

599107

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

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We

RHONE-POULENC CHIMIE., of
25, Quai Paul Doumer, 92408
Courbevoie Cedex, France.

hereby apply for the grant of a Standard Patent for an invention entitled:

"RESILIENT SILICONE ELASTOMER SUPPORT AND ITS USE"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

<u>Number</u>	<u>Convention Country</u>	<u>Date</u>
Nil	Nil	Nil

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 1.5.90

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 1st day of June 19 87

H. W. Rimington

To: THE COMMISSIONER OF PATENTS

.....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

LOGGED AT SUB-OFFICE
= 1 JUN 1987
Melbourne

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

Insert title of invention.

In support of the Application made for a patent ~~XXXXXX~~ for an invention entitled: "Resilient Silicone Elastomer Support and its Use"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I Jean-Louis SEUGNET, ~~XXXX~~

of: RHONE-POULENC CHIMIE, a French Body Corporate of: 25, Quai Paul Doumer, 92408 COURBEVOIE Cedex, France.

Cross out whichever of paragraphs 1(a) or 1(b) does not apply 1(a) relates to application made by individual(s) 1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows:-

~~I am the applicant for the patent~~ or (b) I am authorized by

RHONE-POULENC CHIMIE

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

the applicant ~~XXXX~~ for the patent ~~XXXXXX~~ to make this declaration on its behalf ~~XXXX~~

2(a) relates to application made by inventor(s) 2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) ~~XXXX~~ the actual inventor(s) of the invention or (b)

CLAUDE LAURENT: PAUL ROSTAING and RENE LYOBARD all citizens of France of: 50, Avenue de Parmelan, 74000 - ANNECY, France. Les Charavelles - Bastiment Jonquille, 38200 - VIENNE, France and 71, rue Arthur Rimbaud, 69800 - SAINT-PRIEST, France respectively.

~~XXXX~~ are the actual inventor(s) of the invention and the facts upon which the applicant ~~XXXX~~ is entitled to make the application are as follows:-

State manner in which applicant(s) derive title from inventor(s)

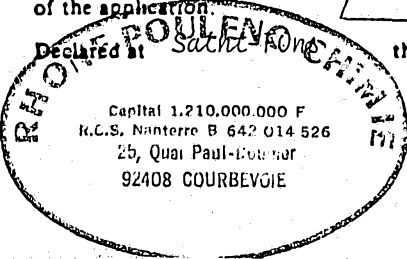
"The applicant would if a patent were granted upon an application made by the inventors, be entitled to have the patent assigned to it.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ^{was} ~~were~~ made in on the by in on the by in on the by

4. The basic application..... referred to in paragraph 3 of this Declaration ^{was} ~~were~~ the first application..... made in a Convention country in respect of the invention the subject of the application.....

Insert place and date of signature.



Declared at ~~Saint~~ this 21 mai 1987 day of

Signature of declarant(s) (no attestation required)

Jean-Louis Seugnet
Jean-Louis SEUGNET
Ingénieur - Brevets

Note: Initial all alterations.

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SILICONE ELASTOMER SUPPORT

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AU 577659 52778/86 C08L 83/04 C08K 13/02 H01B 1/24
AU 509215 20584/76 C08L 83/04 C08K 7/10 C08G 77/38
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(57) Claim

1. Process for shaping sheet metal (as hereinbefore defined), which comprises stamping sheet metal by electroforming using a silicone elastomer support suitable for forming a die for such a process, in which the silicone elastomer is a fluid organopolysiloxane composition which has been crosslinked, at ambient temperature or with heating, by a polycondensation or polyaddition reaction in the presence of a catalyst, and the organopolysiloxane is plasticized with at least one compatible plasticizer, which remains stable and nonmigrating under the stamping conditions, in a quantity such that the plasticized silicone elastomer has a Shore 00 hardness of less than about 40.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

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Complete Specification Lodged:
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amendments made under
Section 49 and is correct for
printing.

Priority:

Related Art:

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Complete Specification for the invention entitled:

"RESILIENT SILICONE ELASTOMER SUPPORT AND ITS USE"

The following statement is a full description of this
invention, including the best method of performing it
known to us:-

The present invention relates to a process for shaping sheet metal by elastoforming.

Although the description which follows concentrates more particularly on the elastoforming of sheet metal, that is to say of thin plates which are generally made of metal, it should nevertheless be understood that the elastoforming process employing the resilient supports of the present invention is not limited to this application.

Thus, the elastoforming process may be used for thin sheets of plastic materials, in particular for sheets consisting of polybutene, polyethylene, chlorinated polyethylene, PVC, chlorinated PVC, ABS (acrylonitrile/butadiene/styrene), polycarbonates, polyphenylene oxide, polysulphones, polychlorotrifluoroethylene, cellulose acetate butyrate, cellulose acetate, nylons, nylon 6 and 66. (See, in particular, "Polymer Engineering and Science", March 1971, vol. 11, No. 2, page 106).

Thus, in the present description and in the claims, the term "sheet metal" should be understood as having a general meaning of "thin plate" or "sheet" without any intention to limit the scope to "metal products", but incorporating all the products having a degree of plasticity like that of metals.



More specifically, the process of the present invention comprises stamping sheet metal by elastoforming using a resilient silicone elastomer support capable of being used as a die in a double-action (mechanical or hydraulic) press such as, for example, that described in European Patent Application EP-A-165,133, mentioned for reference. In that Patent application a process is described for stamping sheet metal blanks of substantially constant thickness, called metal sheets hereinafter, in a double-action press. In the process the metal sheets to be shaped are arranged on a resilient support, particularly of low-hardness silicone elastomer, a first external slide block, or blank-clamp, is applied to the peripheral part of the metal sheet, and then a second middle slide block is applied to the central part of the metal sheet; the peripheral part of this metal sheet is formed by being allowed to slide under the blank-clamp by means of at least one working part of the external slide block so as to compensate in some regions of the finished article for the excess surfaces of unchanged thickness of the initial metal sheet in relation to the volume to be formed and, simultaneously, the middle slide block is moved to form the angular spaces of the middle part of the metal sheet by applying the metal sheet against the surfaces of the middle part of the support. In the process of the above type, in the case where metal



sheets having angular spaces and especially sheets of steel of a high elastic limit (for which $E = 40 \text{ kg/mm}^2$) and which are extra-thin (thickness below approximately 0.5 mm) are to be stamped in mass production, the low-hardness resilient support
5 creeps in order to deform the middle part of the metal sheet, during the action of the working part of the external slide block on the metal sheet, so as to give it a surface which is substantially equal to the surface of the finished component to be produced. The middle
10 slide block is then moved to form the angular spaces of the middle part of the metal sheet by final creep flow of the support.

According to an alternative form, a first external slide block is applied to the peripheral part of the
15 metal sheet, and then a second middle slide block is applied to the middle part of the metal sheet; the peripheral part of the metal sheet to be formed is arranged on a lower blank-clamp forming a container for the resilient support and whose upper face for holding the metal
20 sheet is situated at a level which is higher than that of the working face of the resilient support; the first external slide block, whose body has a diameter which is smaller than the lower blank-clamp and which at its periphery comprises an upper blank-clamp interacting
25 with the lower blank-clamp in order to clamp the metal

sheet, is applied, the descent of the external slide block is continued against the resilient support to produce the dropping of an edge of the metal sheet blank and creep flow of the mass of the resilient cushion is produced in order to deform the middle part of the metal sheet so as to give it a surface which is substantially equal to the surface of the finished component to be produced, and then the middle slide block is moved to form the angular spaces and the middle part of the metal sheet by final creep flow of the support. This alternative form is the subject of French Patent Application 85/17,957, filed on 4 December 1985.

On page 11 of Patent Application EP-A-165,133 it is indicated that the resilient support should have a Shore hardness of less than 30 and preferably greater than 10, and that it may consist of a silicone elastomer, at least partly covered, if desired, with a relatively thin skin (for example 10 to 15 mm) of a stronger and harder material such as a silicone of Shore hardness 50 or of Teflon having advantageous antifriction properties.

When the abovementioned process is being used, the resilient support is subjected to stresses. The pressures may reach 500 bars and more. Pressures which are generally used are between 2 and 200 bars. The operating rates of the presses are generally between 10 and 60 strokes per minute. The support may furthermore

be subjected to a volume deformation of 100%, which corresponds to a movement of 50% of the substance. In view of these conditions of use, this resilient support must have, in particular, the following properties:

- 5 - being free from the hazards and the limitations of the hydraulic fluids used for hydroforming under very high pressure,
- being resilient with a high rate of relaxation after deformation (elastic recovery of less than one second),
- 10 - having a low energy of deformation and a low hardness,
- being very slightly compressible (degree of compressibility of less than 5% under 500 bars),
- being resistant to abrasion and to tearing,
- having adequate fatigue and ageing resistance,
- 15 - having a sufficient heat resistance when heated by friction,
- having a low heating effect during the deformations involved in the process,
- not contaminating the formed surfaces, particularly
- 20 when these surfaces are to be painted, and
- being handleable.

In the abovementioned Patent Application EP-A-165,133 it is indicated that silicones of Shore hardness of less than 30 can be used but no explicit indication

25 is given of the means permitting the production of a resilient silicone elastomer support of appropriate hardness and combining all the properties listed above.

In the following, the percentages and parts are on a weight basis, unless stated otherwise.

The present invention provides a process for shaping sheet metal (as hereinbefore defined), which
5 comprises stamping sheet metal by elastoforming using a silicone elastomer support suitable for forming a die for such a process, in which the silicone elastomer is a fluid organopolysiloxane composition which has been cross-
linked, at ambient temperature or with heating, by a
10 polycondensation or polyaddition reaction in the presence of a catalyst, and the organopolysiloxane is plasticized with at least one compatible
plasticizer, which remains stable and nonmigrating under the stamping conditions, in a quantity such that the
15 plasticized silicone elastomer has a Shore 00 hardness of less than about 40, preferably less than 30. This hardness is determined with the aid of a hardness gauge calibrated according to the ASTM standard D 2 240.

It has been found that not all silicone elastomers
20 are suitable for stamping sheet metal by elastoforming, and that it is necessary to use an elastomer of the aforesaid kind made by crosslinking, preferably by casting, a fluid organopolysiloxane composition which crosslinks either at ambient temperature or when heated
25 to a temperature which is generally below 150°C, by polycondensation or by polyaddition reaction in the presence of a suitable metallic or organic catalyst.



The ~~organic or inorganic~~ plasticizer, which remains stable and nonmigrating under stamping conditions, may be an organic or mineral hydrocarbon oil, diorganopolysiloxane oil, mixed organic/diorganopolysiloxane polymer
5 or an organic plasticizer compatible with silicones, such as a polyoxyalkylene/polyorganosiloxane block copolymer, a polyalkylbenzene obtained by the alkylation of benzene with olefins containing a long linear or branched chain, in particular olefins containing 12 carbon atoms and
10 derived from propylene polymerization, described, for example, in French Patents FR-A-2,392,476 and FR-A-2,446,849, a polybutylene of low molecular weight described in French Patents FR-A-2,256,231, FR-A-2,393,831 and FR-A-2,405,985, or a petroleum cut with a boiling
15 point, preferably higher than 200°C, consisting of a mixture of aliphatic and/or aromatic hydrocarbons.

A preferred plasticizer is a diorganopolysiloxane oil of a viscosity between 0.65 and 5,000 mPa s at 25°C, preferably between 5 and 1,000, in particular a diorganopolysiloxane consisting of a concatenation of repeat
20 units of formula R_2SiO , and blocked at each end of its chain by a unit of formula $R_3SiO_{0.5}$, in which the radicals R are chosen from C_1-C_{10} hydrocarbon radicals such as methyl, ethyl, propyl and octyl radicals, and phenyl,
25 chlorophenyl and 3,3,3-trifluoropropyl radicals.



More specifically, the radicals R are chosen from the group consisting of methyl, chlorophenyl and 3,3,3-trifluoropropyl radicals, at least 50% of the number of radicals R being methyl radicals, not more than 5 30% of the number being chlorophenyl and 3,3,3-trifluoropropyl radicals.

The above oils are available from silicone manufacturers. In addition, they may be readily prepared by polymerization and rearrangement, with the aid of alkaline or acidic catalysts, of an appropriate mixture of diorganocyclopolysiloxanes and of straight-chain diorganopolysiloxanes of low molecular weight (United States Patents 10 2,875,172 and 2,954,357). These oils may be used by themselves or mixed with organic plasticizers.

15 The plasticizer may be introduced into the cross-linked network of the silicone elastomer by addition of the plasticizer to the fluid organopolysiloxane composition before crosslinking.

20 Another, less convenient but nevertheless feasible method is to soak the crosslinked silicone elastomer in the plasticizer.

The maximum quantity of plasticizer is defined, for each type of plasticizer associated with a particular silicone elastomer, as the quantity above which the 25 organopolysiloxane composition no longer crosslinks.

The minimum quantity of plasticizer to be added is defined by the quantity above which a Shore 00 hardness of less than 40, preferably less than 30, is obtained.

5 Surprisingly and unexpectedly, it is found that the plasticizer, especially when it is a silicone oil, remains incorporated into the elastomer network even when the latter is subjected to the very severe pressure conditions of elastoforming.

10 The fluid organopolysiloxane compositions which are capable of being crosslinked by casting in the presence of a metal or organic catalyst are the compositions which appear in most cases in the form of two-component (or 2-pack) compositions which crosslink either
15 by polyaddition reactions substantially by the reaction of $\equiv\text{SiH}$ groups carried by a silane or a straight-chain or branched organopolysiloxane, or of vinyl groups bonded to the silicon atoms of an organopolysiloxane, in the presence of a compound of a platinum group metal, or
20 by polycondensation reactions of an alpha,omega-dihydroxydiorganopolysiloxane oil with a crosslinking agent, which is a silane bearing at least three hydrolysable groups (generally alkoxy groups) or a polyalkoxysilane originating from the partial hydrolysis of this silane,
25 in the presence of a metal catalyst, generally a tin compound and/or an organic compound such as amines.

These compositions may additionally, but not necessarily, comprise an inorganic filler, preferably some or all of which is a reinforcing or semireinforcing siliceous filler. This reinforcing or semireinforcing
5 filler may be, among others, pyrogenic silica, precipitated silica, ground quartz, diatomaceous silicas, or talc. Extenders which may be employed are, in particular, calcium carbonate, mica, aluminium oxide, glass fibres and ballotini.

10 At least a proportion of the filler may be advantageously treated with a siloxane such as octamethylcyclotetrasiloxane, with a silazane such as hexamethyldisilazane, or with a silane such as the chlorosilanes.

Fluid polyaddition compositions which may be
15 used to produce resilient supports are, for example, those described in United States Patents 3,220,972, 3,697,473 and 4,340,709, which are mentioned as reference.

Fluid polycondensation compositions which may be used to produce resilient supports are, for example,
20 those described in United States Patents 3,888,815, and 4,064,096 and French Patent Specification FR-A-2,300,114, which are mentioned as reference.

The fluid polyaddition compositions which are still more preferred comprise:

25 A. a vinylated diorganopolysiloxane oil with a viscosity of between 100 and 100,000 mPa s at 25°C, containing at least two vinyl radicals per molecule, the remaining radicals being chosen from methyl, ethyl,

phenyl and 3,3,3-trifluoropropyl radicals, at least 60% of the number of the organic radicals being methyl radicals;

5 B. an organopolysiloxane containing at least 3 $\equiv\text{SiH}$ groups per molecule, chosen from branched organopolysiloxanes and straight-chain diorganopolysiloxanes;

10 C. if desired, a coupling agent, which is a straight-chain diorganopolysiloxane containing two SiH groups per molecule, the ratio of the number of $\equiv\text{SiH}$ groups in B. + C. to the number of the vinyl radicals in A. being between 0.7 and 2;

D. if desired, a reinforcing or semireinforcing inorganic filler, preferably a proportion of which is treated;

15 E. a catalytically effective quantity of a platinum or platinum group catalyst. This quantity, calculated as the weight of platinum metal, is generally between 2 and 300 ppm based on the weight of A.

20 As examples of catalyst which can be used, there may be mentioned in particular: chloroplatinic acid H_2PtCl_6 , the platinum/vinyl siloxane complexes described in French Patent Specification FR-A-1,480,409, United States Patents 3,715,334, 3,775,452 and 3,814,730 and the complexes of platinum with an organic product
25 which are described in European Patent Specifications EP-A-188,978 and EP-A-190,530;

F. a plasticizer which is a diorganopolysiloxane with a viscosity between 5 and 3,000 mPa s at 25°C, preferably between 10 and 1,500, in which the organic radicals are chosen from C₁-C₁₀ alkyl, phenyl, chloro-phenyl and 3,3,3-trifluoropropyl radicals, at least 80% of the number of these radicals being methyl radicals.

The organopolysiloxane compositions containing the components A, B, C, D and E are well known and are described in detail, particularly in the abovementioned 10 United States Patents 3,697,473 and 4,340,709.

From 5 to approximately 400 parts of oil F., preferably from 20 to 200 parts per 100 parts of compositions A + B + C + D + E may be added so as to adjust the hardness to the desired value, which is below 40 15 (Shore 00 hardness).

The hardness may also be regulated by means of the quantity of added filler. In general, 0 to 60 parts of D. are added per 100 parts of A. The expert will have no difficulty in producing an elastomer having the 20 target Shore 00 hardness, chiefly by making use of the quantities of D and of F.

The composition charged with oil F. may be supplied in a single pack or in two packs.

To enable it to be supplied in a single pack, it 25 is necessary to add a platinum inhibitor, for example those described in United States Patent 3,445,420 or European Patent Specification EP-A-146,422, which are

mentioned for reference.

As fluid organopolysiloxane composition which is supplied in two packs and which crosslinks by polycondensation reactions, there are more particularly
5 chosen the compositions comprising:

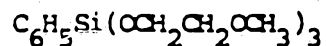
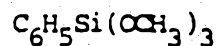
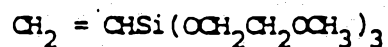
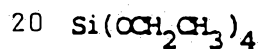
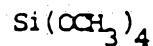
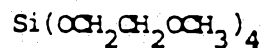
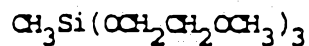
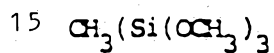
1. at least one alpha,omega-dihydroxydiorganopolysiloxane polymer with a viscosity of 20 to 500,000 mPa s at 25°C in which the organic radicals are chosen from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl
10 radicals, at least 60% of the number being methyl radicals, up to 20% of the number being phenyl radicals and not more than 2% of the number being vinyl radicals;
2. if desired, a reinforcing or semireinforcing inorganic filler;
- 15 3. at least one crosslinking agent chosen from polyalkoxysilanes and polyalkoxysiloxanes. In general, 0.5 to 15 parts of agent 3. are used per 100 parts of oil 1.;
- 20 4. a catalytically effective quantity of a tin catalyst. This quantity is generally from 0.005 to 1 part (calculated as the weight of tin metal) per 100 parts of oil 1.; and
- 25 5. a plasticizer which is a diorganopolysiloxane with a viscosity of between 5 and 3,000 mPa s at 25°C, preferably between 10 and 1,500, in which the organic radicals are chosen from C₁-C₁₀ alkyl, phenyl, chlorophenyl, vinyl and 3,3,3-trifluoropropyl radicals,

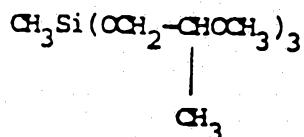
at least 8% of the number of these radicals being methyl radicals.

The two-component compositions comprising the above components 1 to 4 are well known to the expert and are described in detail, particularly in the abovementioned French Patent Specification FR-A-2,300,114 and in United States Patent 3,642,685, British Patent Specification GB-A-1,024,234 and European Patent Specification EP-A-184,522.

The crosslinking agents 3 are well-known products, described in particular in French Patent specifications FR-A-1,330,625, FR-A-2,121,289, FR-A-2,121,531 and FRA-A-2,458,572, which are mentioned for reference.

It is possible, for example, to use the silanes of formula:





Among the crosslinking agents 3, those more particularly preferred are alkyltrialkoxysilanes, alkyl silicates and alkyl polysilicates in which the organic radicals are alkyl radicals containing from 1 to 4 carbon atoms.

The alkyl silicates may be chosen from methyl silicate, ethyl silicate, isopropyl silicate, n-propyl silicate and polysilicates chosen from the products of partial hydrolysis of these silicates; these are polymers consisting of a high proportion of repeat units of formula $(\text{R}^4\text{O})_2\text{SiO}$ and a low proportion of repeat units of formula $(\text{R}^4\text{O})_3\text{SiO}_{0.5}$, $\text{R}^4\text{OSiO}_{1.5}$ and SiO_2 ; the symbol R^4 denoting methyl, ethyl, isopropyl and n-propyl radicals. They are usually characterized on the basis of their silica content, which is established by determining the product of complete hydrolysis of a sample.

The polysilicate used may be, in particular, a partially hydrolysed ethyl silicate marketed under the trademark "Ethyl Silicate-40" [®] by Union Carbide Corporation, or a partially hydrolysed propyl silicate.

Compound 4 is a tin catalyst compound which is employed or proposed for catalysing a composition of

this type, and which may be, in particular, a tin salt of a mono- or dicarboxylic acid. These tin carboxylates are described particularly in the work by Noll (Chemistry and Technology of Silicones, page 337, Academic Press, 1968, 2nd edition). Dibutyltin naphthenate, octanoate, oleate, butyrate and dilaurate, and dibutyltin diacetate may be mentioned in particular.

It is also possible to use the salts of monocarboxylic acids branched on an aliphatic carbon atom in the alpha position in relation to the carboxyl group and containing at least 8 carbon atoms per molecule, such as described in French Patent Specification FR-A-2,066,159, particularly dibutyltin diversatate.

The tin catalyst compound used may also be the product of reaction of a tin salt, especially a tin dicarboxylate, with ethyl polysilicate, as described in United States Patent 3,186,963. It is also possible to use the product of reaction of a dialkyldialkoxysilane with a tin carboxylate, as described in United States Patent 3,862,919.

It is also possible to use the product of reaction of an alkyl silicate or of an alkyltrialkoxysilane with dibutyltin diacetate, as described in Belgian Patent Specification BE-A-842,305.

In order to adjust the hardness to the required value, which is below 40 (Shore 00 hardness), there may be added from 50 to 500 parts of oil 5, preferably from 80 to 250 parts per 100 parts of composition 1 + 2 + 3

+ 4. This hardness may also be adjusted using the quantity of added filler. Between 0 and 50 parts of fillers are generally added per 100 parts of oil 1.

In one embodiment of the invention at least a portion of the 5 surface of the resilient support, in particular that in contact with the slide blocks and the sheet metal, is enclosed by a protective membrane of harder elastomer made, for example, of polyurethane, polybutadiene or natural or synthetic rubber of Shore A hardness greater than 30 and 10 preferably below 90, preferably between 35 and 80, and generally between 0.5 and 25 mm in thickness.

This membrane is particularly useful for ensuring the sealing of the die when the pressure increases and makes it possible to avoid contamination of the metal sheet by the silicones. In addition, in the case 15 where the resilient supports are very soft, it enables these supports to be readily handled.

The material of which this membrane is made must have elastic recovery properties which are as close as 20 possible to those of the resilient support, in order not to disturb its operation.

This membrane also extends the useful life of the resilient support.

The composite silicone resilient support of the 25 above type may be produced in various ways:

1. The elastomer may be cast in a receptacle formed by the membrane of harder, rigid elastomer,

of suitable dimensions such that the composite resilient support is arranged in the plate container (called die container hereinafter) receiving the slide blocks of the press.

5 2. The elastomeric composition which is to form the membrane may be sprayed and crosslinked on the inner walls of the die container and then the elastomeric silicone composition may be cast and crosslinked, and then a film of polyurethane may be arranged or bonded on the
10 upper face of the soft crosslinked support, for example using a silicone adhesive.

3. A continuous membrane layer may be arranged around the silicone elastomer resilient support using rotational moulding, or using overmoulding in a press.

15 4. The elastomeric composition may be cast and crosslinked directly in the die container and then the membrane may be arranged or bonded to the free outer surface of the resilient support.

20 Although polyurethane and rubber films produce the best results, they can nevertheless be replaced with Teflon, with a silicone elastomer, and the like.

The resilient support may consist of one or more resilient members arranged side by side and/or superposed inside the die container.

The following examples illustrate the invention. The double-action press used in these examples is of the type described in Figures 5 to 9 of the abovementioned European Patent Specification EP-A-165,133. The component 5 produced is similar to that shown in Figure 11 of the same specification.

EXAMPLE 1:

The following organopolysiloxane composition A₁ is cast in cylindrical metal moulds with an internal diameter of 320 mm and a height of 50 mm:

- 100 parts of dimethylpolysiloxane oil with a viscosity of 600 mPa s at 25°C, containing dimethylvinylsiloxy end groups (0.4% by weight of vinyl groups),
- 41.5 parts of pyrogenic silica with a specific surface area of 300 m²/g, treated with hexamethyldisilazane,
- 4 parts of a trimethylsiloxy-blocked dimethylpolysiloxane copolymer containing hydromethylsiloxy repeat units in the chain (0.24% by weight of hydrogen atoms bonded to silicon) and containing approximately 120 silicon atoms per molecule,
- 4 parts of a dimethylpolysiloxane polymer containing dimethylhydrosiloxy end groups with a viscosity of 30 mPa s at 25°C,
- 20 ppm of platinum in the form of a platinum complex prepared from chloroplatinic acid and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane as described in Example 4 of Patent US-A-3,814,730, and

- 0.1% by weight of 2-octyn-3-ol inhibitor, based on the total weight of the composition.

During the casting, 110 parts of dimethylpolysiloxane oil blocked with a trimethylsiloxy unit at each of its ends with a viscosity of 50 mPa s at 25°C are mixed with 100 parts of the above composition A₁. The mixture crosslinks after heating for two hours at 60°C.

Very good homogeneity of the crosslinked product is noted, and this is typical of good plasticizer miscibility.

4 cylindrical elastomer supports with a Shore 00 hardness value of 18, 24 hours after crosslinking, are obtained, and are stacked to fill the interior of the die container of the double-action press. A component identical to that of Figure 11 of European Patent specification EP-A-165,133 is produced using a sheet of HEL steel, $E = 60 \text{ kg/mm}^2$, 40/100 mm in thickness.

The drawing depth is 80 mm, the pressure is 100 bars, 20 blanks are formed per minute, and 300,000 blanks are formed without changing the resilient support and without stopping the press. The support plasticizer has not exuded.

The components produced are of substantially constant thickness, without wrinkles at the angles and show no defect in the region of the die entry radii.

EXAMPLES 2 TO 5:

To perform these examples, the procedure of Example 1 is repeated, except that a more viscous silicone plasticizer is employed. X parts by weight of tri-5 methylsiloxy-blocked dimethylpolysiloxane oil with a viscosity of 100 mPa s at 25°C are added during the casting to 100 parts of the composition A₁ described in Example 1.

The mixture crosslinks after heating for two 10 hours at 80°C. Very good plasticizer miscibility is noted.

The Shore 00 hardness (SH 00) is determined 24 hours after crosslinking. The plasticizer does not exude after use in the press.

15 The results are collated in Table I below:

TABLE I

Example	2	3	4	5
A ₁	100	100	100	100
Plasticizer X	37	46	110	140
SH 00 - 24 h	38	34	17	9

20

EXAMPLES 6 TO 8:

The procedure of Example 1 is repeated, except

that, during the casting in the mould, there are added to 100 parts of composition A1 X parts by weight of an organic plasticizer which is a polyalkylbenzene produced by the alkylation of benzene using olefins derived from the polymerization of propylene and marketed by the French company Petrosynthese under the trade name of Alkylat 150 DT ^(R).

The Shore 00 hardness (SH 00) is measured after eight hours following the crosslinking.

The miscibility (G: good, M: mediocre) and the exudation (N: none, S: slight) are assessed visually on the press under the conditions employed in Example 1. The results are collated in Table II below:

TABLE II

Example	6	7	8
A1	100	100	100
Alkylat 150 DT	20	30	40
SH 00 - 8 h	28	10	4
Miscibility	G	G	G
Exudation	S	S	S



EXAMPLE 9:

A mixture is cast in a rectangular die container which has a continuous internal coating of 3-mm thick polyurethane of Shore A hardness 55, of internal dimensions 790 mm x 358 mm and 200 mm in height, a fluid organopolysiloxane composition prepared beforehand in the following manner:

the following dough is prepared in a multiblade mixer maintained under a nitrogen atmosphere:

- 10 - 100 parts of a dimethylpolysiloxane oil with a viscosity of 500 mPa s at 25°C, blocked at each end with a $(\text{CH}_3)_3\text{SiO}_{0.5}$ unit,
- 40 parts of a pyrogenic silica of specific surface area 200 m²/g containing 1.5% of adsorbed water,
- 15 - 32 parts of distilled water, and
- 80 parts of hexamethyldisilazane.

This mixture is stirred for 6 hours at 20°C and is then devolatilized by being heated for 6 hours at 153°C under a stream of nitrogen.

20 The following are then added to the mixture, cooled to approximately 80°C:

- 100 parts of an alpha,omega-dihydroxydimethylpolysiloxane oil with a viscosity of 14,000 mPa s at 25°C,
- 2 parts of alpha,omega-dihydroxydimethylpolysiloxane
- 25 oil with a viscosity of 50 mPa s at 25°C, and
- 100 parts of ground quartz with a specific surface

area of $5 \text{ m}^2/\text{g}$, a mean particle diameter of 5 micrometres and containing 1% of adsorbed water.

The whole is compounded for two hours and is then ground.

5 To 1,000 parts of the above dough there are added and mixed in the die container 1,003 parts of a mixture consisting of:

- 1,000 parts of dimethylpolysiloxane oil blocked with trimethylsiloxy units at each end, with a viscosity of 10 100 mPa s at 25°C ,
- 2.4 parts of ethyl polysilicate, and
- 0.6 part of dibutyltin dilaurate.

The mixture crosslinks in 24 hours, cold.

Very good plasticizer miscibility is noted.

15 The resilient support has a Shore 00 hardness of 30, 24 hours after crosslinking.

After crosslinking, a polyurethane film with a Shore A hardness of 55 and 3 mm thick is bonded to the entire free upper surface of the resilient support, de-
20 fined by the edge of the polyurethane container, using a silicone adhesive.

The same sheet metal blanks as in Example 1 are used in order to elastoform components of the same shape.

The drawing depth is 100 mm.

25 The pressure is 100 bars, 20 blanks per minute are formed and 200,000 blanks are formed without stopping the press and without changing the resilient support.

The components produced are of the same quality as that obtained in Example 1.

The plasticizer has not exuded from the support.

EXAMPLE 10:

5 A composition C₁ is prepared by mixing:

- 100 parts of an alpha,omega-dihydroxydimethylpolysiloxane oil with a viscosity of 60,000 mPa s at 25°C,
 - 95 parts of a dimethylpolysiloxane oil blocked with a (CH₃)₃SiO_{0.5} unit at each end, with a viscosity of 50 mPa s
- 10 at 25°C, and
- 135 parts of ground quartz with a particle size distribution between 0.5 and 10 micrometres, containing 400 ppm of water.

2 parts of ethyl polysilicate and 0.35 parts of

15 dibutyltin dilaurate are added to 100 parts of the above composition C₁. A composition C₂ is obtained.

During the casting, 60 parts of a dimethylpolysiloxane oil blocked with a (CH₃)₃SiO_{0.5} unit at each end, with a viscosity of 100 mPa s at 25°C, are added to 100 parts of composition C₂. The whole crosslinks at ambient

20 temperature in the same cylindrical mould as that used in Example 1.

After 24 hours the Shore 00 hardness is 26. The miscibility of the plasticizing oil is very good and

25 this oil does not exude even after use in the press under the same conditions as in Example 1.

EXAMPLES 11 AND 12:

The procedure of Example 10 is repeated, except that X parts of the same plasticizing oil are added during the casting to 100 parts of composition C₂.

5 The miscibility is good and no exudation is noted. The Shore 00 hardness is measured after 24 hours following crosslinking.

The results are collated in Table III below:

TABLE III

Example	11	10	12
C ₂	100	100	100
Plasticizer X	40	60	100
SH 00	35	26	12

EXAMPLES 13 TO 16:

15 These examples are performed by starting with 100 parts of composition C₂ described in Example 10 and adding, during the casting, X parts by weight of an alkylate which is a polyalkylbenzene produced by the alkylation of benzene using olefins produced by the polymerization of propylene and marketed by the Société Fran-

20

çaise de Petrosynthèse under the trade name Alkylat 150 DT ^(R). The composition is cast in the cylindrical mould used in Example 1. The Shore 00 hardness is measured. The miscibility (G: good, M: mediocre) and the exudation (N: none, S: slight) are assessed visually in the press under the use conditions of Example 1.

The results are collated in Table IV below (SH 00 = Shore hardness (0)):

TABLE IV

Example	13	14	15	16
C ₂	100	100	100	100
Alkylat	30	40	50	60
SH 00	40	38	35	28
Miscibility	G	G	G	G
Exudation	S	S	S	S

EXAMPLES 17 TO 25:

The operations which are exactly the same as in Examples 12 to 16 are performed, except that the alkylate is replaced with a trimethylsiloxy-blocked copoly-

mer containing dimethylsiloxy and tetrachlorophenylsiloxy repeat units, marketed by Rhône-Poulenc under the trade name Huile 508 V 70 and originating from the cohydrolysis of tetrachlorophenyltrichlorosilane, dimethyldi-
5 chlorosilane and trimethylchlorosilane. The Shore 00 hardness is measured after 24 hours.

The results are collated in Table V below:

TABLE V

Example	17	18	19	20	21	22	23	24	25
C ₂	100	100	100	100	100	100	100	100	100
508 V 70 X	30	30	40	50	60	70	80	90	100
SH 00 - 24 h	40	39	33	30	25	22	15	12	6
Miscibility	G	G	G	G	G	G	G	G	G
Exudation	N	N	N	N	N	N	N	N	N

15 EXAMPLES 26 TO 32:

Operations which are exactly the same as in Examples 12 to 16 are performed, except that the alkylate is replaced by a petroleum cut with a boiling point of approximately 250°C, consisting essentially of ali-

phatic hydrocarbons and marketed by the company Esso-Chimie under the tradename Exsol D 100 [®].

The Shore 00 hardness is measured after 24 hours and after 15 days (following crosslinking at ambient temperature).

The results are collated in Table VI below:

TABLE VI

Example	26	27	28	29	30	31	32
C ₂	100	100	100	100	100	100	100
Exsol-X	40	50	60	70	80	90	100
SH 00 - 24 h	40	35	25	-	-	-	-
SH 00 - 15 d	40	38	30	20	15	5	2
Miscibility	G	G	G	G	G	G	G
Exudation	N	N	N	N	N	N	N

15 EXAMPLES 33 TO 37:

Operations which are exactly the same as in Examples 12 to 16 are performed except that the alkylate is replaced with a polybutylene of low molecular weight

(approximately 455) marketed by the company B.P. Chimie under the trade name Napvis D07[®].

The Shore 00 hardness is measured after 8 hours following crosslinking at ambient temperature.

5 The results are collated in Table VII below:

TABLE VII

Example	33	34	35	36	37
C2	100	100	100	100	100
D 07 X	30	40	50	60	70
SH 00	40	35	30	25	25
Miscibility	G	G	G	G	G
Exudation	N	S	S	S	High

10

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for shaping sheet metal (as hereinbefore defined), which comprises stamping sheet metal by electroforming using a silicone elastomer support suitable for forming a die for such a process, in which the silicone elastomer is a fluid organopolysiloxane composition which has been crosslinked, at ambient temperature or with heating, by a polycondensation or polyaddition reaction in the presence of a catalyst, and the organopolysiloxane is plasticized with at least one compatible plasticizer, which remains stable and nonmigrating under the stamping conditions, in a quantity such that the plasticized silicone elastomer has a Shore 00 hardness of less than about 40.

2. A process according to claim 1, in which the silicone elastomer support has a Shore 00 hardness of less than 30.

3. A process according to claim 1 or 2 in which the plasticizer is organic or mineral hydrocarbon oil, a diorganopolysiloxane oil, an organic plasticizer or a mixed organic/diorganopolysiloxane polymer.

4. A process according to claim 1 or 2, in which the plasticizer is a diorganopolysiloxane oil with a viscosity of 0.65 to 5,000 mPa s at 25°C.

5. A process according to claim 1 or 2 in which the plasticizer is a diorganopolysiloxane oil with a viscosity of 5 to 1000 mPa s at 25°C.



6. A process according to any

of claims 1 to 5 in which the silicone elastomer is the product of crosslinking an organopolysiloxane composition comprising:

A. a vinylated diorganopolysiloxane oil with a viscosity of between 100 and 100,000 mPa s at 25°C, containing at least two vinyl radicals per molecule, the other radicals being chosen from methyl, ethyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 60% of the number of the organic radicals being methyl radicals;

B. an organopolysiloxane containing at least 3 $\equiv\text{SiH}$ groups per molecule, chosen from branched organopolysiloxanes and straight-chain diorganopolysiloxanes;

C. optionally a coupling agent, which is a straight-chain diorganopolysiloxane containing two $\equiv\text{SiH}$ groups per molecule, the ratio of the number of $\equiv\text{SiH}$ groups in (B) + (C) to the number of the vinyl radicals in (A.) being between 0.7 and 2;

D. a reinforcing or semireinforcing inorganic filler;

E. a catalytically effective quantity of a platinum group metal catalyst; and

F. a plasticizer which is a diorganopolysiloxane with a viscosity of 5 to 3,000 mPa s at 25°C, in which the organic radicals are chosen from C_1 - C_{10} alkyl, phenyl, chlorophenyl and 3,3,3-trifluoropropyl radicals, at least 80% of the number of these radicals being methyl



radicals.

7. A process according to claim 6 in which the plasticizer F. has a viscosity of 10 to 1500 mPa s at 25°C.

8. A process according to claim 6 or 7, in which the silicone elastomer includes 5 to 400 parts of plasticizer F per 100 parts of (A + B + C + D + E).

9. A process according to claim 8, in which the silicone elastomer includes 20 to 200 parts of plasticizer F per 100 parts of (A + B + C + D + E).

10. A process according to any one of claims 1 to 5, in which the silicone elastomer is the product of crosslinking an organopolysiloxane composition comprising:

a. at least one alpha,omega-dihydroxydiorganopolysiloxane polymer with a viscosity of 20 to 500,000 mPa s at 25°C, in which the organic radicals are chosen from methyl, vinyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 60% of the number being methyl radicals, up to 20% of the number being phenyl radicals, and not more than 2% of the number being vinyl radicals;

b. a reinforcing or semireinforcing inorganic filler;

c. at least one crosslinking agent chosen from polyalkoxysilanes and polyalkoxysiloxanes;

d. a catalytically effective quantity of a tin catalyst; and



e. a plasticizer which is a diorganopolysiloxane with a viscosity of 5 to 3,000 mPa s at 25°C, in which the organic radicals are chosen from C₁-C₁₀ alkyl, phenyl, chlorophenyl, vinyl and 3,3,3-trifluoropropyl radicals, at least 80% of the number of these radicals being methyl radicals.

11. A process according to claim 10 in which the viscosity of the plasticizer (e) is 10 to 1500 mPa s at 25°C.

12. A process according to claim 10 or 11, in which the silicone elastomer comprises 50 to 500 parts of plasticizer (e) per 100 parts of (a + b + c + d).

13. A process according to claim 12, in which the silicone elastomer comprises 80 to 250 parts of plasticizer (e) per 100 parts of (a + b + c + d).

14. A process according to any one of the preceding claims, in which at least a proportion of the surface of the silicone elastomer support is enclosed with a membrane of hard elastomer with a thickness of between 0.5 and 25 mm and with Shore A hardness of 30 to 90.

15. A process according to claim 14 in which the hard elastomer has a Shore A hardness of 35 to 80.

16. A process according to claim 14 or 15 in which the hard elastomer is polyurethane, a polybutadiene or natural rubber.

17. A process according to any one of the preceding claims, in which the silicone elastomer support



consists of several resilient members arranged side by side and/or superposed inside a die container.

18. A process according to claim 1 substantially as described in any one of the foregoing Examples.

19. Process according to claim 1, in which the silicone elastomer support is prepared by introducing the plasticizer into the organopolysiloxane composition and then crosslinking the latter.

20. Process according to any one of claims 1 to 19, in which the sheet metal is elastoformed in a double-action press.

21. Sheet metal shaped by elastoforming by the process of any one of claims 1 to 20.

Dated this 30th day of March, 1990.

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