if necessary by homogenization of the latex. The compounded latex is then pre-vulcanized in the pre-vulcanization step 3. Next, the pre-vulcanized latex is transferred into a chain dipping unit 4, where it or the semi-finished product passes through the stages of dipping 5, beading 6, wet-leaching 7, drying 8, optional dry leaching 9, optional powdering 10, stripping 11, packing 12, quality control 13 and optional sterilization 14. The dipping formers undergo cleaning 15, coagulant dipping 16 and drying 17 prior to repeated dipping in latex.

The dipping formers are usually made of porcelain, but may also be made of glass, stainless steel or plastic. A clean surface for this dipping former is a criterion for homogenous deposition of the latex film in the subsequent dipping process. Both alkali and acid solutions, oxidizing compounds, surfactants and often a combination of these cleaning chemicals is used to degrease and clean the dipping formers.

The composition of the coagulation tank is also a parameter for the layer thickness of the deposited latex film. The coagulation tank is composed of the coagulants (usually $CaNO_3$, optionally also $CaCl_2$), the releasing agent ($CaCO_3$) and the wetting agent (cationic surfactants). The releasing agent facilitates removal of the glove from the dipping former, but in some powder-free processes, other inorganic salts and sometimes even polymers may be used, as is known from the prior art.

The positive metal ions deposited on the surface of the dipping former discharge them and then subsequently coagulates the negatively stabilized NR latex, as soon as the former is dipped into the pre-crosslinked latex. Different film thicknesses are obtained as a function of the dipping period and the concentration of the metal ions.

Gloves are produced with a rolled edge on the lower shaft end. To this end, a portion of the deposited film with is rolled together mechanically by rotating brushes during the beading stage 6. Because of the stickiness of the film, the rolled beaded edge is held together during the entire production process.

The wet latex film is provided with mechanical strength by a brief drying period before wet leaching 7 is carried out. Dipping the latex films into a warm water tank washes out some proteins in addition to the coagulants ($CaNO_3/CaCl_2$).

In order to produce powder-free gloves, instead of the powdering stage 10, a surface treatment may be provided, for example by chlorination, in order to improve donning and doffing of the gloves. Lubricant coatings are also possible, however.

Since dipping processes for gloves are known from the prior art, a skilled person is referred to EP 0 856 294 A, for example, in particular Figures 4 and 5 of this EP-A document, as well as to the relevant discussions in column 14, line 38 to column 18, line 51, in particular in relation to discussions relating to coagulation, dipping in latex, various washing processes, various post-treatments such as, for example, chlorination or halogenation of the surface of the gloves or the latex, roughening of the surface or the provision of powderless gloves etc. This avoids unnecessary repetition of the prior art in connection with the present invention and therefore at least in this regard, EP 0 856 294 A1 forms part of the disclosure of the present application.

Figure 2 shows a preferred variational embodiment of a pre-crosslinking device 18. In the installation of Figure 1, this is disposed between the mixing stage 2 and the dipping stage 5, wherein the pre-crosslinking device 18 may also include the mixing stage 2.

In this variation, the pre-crosslinking device 18 comprises two reactors 19, 20, in particular falling film reactors, which are connected one behind the other in the direction of flow of the latex—arrow 21, so that the latex passes through two exposure cycles during pre-crosslinking, i.e. is exposed twice to irradiation with UV and/or visible light. Radiation sources 22, 23 are also disposed in the reactors 19, 20, in particular Hg high pressure vapour lamps. Additional containers may be disposed before and/or between and/or after the reactors 19, 20, for example three containers 24, 25 and 26 as in the case of the variational embodiment according to

Figure 2. Said containers may, for example, be used for dosing (additional) process chemicals, for example the photoinitiator and/or co-crosslinking agent, or as an intermediate storage container for the mixed or pre-cross-linked latex. Furthermore, said container(s) 24, 25 might contain the photoinitiator as a pre-emulsion or pre-dispersion, possibly with an appropriate emulsifying agent. As an example, as already mentioned, surfactants may be used as the emulsifying agents.

Furthermore, at least one conveying device 27 may be provided, by means of which the latex is conveyed by pre-crosslinking device 18. In the embodiment of Figure 2, a second conveying device 28 is provided for this purpose, arranged in the direction of flow - arrow 21 - between the two reactors 19, 20. As an example, the conveying devices 27, 28 may be formed by eccentric worm pumps.

Furthermore, appropriate controllers, valves, etc. may be disposed at the corresponding locations for the purposes of controlling and/or regulation.

This cascade of reactors of Figure 2 has the advantage that two-stage pre-crosslinking of the latex may be carried out continuously. However, it is also possible to carry out said pre-crosslinking with only one reactor 19, whereupon the latex then has to be guided in a circuit to allow for multiple exposure.

Instead of falling film reactors, dipping reactors may also be used, for example, into which the irradiation source 23 dips.

Figure 3 diagrammatically shows a variational embodiment of a post-crosslinking device 29. Two dipping formers 30, 31 are shown, as well as six irradiation units 32 to 37. Preferably, this post-crosslinking unit 29 is disposed in the region of the edges 6 of the installation 1 (Figure 1) since, if gloves are produced, a rotational movement - arrow 39 - is superimposed on the translational forwards movement - arrow 38 in this embodiment, whereupon the irradiation may become more uniform; in particular, "shadowed" areas in the fingers may be illuminated more effectively.

In general, it should be noted that the post-crosslinking device 29 does not necessarily have to be disposed in this position in the installation 1 (Figure 1), but may also be placed at a different point after the dipping 5 or shaping of the latex. In addition, it is not necessary to use six irradiation units 32 to 37; just one irradiation unit 32 may also be used, in particular for products with a simple geometry, for example with flat films, or a number other than six, for example two, three, four, five, seven, etc.

Preferably, here too and for the reason given above, Ga-doped Hg-high pressure vapour lamps are used as the irradiation units 32 to 37. However, other UV or UV/visible emitters may be used, for example those mentioned above.

If the post-crosslinking device 29 is situated at a different position in a production installation for crosslinked elastomer (products), it is also possible to provide an additional rotational direction in order to homogenize the irradiation.

Preferably, a drying unit, for example a drying chamber or hot air oven, is provided (not shown) prior to dipping 5 and after the pre-crosslinking device 18 in the installation 1 (figure) because, when the invention was being developed, it was observed that higher tear strengths could be obtained if the maximum residual moisture content was at the aforementioned levels.

Figures 4 to 6 show various options for the irradiation of dipping formers 30 provided with a latex film 30. Thus, Figure 4 shows irradiation at a right angle, whereas Figures 5 and 6 show irradiation at an angle 40 of 30°. To form the angle 40, the dipping former 30 is accordingly inclined relative to the reference plane (the horizontal plane in the example of Figures 5 and 6).

By using dose measuring strips disposed at various points of the hand shape (both the spaces between the fingers and on the hand surface), it was discovered that even with simple illumination perpendicular to the hand shape (Figure 4), critical areas could also be illuminated; the dose distribution in this case was in the region of 1:6 (see Table 1). Inclining the hand shape at 30° to the UV emitter substantially reduced the dose distribution (in the region of 1:3 to 1:4).

Table 1

Position 1					
Measurement point	1	2	3	4	5
Dose [mJ/cm2]	30	30	30	20	120
Plus position 2					
Measurement point	1	2	3	4	5
Dose [mJ/cm2]	100	100	30	30	200
Plus position 3					
Measurement point	1	2	3	4	5
Dose [mJ/cm2]	100	100	70	70	>200

The same was observed for the back of the hand.

For geometrically more complex formers, it is also an advantage if more than one irradiation source is used, wherein the irradiation sources are disposed at different angles—dependent on the geometry—to the former and/or if the former is rotated during irradiation, wherein in this case too, the angle of inclination of the former to the irradiation source may be varied during irradiation if necessary.

By means of the irradiation sources 22, 23 or the irradiation units 32 to 37, energy is transferred to the photoinitiator in the form of photons, i.e. its molecules, and in this manner, radical formation from the molecules of the photoinitiator can be initiated. The radicals which are formed can then break double bonds which are in the latex molecules, for example in the main chain and/or in a side chain in accordance with a radical reaction mechanism, and thus bring about crosslinking via initiator molecules or directly between the elastomer molecules.

In addition, according to an additional variational embodiment, it is possible to add at least one auxiliary substance to the polymer dispersion and/or pre-emulsion. This auxiliary substance may, for example, be a crosslinking auxiliary agent (co-crosslinking agent). As an ex-

ample, it is possible to use a thiol and/or a selenol as a crosslinking auxiliary agent. Preferably, the thiol comprises two or more SH groups, whereupon the possibility of the so-called thiolene addition reaction occurring arises, which generates crosslinking sites in the polymer. In this manner, the crosslinking reaction can be accelerated. In addition to this crosslinking auxiliary agent, it is also possible to add additional crosslinking auxiliary agents or additional auxiliary agents such as, for example, sensitizers, hydrogen donors, various process additives such as, for example, stabilizers, antifoaming agents, dispensing agents, emulsifiers, coagulating agents, crosslinking chemicals, colorants and also fillers to the polymer dispersion or at least in part to the pre-emulsion, wherein these reagents are at least for the most part known from the prior art; at this point, a skilled person is referred to the pertinent literature, for example to the Applicant's document EP 0 856 294 A1 or to the publication "Kautschuktechnologie" [Rubber technology] (Röthemeyer/Sommer, Carl Hanser Verlag 2001).

At least a portion of the pre-emulsion or the pre-dispersion may be added to the polymer dispersion prior to the start of pre-crosslinking reaction and/or post-crosslinking reaction. Similarly, it is possible to add at least a portion of it during reaction of said polymer dispersion, for example in small amounts, such as in droplets.

The irradiation sources 22, 23 and the irradiation units 32 to 37 may emit light in the spectral region which has already been described, i.e. in particular between 200 nm and 550 nm or 250 nm and 475 nm or 275 nm and 400 nm.

With respect to the photoinitiator or possible mixtures of different photoinitiators, reference is made in this regard to the discussions above.

Both the irradiation sources 22, 23 and the irradiation units 32 to 37 as well as various agitators or optional further components of the installation 1 may be operatively connected with a control and/or regulating device (not shown) such as, for example, a PC or, in general, a data processing system, so that if necessary, automation or processing with variable reaction parameters can be carried out completely automatically. As an example, in order to change the temperature, an appropriate prior art heating and/or cooling device may be disposed on or in the reactor(s) 19, 20.

It is also possible to carry out pre-crosslinking and/or post-crosslinking at a pressure which differs from atmospheric pressure, for example at low pressure; it is also possible to carry out the crosslinking reaction under high pressure, and to this end, at least one of the reactors 19, 20 or the post-crosslinking device 29 may be designed accordingly, i.e., for example, vacuum-tight, or indeed suitable for carrying out high pressure reactions, i.e. for example with reinforced walls.

On at least one surface, the falling film reactor comprises suitable safeguards such as a viewing window, for example, in order to allow the electromagnetic irradiation to penetrate into the interior of the reactor or reactors 19, 20. Furthermore, it is possible to form the latter at least in part from a UV-transparent material such as, for example, (quartz) glass or plastic.

The irradiation sources 22, 23 may, however, also be disposed on the inside of the falling film reactor, so that the polymer dispersion is exposed from the inside out.

Clearly, it is possible for pre-crosslinking and/or post-crosslinking of the latex or the latices to be carried out separately, i.e. independently of the additional production installation for latex products.

Concerning the photoinitiators used, the various auxiliary substances and their concentrations or proportions as well as the latices which can be used and their proportion in the polymer dispersion, reference is made at this juncture to the above general discussions in order to avoid unnecessary repetition.

In the context of the invention, the solids used may be dissolved in a solvent and/or emulsified or dispersed in water.

In the context of the invention, it is also possible to carry out a post-treatment after shaping, for example by heating, illuminating or extraction.

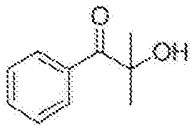
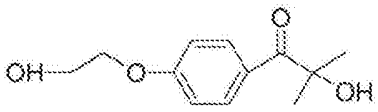
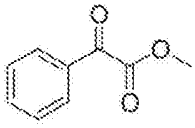
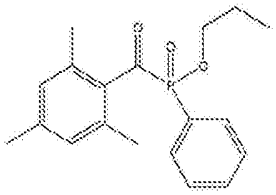
The tear strengths of the latex films produced in the context of the invention may be in the range 25 N/mm^2 to 30 N/mm^2, particularly for natural rubber, with an elongation at break of 800%-900%.

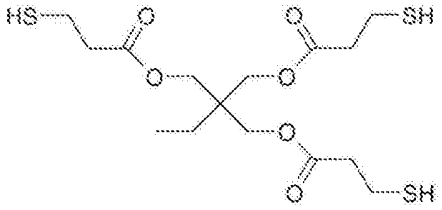
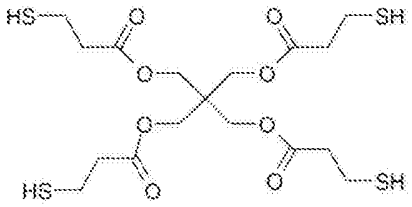
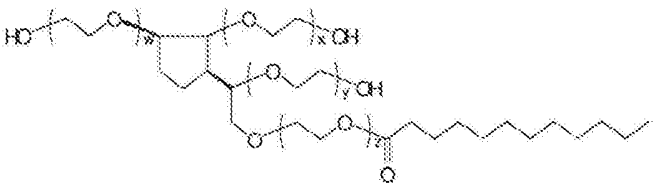
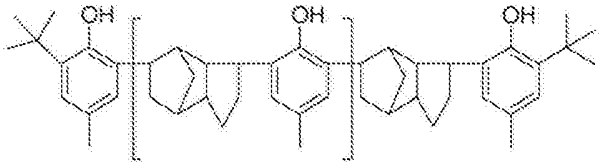
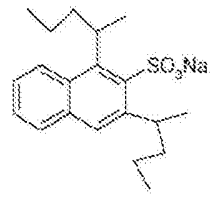
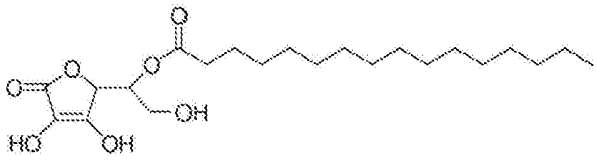
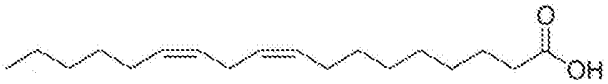
It is also possible to carry out the radiative chemical crosslinking both continuously and discontinuously.

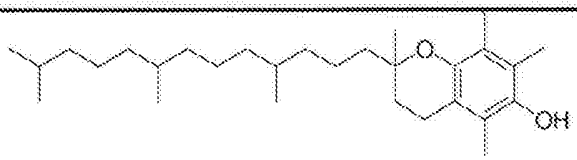
Several examples are described below which were carried out in the context of the invention. However, a description of all of the experiments carried out would be beyond the scope of the present description. Restriction to the examples below does not mean that the invention is restricted to them. Rather, the scope of the invention with respect to the latices or chemicals used and their proportions is within the ranges defined above.

The following materials or chemicals were used:

Materials	Detailed description
NR-Latex	High ammonia NR-Latex / 60 % drc.
IR-Latex	Kraton® IR-401 Latex / 60 % drc.
Coagulation tank	CaCl2 solution (10 wt %) in water/additives: chalk, wetting agents
Lubricant tank	Mixture of silicon, acrylate and polyurethane components

Chemical	Manufacturer	Structural formula
Photoinitiators		
Genocure DMHA	Rahn AG	
Irgacure 2959	Rahn AG	
Genocure MBF	Rahn AG	
Lucirin TPO L	BASF	

Co-crosslinking agent		
Trimethylolpropane-tris-3-mercaptopropionate	Bruno Bock Thiochemicals	
Pentaerythritol tetrakis-3-mercaptopropionate	Bruno Bock Thiochemicals	
Other chemicals		
Tween 20	Sigma-Aldrich	
Ralox LC®	Solvadis	
Nekal BX	BASF	
Ascorbyl palmitate	Sigma-Aldrich	
Linoleic acid	Sigma-Aldrich	

α-Tocopherol	Sigma-Aldrich	

Example 1: UV Crosslinking of Natural Rubber (NR latex)

UV pre-crosslinking in falling film reactor:

(The abbreviation phr stands for parts per hundred parts rubber)

Process parameter		Process parameter	
Emitter output (Hg-high pressure lamp) [W]	3000	Conveying speed [l/min]	1.28
Number of exposure cycles	2	Layer thickness (falling film) [mm]	0.45 – 0.6
Photoinitiator	Genocure DMHA (0.5 – 1.0 phr)	Solids content (latex) [drc.]	40
Thiol crosslinking agent	Tris-thiol (1.0 phr)	Cooling water pressure [bar]	0.6

Dipping:

Process parameter		Process parameter	
Liquid latex storage period (pre-crosslinked) [days]	0 - 1	Drying temperature [°C]	120
Stabilizer	Ralox LC (0.5 phr)	Drying period [min]	20

Subsequent dosing prior to dipping	
Process parameter	Process parameter

Photoinitiator	Genocure DMHA (1,0 – 1,4 phr)	Thiol crosslinking agent	Tetra-thiol (1.0 phr)
Post-crosslinking Process parameter			
Irradiation dose [J/cm²]	~ 5		

During the crosslinking experiments, NR latex was pre-cross-linked once, twice and three times at an irradiative power of 3000 W, whereby after each exposure cycle, latex samples were directly removed at the outflow valve. The results are shown in Figure 7 and Figure 8. Sterile samples (squares) and non-sterile samples (triangles) were measured. The tearing strengths in N/mm^2 (ordinate) are shown in the figures against the number of exposures (abscissa).

It may be concluded from the results that after pre-crosslinking twice, a maximum of the mechanical strengths was obtained (crosslink density was 0.28 $mmol/cm^3$). In this case sterile, non-aged NR latex films (stored for 7 days at 20° C) had a tear strength of 26.5 N/mm^2, whereas after hot air aging, the mechanical properties diminished to 22.0 N/mm^2.

With a single exposure cycle, the crosslink density (0.19 $mmol/cm^3$) was apparently too low, so that the subsequently dipped latex films had much lower tear strengths (21 N/mm^2) associated with a poorer aging resistance (13-15 N/mm^2).

After a third exposure pass, a reduction in the tear strength was also observed, since over-crosslinking (crosslink density was 0.49 $mmol/cm^3$) led to a reduction in the mechanical strength, whereas the aging resistance of an over-cross-linked NR latex film was much higher compared with an under cross-linked film (one exposure cycle).

It was also found that crosslinking (pre-crosslinking and/or post-crosslinking) in an inert gas atmosphere (argon or nitrogen) after the second or third exposure cycle led to an increase in the mechanical strength of up to 5 N/mm^2.

In addition, drying the latex films at room temperature instead of at a raised temperature could result in tear strengths up to 5 N/mm^2 higher.

Finally, by means of post-crosslinking, tear strengths of up to 33 N/mm^2 could be obtained, whereas with an irradiation dose of over 5 J/cm^2, the first degradation reactions could be observed in connection with oxygen in the air, which lead to a reduction of the tear strength.

Example 2: UV Crosslinking of IR Latex

UV-pre-crosslinking in the falling film reactor			
Process parameter		Process parameter	
Emitter output (Hg-high pressure lamp) [W]	800	Conveying speed [l/min]	1,28
Number of exposure cycles	2	Layer thickness (falling film) [mm]	0,45 - 0,6
Photoinitiator	Lucirin TPO L (0,5 - 1,0 phr)	Solids content (latex) [drc.]	40
Thiol crosslinking agent	Tetra-thiol (0.2 – 1.0 phr)	Cooling water pressure [bar]	0,6

Dipping			
Process parameter		Process parameter	
Liquid latex storage period (pre-crosslinked) [days]	< 1	Residual moisture content [%]	< 4
Antioxidant[1]	Ralox LC (0,5 phr)	Stabilizer	Nekal BX (1,25 phr)

Subsequent dosing prior to dipping			
Process parameter		Process parameter	
Photoinitiator	Lucirin TPO L (1,0 – 1, 5 phr)	Thiol crosslinking agent	Tetra-thiol (0.9- 1.4 phr)

Post-crosslinking Process parameter	
Irradiation dose [J/cm²]	~ 4 - 13
UV light source	Ga doped Hg emitter

1…optionally also 0.5 phr α-tocopherol

drc. … dry matter content

Generally, it should be noted that the power output of the emitters of the invention in the pre-crosslinking stage was between 300 W and 3000 W, in particular between 400 W and 1000 W, and in the post-crosslinking stage, it was between 2500 W and 4500 W, in particular between 3000 W and 3500 W, wherein it is advantageous for pre-crosslinking to be carried out at a lower power. In order to obtain better film formation, particularly with IR-latices, it is advantageous for the power output of the emitters for pre-crosslinking not to exceed approximately 800 W. However, it should be noted that the emitter power output used can vary from the values given by way of example as a function of the geometry of the irradiating installation.

In addition, adding surfactants in the pre-crosslinking stage, in particular surfactants with unsaturated C—C bonds such as linoleic acid, for example, may improve formation of the film.

Furthermore, in particular with IR latices, film formation by adding radical scavengers such as ascorbyl palmitate (in a proportion of 0.25 phr to 2 phr, in particular 0.5 phr to 1 phr), for example, could be improved so that crack-free films were obtained even after drying. Ascorbyl palmitate has the property of accumulating on the surface of the latex particles.

Because of the allergy potential of the products and the efficiency of the method, it is desirable to use as few chemicals as possible, but for high mechanical strengths (>20 N/mm^2), at least 1.0 phr of Genocure DMHA and 1.0 phr of tetra-thiol are preferred. These tear strengths could be improved in the absence of a stabilizer.

Ralox LC used, for example, as the substituted BHT derivative, in this case traps the initiator radicals during post-vulcanization very effectively, whereby the thiol-ene crosslinking is primarily inhibited at a low concentration of the process chemicals (post-doping with 1.0 phr of Genocure DMHA and 1.0 phr of tetra-thiol).

Using Lucirin TPO L as a photoinitiator has the advantage that, because of its absorption into the visible wavelength range, on the one hand irradiation can be used efficiently for post-crosslinking, and on the other hand, long-wavelength light can penetrate into deeper layers, whereupon a more homogenous crosslinking may be obtained over the latex film.

An improvement to the aging resistance of UV crosslinked (pre-plus post-crosslinking) IR-latex films could be obtained with α-tocopherol (vitamin E), which occurs as an essential compound in the metabolism of the human body, and therefore is advantageous having regard to allergological tolerance. The proportion of vitamin E may be between 0.2 phr and 1 phr.

However, in the context of the invention, the addition of vitamin E as a stabilizer is not restricted to IR latices. In general, vitamin E can also be used for this purpose in other latices.

Vitamin E also has the advantage that it - surprisingly - does not inhibit or only slightly inhibits the thiol-ene reaction.

To improve the stability of the latex mixture, a naphthyl sulphonate (Nekal BX; 0.2 phr-2.5 phr) may be added, for example, whereupon the conveyability of the latex through smaller deposits in the installation 1 can be considerably improved.

Furthermore, it is advantageous if the level of pre-crosslinking is between 80% and 120%, in particular between 80% and 90%. In addition, the crosslink density is determined in order to estimate the degree of crosslinking, since this parameter can be determined rapidly, in order to characterize the progress of the photochemical crosslinking reaction.

The crosslink density provides more exact information about the density of crosslinking and the average molecular weight of the polymer chains between the individual crosslinking sites.

In addition, the degree of swelling of the UV-crosslinked latex films is determined by means of the Flory Rehner method.

About 60 mg of the crosslinked latex film were swollen in 3 ml of toluene for 48 h at 30° C in a drying cabinet. Next, the films were filtered through a filter paper and dipped several times in diethyl ether. 30 s after removing the sample from the diethyl ether, the latex film was weighed (± 0.5 mg) and the sample was dried at 70° C in the drying cabinet to constant weight, then weighed again. The density of crosslinking was then determined by means of the Flory Huggins interaction parameter between the solvent and polymer using the following set of equations.

$$\overline{M_C} = -V_1 \rho_p \frac{\phi_p^{1/3} - \frac{\phi_p}{2}}{\ln(1-\phi_p) + \phi_p + \chi_1 \phi_p^2}$$

$$\frac{1}{\phi_p} = 1 + \frac{W_s}{W_p} \frac{\rho_p}{\rho_s}$$

$\overline{M_C}$ average molar mass of the polymer chains between the crosslinking sites

V_1 molar volume of the solvent

ϕ_p volume fraction of the polymer

χ_1 Flory Huggins interaction parameter between the solvent and polymer

W_s mass of the absorbed solvent

W_p mass of the dry polymer

ρ_s density of the solvent

ρ_p density of the polymer

The mechanical strengths of the latex films were determined in accordance with ASTM standard D412-98a (Annu. Book ASTM Stand. 09.01 (2002)). The tear strength was used as the characteristic parameter. For the mechanical tensile testing, 3-4 test specimens (web width: 3 mm) were stamped out of a latex film. The thickness of the web was determined by means of

a micrometre screw (arithmetic mean of 10 measurements) and entered manually into the measurement software. In order to evaluate the tear strength, the arithmetic mean of the test specimens of a sample were used.

In order to determine the resistance of the elastomers during sterilization, they were irradiated with a Co60 source at a dose of 25 kGy. After the gamma-sterilized latex films had been produced, the tear strengths were determined both before and after hot air aging (7 days at 70° C, in accordance with EN 455/2) using the tensile testing machine.

The exemplary embodiments show possible variational embodiments of the invention, but it should be noted at this juncture that the invention is not restricted to the variational embodiments which have been shown in particular but rather, various combinations of the individual variational embodiments are also possible and because of the teaching regarding technical procedure in the present invention, this possibility of variation lies within the ability of a person who is skilled in this technical field.

Finally, as a point of formality, it should be noted that for a better understanding of the construction of the pre-crosslinking device 18 and the post-crosslinking device 29, these and its components have occasionally not been drawn to scale and/or have been enlarged and/or reduced in size.

List of reference numerals

1 Installation
2 Mixing step
3 Pre-vulcanization step
4 Chain dipping installation
5 Dipping

6 Beading
7 Wet leaching
8 Drying
9 Dry leaching
10 Powdering

11 Stripping
12 Packing
13 Quality control
14 Sterilization
15 Cleaning

16 Coagulant dipping
17 Drying
18 Pre-crosslinking device
19 Reactor
20 Reactor

21 Arrow
22 Irradiation source
23 Irradiation source
24 Container
25 Container

26 Container
27 Conveying device
28 Conveying device
29 Post-crosslinking device
30 Dipping former

31 Dipping former
32 Irradiation unit
33 Irradiation unit
34 Irradiation unit
35 Irradiation unit

36 Irradiation unit
37 Irradiation unit
38 Arrow
39 Arrow
40 Angle

9491D

EP 2 408 849 B1

ELJÁRÁS TÉRHÁLÓS ELASZTOMER ELŐÁLLÍTÁSÁRA

Szabadalmi igénypontok:

1. Eljárás térhálós elasztomer előállítására legalább egy térhálósítható polimert tartalmazó polimer diszperziónak ultraibolya (UV fény) és/vagy látható spektrumtartományban levő elektromágneses besugárzással, ahol a térhálósítást legalább két lépésben, elő-térhálósításként és utó-térhálósításként végezzük, és legalább egy fotoiniciátort adunk a polimer diszperzióhoz az elő-térhálósítás előtt a térhálósítási reakció kiváltására, azzal jellemezve, hogy még egyszer legalább egy fotoiniciátort adunk az elő-térhálósított polimer diszperzióhoz az utó-térhálósítás előtt és/vagy az utó-térhálósítás alatt, és az utó-térhálósítást szintén az ultraibolya (UV fény) és/vagy látható spektrális tartományban levő elektromágneses besugárzással végezzük.

2. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy az elő-térhálósításban hozzáadott legalább egy fotoiniciátor mennyisége maximálisan azonos, előnyösen kisebb, mint az utó-térhálósításban alkalmazott legalább egy fotoiniciátor mennyisége.

3. A 2. igénypont szerinti eljárás, azzal jellemezve, hogy a legalább egy fotoiniciátor részaránya az elő-térhálósításra szolgáló polimer diszperziónál 0,2 phr és 5,0 phr között van.

4. A 2. vagy 3. igénypont szerinti eljárás, azzal jellemezve, hogy a legalább egy fotoiniciátor részaránya az utó-térhálósításra szolgáló polimer diszperziónál 0,5 phr és 5,0 phr között van.

5. Az 1-4. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy a polimer diszperziót legalább kétszer sugározzuk be az elő-térhálósítás során.

6. Az 1-5. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy legalább egy fotoiniciátort alkalmazunk, amelyet a 2-hidroxi-2-metil-1-fenilpropanon, fenilglioxálsav-metil-észter, 2,4,6-trimetilbenzoilfenilfoszfinsav-etil-észter, metilbenzoilformiát, 1-[4-(2-hidroxietoxi)-fenil]-2-hidroxi-metil-1-propanon-1-on, 2-dimetilamino-2-(4-metilbenzil)-1-(4-morfolin-4-ilfenil)-bután-1-on, 2-metil-1-[4-(metiltio)fenil]-2-morfolinopropán-1-on, 2,4,6-trimetilbenzoil-difenilfoszfin-oxid által alkotott csoportból választunk.

7. Az 1-6. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az elő-térhálósítást filmen, különösen maximum 2 mm rétegvastagságú filmen végezzük.

8. Az 1-7. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az utó-térhálósításhoz legalább két sugárforrást alkalmazunk.

9. Az 1-8. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az utó-térhálósítást nagyobb sugárdózissal végezzük, mint az elő-térhálósítást.

10. A 9. igénypont szerinti eljárás, azzal jellemezve, hogy az utó-térhálósítást olyan sugárdózissal végezzük, amely az elő-térhálósításhoz alkalmazott sugárdózis 150 %-a és 500 %-a között van.

11. Az 1-10. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az elő-térhálósításhoz és/vagy utó-térhálósításhoz legalább egy társ-térhálósítót adunk, amely legalább egy tiolcsoportot tartalmaz.

12. A 11. igénypont szerinti eljárás, azzal jellemezve, hogy az elö-térhálósításban a legalább egy társ-térhálósító hozzáadott mennyisége maximum azonos, előnyösen kisebb, mint az utó-térhálósításhoz alkalmazott legalább egy társ-térhálósító mennyisége.

13. A 12. igénypont szerinti eljárás, azzal jellemezve, hogy az elő-térhálósításra szolgáló polimer diszperziónál a legalább egy társ-térhálósító részaránya 0,5 phr és 2,0 phr között van.

14. A 12. vagy 13. igénypont szerinti eljárás, azzal jellemezve, hogy az utó-térhálósításra szolgáló polimer diszperziónál a legalább egy társ-térhálósító részaránya 0,5 phr és 2,5 phr között van.

15. A 11-14. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy társ-térhálósítóként trimetilolpropán-trisz-3-merkaptopropionátot vagy pentaeritrit-tetrakisz-3-merkaptopropionátot alkalmazunk.

16. Az 1-15. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy legalább egy öregedésgátló szert adunk az elő-térhálósított polimer diszperzióhoz az utó-térhálósítás előtt.

17. A 16. igénypont szerinti eljárás, azzal jellemezve, hogy öregedésgátló szerként E vitamint és/vagy a sztérikusan gátolt fenolt alkalmazunk.

18. Az 1-17. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az elő-térhálósítás és az utó-térhálósítás között az elő-térhálósított elasztomer szárítását végezzük el maximum 6 % maradék-nedvességtartalomig.

19. Az 1-18. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy legalább egy olyan felületaktív anyagot adunk a polimer diszperzióhoz az elő-térhálósítás előtt, amelynek legalább egy fotokémiailag aktív centruma, különösen kettős kötése van.

20. Az 1-19. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy a besugárzáshoz galliummal dópolt nagynyomású higanygőzlámpát alkalmazunk.

21. Az 1-20. igénypontok egyike szerinti eljárás, azzal jellemezve, hogy az utó-térhálósítást közömbös gázatmoszférában végezzük.

22. Eljárás mártott cikk előállítására legalább egy látexből, ahol egy külső konturral rendelkező formát, amely megfelel az előállítandó mártott cikknek, egy előre meghatározott ideig mártófürdőbe mártunk, amely tartalmaz legalább egy látexet,

és utána a mártott cikket keményítjük és/vagy szárítjuk, azzal jellemezve, hogy a látexet térhálósítjuk az 1-21. igénypontok egyike szerinti eljárással.

23. A 22. igénypont szerinti eljárás, azzal jellemezve, hogy a látex formálását a forma mártófürdőbe merítésével a látex elő-térhálósítása és utó-térhálósítása között végezzük.

24. A 23. igénypont szerinti eljárás, azzal jellemezve, hogy az utó-térhálósítást a formán végezzük.

25. Berendezés merített cikk előállítására látexből, amely tartalmaz reaktort (19), legalább egy merítő formát (30) és legalább egy merítő fürdőt, ahol legalább egy sugárforrás (22) van hozzárendelve a reaktorhoz (19) az ultraibolya (UV fény) és/vagy látható spektrális tartományban levő elektromágneses sugárzás kibocsátására, azzal jellemezve, hogy a legalább egy bemerítő fürdő után további sugárforrás van elrendezve az ultraibolya (UV fény) és/vagy látható spektrális tartományban levő elektromágneses sugárzás kibocsátására.

26. A 25. igénypont szerinti berendezés, azzal jellemezve, hogy a legalább egy bemerítő fürdő után forgó egység van elrendezve, amellyel a merített cikkek forgathatók, legalább részben, és a további sugárforrás a forgó egységhez van hozzárendelve.

27. A 25. vagy 26. igénypont szerinti berendezés, azzal jellemezve, hogy legalább két további sugárforrás van elrendezve egymás mögé a mártott cikkek szállítási irányában.

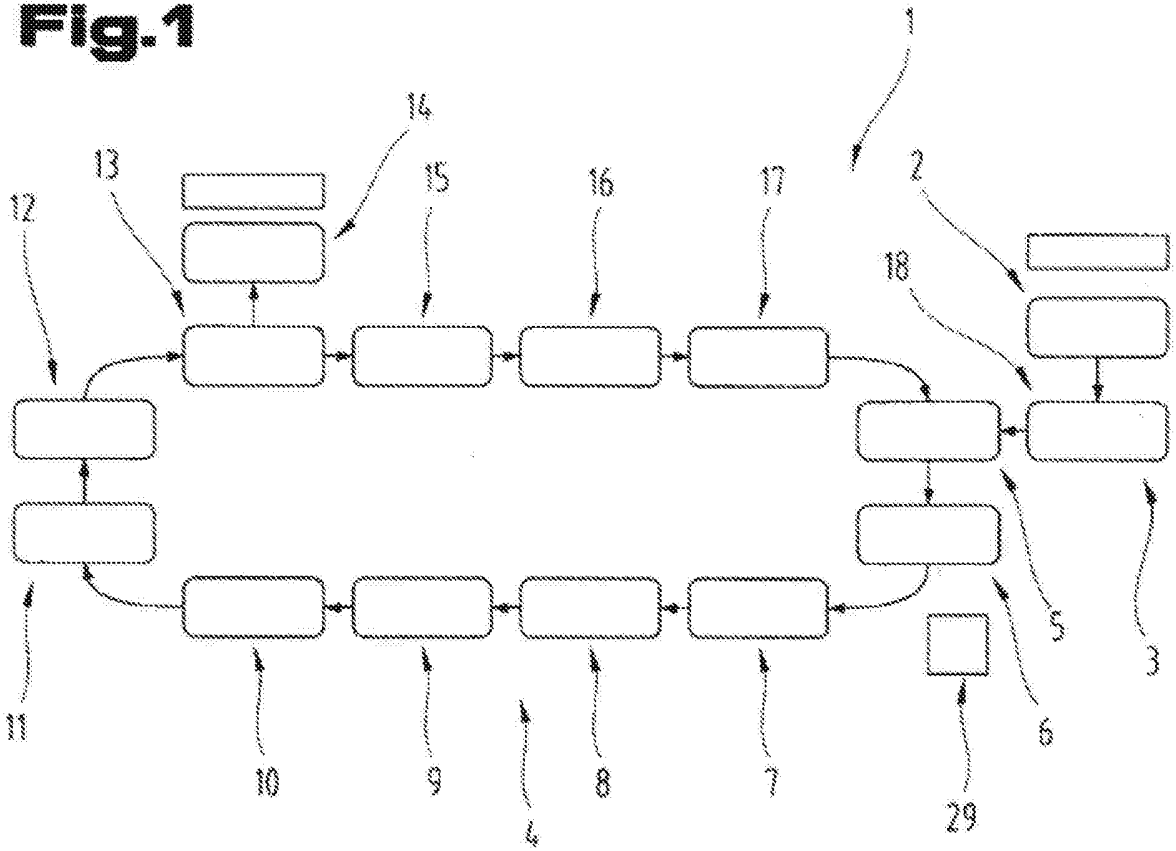
28. A 25-27. igénypontok egyike szerinti berendezés, azzal jellemezve, hogy az első sugárforrás (19) és/vagy a további sugárforrás galliummal dópolt nagynyomású higanygőzlámpa.

29. A 25-28. igénypontok egyike szerinti berendezés, azzal jellemezve, hogy legalább két reaktor (19, 20), mindegyik legalább egy első sugárforrással (22, 23), van egymás mögött elrendezve a termelési irányban.

30. A 29. igénypont szerinti berendezés, azzal jellemezve, hogy a két reaktor (19, 20) között legalább egy tartály (24) van elrendezve, amely adott esetben tartalmaz keverőt.

31. Kesztyű térhálósított elasztomerből, azzal jellemezve, hogy az 1-24. igénypontok egyike szerinti eljárással van előállítva, és szakítószilárdsága legalább 14 N/mm^2.

Fig.1


1
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29

Fig.2

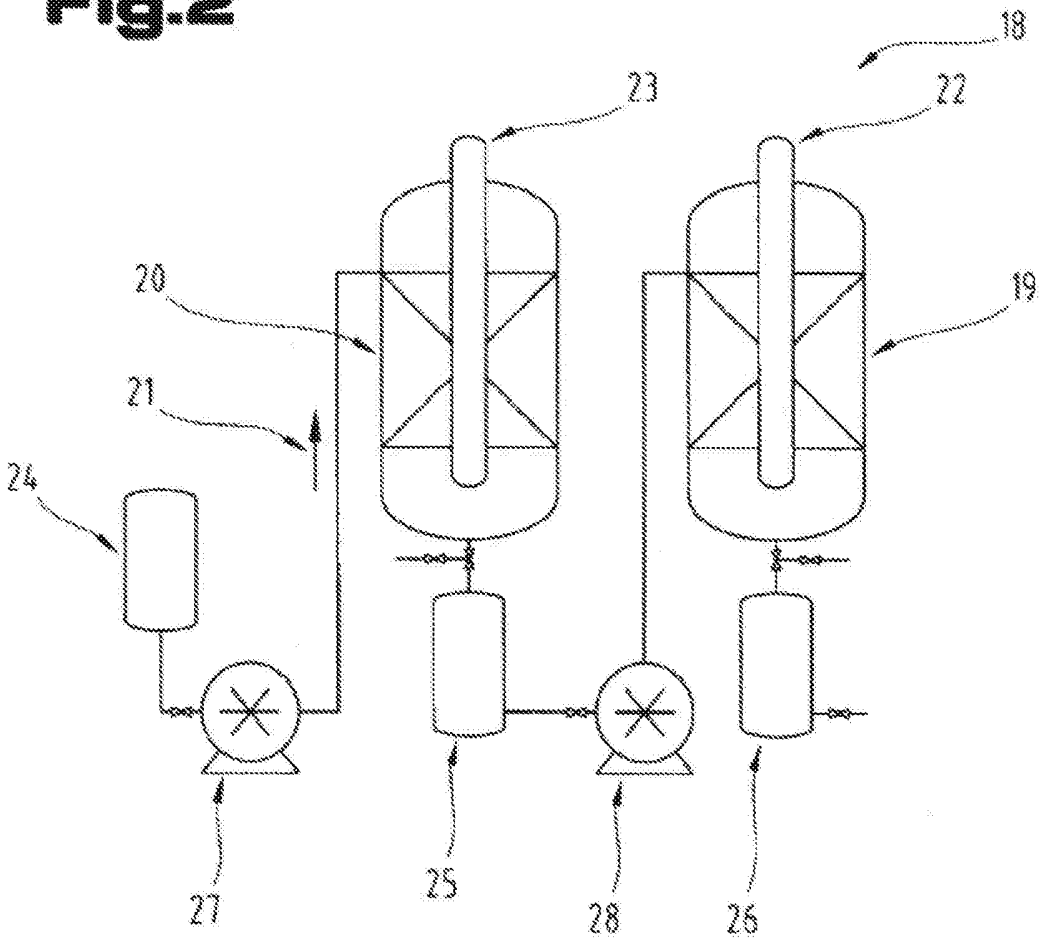
18
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Fig.3

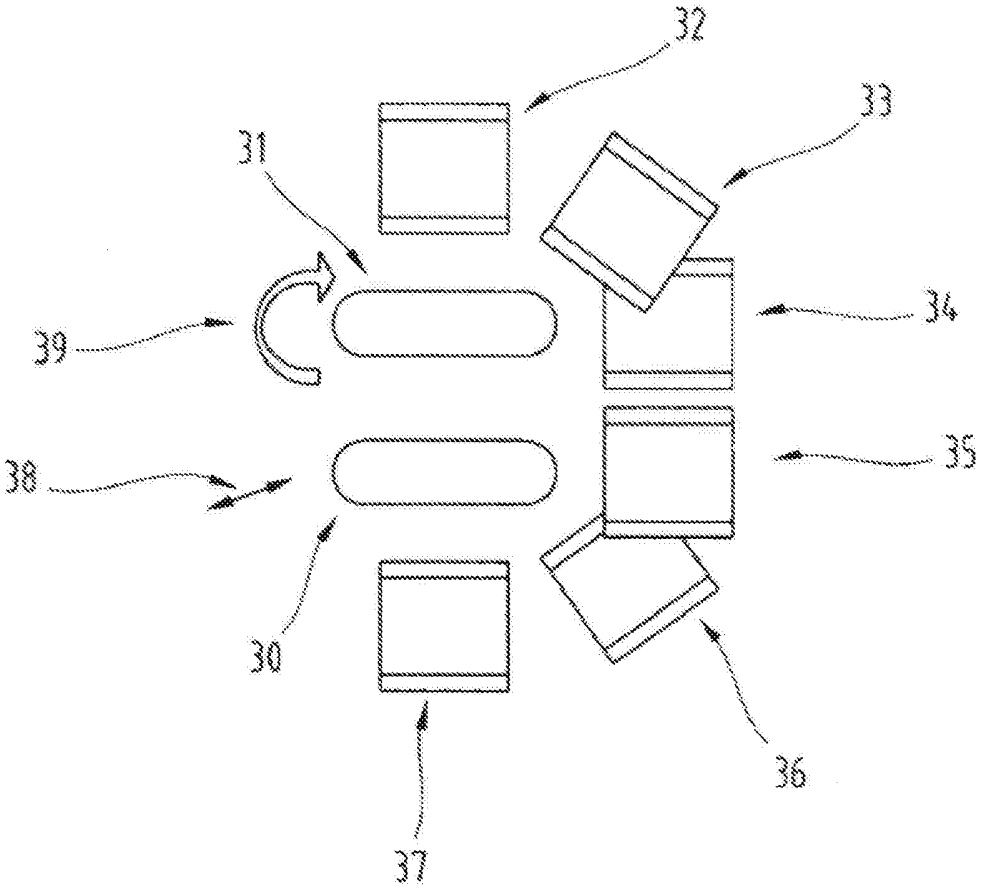


Fig.4 Fig.5 Fig.6

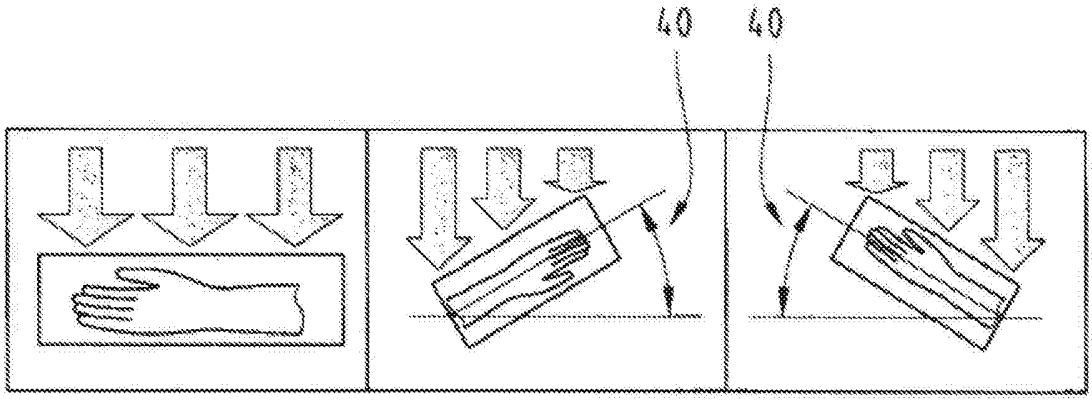
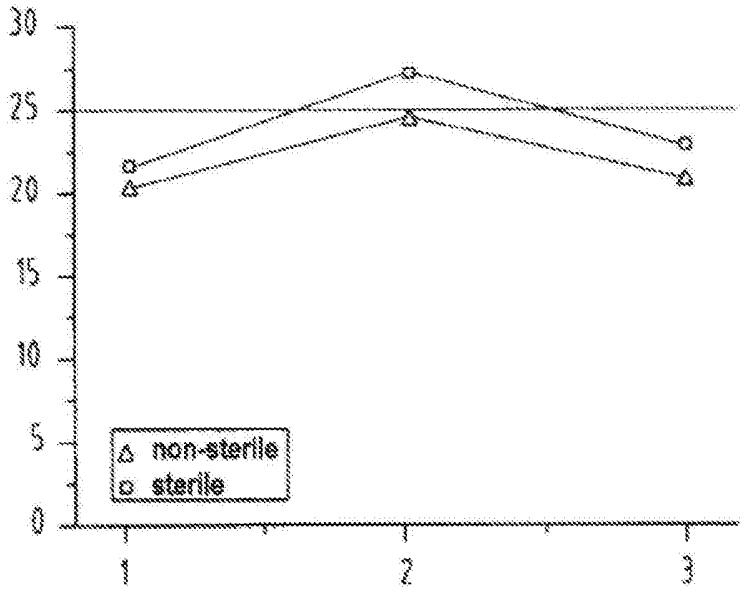


Fig.7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25
20
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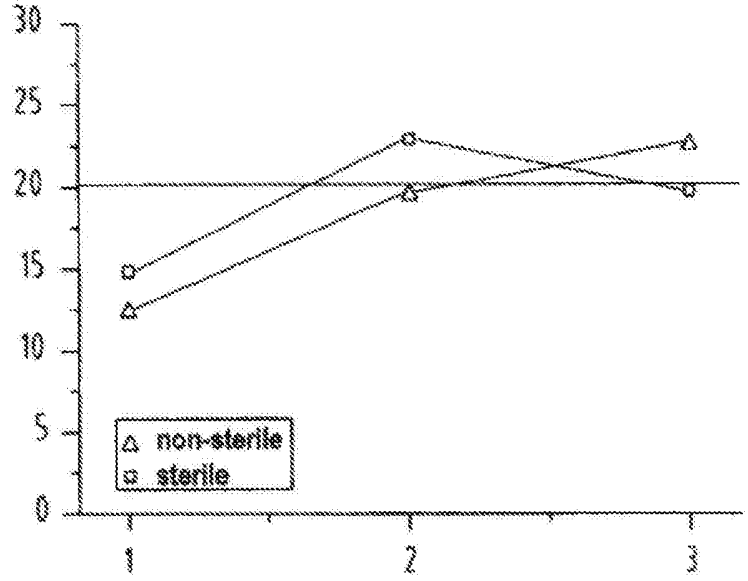
5
0
1
2
3
non-sterile
sterile

Fig.8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non-sterile
sterile