A METHOD OF PRODUCING A SILICONE RUBBER ITEM AND THE PRODUCT OBTAINABLE BY THE METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a method of producing a silicone rubber item, such as a medical item or other silicone items where high quality is important.

Silicone rubber has been used in a variety of fields as medical instruments, building materials, electric and electronic parts, automotive parts, and business machine parts because of its superior properties including physiological inertness (non-toxicity), weather resistance, durability, release properties, and heat resistance.

Silicone rubber item may today be produced in many ways using various starting materials and curing systems. US 5519082 discloses a silicone rubber composition that cures through hydrosilylation. This reaction type is known as the addition curing type. US 5973030 discloses production of liquid silicone rubber compositions. EP 384 609 and US 6020449 disclose single-component silicone rubber mixtures (RTV1) which readily cure simply by heating, leading to a very high production yield. Two component silicon rubbers are also very popular.

The methods of producing silicone rubber items in general comprise a step of curing the composition which is most often a process which requires or is speeded up using heat.

After the curing is terminated it has for a lot of applications been found necessary to treat the cured silicone rubber item with heat, for removing undesired and often bad smelling residuals. This heat treatment process can often be very time consuming up to several hours, and requires large production space and heating chambers.

In particular in LSR silicon rubber items, which are used in medical applications, it has been found essential to subject the items to a post-heat treatment or a post-vulcanisation, also referred to as post-curing, in order to reduce the amount of silicon oil residues. The

LSR articles have thus been subjected to 2 or even further hours of heat treatment at e.g. at 200 °C under air or oxygen flow.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an improved method for producing a silicone item, in which method the post-heat treatment may be reduced or even eliminated.

The method provided according to the invention is much faster than the prior art method, and furthermore it will in most circumstances require less working space.

Also it has been found that the method according to the invention results in a silicone item with a very low amount of undesired residuals as compared to silicone item produced using prior art methods.

The inventors of the present invention have thus found than by subjecting the silicone rubber item to a cold tempering including extracting the silicone material using a carbon dioxide containing solvent, a much more effective and fast method of producing the silicone rubber item can be provided.

The method according to the invention is defined in the claims. The invention also comprises a silicone rubber item obtainable using the method.

DETAILED DESCRIPTION OF THE INVENTION

The term 'silicone rubber item' is meant to include all items having at least some silicone material. Silicone rubber item thus also includes composites where one of the composite materials is a silicone rubber material, e.g. the composite of a thermoplastic resin bonded to a silicone rubber integrally as described in US 6800372 or US6613440. The weight of the silicone rubber item as used in the definitions in this description and claims should, however, include only the weight of the silicone rubber part of the composite material.

According to the invention it is preferred that the silicone rubber item should have at least one non-coated surface. This means that at least one surface area of silicone rubber

should not be coated with paint or another material directly bonded to the surface (not including packing material, which is to be removed in use).

In one embodiment the silicone rubber item has at least one non-coated surface at least during the cold tempering. After the cold tempering this non-coated surface may be covered or coated. In one embodiment this non-coated surface remains uncoated except for potential packing material. It has thus been found that the surface of the silicone item produced according to the present invention is very clean and does not exude residual oils which might cause irritation to the body if the silicone item is used against the body e.g. against the skin or mucous membranes.

The silicone item may in principle be any type of items such as tubes, catheters, cable insulations, keypads, gaskets, parts for infant care and feeding (soothers, bottle closures), parts for use in the automotive, telecom and medical sector, films, contact lenses and etc. In particular the method according to the invention is useful for producing silicone rubber items of high quality demands, such as items which should be approved under government regulations e.g. FDA, UBA, Japanese Pharmacopoeia and other relevant regulations concerning material requirements for silicone items designed for medical, implant, direct and indirect food contact and disposable use.

The method of the invention has further been found to be useful in the production of silicone items which heretofore were only produced by casting, due to fragile shapes such as thin material walls e.g. contact lenses and similar items. Since the cold tempering is performed effectively at such low temperatures the items with fragile shapes can withstand the extraction treatment without altering shape.

The method according to the invention comprises the steps of
i) shaping the silicone rubber item by injection moulding and
ii) subjecting the injection moulded item to a cold tempering,

wherein the cold tempering includes feeding the injecting moulded item into a reactor, and subjecting the injection moulded item to an extraction treatment using carbon dioxide containing solvent at a pressure between 10 and 50 bars, wherein the item has an initial temperature below 60 °C in the extraction step, and in at least a part of the extraction time

the item has a temperature below 25 °C and a pressure between 10 and 50 bars so that the carbon dioxide is in its liquid state.

In one embodiment the initial temperature is 30 °C or below.

The step of shaping may in addition to the injecting moulding comprise other manipulation steps. In one embodiment the shaping step comprises providing the item with a slit or hole extending at least partly through the material of the item. This slit or hole may preferably be provided in the injection moulding step or it may in one embodiment be provided after the injection moulding step e.g. using a cutting tool.

When the item is an item with such a slit or hole e.g. a slit or a hole in an infant feeding devise, the method of the invention has the additional benefit that this slit or hole can be provided before the cold tempering, because the cold tempering is performed under conditions where the silicone item is performed at low temperatures whereby this slit or hole will not collapse or close.

It is preferred that the temperature is kept below 60 °C, such as below 50 °C, such as below 25 °C, such as between 5 and 22 °C, such as between 8 and 20 °C. In one embodiment the temperature during the cold tempering is between 8 and 15 °C for the major part of the time.

In particular it is preferred that the temperature is kept below about 25 °C, because this has shown to give the most optimal extraction, and furthermore the item can be packed directly after the treatment with no need for intermediate cooling. This is both beneficial with respect to production time, but also with respect to the quality of the item as it will be explained further later in the description.

In one embodiment the cold tempering step is initiated at a relative high temperature and the item may be transported directly from the injection moulding to the cold tempering reactor. The initial temperature may be up to 60 °C. After the item is placed in the cold tempering reactor the temperature is allowed to fall during the cold tempering step to terminate the cold tempering step at a temperature below 25 °C. The temperature fall may be provided by active cooling or by passive cooling.

In one embodiment the cold tempering step is initiated at a temperature above 50 °C, e.g. around 60 °C.

In one embodiment the temperature drops by up to 50 °C, such as up to 25 °C, such as between 1 and 50 °C, such as between 5 and 25 °C during the cold tempering step.

In one embodiment the carbon dioxide containing solvent converts from gas to its liquid state during the cold tempering.

In one embodiment the cold tempering includes subjecting the silicone rubber item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor under a pressure of between 5 and 50 bars, and a temperature of between 0 and 60 °C.

In one preferred aspect of the invention extraction treatment comprises subjecting the silicone rubber item to an extraction treatment with a carbon dioxide containing solvent in liquid state. Thus, it has surprisingly been found that performing the extraction treatment using the carbon dioxide containing solvent in liquid state is highly effective, even if the pressure is kept relatively low. Thus according to the invention it is preferred that the extraction treatment is performed at a pressure of between 5 and 50 bars, such as between 10 and 50 bars, preferably between 20 and 50 bars, such as between 25 and 50 bars, more preferably between 30 and 50 bars. By using this relatively low pressure, it has surprising been found that the extraction of oil residuals is very effective and very fast compared to using other extraction methods e.g. using supercritical solvents, and simultaneously the requirements to the equipment and in particular the pressure reactor are highly reduced as compared to the cost connected with a pressure reactor for supercritical extraction.

In one embodiment the pressure is kept around 45 bars or below, which in practice has shown to be a sufficient pressure for a fast and effective extraction, in particular when the temperature is kept in the interval 8-15 °C in most of the extraction time.

It is thus in one embodiment it is preferred that the pressure during the entire cold tempering step is kept below 45 bars and preferably in the range around 30-35 bars.

In one embodiment the pressure is kept around 45 bars +/- 5 bars.

The pressure may be pulsed during the extraction, e.g. such that the pulsed pressure has variations from top to bottom of a pulse of up to 10 bars, such as up to 5 bars, such as up to 2 bars.

The pulsation may speed up the extraction. However, in order to avoid damaging the material the pulsation should not be too fast, since this may result in internal damaging of the silicone rubber material.

In one embodiment the pulsed pressure preferably have a frequency of up to 10 pulses per minutes, such as 2 pulses per minute, wherein one pulse includes decreasing from one pressure top (high pressure peak) to the pressure bottom (low pressure peak) and back to the pressure top.

The extraction treatment may preferably be performed for at least 0,5 minutes, such as at least 1 minute, such as at least 2 minutes, such as at least 4 minutes, such as at least 10 minutes.

The optimal extraction treatment time depends on the type of silicone rubber, including its production method. However, the optimal extraction treatment time depends even more on the shape and thickness of the silicone rubber material.

Test performed on different shapes of silicone rubber items have shown that the optimal extraction treatment time for an item is to subject the silicone rubber item to a treatment with a carbon dioxide containing solvent for at least 0.1 minute per Maximal Shortest Distance to Surface (MSDS) in millimetres. In this connection the term MSDS means the maximal shortest distance to a surface point for any point of material of the item. Preferably the extraction treatment comprises subjecting the item to a treatment with a carbon dioxide containing solvent in liquid state for at least 0.3 minute, such as at least 1.0 minute, such as at least 1.5 minutes, such as at least 2 minutes per MSDS.

In one embodiment the method of the invention comprises the step of subjecting the items to movement during the cold tempering. This movement may e.g. be proformed by applying a mechnical stirring system inside the chamber or by roatation of the chamber itself (tumbler).

In one embodiment the reaction chamber formed as a tumbler is rotated with a rate of 1 – 50 Hz (1 Hz = 2.4 rpm), such as at a rate of 1-10 Hz during the extraction.

For improving the tumbler effetc the inside of the tumbler may in one embodiment comprise protruding elements attached to the walls, also referred to as "wings". Such wings result in an even more improved effect of extraction due to an improved mixing of the items with the liquid.

In one preferred aspect of the invention the product item is packed. This method thus comprises the steps of

i) shaping the silicone rubber item,

ii) subjecting the injection moulded item to a cold tempering, and

ii) packing the item in a packing material.

The packing material will in general provide a barrier against silicone oil residuals. In other words, silicone oils cannot freely escape from the surface of a packed item as fast as it would have if it had not been packed. Normally, for prior art silicone rubber materials some of the silicone oils migrates through the silicone rubber material and escapes – if the silicone rubber material is not packed – to the environment several months after production e.g. 12 month or even longer, in particular if the silicone rubber material has not been heat treated sufficiently or cold tempered as according to the present invention. This slow migration/evaporation from the silicone rubber material provides the silicone rubber material with an unpleasant smell, and furthermore, if the silicone rubber material is to be used in contact with the human body, this slow migration/evaporation may cause irritation, eczema, bad taste or similar unpleasant effects.

Therefore the method according to the invention is particularly useful for the production of silicone rubber items which are to be packed.

In one embodiment the packing material used in the packing step has a permeability of the silicone oil hexamethylcyclotrisiloxane (D3) of up to 10 g/m^2 x 24h, such as up to 5 g/m^2 x 24h, such as up to 1 g/m^2 x 24h, such as up to 0.1 g/m^2 x 24h. For some items it is desired that the packing material is impermeable to hexamethylcyclotrisiloxane (D3).

In one embodiment the method of the invention includes packing the silicone rubber item in a packing material with a water vapour permeability (DIN 53122) of up to 100 g/m^2 x 24h, such as up to 50 g/m^2 x 24h, such as up to 25 g/m^2 x 24h, such as up to 10 g/m^2 x 24h. For some silicone rubber items, it is desired that the moisture levels is kept low and that the item is protected against moisture prior to use. In such situation it is preferred that the packing material has an even lower water vapour permeability e.g. below 1 g/m^2 x 24h, or even below 1 mg/m^2 x 24h.

In one embodiment the method of the invention includes packing the silicone rubber item in a packing material which is essentially impermeable to bacteria and viruses. This method is in particular preferably for silicone rubber items for medical use such as catheters, contact lenses and feeding (soothers, bottle closures, tests, dummies) and similar items for use in contact with the human body.

In one embodiment the packing step comprises packing the item in a sealed packing material, whereby the packing material provides a barrier against free flow of air. For silicone rubber items for medical use, the sealed packing material may preferably provide a gas-tight package.

In principle the packing step may be performed any time after termination of the cold tempering step. But for most productions it is desired that the packing step is performed relatively soon after the cold tempering step in order to reduce needs for excessive factory space and space for intermediate storing.

In one embodiment it is therefore desired that the packing step is performed within 60 minutes from termination of the cold tempering step, preferably within 40 minutes, such as within 20 minutes, such as within 10 minutes, more preferably within 5 minutes.

If the cold tempering step is terminated at elevated temperatures e.g. above 40 °C, the silicone rubber item may need to cool down prior to packing. However, if the cold tempering step is performed or terminated at temperatures about or below 40 °C it may not be necessary to cool down the silicone rubber item prior to packing. This further has the beneficial effect that the silicone rubber item main be kept very clean or even essentially sterile up to the packing step, and if the packing step is performed under sufficiently clean circumstances the packed product may be very clean. For products for

medical use this is a very beneficial effect. Some products, e.g. catheters and contact lenses produced using prior art methods, must be subjected to further sterilisation after packing. For similar products produced using the present method this sterilisation can be avoided, in particular if the packaging is performed immediately after termination of the cold tempering step.

In one embodiment it is thus preferred that the silicone rubber item is packed after the cold tempering with no further intermediate treatments, in particular with no additional surface treatments.

In one embodiment the shaped silicone rubber item is mounted with another part e.g. a teat is mounted with a base of another polymer. This mounting may in one embodiment be performed prior to the cold tempering step, which means that the cold tempered product may be packed directly after termination of the cold tempering step.

In another embodiment the mounting with another part is performed after the cold tempering step.

During the cold tempering step, carbon dioxide will penetrate into the silicone rubber material. In one embodiment it is desired that the packing step is performed sufficiently shortly after the cold tempering step for the item to still comprise releasable carbon dioxide. This carbon dioxide will then be released within the package. The packing step may e.g. be performed sufficiently shortly after the cold tempering step for the item to still comprise sufficient carbon dioxide so that the item releases at least 0.01 % by weight, such as at least 0.1% by weight or even at least 0.5% of weight of carbon dioxide relative to the weight of the item within the first hour after the package has been sealed.

In situation where the silicone rubber item is only partly cured prior to the cold tempering step, the extraction performed during the cold tempering step may result in visible area of air bubbles within the material resulting from the removed silicon oil residuals. For some products this may be desired. For other product this may not be desired, and thus a visible test can show if the curing level is sufficiently high, i.e. the amount and size of visible air bubbles is below a desired level or not present at all.

The silicone rubber material for the silicone rubber item may in principle be any type of silicone rubber, in particular polyorganosiloxanes with a backbone consisting of alternating silicon and oxygen atoms.

The silicone rubber may be produced from silicone fluids. Silicone fluids are linear polymers whose chains contain between 2 and well over 1,000 silicon atoms, each of which is linked to the next by an oxygen atom. Unlike mineral oils, silicone fluids change very little in viscosity over a wide temperature range.

In one embodiment the silicone rubber is produced from a precursor silicon mixture comprising one or more silicone components. Preferably the silicone precursor mixture comprises one or more of the silicone components selected from the group consisting of dialkylsilicone elastomers wherein alkyl means hydrocarbon side groups of 1-12 carbon atoms such as methyl, ethyl, hexyl, and octyl; vinyl silicone elastomers; phenyl silicone elastomers; nitrile silicone elastomers; fluorosilicone elastomers, room temperature vulcanising (RTV) silicone elastomers; liquid silicone elastomers (LSR); borosilicone elastomers; the precursor silicon mixture preferably comprises dimethyl silicone elastomers.

In one embodiment the constituents for the precursor mixture comprise long-chain polysiloxanes, catalysts, crosslinking agents and various fillers, such as fumed silica (HDK), quartz, chalk and kaolin, as well as other additives such as pigments, adhesion promoters, and the like.

According to the type of useful vulcanization (crosslinking agent and temperature) and the viscosity of the base polymers silicone rubbers may classified as follows:

RTV-1 silicone rubbers are one-component, ready-to-use, room-temperature vulcanizing systems. They may comprise polydimethylsiloxanes, crosslinking agents, fillers, and auxiliaries. After shaping, crosslinking is initiated by contact with atmospheric moisture and proceeds with the elimination of by-products.

RTV-2 silicone rubbers are two-component, pourable, spreadable or kneadable compounds that cure to highly flexible silicone vulcanizates on addition of crosslinking agent.

In one embodiment the silicone rubber material may be made from High Temperature Vulcanisates (HTV) Liquid silicone rubbers two-component system. As the name suggests, HTV silicone rubbers are vulcanized at high temperatures e.g. by injection moulding, in the presence of organic-peroxide curing agents.

In one embodiment the precursor mixture comprises one or more thermoplasts, the one or more thermoplasts preferably being selected from the group consisting of polyurethane, polyamide and polyolefins.

In one embodiment the precursor mixture comprises one or more catalyst, such as a metal catalyst (e.g. platinum catalyst), and/or organic peroxides such as dibenzoyl, dicumyl and di-tertiary butyl peroxide.

The silicone precursor mixture may comprise one or more filler material, such as filler materials selected from the group of metals such as, aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc; metal oxides/ hydroxides such as alumina trihydrate, oxides of aluminum, tin, lead, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, antimony and zinc; metal salts, such as phosphates, sulfides, and sulfates; minerals such as spodumene, mica, montmorillonite, kaolinite, bentonite, hectorite, beidellite, attapulgite, chrysolite, garnet, saponite, and hercynite; ceramic materials such as hydrated or anhydrous silicas, silica, silicate glass, quartz, calcium silicates, calcium-magnesium silicates, barium silicates, sodium-alumino-silicates, calcium-alumino-silicates, calcium-sodium-alumino silicates; clays (aluminum silicates) such as halloysite, montmorillonites including sodium and magnesium bentonites; synthetic or natural zeolites; and synthetic or natural talcs (magnesium silicates); and organic materials such as carbon black; graphite, granulated or milled thermoplastics or thermosets such as recycled or virgin polymer resin or rubber; wood-derived materials such as lignin, lignosulfates, Kraft lignin, cellulose and mixtures thereof.

The filler material may in principle have any shape and size e.g. in the form of particles or fibers or mixtures thereof. The filler material may be solid, hollow or porous. Useful fillers

are e.g. described in US 4,740,538, US 5,332,429, US 5,968,652, US 2001/00366617, US 5,861,445 and US 4,740,538.

In one embodiment it is preferred that the item is shaped using injection moulding. The temperature and the residence time in the moulding tool may vary dependent on the material and the shape of the injection moulded item. Thicker items normally require longer residence time.

In one embodiment the injection moulding is performed with residence times in the moulding tool of 10-50 seconds at 150-200 °C.

In one embodiment the injection moulding is performed with residence times in the moulding tool of 30-90 seconds at temperatures between 80 and 150 °C.

In one embodiment the injection moulding is performed with residence times in the moulding tool of more than 60 seconds at temperatures below 80 °C.

The injection moulded silicone rubber item may in one embodiment be subjected to the cold tempering step directly from the injection moulding step.

The cold tempering step may e.g. be performed batch-wise. In one embodiment the cold tempering step is performed batch-wise and this cold tempering step is performed physically separately from the shaping machinery. In this embodiment it may be desired that the shaped silicone rubber item is transported from the shaping equipment to a pressure reactor e.g. in a rack adapted to the shape of the silicone rubber items to be treated in the cold tempering step. The rack may be adapted to the silicone rubber items so that the major part, such as preferably above 60 %, e.g. above 75 % or even above 85 % of the surface of the silicone rubber items is free of contact while still being supported by the rack.

The carbon dioxide containing solvent may preferably comprise at least 80 % by weight, such as at least 85 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of carbon dioxide

In one embodiment essentially all of the solvent is constituted by carbon dioxide containing solvent. In one embodiment it is preferred that the carbon dioxide containing solvent comprises at least 1 %, such as at least 5 % by weight of another composition e.g. a surfactant.

In one embodiment the solvent comprises at least one surfactant selected from the group consisting of perhalogenated and wholly or partly fluorinated surfactants, such as CF_3 $(CF_2)_a$ CH_2 CH_2 C(O)OX, a= 1-30, polypropylene glycol surfactants, optionally containing up to 75% of weight polyethylene glycol groups, such as $HO(CH_2$ $CH(CH_3)O)_i$ $(CH_2$ CH_2 $O)_i$ R, i=1-20 and R = alkyl such as methyl, ethyl, propyl, butyl, or alkyls containing 6-20 carbon atoms such as tetradecyl or hexadecyl, perhaloether surfactants, such as CF_3 $(CF_2$ CF_2 $O)_r$ $(CH_2$ CH_2 $O)_t$ H, r=1-30 and t =1-40, sorbitan esters, mono- and polyesters of carbonic acid, and polydimethylsiloxane surfactants.

In one embodiment the solvent comprises at least one surfactant selected from the group consisting of poly(1,1'-dihydroperfluorooctyl acrylate)-b-(poly)styrene, poly(1,1'-dihydroperfluorooctyl acrylate-b-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-b-methyl methacrylate), poly(1,1'-dihydroperfluorooctyl acrylate-b-vinyl acetate), poly(1,1'-dihydroperfluorooctyl acrylate-b-vinyl alcohol), poly(1,1'-dihydroperfluorooctyl methacrylate-b-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-co-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-co-vinyl pyrrolidone), poly(1,1'-dihydroperfluorooctyl acrylate-co-2-ethylhexyl acrylate), poly(1,1'-dihydroperfluorooctyl acrylate-co-2-hydroxyethyl acrylate), poly(1,1'-dihydroperfluorooctyl acrylate-co-dimethylaminoethyl acrylate), poly(styrene-g-dimethylsiloxane), poly(methyl acrylate-g-1,1'-dihydroperfluorooctyl methacrylate), poly(1,1'-dihydroperfluorooctyl acrylate-g-styrene), perfluorooctanoic acid, and perfluoro(2-propoxy propanoic) acid.

The amount of surfactant in the carbon dioxide containing solvent may preferably be between 0.001 to 30 % by weight, such as between 0.01 and 20 % by weight, such as between 0.1 and 5 % by weight of one or more surfactants.

In one embodiment the carbon dioxide containing solvent may comprise a co-solvent e.g. a co-solvent selected from the group consisting of methane, ethane, propane, ammonia butane, n-pentane, hexanes, cyclohexane, n-heptane, ethylene, propylene, methanol, ethanol, isopropanol, xylenes, chlorotrifluoromethane, trichlorofluoromethane,

perfluoropropane, chlorodifluoromethane, sulfur hexafluoride, nitrous oxide, N-methyl pyrrolidone, acetone, esters of carbonic acid, organosilicones, terpenes, paraffins, and mixtures thereof. The amount of the co-solvent may e.g. be up to about 20 % by weight, such as about 15 % by weight, such as about 10 % by weight, such as about 5 % by weight of the carbon dioxide containing solvent.

In the extraction step at least a part of the silicone oil residues in the silicone rubber item is extracted. In particular it is desired to extract the low molecular weight silicone oil residues from the silicone rubber item as it is these low molecular weight silicone oil residues, e.g. compounds with molar weights ranging from about 70 up to 3000 and higher, representing, a.o. D3, D4, D5 a.s.f. and other cyclic or non-cyclic siloxanes, which are migrating out of the silicone rubber material and cause the silicone rubber item to smell and/or to exude undesired components during use.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 3000.

Extractable residual silicone oils having a molecular weight below 3000 are defined as the residual silicone oils having a molecular weight below 3000 which are extractable using heat. As used herein the extractable residual silicone oil is the oil which is extracted from a silicone rubber item by subjecting it to a heat treatment at 200 °C for 4 hours in a reactor of 1 L volume per 100 g silicone rubber item prior to the treatment and with an air flow through the reactor of 1 L/min per litre reactor volume.

In one embodiment of the invention the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 1000, wherein the extractable residual silicone oils having a molecular weight below 1000 are defined as the residual silicone oils having a molecular weight below 1000 which are extractable using heat as disclosed above.

In one embodiment of the invention the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 500, wherein the extractable residual silicone oils having a molecular weight below 500 are defined as the residual silicone oils having a molecular weight below 500 which are extractable using heat as disclosed above.

In one embodiment of the invention the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 200, wherein the extractable residual silicone oils having a molecular weight below 200 are defined as the residual silicone oils having a molecular weight below 200 which are extractable using heat as disclosed above.

In one embodiment of the invention the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 10% by weight, such as at least 25% by weight, such as at least 40% by weight, such as at least 60% by weight of the weight of those residual silicone oils, irrespective of molecular weight, which can be extracted using Soxleth extraction of the non-extracted silicone item using acetone.

The soxlet extraction should be performed using at least 10 ml acetone per 1 g silicone rubber. The silicone rubber should be scared into small pieces of less than 1 cm^3. The extraction time is set to 2 hours followed by a rinse cycle of 20 minutes and a short distillation step. Afterwards the extracts are dried at 50 °C to constant weight. Extracted silicone oils may be subjected to further analysis.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 0.05 % silicone oil containing residual by weight, such as 0.1 % silicone oil containing residual by weight, such as at least 0.2 % by weight,

such as at least 0.5% by weight silicone oil containing residual by weight of the total item. The silicone oil containing residual also includes a small amount of water.

If only silicone oil is to be extracted the silicone rubber item could be subjected to a 2 hour drying step at 50 °C.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 0.005 % by weight of silicone oils having a molecular weight below 3000, such as 0.01 % silicone oil by weight, such as at least 0.02 % by weight of silicone oils having a molecular weight below 3000 relative to the weight of the total item. The extracted oil may be collected using a cold trap.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 0.001 % by weight of silicone oils having a molecular weight below 1000, such as 0.005 % silicone oil by weight, such as at least 0.01 % by weight of silicone oils having a molecular weight below 1000 relative to the weight of the total item.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 0.0005 % by weight of silicone oils having a molecular weight below 500, such as 0.001 % silicone oil by weight, such as at least 0.002 % by weight of silicone oils having a molecular weight below 500 relative to the weight of the total item.

In one embodiment the cold tempering includes subjecting the item to an extraction treatment to thereby remove at least 0.0001 % by weight of silicone oils having a molecular weight below 200, such as 0.0005 % silicone oil by weight, such as at least 0.001 % by weight of silicone oils having a molecular weight below 200 relative to the weight of the total item.

For silicone rubber items for medical use including catheters, contact lenses and feeding (soothers, bottle closures, tests, dummies) and similar items for use in contact with the human body, it may be desired that the cold tempering includes subjecting the item to an extraction treatment to thereby remove a sufficient amount of the low molecular weight residues for meeting government regulations e.g. FDA, UBA, Japanese Pharmacopoeia

and other relevant regulations concerning material requirements for silicone items designed for medical, implant, direct and indirect food contact and disposable use. In particular it may be desired that the cold tempering includes subjecting the item to an extraction treatment to thereby remove a sufficient amount of the low molecular weight residues for meeting the FDA Regulation 21 CFR 177.2600 as of April 1, 2004.

During the cold tempering it has in one embodiment been found that by introducing additional gas which may e.g. be inert or it may be reactive, the extraction time may be reduced. Thus, in one embodiment it is desired that the cold tempering includes subjecting the item to an extraction treatment wherein a gas is introduced into the reactor during the extraction treatment, where it is released to thereby create a pressure gradient from the bulk of the item to the surrounding solvent, thereby creating a flow of solutes from the item to the solvent. The gas may e.g. be nitrogen, oxygen or Helium. The amount of gas may preferably be at least 0.1 mol, such as at least 0.5 mol, such as at least 1 mol gas per litre reactor volume.

The extraction effect during the extraction treatment may further be increased by providing turbulence within the reactor e.g. by stirring or preferably by rotation and/or shaking the pressure reactor.

When performing the cold tempering it has also been observed that the pressure and temperatures during the cold tempering may be regulated so that the cold tempering includes removal of particles such as dust and silicone dioxide, and removal of any mould release agents and lubricating chemicals used during extrusion or moulding or shaping, combined with the process of cold tempering.

In one embodiment the cold tempering includes deposition and optional cross-linking of materials and substances within the silicone rubber item, such materials and substances selected from the group of pigments and dyes, as well as organic monomers and suitable cross-linking agents and radical starters such as olefins such as ethylene and propylene and butadiene, vinyl compounds such as vinyl acetate, vinyl-pyrrolidinone, styrene, acrylic compounds, epoxides such as propylene oxide and diglycidylethers, urethane precursors such as glycols and diisocyanates.

Further information concerning deposition and optional cross-linking within the silicone rubber material of the silicone rubber item can be found in WO 03068846 and PA 2003 01027 (PCTDK04000476).

In one embodiment the cold tempering step comprises partial removal or chemical derivatisation of one or more of the compounds selected from the group consisting of organic peroxides, decomposition products of organic peroxides, platinum catalyst or ligands of platinum catalysts, unreacted silanes, cross-linkers and silanols of molecular weights below 3000. Chemical derivatisation is understood to be addition of chemical groups, i.e. one or more chemical groups are bonded to one or more of the compounds selected from the group consisting of organic peroxides, decomposition products of organic peroxides, platinum catalyst or ligands of platinum catalysts, unreacted silanes, cross-linkers and silanols of molecular weights below 3000. The one or more chemical groups will typically be decomposition product from one or more components within the silicone rubber material.

The invention also relates to the silicone rubber item obtainable by the method of the invention. In particular the invention relates to silicone rubber items selected from the group consisting of extruded products: tubes, catheters, cable insulations, injection moulded products: keypads, gaskets, parts for infant care and feeding (soothers, bottle closures), parts for use in the automotive, telecom and medical sector, films and contact lenses.

EXAMPLES

Example 1

Injection moulded silicone rubber plates of 1, 2 and 3 mm thickness (other dimensions 15cm * 4 cm) were used as standard in cold tempering step experiments. The raw materials were 2 component (A and B) LSR (liquid silicone rubber), e.g. available from Wacker under the tradename Elastosil, furthermore peroxide-vulcanised silicone rubber was studied.

Hardnesses of all rubbers investigated ranged from 90 Shore A, 70 Shore A, 50 Shore A, 20 Shore A and 10 Shore A.

The extraction parameters were as follows: items were placed in a 10 litre reactor, liquid CO_2 was added, and extraction proceeded under stirring of CO_2, rotation of the holding device in which the rubber items were placed, or rotation of the complete reactor, for 5, 10, 15 or 40 minutes at 8-15 °C and a pressure of 30-45 bars. The pressure could be varied during the extraction by adding other gases such as nitrogen, oxygen or helium. The extraction was terminated by transferring the liquid from the reactor to a distillation tank or to atmosphere. The residual pressure was decreased at varying rates, such as 40 bar/minute or as low as 2 bar/minute.

Observations:

The rate of decompression was found to be critical for the mechanical integrity of rubbers with hardnesses below 40 Shore A and in particular for rubbers below 10-20 Shore A. All rubber items (which typically are opaque or transparent) are at least partly white, presumably because CO2 has swollen the interstitial volumes within the bulk polymer. With decay times of typically minutes the items resume their original colour, and a clear correlation is found with the weight loss (in the order of 1-3% of the weight of the polymer), i.e. gas migrating out of the polymer into atmosphere. Most polymer items show in addition to the white colour "bubbles" (ca. 1 mm size) which disappear completely from harder rubbers but may persist in the case of rubbers softer than 20 Shore A. Furthermore, mechanical delamination occurs in soft rubbers, especially in thicker parts and especially if the rate of decompression is faster than 10 bar/minute.

Upon equilibration (i.e. weight constant after gas evaporation), the rubber items have lost 0.2-1.8% weight whereby the weight loss is clearly related to extraction time and thickness of the polymer. The weight loss is related to the absolute amount of silicone oils which can be measured in control experiments using Soxleth extraction of rubber using acetone or methylethylketone (MEK) as solvents. Typically, 75 % of the absolute amount of oil as measured by Soxleth extraction is extracted using liquid CO_2 within 20 minutes of extraction. Furthermore, rotation speed, pressure pulsing, surfactant addition, CO_2 cycling (removal, distillation, replacement) etc. affect the rate of extraction.

Mechanical properties were, in general, only marginally affected by extraction. Elongation at break, tensile strength, modulus, compression set, permanent deformation upon elongation and the like were not changed within experimental error. A 3-10% increase in

oxygen permeability was found for extracted silicone versus non-extracted silicone.

Example 2

Plates as used in example 1 but made of peroxide-vulcanised silicone were extracted according to procedures described above and simultaneously impregnated using blue pigments, such as Victoria B or phtalocyanin based pigments. The purpose of the experiment was partly to extract compounds which cause yellow colour directly and which increase the rate of yellowing upon ageing. As result, the intensity of the yellow colour is reduced by direct extraction, the yellowing by ageing is slowed down, and the impregnation of blue pigments is found useful for compensating the yellow colour. The weight increase by pigment addition is too low to be measurable.

Example 3

Analysis of silicone rubber samples after CO_2-extraction by acetone-extraction (soxleth). In CO_2-extraction it is not simple to collect the extracted low molecular silicone oils and it may be simpler to calculate the amount of removed residues by weighing the samples. To get more specific values we extracted the CO_2-cured samples in acetone in a Büchi Universal Extraction Unit B811 and calculated the amount of extractable silicon oils from the weight of the extract.

150 ml acetone per sample (Fischer Chemicals, 0.042 % water) was used. The samples were scared into small pieces and there was used 1.5 to 6 g of the sample for analysis. Repeat determinations were made. The extraction time is about 2 hours followed by a rinse cycle of 20 minutes and a short distillation step. Afterwards the extracts were dried for 2 hours at 50 ˚C and weighed. The amount of CO_2 extracted silicone oils is calculated from the difference between the amount of silicone oils extracted from untreated samples and the amount from treated samples.

The following samples were analyzed:

	Original sample, acetone extract [wt %]	Post cured in liquid CO_2, acetone extract [wt%]	
Injection moulded plates (e.g. Wacker elastosil)	1.70	0.29	
Baby pacifier/comforter (e.g. Avent)	2.57	1.53 (20 min CO_2 extraction)	1.13 (2x20 min. CO_2 extraction)
Silicone valve (e.g. Avent)	3.52	0.90	

Up to 80% of the absolute amount of the low molecular residues is removed in liquid CO_2 extraction.

Example 4

Large soothers and small pacifiers were extracted in the Cold Tempering process with the following conditions:

All soothers had been proved with a cut before the Cold Tempering.

20 to 25 kg of soothers were filled into bags (nylon, 5 kg in each bag), that were filled into the extraction chamber / tumbler. The chamber was closed and pressurized to 42-50 bar, the temperature decreased to 8-15˚C. The tumbler was rotating with 3 Hz (7.2 r.p.m). After 15-25 minutes the liquid CO_2 was pumped out of the chamber, destilled, depressurized and leaded back into the chamber that was again pressurized to 42-50 bar. After another 25 minutes tumbling the liquid CO_2 was again removed from the chamber and after depressurizing the chamber was opened and the samples taken out.

Results:

100 % of the cuts were still open after the treatment process in liquid CO_2.

The soothers and pacifiers were investigated after the standard EN 14350/2

This standard says, that the volatiles in a soother or pacifier has to be under a amount of 0.5 %.

Volatile weight loss[%]	Not tempered	After 1st cycle (15-25 min)	After 2nd cycle (40-50 min)
Small pacifiers, 25.6 kg (11800 items)	0.670 (StD 0.048)	0.442 (StD 0.029)	0.266 (StD 0.026)
Large soothers, 19.2 kg (1600 items)	1.036 (StD 0.033)	0.606 (StD 0.037)	0.400 (StD 0.034)
Large soothers, 25 kg (4150 items)	0.889 (StD 0.024)	0.753 (StD 0.027)	0.265 (StD 0.089)

To shorten the batch time it is also possible to take off the liquid CO_2 after the first cycle without depressurizing the chamber. A variation of the cycle times may be desired as e.g. 1. cycle 10 minutes, 2. cycle 20 minutes and vs.

CLAIMS

1. A method of producing a silicone rubber item, said method comprising the steps of
i) shaping the silicone rubber item using injection moulding and
ii) subjecting the injection moulded item to a cold tempering,

wherein the cold tempering includes feeding the injecting moulded item into a reactor, and subjecting the injection moulded item to an extraction treatment using carbon dioxide containing solvent at a pressure between 10 and 50 bars, wherein the item has an initial temperature below 60 °C in the extraction step, and in at least a part of the extraction time the item has a temperature below 25 °C and a pressure so that the carbon dioxide is in its liquid state.

2. A method according to claim 1, wherein the silicone rubber item has at least one non-coated surface at least during the cold tempering.

3. A method according to any one of the claims 1 and 2, wherein the shaping step comprises providing the item with a slit or hole extending at least partly through the material of the item, said slit or hole may preferably be provided in the injection moulding step or after the injection moulding step e.g. using a cutting tool.

4. A method according to any one of the preceding claims, wherein the extraction treatment comprises subjecting the item to a treatment with a carbon dioxide containing solvent in liquid state for at least 0.5 minutes, such as at least 2 minutes, such as at least 4 minutes, such as at least 10 minutes.

5. A method according to any one of the preceding claims, wherein the extraction treatment comprises subjecting the item to a treatment with a carbon dioxide containing solvent in liquid state for at least 0.1 minute per Maximal Shortest Distance to Surface (MSDS) in millimetres, wherein the MSDS is the maximal shortest distance to a surface point for any point of material of the item, preferably the extraction treatment comprises subjecting the item to a treatment with a carbon dioxide containing solvent in liquid state least 0.3 minute, such as at least 1.0 minute, such as at least 1.5 minutes, such as at least 2 minutes per MSDS.

6. A method according to any one of the preceding claims, wherein the method comprises the steps of

i) shaping the silicone rubber item,

ii) subjecting the injection moulded item to a cold tempering, and

ii) packing the item in a packing material providing a barrier against silicon oil residuals.

7. A method according to claim 6, wherein the packing material has a water vapour permeability (DIN 53122) of up to 100 g/m^2 x 24h, such as up to 50 g/m^2 x 24h, such as up to 25 g/m^2 x 24h, such as up to 10 g/m^2 x 24h.

8. A method according to any one of the claims 6 and 7, wherein the packing material has a permeability of the silicone oil hexamethylcyclotrisiloxane (D3) of up to 10 g/m^2 x 24h, such as up to 5 g/m^2 x 24h, such as up to 1 g/m^2 x 24h, such as up to 0.1 g/m^2 x 24h.

9. A method according to any one of the claims 6-8, wherein the packing material is essentially impermeable to bacteria and viruses.

10. A method according to any one of the claims 6-9, wherein the packing step comprises packing the item in a sealed packing material, whereby the packing material provides a barrier against free flow of air, preferably the sealed packing material provides a gas-tight package.

11. A method according to any one of the claims 6-10, wherein the packing step is performed within 60 minutes from termination of the cold tempering step, preferably within 40 minutes, such as within 20 minutes, such as within 10 minutes, more preferably within 5 minutes, most preferably the packaging is performed immediately after termination of the cold tempering step.

12. A method according to any one of the claims 6-11, wherein the packing step is performed sufficiently shortly after the cold tempering step for the item to still comprise releasable carbon dioxide which will be released within the package, the item preferably releases at least 0.01 % by weight, such as at least 0.1% by weight or even at least 0.5% of weight of carbon dioxide relative to the weight of the item within the first hour after the package has been sealed.

13. A method according to any one of the preceding claims, wherein the silicon rubber item is made from a precursor silicon mixture comprising one or more silicone components, preferably said a precursor silicon mixture comprises one or more of the silicone components selected from the group consisting of dialkylsilicone elastomers wherein alkyl means hydrocarbon side groups of 1-12 carbon atoms such as methyl, ethyl, hexyl, and octyl; vinyl silicone elastomers; phenyl silicone elastomers; nitrile silicone elastomers; fluorosilicone elastomers, room temperature vulcanising (RTV) silicone elastomers; liquid silicone elastomers (LSR); borosilicone elastomers; the precursor silicon mixture preferably comprises dimethyl silicone elastomers.

14. A method according to claim 11 wherein the precursor mixture comprises one or more thermoplasts, the one or more thermoplasts preferably being selected from the group consisting of polyurethane, polyamide and polyolefins.

15. A method according to any one of the claims 11 and 12 wherein the precursor mixture comprises one or more catalyst, such as a metal catalyst (e.g. platinum catalyst), and/or organic peroxides such as dibenzoyl, dicumyl and di-tertiary butyl peroxide.

16. A method according to any one of the preceding claims, wherein the injection moulding is performed with residence times in the moulding tool of 10-50 seconds at 150-200 degree Celsius, or 30-90 seconds at temperatures between 80-150 degree C, or more than 60 seconds at temperatures below 80 degree C.

17. A method according to any one of the preceding claims, wherein the cold tempering is performed batch-wise, said cold tempering preferably being performed physically separately from the shaping machinery.

18. A method according to any one of the preceding claims wherein the carbon dioxide containing solvent comprises at least 80 % by weight, such as at least 85 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of carbon dioxide

19. A method according to any one of the preceding claims wherein carbon dioxide containing solvent comprises at least one surfactant, preferably selected from the group consisting of perhalogenated and wholly or partly fluorinated surfactants, such as CF_3

$(CF_2)_a$ CH_2 CH_2 C(O)OX, a= 1-30, polypropylene glycol surfactants, optionally containing up to 75% of weight polyethylene glycol groups, such as HO(CH2 CH(CH3)O)$_i$ (CH_2 CH_2 O)i R, i=1-20 and R = alkyl such as methyl, ethyl, propyl, butyl, or alkyls containing 6-20 carbon atoms such as tetradecyl or hexadecyl, perhaloether surfactants, such as CF_3 (CF_2 CF_2 O)$_r$ (CH_2 CH_2 O)$_t$ H, r=1-30 and t =1-40, sorbitan esters, mono- and polyesters of carbonic acid, and polydimethylsiloxane surfactants.

20. A method according to any one of the preceding claims wherein carbon dioxide containing solvent comprises a surfactant, preferably selected from the group consisting of poly(1,1'-dihydroperfluorooctyl acrylate)-b-(poly)styrene, poly(1,1'-dihydroperfluorooctyl acrylate-b-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-b-methyl methacrylate), poly(1,1'-dihydroperfluorooctyl acrylate-b-vinyl acetate), poly(1,1'-dihydroperfluorooctyl acrylate-b-vinyl alcohol), poly(1,1'-dihydroperfluorooctyl methacrylate-b-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-co-styrene), poly(1,1'-dihydroperfluorooctyl acrylate-co-vinyl pyrrolidone), poly(1,1'-dihydroperfluorooctyl acrylate-co-2-ethylhexyl acrylate), poly(1,1'-dihydroperfluorooctyl acrylate-co-2-hydroxyethyl acrylate), poly(1,1'-dihydroperfluorooctyl acrylate-co-dimethylaminoethyl acrylate), poly(styrene-g-dimethylsiloxane), poly(methyl acrylate-g-1,1'-dihydroperfluorooctyl methacrylate), poly(1,1'-dihydroperfluorooctyl acrylate-g-styrene), perfluorooctanoic acid, and perfluoro(2-propoxy propanoic) acid.

21. A method according to any one of the preceding claims wherein carbon dioxide containing solvent comprises from 0.001 to 30 % by weight, such as between 0.01 and 20 % by weight, such as between 0.1 and 5 % by weight of one or more surfactants.

22. A method according to any one of the preceding claims wherein the carbon dioxide containing solvent comprises a co-solvent preferably selected from the group consisting of methane, ethane, propane, ammonia butane, n-pentane, hexanes, cyclohexane, n-heptane, ethylene, propylene, methanol, ethanol, isopropanol, xylenes, chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, sulfur hexafluoride, nitrous oxide, N-methyl pyrrolidone, acetone, esters of carbonic acid, organosilicones, terpenes, paraffins, and mixtures thereof.

23. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon

dioxide containing solvent in a pressure reactor under a pressure of between 10 and 50 bars, and a temperature of between 0-60 °C. preferably the cold tempering includes extraction with a carbon dioxide at 8-15 ˚C and 42-50 bars for the major part of the extraction time.

24. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor under a pressure of between 10 and 50 bars, and a temperature of between 0-25 °C.

25. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor under a pressure of between 10 and 50 bars, such as between 20 and 50 bars, preferably between 25 and 50 bars, such as between 30 and 50 bars such as between 40 and 50 bars.

26. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor wherein the pressure is pulsed, the pulsed pressure preferably having variations from top to bottom of a pulse of up to 10 bars, such as up to 5 bars, such as up to 2 bars.

27. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor wherein the pressure is varied or pulsed, the pulsed pressure preferably having a frequency of up to 10 pulses per minutes, such as 2 pulses per minute

28. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment with a carbon dioxide containing solvent in a pressure reactor at a temperature below 25 °C, preferably below 22 °C, more preferably between 5 and 20 °C, preferably between 8 and 15 ˚C

29. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove

at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 3000, wherein the extractable residual silicone oils having a molecular weight below 3000 are defined as the residual silicone oils having a molecular weight below 3000 which are extractable.

30. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 1000, wherein the extractable residual silicone oils having a molecular weight below 1000 are defined as the residual silicone oils having a molecular weight below 1000 which are extractable.

31. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 500, wherein the extractable residual silicone oils having a molecular weight below 500 are defined as the residual silicone oils having a molecular weight below 500 which are extractable.

32. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 50 % by weight, such as at least 60 % by weight, such as at least 70 % by weight, such as at least 80 % by weight, such as at least 90 % by weight, such as at least 95 % by weight, such as at least 99 % by weight of the extractable residual silicone oils having a molecular weight below 200, wherein the extractable residual silicone oils having a molecular weight below 200 are defined as the residual silicone oils having a molecular weight below 200 which are extractable.

33. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 10% by weight, such as at least 25% by weight, such as at least 40% by weight, such as at least 60% by weight of the weight of those residual silicone oils, irrespective of molecular weight, which can be extracted using Soxleth extraction of the non-extracted silicone item using acetone.

34. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 0.05 % silicone oil by weight, such as 0.1 % silicone oil by weight, such as at least 0.2 % by weight, such as at least 0.5% by weight silicone oil by weight of the total item.

35. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 0.005 % by weight of silicone oils having a molecular weight below 3000, such as 0.01 % silicone oil by weight, such as at least 0.02 % by weight of silicone oils having a molecular weight below 3000 relative to the weight of the total item.

36. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 0.001 % by weight of silicone oils having a molecular weight below 1000, such as 0.005 % silicone oil by weight, such as at least 0.01 % by weight of silicone oils having a molecular weight below 1000 relative to the weight of the total item.

37. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 0.0005 % by weight of silicone oils having a molecular weight below 500, such as 0.001 % silicone oil by weight, such as at least 0.002 % by weight of silicone oils having a molecular weight below 500 relative to the weight of the total item.

38. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove at least 0.0001 % by weight of silicone oils having a molecular weight below 200, such as 0.0005 % silicone oil by weight, such as at least 0.001 % by weight of silicone oils having a molecular weight below 200 relative to the weight of the total item.

39. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment to thereby remove a sufficiently amount of the low molecular weight residues for meeting the FDA Regulation 21 CFR 177.2600 as of April 1, 2004the EN standards EN 14350/2, August 2004 and EN 1400-1, September 2002.

40. A method according to any one of the preceding claims wherein the cold tempering step includes subjecting the item to an extraction treatment wherein the extraction treatment is performed for at least 1 minute, such as at least 2 minutes, such as at least 5 minutes, such as at least 10 minutes.

41. A method according to any one of the preceding claims, wherein the cold tempering step includes subjecting the item to an extraction treatment wherein the extraction treatment is performed for least 0.1 minute per Maximal Shortest Distance to Surface (MSDS) in millimetres, wherein the MSDS is the maximal shortest distance to a surface for any point of material of the item, preferably the extraction treatment comprises subjecting the item to a treatment with a carbon dioxide containing solvent in liquid state for least 0.3 minute, such as at least 1.0 minute, such as at least 1.5 minutes, such as at least 2 minutes per MSDS.

42. A method according to any one of the preceding claims, wherein the cold tempering step includes subjecting the item to an extraction treatment wherein a gas is introduced into the reactor during the extraction treatment, where it is released to thereby create a pressure gradient from the bulk of the item to the surrounding solvent, thereby creating a flow of solutes from the item to the solvent, the gas preferably being nitrogen, oxygen or Helium.

43. A method according to any one of the preceding claims, wherein the cold tempering step includes removal of particles, such as dust and silicone dioxide, and removal of at least some of the mould release agents and lubricating chemicals used during extrusion or moulding or shaping.

44. A method according to any one of the preceding claims, wherein the cold tempering step includes deposition and optional cross-linking of materials and substances within the

silicone rubber item, such materials and substances being selected from the group of pigments and dyes, as well as organic monomers and suitable cross-linking agents and radical starters such as olefins such as ethylene and propylene and butadiene, vinyl compounds such as vinyl acetate, vinyl-pyrrolidinone, styrene, acrylic compounds, epoxides such as propylene oxide and diglycidylethers, urethane precursors such as glycols and diisocyanates.

45. A method according to any one of the preceding claims, wherein the cold tempering step comprises partial removal or chemical derivatisation of one or more of the compounds selected from the group consisting of organic peroxides, decomposition products of organic peroxides, platinum catalyst or ligands of platinum catalysts, unreacted silanes, cross-linkers and silanols of molecular weights below 3000, whereby chemical derivatisation is understood to be addition of chemical groups.

46. A silicone rubber item obtainable by the method according to any one of the claims 1 - 45.

47. A silicone rubber item according to claim 46 wherein the item is selected from the group consisting of extruded products: tubes, catheters, cable insulations, injection moulded products: keypads, gaskets, parts for infant care and feeding (soothers, bottle closures), parts for use in the automotive, telecom and medical sector, films and contact lenses.

48. A silicone rubber item according to any one of the claims 46 and 47, wherein the item has at least one non-coated surface adapted to be brought into contact with the human or animal body, said item preferably being selected from the group consisting of catheters, parts for infant care and feeding (soothers, bottle closures) and contact lenses.