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(71) Applicant: **RADIUM FOAM B.V.** [NL/NL]; Fort Willemweg 61, 6219 PA Maastricht (NL).

(72) Inventor: **BASTIAENS, Rik**; c/o Fort Willemweg 61, 6219 PA Maastricht (NL).

(74) Agent: **JANSEN, C.m.**; V.O., Carnegieplein 5, 2517 KJ Den Haag (NL).

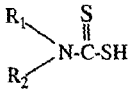
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(54) Title: VULCANIZATION ACCELERATOR COMPOSITION FOR LATEX FOAM RUBBER



(I)

(57) Abstract: The invention relates to a process for producing a vulcanized foamed open cell comfort product, wherein a vulcanizable rubber latex foam composition comprising a rubber latex, a sulfur-containing vulcanizing agent and at least one vulcanization accelerator, is subjected to foaming, gelling and vulcanization. The vulcanization accelerator comprises 0.25-10.0 parts per hundred based on the total weight of the foam composition of a compound which responds to formula (I) or a zinc salt of this compound: wherein R_1 and R_2 may be the same or different, but preferably are the same, wherein each of R_1 and R_2 may be an alkyl or a cycloalkyl group having a hydrocarbon chain containing between 1 and 9 carbon atoms, or an arylalkyl group comprising 6-12 carbon atoms, preferably an arylakylgroup having an aryl moiety with one or two alkyl groups each having 1 to 5 carbon atoms in the ocposition. The vulcanization accelerator further comprises 0.01 - 10.0 parts per hundred based on the total weight of the foam composition of a thiazole or the zinc salt thereof.

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Vulcanization accelerator composition for latex foam rubber.

The present invention relates to a process for producing a vulcanized foamed open cell comfort product, wherein a vulcanizable rubber latex foam composition comprising a liquid rubber latex, a sulfur-containing vulcanizing agent and at least one vulcanization accelerator, is subjected to foaming, gelling and vulcanization, according to the preamble of the first claim.

Natural and synthetic elastomer or rubber latex compositions are employed in the production of a wide variety of products, such as foam backings for carpets, dipped goods, extruded threads, adhesives, shoulder straps, impact protection pads, helmet cushioning and molded foams. For bedding products the typical range is 30 - 100 kg/m^3 and a hardness of 5 - 105 lbf. Each of the afore-mentioned applications has its own demands in relation to the physical properties of the foam, for example elongation at break, tensile strength, hardness, density, sag factor, fatigue at constant load pounding. Depending on the nature of the application, the latex composition will be processed using dipping, extrusion and molding, for example slush molding.

Latex foam is a particularly suitable base material for the production of products or structures used in comfort products, such as mattresses, pillows, furniture cushions, toppings over springs. These comfort products are often called cushioning products. The exceptional high resilience and low creep in compression characteristics suit the use of latex foam in these soft comfort products.

An important property of a latex foam comfort product is its density, which generally varies between 30 and 100 kg/m^3 when measured according to ISO 845, its hardness, in particular the ILD hardness measured according to ASTM 1055D-4 section 20-23, i.e. the resistance to compression is usually between 5 and 105 lbf, its tensile strength generally between 40 and 150 kPa, and its elongation at break which generally varies between 200 and 350 %. An important property of a latex foam product is its density, as there is a correlation between hardness and density (weight per

volume): the more the density decreases, the lower the hardness will be. According to the ASTM 1055-D Standard in particular ASTM 1055D-4 section 20-23, the ILD hardness (Indentation Load Deflection) equals the force (lbf) needed to compress a mattress for 25% with a 50 square inch or 322 cm^2 circular stamp.

Another important goal to be achieved by latex foam comfort products is that the structure should be capable of optimally dispersing the pressure without peak pressure points. Initially a comfort product, for example a mattress, should be soft to the touch and then increasingly offer resistance and support after further compression. To evaluate this property, the property of "sag factor' was introduced via the ISO 2439 standard, which equals the relation between 65% indentation compared to 25% indentation. A sag factor of around 3 is said to give an ideal sleeping comfort.

Industrial production of rubber latex foam comfort products nowadays generally proceeds using one of two long established processes, the so-called Dunlop and Talalay process. Rubber latex foam is usually prepared by compounding a latex of natural rubber, synthetic rubber or a mixture of natural and synthetic rubber compositions all with a vulcanization system and other compounding ingredients for imparting desired properties to the latex foam rubber.

To achieve vulcanization, the latex foam composition will generally comprise a vulcanizing agent, which will usually be sulphur based, a vulcanization activator for the vulcanizing agent for example ZnO, a vulcanization accelerator and other additives such as antioxidants, dispersants. Commonly used vulcanization accelerators include zinc mercaptobenzothiazole and/or zinc diethyldithiocarbamate, but others may be used as well. In latex foam production process vulcanization is usually carried out at a temperature between 80°C 125°C.

A frequently used primary vulcanization accelerator is zinc diethyldithiocarbamate (ZDEC). ZDEC is often incorporated in rubber compositions to enable the zinc oxide present in the latex composition

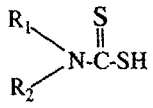
to assist gelation. The main function of ZDEC is however to activate cross-linking of sulfur with the rubber polymer of the latex composition. While the presence of ZDEC is important to achieve a fast curing rate of the latex foam and good mechanical foam properties, increased pressure in relation to environmental and safety issues, requests urging towards a reduction or elimination of the use of ZDEC are taking ground, particularly in Europe. The Environmental Protection Encouragement Agency's (EPEA) cradle-to-cradle methodology has listed ZDEC in the red category. Hence its use should no longer be continued as it is suspected to form hazardous N-nitrosamines in certain conditions.

The occurrence of hazardous N-nitrosamines in articles made of vulcanized rubber is attributed to the fact that ZDEC remains behind in the rubber polymer latex, after vulcanization has been terminated. ZDEC may be hydrolyzed to produce a secondary amine which in turn reacts with NOx, nitrites or other NOx in the environment to produce hazardous N-nitrosamines. Certain of these N-nitrosamines are carcinogenic, and a problem arises when they remain behind in the finished foam, in particular when the finished foam comes into close contact with the human body. Many countries have therefore severely restricted the maximum permissible concentration of certain N-nitrosamines in vulcanized rubber articles, in particular N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodi-n-butylamine and N-nitrosomethylphenylamine.

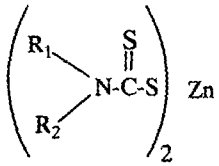
Other vulcanization accelerators exist, which do not present the problem of producing nitrosamine. Examples hereof but not solely include zinc isopropylxanthogenate, thiophosphate compounds, thiazole compounds, benzothiazolesulphenamide compounds and guanidine compounds. Zinc isopropylxanthogenate presents the problem of showing low storage stability, an offensive smell and it gives poor vulcanization properties. Guanidine compounds are not able to provide desired vulcanization properties (Polymer Digest, 1991, 1, p65).

EP915133 discloses dip-forming vulcanizable rubber latex compositions comprising a sulfur-containing vulcanizing agent

and zinc dibenzyldithiocarbamate as vulcanization accelerator, to manufacture vulcanized unsaturated nitrile rubber article without producing nitrosamine. In dip-forming, the latex composition is processed into thin-walled products like membranes; the composition is not subjected to coagulation or gelling and does therefore not contain a gelling agent. The density will often be higher than 100 kg/m^3. According to EP915133, dithiocarbamic acid produces only a negligible amount of nitrosamine or secondary amines which are precursors of nitrosamine. According to EP915133 the occurrence of cracks may be avoided and good surface luster and vulcanization properties can be obtained with a vulcanizable dip-forming rubber latex composition which comprises an unsaturated nitrile-conjugated diene copolymer rubber latex, a sulfur-containing vulcanizer and at least one vulcanization accelerator selected from (i) dithiocarbamic acid compounds represented by the formula (1) and (ii) zinc dithiocarbamate compounds represented by the formula (2) below, and an optional thiazole compound vulcanization accelerator



(Formula I)



(Formula II)

In formula I and II, R_1 and R_2 are hydrocarbon groups having at least 6 carbon atoms which may be the same or different. In particular, R_1 and R_2 are an alkyl or cycloalkyl group which may have a branch, an aryl group which may have a substituent, and a benzyl group which may have one or two alkyl groups each having 1 to 5 carbon atoms in the α-carbon atom. Specific examples of compounds according to formula (1) and (2) include dibenzyldithiocarbamic acid, di-2-ethylhexyldithiocarbamic acid), diphenyldithiocarbamic acid and dicyclohexyldithiocarbamic acid, and their zinc salts. Dibenzyldithiocarbamic acid and its zinc salt are especially preferred.

US3.968.285 discloses a latex composition for use in carpet backing, foam drapery fabrics and clothing. The latex composition has a solids content of between 55% and 85% by weight and may be used or foamed

in the conventional manner and produce curable and gellable foams. The composition comprises a curable or cross-linkable, natural or synthetic polymer for example an elastomeric latex, a curing system, such as curing agents like sulfur and activators like zinc oxide, where required, crosslinking agents and similar materials in conventional amounts; a volatile base such as ammonia, either naturally present, or as in natural latex added; and an accelerator which is inhibited from accelerating the curing system in the presence of ammonia, such as zinc dibenzyl dithiocarbamate. Gelling is carried out be heating the composition, ammonia is driven off by heating to a temperature of between 70-90 F (21 - 32 °C). The composition further contains a siloxane heat-sensitizing agent. The latex compositions may be cured through the removing of the ammonia, typically by heating to a temperature of between 200 and 400°F, thereby permitting the accelerator to function and the curing mechanism to proceed. Example 1 discloses a latex composition comprising 100 parts by weight of latex, 2.5 parts by weight of ZMBT and 1.05 parts by weight of ZBEC, which corresponds to a molar ratio ZBEC/ZMBT of 0.31.

US6.187.829 discloses heat-gellable latex compositions for the production of carpet backing, comprising a vulcanizable latex rubber dispersion, an amount of a vulcanizing agent sufficient to vulcanize the latex rubber, an amount of ammonia sufficient to prevent gelation of the latex rubber, an amount of a gelling agent sufficient to gel the latex rubber, the gelling agent comprising the reaction product of zinc chloride and an ammonium-containing compound, and an amount of an accelerator sufficient to accelerate vulcanization of the latex rubber, the accelerator comprising zinc dibenzyldithiocarbamate and Z(MBT) in equal weight percentages.

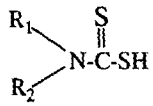
There is still a need to a process for producing vulcanized foamed open cell comfort products, with a minimal risk to the formation of hazardous nitrosamine from the vulcanization accelerator used.

The present invention therefore seeks to provide a process for producing a vulcanized open cell foamed latex comfort product with which the risk to the formation of the hazardous nitrosamine from the

vulcanization accelerator used in the process may be minimized, and at the same time permits to provide latex foams with desirable mechanical properties.

This is achieved according to the present invention with a process which shows the technical features of the characterizing portion of the first claim.

Thereto the process for of the present invention is characterized in that the at least one vulcanization accelerator comprises 0.25-10.0 parts per hundred based on the total weight of the foam composition of a compound which responds to formula (I) or a zinc salt of this compound :



wherein R_1 and R_2 may be the same or different, but preferably are the same, wherein each of R_1 and R_2 may be an alkyl or a cycloalkyl group having a hydrocarbon chain containing between 1 and 9 carbon atoms, or an arylalkyl group comprising 6-12 carbon atoms, preferably an arylakylgroup having an aryl moiety with one or two alkyl groups each having 1 to 5 carbon atoms in the α-position,

wherein the vulcanization accelerator further comprises 0.01 – 10.0 parts per hundred based on the total weight of the foam composition of a thiazole or the zinc salt thereof,

wherein the molar ratio of the compound of formula I to the thiazole or their zinc salts ranges from 1 to 6 and vulcanization is carried out at a temperature of between 80 and 125°C.

In a preferred embodiment, the molar ratio of the compound of formula I to the thiazole or their zinc salts ranges from 1 to 5, preferably from 1 to 4, most preferably from 1 to 3.

If the ratio of the compound of formula I to the thiazole or their zinc salts takes a value higher than 6 or higher then 5, the risk increases to over-curing of the foam and to the formation of brittle foam, difficult to remove from the mold and showing an increasing risk to being damaged upon removal of the foam rom the mold. Also, the physical properties

of the vulcanized foam which are envisaged for these products may hardly or not be achieved, as there is a risk that the compression set increases to undesirable values. With at too high ratio of the compound of formula I to the thiazole or their zinc salts also the risk to blooming of the foamed product increases, most probably because of the limited solubility of the dithiocarbamate.

Optimal results are achieved if the ratio of the compound of formula I to the thiazole or their zinc salts is maximum 4, preferably maximum 3. With a too small ratio of the compound of formula I to the thiazole or their zinc salts, i.e. a ration < 1, the risk increases to the occurrence of a permanent reduction of the thickness of the foam upon washing at the end of the production process to remove any remaining reactants.

Vulcanization may be carried out in a temperature range of between 80 and 125°C. Preferably however vulcanization is carried out in a temperature range of between 90 and 125°C, preferably between 100 and 120°C, more preferably between 105 and 120, most preferably between 105 and 115°C.

A preferred thiazole or zinc salt thereof is a mercaptobenzothiazole or a zinc salt thereof, in particular 2-mercaptobenzothiazole or a zinc salt thereof.

In a preferred embodiment each of R_1 and R_2 or both may be an alkyl group having 1, 2, 4 or 9 carbon atoms, for example methyl, ethyl, butyl, nonyl or isononyl, or an arylakylgroup having an aryl moiety comprising one or two alkyl substituents in the α-position, each of the alkyl substituents having independently of one another 1 to 5 carbon atoms. If so desired, mixtures of two or more of the afore mentioned compounds may be used as well, wherein the molar ratio of the individual compounds may be varied taking into account their individual activation temperature and the envisaged degree of vulcanization. Preferably however use is made of di-isononyldithiocarbamate or its zinc salt, or of dibenzyldithiocarbamate or its zinc salt or of a mixture containing two or more of these compounds.

Preferably the concentration of the dithiocarbamate vulcanization accelerator, in particular the concentration of the dibenzyldithiocarbamate or the di-isononyldithiocarbamate or their zinc salt varies from 0.25-5.0 parts per hundred, preferably from 0.5-5.0 parts per hundred, more preferably 0.5-4.0, most preferably 1.0-4.0 parts per hundred, in particular from1.0-3.0 parts per hundred, more in particular from 1.5-3.0 parts per hundred based on the total weight of the foam composition, in order to achieve optimum foaming and a desired degree of vulcanization.

The concentration of 2-mercaptobenzothiazole or its zinc salt preferably varies from 0.025 – 7.5 parts per hundred based on the total weight of the foam composition, more preferably 0.025 – 5.0, most preferably 0.5-2.5 or even 0.5-2.0 parts per hundred.

The use of the claimed mixture of vulcanization accelerators, permits reducing the risk to the production of hazardous carcinogenic nitrosamines to a minimum and still obtain a vulcanized foamed open cell comfort product with a desired degree of vulcanization and the desired physical properties. The latex foam composition of this invention presents the advantage that it does not give an offensive smell, and does not produce unwanted color; in particular the risk to yellowing of the product may be reduced to a minimum which is a significant commercial value.

Without wanting to be bound by this theory, the inventors believe that in the process of the present invention, the thiazole will usually act as the secondary vulcanization accelerator, capable of facilitating the onset of the vulcanization reaction already at a low temperature of about 100°C. Once the vulcanization reaction has been initiated, the compound of formula I may take over and act as the primary vulcanization accelerator which ensures that vulcanization is continued to a desired degree within a reasonably short time frame.

The use of the claimed mixture of vulcanization accelerators permits to achieve the desired degree of vulcanization within a reasonably short time frame, in the temperature range conventionally used in the rubber latex foam production processes, such as the Talalay and Dunlop

process, i.e. 80-125°C and at a reasonable cost. Whereas a thiocarbamate or its zinc salt is a vulcanization accelerator which is capable of providing a substantially complete vulcanization, it is relatively expensive when compared to a thiazole, in particular mercaptobenzothiazole or its zinc salt. In addition a thiocarbamate or its zinc salt (ZBEC) will usually need a relatively high temperature and require additional heating in order to be activated, and the acceleration rate provided by it is slower when compared to a thiazole, in particular when compared to mercaptobenzothiazole.

Activation of vulcanization of a rubber latex foam composition by a thiazole, in particular mercaptobenzothiazole (ZMBT) or its zinc salt, with the purpose of producing a vulcanized foamed open cell comfort product, may be achieved at lower temperatures and the acceleration achieved is faster when compared to vulcanisation in the presence of a thiocarbamate alone, in particular dibenzyldithiocarbamate or di-isononyl dithiocarbamate or a zinc salt thereof. Usually however only an incomplete vulcanization may be achieved when using MBT or ZMBT alone. Without wanting to be bound by this theory, the inventors assume that the presence of the thiocarbamate ensures that the onset of the activation of the vulcanization may be achieved at the relatively low vulcanization temperatures described above. Once vulcanization has been initiated at lower temperature, the thiazole vulcanisation accelerator, in particular the mercaptobenzothiazole or its zinc salt, which normally activates at higher temperatures, gets activated as well at this lower temperature and ensures that substantially complete vulcanization may be achieved in a desirable low temperature range as described above within the desirable conventional time frame, at a suitable overall reaction rate.

The present invention further presents the advantage that the rubber latex composition of the present invention does no longer contain hazardous amounts of ZDEC, and may therefore be fully recycled at minimum, even no risk to producing unwanted of non-recyclable side products, and is thus suitable for the production of foams according to the cradle to cradle principle. Recycling of vulcanized rubber latex foam usually

involves de-vulcanization and reducing the size of the material into material particles which are suitable to be recycled, for example processed into other compounds. Moreover, when recycling the rubber latex composition of the present invention, there is a minimum risk to deteriorating the quality of the rubber latex material. In particular upon recycling the air resistance and compression set of the recycled particles are not adversely affected, as well as the hysteresis, the dynamic fatigue hardness loss and height loss over time, the compression set and ball rebound. A rubber latex foam according to the present invention meets the ecological demands for baby products, is environmentally friendly, healthy and hygienic, it is completely free from petrochemical substances.

By using as a vulcanization accelerator a mixture of a dithiocarbamate or its zinc salt, and mercaptobenzothiazole or its zinc salt the temperature at which vulcanization is carried out may be kept relatively low, i.e. within a range of about 80-125°C, often between 90 and 125°C or between 100 and 120°C or between 105 and 120°C or between 105 and 115°C, and therefore vulcanization may be achieved by using heat as a main energy source. This is unexpected as the use of dibenzyldithiocarbamate or its zinc salt (ZBEC) normally requires an elevated activation temperature, often about 135°C, which conventionally is achieved by the use of steam. Thus, the use of the claimed mixture of dibenzyldithiocarbamate or its zinc salt, and mercaptobenzothiazole or its zinc salt as vulcanization accelerator permits achieving a sufficiently complete degree of vulcanization at acceptable costs for the vulcanization accelerator and provides an economically feasible process in view of energy costs. The higher costs of for example dibenzyldithiocarbamate or di-isononyldithiocarbamate or its zinc salt may be compensated by using it in a mixture with the cheaper mercaptobenzothiazole or its zinc salt.

The use of the relatively low vulcanization temperature has the effect that drying of the foam during the processing to achieve vulcanization may be kept within desirable limits. Therewith the risk to a too high degree of drying which would involve the risk to the formation of a brittle foam, which is easily damaged certainly upon removal from a mold, and

which may be difficult to remove from a mold, may be reduced to a minimum. Thus vulcanized foam may be obtained with the desired quality in terms of mechanical and physical properties.

The inventors have further observed that the present invention permits to produce latex rubber foams of which the fatigue of the vulcanized foam, measured by applying a constant load pounding (measured according to ISO 3385 method), which is desired for these products is not adversely affected but may even be improved. In particular, the weaker foam strength provided by the dithiocarbamate or its zinc salt may be compensated and even be enhanced by the presence of the 2-mercaptobenzothiazole or its zinc salt, which tends to impart rigidity to the foam. By varying the dithiocarbamate and mercaptobenzothiazole concentration within the ranges indicated, the foam strength may be tailored as desired. With "fatigue" is meant a permanent loss of initial hardness and height of a foam sample after repeated application of load or pressure to the foam sample. "Fatigue" is commonly expressed as a percentage of the original foam hardness and height.

The amount of the vulcanization accelerator may be varied within wide ranges, and is preferably selected such that a sufficient degree of vulcanization can be attained and the desired mechanical strength and other physical properties required for vulcanized rubber articles may be obtained. Usually the total amount of the vulcanization accelerator is 0.1 to 20 parts per hundred, preferably 0.1 to 10 parts per hundred based on the solid content in the copolymer rubber latex, preferably 2-5 parts per hundred.

Detailed description of the invention.

The present invention in particular relates to process for producing a vulcanized foamed open cell product, wherein a vulcanizable rubber latex foam composition comprising a liquid rubber latex, a sulfur-containing vulcanizing agent, at least one vulcanization accelerator and soap is subjected to foaming, vulcanizing and the usual further processing to achieve a commerical foam.

The vulcanizable rubber latex foam composition used in the process of this invention will usually contain the conventional components, known to the skilled person. The vulcanizable rubber latex foam composition used in the process of this invention will usually contain a rubber latex, a sulfur-containing vulcanizing agent, at least one vulcanization accelerator, a foaming or blowing agent and a gelling agent.

Thereby, the latex may be any natural rubber latex or a mixture of two or more varieties of natural latices, a synthetic latex or a mixture of two or more varieties of synthetic rubber latices, or blend of natural rubber latex and synthetic rubber latex.

Many vulcanizing agents are known to the skilled person, many of them are suitable for use with an elastomeric latex and the particular curing or vulcanizing agent is not critical to the present invention. Suitable sulfur-containing vulcanizing agents for use in this invention include sulfur, sulfur donors and sulfur-containing compounds which are generally used as a sulfur-containing vulcanizing agents for polymer rubber latexes and which are well known to the skilled person. Examples of vulcanizing agents suitable for use with this invention include sulfur such as powdery sulfur, flower of sulfur, precipitated sulfur, colloidal sulfur, surface-treated sulfur and insoluble sulfur, sulfides; and sulfur-containing compounds such as sulfur chloride, sulfur dichloride, morpholine disulfide, an alkylphenol disulfide, N,N'-dithiobis(hexahydro-2H-asepinone-2), phosphorus-containing polysulfide, high-molecular-weight polysulfide, tetramethylthiuram disulfide, selenium dimethyldithiocarbamate and 2-(4'-morpholinodithio) benzothiazole, TMTD, TETD to include thiazoles, i.e., ZMBT. The concentration of the vulcanizing agent may vary within wide ranges. The amount of the sulfur-containing vulcanizing agent contained in the latex composition of this invention is not critical to the invention, but will usually vary from 1-5, preferably 1.5 to 3 parts per hundred (phr) of uncompounded latex solids, more preferably between 2 – 2.5 phr depending on the product requirements.

The latex foam composition used in the process of this invention may contain one or more vulcanization activators. Suitable

examples include zinc oxide and magnesium oxide which can be used in a manner similar to the conventional sulfur vulcanization method. Active zinc oxide can be used as the zinc oxide, but is difficult to disperse. The amount of zinc oxide is suitably determined so that a sufficient vulcanization can be attained and the mechanical strength and other physical properties required for vulcanized rubber articles are obtained, and is not particularly limited. The amount of activator that may be used in the present invention is approximately 0.01-5 parts by weight per 100 parts by weight of uncompounded latex solids.

The vulcanization accelerator contained in the latex foam composition used in the process of this invention may comprise 0.50-10.0 parts per hundred based on the total weight of the foam composition of dibenzyldithiocarbamate or its zinc salt, and 0.01 – 10.0 parts per hundred based on the total weight of the foam composition of 2-mercaptobenzothiazole or the zinc salt thereof. Although the invention does not exclude other compounds which have the effect to accelerate vulcanization, their presence is not preferred and the vulcanization accelerator used with the present invention preferably exclusively consists of

- dibenzyldithiocarbamate or its zinc salt or di-isononyl dithiocarbamate or its zinc salt,
- and 2-mercaptobenzo-thiazole or the zinc salt thereof.

The latex composition used in the process of the present invention may also comprise a gelling agent. Suitable gelling agents are well known to the skilled person. An example of a suitable gelling agent is $Zn(NH_4)_nCl_2$. The amount of gelling agent used may vary within some ranges, and is chosen such that it is sufficient to gel the latex upon removal of a sufficient amount of ammonia; preferably, approximately 0.5-2 parts by weight per 100 parts by weight of uncompounded latex solids. Examples of other suitable gelling agents include polyethers, low molecular weight glycols, silicone polyethers, alkali metal silicofluorides, ammonium or amine salts of carboxylic acids in the presence of a divalent metal ion, preferably zinc.

According to the need, further additives can be incorporated in the latex composition used in the process of the present

invention for imparting desired properties to vulcanized rubber articles, which include, for example, reinforcing materials such as carbon black, silica and talc, fillers such as calcium carbonate and clay, plasticizers, flame retardants, antioxidants and natural fibers.

The latex composition suitable for use with the present invention may comprise either a natural or a synthetic rubber or a mixture thereof. Natural rubber mainly consists of elastomeric polyisoprene, with minor impurities of other organic compounds, and water. It has a large stretch ratio, a high resilience and is waterproof. Other latex compositions suitable for use with the present invention include synthetic latex dispersions. Synthetic rubber may be made by the polymerization of a variety of petroleum-based precursors or monomers. The most prevalent synthetic rubbers are styrene-butadiene rubber (SBR) derived from the copolymerization of styrene and 1,3-butadiene. Other synthetic rubbers are prepared from isoprene (2-methyl-1,3-butadiene), chloroprene (2-chloro-1,3-butadiene), and isobutylene (methylpropene) with a small percentage of isoprene for cross-linking. Other latex compositions suitable for use with the present invention include cis-polyisoprene (IR), Styrene butadiene (SBR), Cis polybutadiene (BR), or Butyl rubber (IIR) (and variants chlorobutyl (CIIR), or bromobutyl (BrIIR) rubber, liquid polybutene (PB); liquid Natural Rubber; liquid cis polyisoprene; liquid cis polybutadiene; liquid styrene butadiene; or any suitable combination of the afore-mentioned latex rubber compositions. Still other latex compositions suitable for use with this invention include elastomeric latex dispersions, for example those based on acrylonitrile, chloroprene, isoprene, butadiene-styrene, butadiene-acrylonitrile, polyacrylonitrile, polyisoprene, polystyrene, polyvinylidene chloride, polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate, co-polymers of the monomers of these resinous polymers, resinous copolymers of these monomers with other copolymerizable monomers, such as C4 -C10 conjugated dienes and blends of two or more of the afore-mentioned materials. The solids content of the latex composition may vary within wide ranges, but is preferably at least 15% by weight total solids before compounding; preferably, about 40%-75% by weight total solids.

Anionic, cationic or non-ionic surfactants can be chosen as a foaming agent, depending on the process requirements whereby anionic surfactants are preferred. Preferred anionic surfactants are fatty acid soaps, fatty alcohol sulfonates and alkylaryl or aralkyl sulfonates, succinates and amido sulfosuccinates. Particularly preferred are alkali metal and ammonium salts of fatty acids and rosin acids and combinations thereof, most preferred are alkali metal salts of fatty acids and rosin acids and combinations thereof.

The order in which the foregoing components of the latex composition of the present invention are mixed with each other is not critical. However, it is preferred to prepare a first blend by mixing the latex, gelling agent and optionally the enhancers, surfactants, pigments, antioxidants, thickeners, dispersants and the like. These ingredients can be blended together in a conventional manner, for example using a mixer, for example a planetary mixer. A second blend which comprises the vulcanization accelerator, the vulcanizing agent and optionally the vulcanization activator may be prepared and mixed with the first blend to form the finished vulcanizable latex foam composition.

According to a preferred embodiment of this method, the vulcanizable latex foam composition used in the process of this invention is subjected to pre-foaming to produce a foam with a desired density, and then poured into a mold with a desired shape, which will usually be similar to the shape of the article that is to be produced from the foam. After the mold has been closed, it is evacuated to allow the latex foam composition to foam to the finally desired density. Thereby, the foam will completely fill the mold. Thereafter, the foam structure is stabilized or fixed by cooling the mold to approximately -30^{0}C. In a next step, carbon dioxide is supplied to the mold to pressurize the mold, and lower the pH of the frozen foamed latex compound to achieve coagulation and gelling. Usually this is carried out at a temperature of -30°C. The foam may than be vulcanized at 80°C-125°C. After vulcanization has been achieved to a desired degree, the vulcanized latex foam article is

removed from the mold, washed to remove any remaining surfactants and other unwanted products and dried.

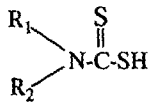
The present invention also relates to a vulcanized foamed open cell rubber latex comfort product obtained with the above-described method, having a ILD hardness of between 5 and 105 lbf measured according to ASTM 1055D-4 section 20-23. The vulcanized foamed open cell rubber latex comfort product of this invention preferably has a density of between 30 and 100 kg/m^3 measured according to ISO 845. The vulcanized foamed open cell rubber latex comfort product obtained with the method of this invention preferably has a SAG value measured according to ISO 2439 of between 2.0 and 5.0, preferably between 2.5 and 4.0.

The vulcanized latex foam of the present invention may be used for a wide variety of applications for example for the production of mattresses, pillows, neck rests, toppers, shock absorbers, shaped parts of shoes, shoe inside soles, garments padding, protectors for sportswear, athletic implements, bike saddles, motorbike saddles, furniture upholstery material, bumpers, automotive dashboards and carpets. The present invention therefor also relates to an article selected from a mattress, pillow, neck rest, topper, shock absorber, shaped part of a shoe, shoe inside sole, garment padding, protector for sportswear, athletic implement, bike saddle, motorbike saddle, furniture upholstery, bumper, automotive dashboard and carpet comprising a vulcanized rubber latex foam as described above and in the claims, or a vulcanized rubber latex foam obtained by the method described above and in the claims, or a foam composition as described above or in the claims.

The present invention also relates to a method for recycling a vulcanized rubber latex foam described above and in the claims, or a vulcanized rubber latex foam obtained by the method described above and in the claims, or a vulcanized rubber latex foam obtained by vulcanization of the foam composition described above and in the claims, wherein the vulcanized rubber is subjected to de-vulcanization and the size of the foam material is reduced to provide material particles which are suitable to be recycled, in particular to be processed into other compounds for example compounds for

producing open cell comfort products such as those described above or compounds for producing rubber slabs. The size of the foam particles to be recycled may vary within wide ranges, depending on the nature of the intended use. De-vulcanized latex foam will be a new virgin rubber slab product for further processing.

The present invention further relates to the use in a vulcanization of a rubber latex foam comfort product of at least one vulcanization accelerator which comprises 0.25-10.0 parts per hundred based on the total weight of the foam composition of a compound which responds to formula (I) or a zinc salt of this compound :



formula (I)

wherein R_1 and R_2 may be the same or different, but preferably are the same, wherein each of R_1 and R_2 may be an alkyl or a cycloalkyl group having a hydrocarbon chain containing between 1 and 9 carbon atoms, or an arylalkyl group comprising 6-12 carbon atoms, preferably an arylakylgroup having an aryl moiety with one or two alkyl groups each having 1 to 5 carbon atoms in the α-position,

wherein the vulcanization accelerator further comprises 0.01 – 10.0 parts per hundred based on the total weight of the foam composition of a thiazole or the zinc salt thereof, wherein the molar ratio of the compound of formula I to the thiazole or their zinc salts ranges from 1 to 6.

The invention is further illustrated in the appending examples and comparative experiments.

In the examples below, use is made of a vulcanization system (Weserland VS), supplied by Weserland GmbH. The vulcanization system comprises sulfur, zinc oxide, antioxidant, ZMBT as

secondary accelerator, and ZBEC as a primary accelerator. Another example is from Synthomer, this vulcanization system (Synthomer VS) comprises sulfur, zinc oxide, ZMBT as secondary accelerator, and ZBEC as a primary accelerator plus other necessary additives to stabilize the dispersion. Yet another example is from Vita Liquid Polymers, this vulcanization system (VLP VS) comprises sulfur, zinc oxide, ZMBT as secondary accelerator, and Arbestab Z as a primary accelerator plus other necessary additives to stabilize the dispersion. Typical properties of Weserland, Synthomer vulcanization systems and Vita Liquid Polymers systems are shown in Table 1 below.

Table 1. Product	VLP VS	Weserland VS	Synthomer VS
Appearance	Yellowish dispersion	Yellowish dispersion	Yellowish dispersion
Solids Content	59-61	56-58	60-62
pH-value	8-11	8.5-10.5	9-10
Viscosity	1500-2500	1500-2500	1500-1650
Particle size (µm) D50	<40	< 2 <15	<2 <15
Solubility	Dilutable with water	Dilutable with water	Dilutable with water

As ZBEC is known to activate at high temperatures (>100°C) and proceeds in a much slower speed as compared to the ultra fast ZDEC, Arbestab Z and ZMBT accelerators, the use of secondary accelerator ZMBT was increased to be able to have curing in a typical operating curing temperatures of 100 – 125°C in 10 minutes.

The ingredients of the foam composition as listed in table 2, 3, 4, 5, 6 and 7 of respectively example 1 and 2 below, comprising the latex, soap, vulcanization system and other additives were compounded in a mixing tank and allowed to mature for 2 hours. The resulting compound was then frothed to the required density and poured in a mold to fill about 20 - 30% of the mold's volume. The mold was then closed and the frothed compound

was allowed to expand inside the mold by applying vacuum in the system. Once vacuum was complete, the latex was flash frozen to -30°C to set the foam inside the mold and to avoid settling of the latex. Carbon dioxide was introduced in the mold to effect gelling of the foam thereby setting completely its structure. The frozen foam was then thawed by slowly heating the foam to 15°C and then 30°C and the foam was finally vulcanized at 80 – 125°C for 8-15 minutes. The resulting foam was then withdrawn from the mold, washed, dried, and post-vulcanized prior to final quality check.

Typical formulations to illustrate the invention are shown in the following examples.

EXAMPLE 1.

Table 2

Material	phr
Synthetic Latex	60
Natural Latex	40
Thickener	1
Weserland VS	8.
Soap	3

Table 3	
Material	phr
Synthetic Latex	60
Natural Latex	40
Anti-oxidant	1
Thickener	0.8
Synthomer VS	10
Soap	3

Table 4	
Material	phr
Synthetic Latex	60
Natural Latex	40
Anti-oxidant	1
Thickener	1
Vita Liquid Polymers VS	7
Soap	3

In Table 2 above, Synthetic Latex, e.g., Lipolan F2420, is a cold polymerized styrene-butadiene latex, commercially available from Synthomer Deutschland GmbH, Marl, Germany; Natural latex which can originate from Hevea Brasiliensis rubber tree, Guayule plant, or Russian Dandelion; Thickener is a viscosity modifier ingredient prepared by mixing Tylose NS 299 KG4 (SE Tylose GmbH & Co. KG, Wiesbaden, Germany) and sodium dodecyl sulphate (commercially available as Serdet NL 30 from Elementis Specialties Netherlands B.V., Delden, Netherlands) with water; Weserland VS is a complete vulcanization system with sulphur, zinc oxide, stabilizers, and accelerators ZBEC and ZMBT, commercially available from Weserland GmbH, Hannover, Germany; Synthomer VS is a complete vulcanization system with sulphur, zinc oxide, antioxidant, stabilizers, and accelerators ZBEC and ZMBT, commercially available from Synthomer, Oss, The Netherlands; Vita Liquid Polymers VS is

a complete vulcanization system with sulphur, zinc oxide, stabilizers and accelerators Arbestab Z and ZMBT, commercially available from Vita Liquid Polymers, Manchester, United Kingdom. Anti-oxidant (Wingstay L) is an anti-oxidant system commercially available from Synthomer, Oss, The Netherlands; and Soap is an ammonium ricinoleate type commercially available from Govi NV, Gent, Belgium.

In the above "phr" means parts per hundred on dry rubber.

All materials were mixed and the compound was allowed to mature for about 2 hours. The matured compound was then processed as described in the United States patent to Talalay No. 2,432,353 wherein the compound is frothed and poured in the mold and then frozen immediately to avoid drainage of the foam. The foam was then coagulated with an acid gas, in this case, a carbon dioxide gas and then the coagulated foam is then vulcanized at 110°C-120°C.

The resulting foam has good physical and mechanical properties and has comparable properties as that of a product with normal vulcanization systems. The physical and mechanical properties of the foam are summarized in table 8 below.

EXAMPLE 2.

Table 5

Material	Phr
Natural Latex	100
Soap	3
Slipol U57	1.5
Weserland VS	8
Thickener	1

Table 6	
Material	Phr
Natural Latex	100
Soap	3
Synthomer VS	10
Anti-oxidant	1.5
Thickener	1

Table 7	
Material	phr
Natural Latex	100
Soap	3
Vita Liquid Polymers VS	7
Anti-oxidant	1.5
Thickener	1

Natural latex which can originate from Hevea Brasiliensis rubber tree, Guayule plant, or Russian Dandelion; potassium oleate is a soap stabilizer commercially available from Govi NV, Gent, Belgium; Slipol U57 is another natural latex stabilizer commercially available from Weserland GmbH, Hannover, Germany; Weserland VS is a complete vulcanization system with elemental sulphur, zinc oxide, antioxidant, stabilizers, and accelerators ZBEC and ZMBT also commercially available from Weserland GmbH, Hannover, Germany; Synthomer VS is a complete vulcanization system with sulphur, zinc oxide, stabilizers, and accelerators ZBEC and ZMBT, commercially available from Synthomer, Oss, The Netherlands; Vita Liquid Polymers VS is a complete vulcanization system with sulphur, zinc oxide, stabilizers and accelerators Arbestab Z and ZMBT, commercially available from Vita Liquid Polymers, Manchester, United Kingdom; Anti-oxidant (Wingstay L) is a anti oxidant system commercially available from Synthomer, Oss, The Netherlands; thickener is again a viscosity modifier prepared by mixing Tylose NS 299 KG4 (SE Tylose GmbH & Co. KG, Wiesbaden, Germany) and sodium dodecyl sulphate (commercially available as Serdet NL 30 from Elementis Specialties Netherlands B.V., Delden, Netherlands) with water.

The materials in Table 3 are mixed and the resulting compound was allowed to mature for about 2 hours and then foam was prepared according to the procedure above. The resulting products give good physical and mechanical properties.

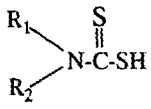
The foregoing data may be also be applied to other conventional lattices containing fillers, and other known modifying materials as long as these said materials can comply to EPEAs criteria for toxicity.

Table 8. Typical Physical and Mechanical Properties of Foams with ZBEC/ZMBT as Compared with Standard Formulations

Description	*Test Standard*	*Standard*	*Example 1 Standard with ZBEC/ZMBT*	*100% Natural*	*Example 2 100% Natural ZBEC/ZMBT*
ILD Hardness (lbf)	ASTM 1055D-4 section 20-23	23.4 – 26.8	23.4	21.1 – 29.0	22.7
Density (kg/m3)	ISO 845	62.0 – 68.0	62.3	64.0 – 75.0	68.0
Elongation at break (%)	ISO 1798	273.6	269.6	274.5	261.2
Tensile strength (kPa)	ISO 1798	84.1	73.9	94.6	83.2
SAG Value	ISO 2439	2.8	2.8	2.9	2.8
Fatigue by constant load pounding Hardness Loss in 24 hrs. (%)	ISO 3385	7.8	14.3	13.5	7.5
Fatigue by constant load pounding Height Loss in 24 hrs. (%)	ISO 3385	1.1	1.1	0.7	0.6

CLAIMS.

1. A process for producing a vulcanized foamed open cell comfort product, wherein a vulcanizable rubber latex foam composition comprising a liquid rubber latex, a sulfur-containing vulcanizing agent and at least one vulcanization accelerator, is subjected to foaming, gelling and vulcanization, characterized in that the at least one vulcanization accelerator comprises 0.25-10.0 parts per hundred based on the total weight of the foam composition of a compound which responds to formula (I) or a zinc salt of this compound :



formula (I)

wherein R_1 and R_2 may be the same or different, but preferably are the same, wherein each of R_1 and R_2 may be an alkyl or a cycloalkyl group having a hydrocarbon chain containing between 1 and 9 carbon atoms, or an arylalkyl group comprising 6-12 carbon atoms, preferably an arylakylgroup having an aryl moiety with one or two alkyl groups each having 1 to 5 carbon atoms in the α-position,

wherein the vulcanization accelerator further comprises 0.01 – 10.0 parts per hundred based on the total weight of the foam composition of a thiazole or the zinc salt thereof,

wherein the molar ratio of the compound of formula I or its zinc salt to the thiazole or its zinc salt ranges from 1 to 6 and vulcanization is carried out at a temperature of between 80 and 125°C.

2. A method according to claim 1, wherein the molar ratio of the compound of formula I to the thiazole or their zinc salts ranges from 1 to 5, preferably from 1 to 4, more preferably from 1 to 3.
3. A method according to any of the previous claims, wherein vulcanization is carried out at a temperature of between 80 and 125°C, preferably between

100 and 120°C, more preferably between 105 and 120°C, most preferably between 105 and 115°C.

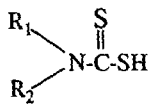
4. A method according to any of the previous claims, wherein the compound according to formula (I) is dibenzyldithiocarbamate or its zinc salt.
5. A method according to any of the previous claims, wherein the compound according to formula (I) is di-isononyldithiocarbamate or its zinc salt.
6. A method according to any of the previous claims, wherein the concentration of the dithiocarbamate or its zinc salt varies from 0.25-5.0 parts, preferably from 0.5-4.0 parts, more preferably from 1.0-3.0 parts per hundred based on the total weight of the foam composition.
7. A method according to any of the previous claims, wherein the thiazole compound is a 2-mercaptobenzothiazole or its zinc salt
8. A method according to claim 7, wherein the concentration of 2-mercaptobenzothiazole or its zinc salt varies from 0.025 – 7.5 parts per hundred, preferably, more preferably 0.025 – 5.0 parts per hundred, most preferably 0.5-2.5 parts per hundred based on the total weight of the foam composition.
9. A method according to any one of the preceding claims, wherein the composition further comprises sulfur containing vulcanizing agent.
10. A method according to any one of the preceding claims, wherein the composition further comprises a vulcanization activator, in particular zinc oxide or magnesium oxide.
11. A method according to any one of the preceding claims, wherein the latex is natural rubber latex or a synthetic rubber latex or blend of natural rubber latex and synthetic rubber latex.
12. A vulcanized foamed open cell rubber latex comfort product obtained with the method according to any one of claims 1-11, having a ILD hardness of between 5 and 105 lbf measured according to ASTM 1055D-4 section 20-23.
13. A vulcanized foamed open cell rubber latex comfort product according to claim 12, having a density of between 30 and 100 kg/m^3 measured according to ISO 845.

14. A vulcanized foamed open cell rubber latex comfort product according to claim 12 or 13 having a SAG value measured according to ISO 2439 of between 2.0 and 5.0, preferably between 2.5 and 4.0.

15. A method for recycling a vulcanized foamed open cell rubber latex comfort product according to any one of claims claim 12-14, or a vulcanized foamed open cell rubber latex comfort product obtained by the method of any one of claims 1 - 12, wherein the vulcanized rubber is subjected to de-vulcanization and the size of the foam material is reduced to provide material particles which are suitable to be recycled, in particular to be processed into other compounds.

16. A comfort article selected from a mattress, pillow, neck rest, topper, shock absorber, shaped part of a shoe, shoe inside sole, garment padding, protector for sportswear, athletic implement, bike saddle, motorbike saddle, furniture upholstery, bumper, automotive dashboard and carpet comprising a vulcanized foamed open cell rubber latex product obtained according to the method of any one of claims 1-11 or a vulcanized foamed open cell rubber latex comfort product according to any one of claims 13-15, or a recycled vulcanized rubber foam obtained by the method of claim 16.

17. Use in a vulcanization of a rubber latex foam comfort product of at least one vulcanization accelerator which comprises 0.25-10.0 parts per hundred based on the total weight of the foam composition of a compound which responds to formula (I) or a zinc salt of this compound :



formula (I)

wherein R_1 and R_2 may be the same or different, but preferably are the same, wherein each of R_1 and R_2 may be an alkyl or a cycloalkyl group having a hydrocarbon chain containing between 1 and 9 carbon atoms,

or an arylalkyl group comprising 6-12 carbon atoms, preferably an arylakylgroup having an aryl moiety with one or two alkyl groups each having 1 to 5 carbon atoms in the α-position,

wherein the vulcanization accelerator further comprises 0.01 – 10.0 parts per hundred based on the total weight of the foam composition of a thiazole or the zinc salt thereof, wherein the molar ratio of the compound of formula I to the thiazole or their zinc salts ranges from 1 to 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2017/050015

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/39 C08K5/47 C08L21/02 C08J9/00 C08J3/24
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C08L C08J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 968 285 A (COFFIN PERLEY A ET AL) 6 July 1976 (1976-07-06) column 4, line 63; claims 1-3, 5, 6, 10, 12, 23; examples 1-5 column 5, lines 3-4 column 5, lines 35-36 column 7, lines 54-55 -----	1-17
X	US 6 187 829 B1 (SELLERS ALAN P [US]) 13 February 2001 (2001-02-13) column 5, lines 14-22; claims 1,2,4-6; tables column 1, lines 15-19 ----- -/--	1-17

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 April 2017	24/04/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lohner, Pierre

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	DEBNATH S C ET AL: "STUDIES ON CURE SYNERGISM. ÖI. EFFECT OF SAFE ZINC DITHIOCARBAMATES ON NR VULCANIZATION ACCELERATED BY THIAZOLE-BASED ACCELERATORS", JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY & SONS, INC, US, vol. 52, no. 5, 2 May 1994 (1994-05-02), pages 597-603, XP000464277, ISSN: 0021-8995, DOI: 10.1002/APP.1994.070520503 Introduction; examples 21-23; table II	1-17
Y	US 2001/004653 A1 (OZAWA YUTAKA [JP] ET AL) 21 June 2001 (2001-06-21) paragraphs [0001], [0009], [0034] - [0040]	1-17
X	US 2011/135909 A1 (IWASE TAKAYUKI [JP] ET AL) 9 June 2011 (2011-06-09)	1-17
Y	paragraphs [0020], [0031], [0032], [0095], [0096], [0050]; claims 1,5; table 1	1-17
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2017/050015

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