# 10. Silicones as Mold-Making Elastomers

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Long ago, people must have realised that clay could be used to take imprints of simple objects like a leaf, or later, a coin. Carefully withdrawing the clay gave a negative of the object or a mold in which other materials like plaster could be cast to reproduce the original. Clay is still used today to make molds, particularly to reproduce museum pieces like statues, not only because it is inexpensive, but also because clay is water washable and unlikely to contaminate or stain any valuable and unique original.

Clay molds are made by applying a layer of clay a few centimetres thick, and not too wet, on the original coated with talc. The clay is covered with plaster to provide a rigid backing or countermold. A fine metallic wire can be laid onto the original surface before applying the clay to help dismantling. This allows the clay mold to be split neatly in smaller parts. If needed, the original is copied in many pieces. After re-assembling the mold and its backing, plaster can be used to fill the clay mold to make copies and disseminate an object that otherwise would be unique and could only be seen by a few. “Does it matter that a copy is being shown and exposed?” the question has been asked. Providing that the copy is properly finished, all the artist's original work will be visually as present in the copy as in the original. So much so, that copies have been stolen from museum displays!

Yet the above technique suffers some shortcomings. Clay does not perfectly wet the original, and details are not perfectly captured. Seals between mold parts are difficult to make, leading to visible imperfections in the copies. The poor recovery after deformation or the clay’s plastic nature creates distortions upon demolding. And such clay molds may be good for making only one copy.

A major improvement was found with the use of elastomers as mold-making materials. These mold-making elastomers are supplied as liquid compositions, usually two-part materials, and are easy to cast around the original. After hardening, they set into a flexible material that can be stretched to ease demolding, even around deep undercuts. However, because of their elastomeric nature, they return to their original shape to give a cavity containing in negative all details of the original surface.

The first reference about the use of silicone molds appeared in the 50s. Mention is made of a composite made of mica or paper and a binder, and shaped around an electrical coil using a silicone mold [1]. The earliest true mold-making application with silicones, where the details of the original surface are being transferred via the mold, appears to be in dental molds, with commercial products available from 1955, and fast-curing compositions later [2].

Compared to molds made of metal and where a cavity must be created with all the details of the desired finished object in negative, elastomers used as mold-making material require little tooling, providing an original object exists and from which a mold can be made. Metal molds perform well when many copies are needed. Molds made from an elastomer are an interesting alternative for short-copy series.

**Process Description**

Different elastomer products are available to prepare molds. Their common and key feature is that they are initially fluid compositions that can be poured around the original before hardening into a solid elastomer. This transformation is obtained by cooling for a thermoplastic elastomer, by water evaporation for a latex emulsion or by a chemical reaction for a two-part reactive system.

The simplest mold is known as the one-piece block mold (see Figure 1):

- The original, master or model is fixed into a container or countermold with appropriate clearance left all around
- After processing of the mold-making elastomer material (melting or mixing), the liquid composition is poured in the space between the original and the countermold
- After hardening and disassembling, a one-piece elastomer block mold is obtained whose internal surface contains in negative all the details of the original

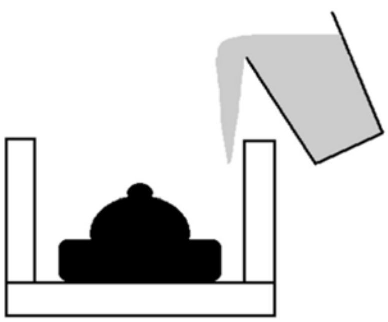
<table>
<tr><td colspan="3">Step 1: Fix the original in its counter-mold; apply a release agent; cast the two-part silicone elastomer after mixing and de-airing the two-part mixture.</td><td colspan="3">Step 2: Allow the two-part silicone elastomer mixture to cure to an elastomer.</td></tr>
<tr><td colspan="3"></td><td colspan="3"></td></tr>
<tr><td colspan="2">Step 3: Dismantle to obtain the one-piece block mold.</td><td colspan="2">Step 4: Cast a suitable copying material (plaster or resin).</td><td colspan="2">Step 5: Dismantle to obtain the copy.</td></tr>
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**Figure 1.** ***Process steps for making a one-piece silicone elastomer block mold (original in black, countermold in white; two-part silicone elastomer mixture and cured silicone mold in light gray; copy in dark gray).***

This one-piece block mold can now be used to cast plaster, polyester or any other suitable material to obtain positive copies of the original (see Figure 2).


**Figure 2.** ***Flexible one-piece block molds: a silicone mold being separated from a PU copy (left); a silicone mold, and two copies, one after and one before finishing (right). Pictures courtesy of Dow Corning.***

But more complex molds are also used. A three-dimensional original (e.g., a statue) can be copied with a mold of two or more pieces (i.e., to render both front and back surfaces, which a simple block mold cannot do). In contrast, skin molds can be used for very large originals that are rather "flat" (e.g., a cathedral door). In this case, the object can be copied with only a thin layer of a thixotropic mold-making material to limit the amount of material used and reduce costs. Here thixotropy can be induced with additives like glycols or silicone polyethers capable of interacting with filler particles present as reinforcing fillers and by hydrogen bonding to give a nonflowing molding material. Such skin molds carry all the details of the original surface but are not self supporting like a block mold. A suitable countermold, usually made of fiberglass-reinforced polyester, must be built directly on top of the skin mold after the mold-making material has hardened.

So, most complex molds are made of many pieces, each of the skin type. Less elastomer is used, but more time is spent preparing the original; that is, hiding or masking some parts of it with clay or plastiline to mold only part of the original surface at a time (see Figure 3).

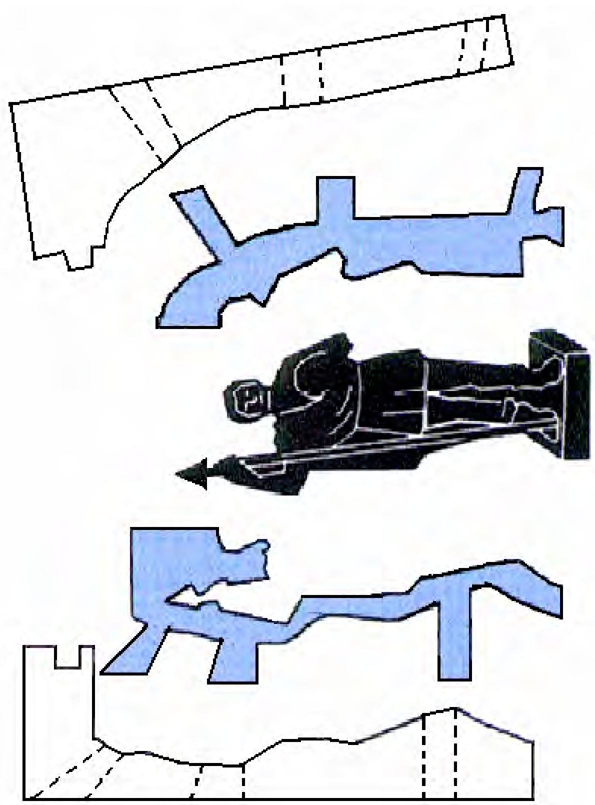

**Figure 3.** ***A complex mold made of two skin pieces (in blue), each with its own supporting countermold (in white) around the original (in black). Protuberances are designed to ensure that the skins adjust properly to their respective countermold parts.***

## Mold-Making Elastomers

Various elastomeric materials are used as mold-making material:

- Thermoplastic, like plasticized PVC, is inexpensive, but the original must allow exposure to high temperatures from the hot melted mold-making material
- Latex-based emulsions of limited stability upon shelf aging or against the heat generated by some copying resins (see further)
- Two-part silicone elastomers

Two-part silicone elastomers have distinctive advantages:

- They are available as two-part materials; that is, as two components to be mixed just prior to use in a fixed ratio such as 10:1 or 1:1 to give a liquid mixture that can be poured or plastered around the original
- Their low surface tension allows them to pick up minute details from the original surface
- They harden, cure or cross-link into high-strength elastomers at room temperature without exotherm, and so do not expose the original to thermal stress
- Because of their low surface energy, various casting materials can be used to make copies without the risk of adhering to the silicone surface; because of the silicone heat stability, resins with strong exotherms can be used

**Two-Part Silicone Mold-Making Elastomers**

PDMS polymers are liquid at room temperature, even those of very high molecular weight. Their low $T_g$ and the flexibility of their backbone make PDMS materials ideal candidates for formulating elastomers. A chemical reaction is yet required to attach or connect the free-flowing PDMS chains to form a solid, three-dimensional network or an elastomer capable of sustaining mechanical deformations. To allow for this, groups that can be reacted between polymer chains via a cross-linker in presence of a suitable catalyst must be present on the silicone polymer chains. Two different cross-linking systems have been developed, referred to as addition cure or condensation cure.

The addition cure is based on vinyl end-blocked PDMS polymers that are cross-linked by a SiH functional PDMS oligomer using a platinum-based catalyst, according to:

$$\sim\sim\sim OM\varepsilon_2\Sigma\iota - XH{=}XH_2 + H{-}\Sigma\iota{\equiv} \xrightarrow{\textit{Pt cat.}} \sim\sim\sim OM\varepsilon_2\Sigma\iota - \mathbf{XH_2{-}XH_2} - \Sigma\iota{\equiv}$$

where ~~~ represents the remaining part of the PDMS chain.

If the SiH functional PDMS contains three or more SiH reactive groups, many PDMS chains can be linked together to form a three-dimensional network. This reaction is an addition cure reaction, and no byproducts are evolved. So molds made using this reaction do not show shrinkage (see further). A platinum-based catalyst is used here and is prone to inhibition problems. Platinum catalysts work because they can bind to the weak electron-donating vinyl groups of the polymer chains. But, if better electron-donating groups are available in the vicinity (e.g., amine or sulphide), these can permanently bind with the platinum catalyst and completely inhibit its activity. Such impurities may come from nearby tools such as sulphur-vulcanized rubber gloves or from the original surface. When encountered, inhibition keeps the two-part addition cure elastomer from cross-linking properly, and it may badly stain the original (a small trial in a nonconspicuous place is recommended).

The condensation cure is based on hydroxy end-blocked PDMS polymers that are cross-linked by an alkoxy silane in presence of a tin catalyst according to:

$$4 \quad \sim\sim\sim Me_2Si - OH + Si(OnPr)_4 \xrightarrow[-\,4\,nPrOH]{\textit{Sn cat.}} \sim\sim\sim Me_2Si - O - \underset{\substack{| \\ O - SiMe_2\sim\sim\sim}}{\overset{\substack{O - SiMe_2\sim\sim\sim \\ |}}{Si}} - OSiMe_2\sim\sim\sim$$

where ~~~ represents the remaining part of the PDMS chains.

Alcohol is evolved during cure, resulting in some material loss and shrinkage (up to 2% linear shrinkage). Molds made using this reaction will not perfectly respect the dimensions of the original. But this reaction is not prone to inhibition except in very rare cases [3].

Advantages and limitations of both addition and condensation cure or cross-linking systems are summarized in Table 1.

**Table 1. Comparison of the Properties of Addition and Condensation Cure Silicone Two-Part Mold Making Elastomers**

| | **Addition cure** | **Condensation cure** |
|---|---|---|
| Inhibition | Possible | Very rare |
| Shrinkage (% linear) | Low (< 0.1) | Medium – high (0.2 – 2) |
| Heat stability | Excellent | Limited |

Two-part silicone elastomers are provided as two-component (Part A and Part B or base and curing agent, the latter sometimes improperly named catalyst) to separate polymer, cross-linker and catalyst from each other. These two components are mixed in a fixed ratio prior to use to allow cross-linking only after mixing. Various additives may be included like fillers (e.g., a high surface area fumed silica with levels up to 25 % w/w), as these dramatically improve mechanical properties, or cure rate control agents to allow for enough time after mixing to handle the mixed material and to have enough "pot life" while casting the two-part material around the original.

**The Art of Mold Making with Two-Part Silicone Elastomers**

Mold making with silicone elastomers is an art. Many aspects are to be considered to preserve the original as well as to create the best possible copies. Originals need little preparation, but they must tolerate the process; staining or removing lustre on an old artifact would be catastrophic. Countermolds are made from various materials, from simple cardboard to fiberglass-reinforced polyesters.

Release agents are used to avoid adhesion from the two-part silicone elastomers onto the original and the countermold, or on any cured silicone surface when making a multipiece mold to avoid adhesion between mold pieces. Release agents are based on soaps in water, petrolatum in organic solvents, organic resins in water or fluoropolymers.

The silicone elastomer is cast after adequate mixing and de-airing under vacuum to eliminate bubbles. Operations range from one casting for a simple block mold to many castings for a multiple-piece mold, with a strong release agent applied on any cured silicone surfaces to avoid subsequent adhesion. "Pegs" may be created to ensure that all mold pieces will adjust to each other properly later, and to minimise defects from seal lines.

Various casting materials can be used to make copies, including plaster, peroxide-cured polyesters, or two-part organic resins like polyurethane or epoxy. Mold life is a critical aspect. Some casting resins can slowly swell the elastomer and cure within the silicone polymer network, actually forming an interpenetrating network (IPN). This can quickly lead to deformations in the copies with respect to the original or worse, adhesion of the copy to the mold. Among other casting materials are low melting point metallic alloys or waxes. Wax copies are used to make ceramic molds for high melting point metals.

Finishing the copy is most important. Thick layers of pigmented coatings are inadequate and would remove all the surface detail transferred from the original to the copy thanks to the silicone elastomers. Silicone elastomers are capable of transferring submicron surface details and render appearance as detailed as velvet or wood structure [4]. So the finishing step is where mold makers can express all their art. Pigments can be included in the casting resin to provide for an adequate starting color, or fillers can be added to adjust density and render feel when handling the object. Lustre on artifacts is developed by very thin coating layers brushed and padded away.

**Application Fields**

Much of the above is related to the use of two-part silicone elastomers for the reproduction of artifacts like museum pieces. The method has been used to reproduce very large objects like a horse with a man statue in France [5], a Chinese dinosaur skeleton [6] or a pair of Easter Island Moai statues [7], all full size! Yet such silicone elastomers are also used in our everyday life as dental impression materials (a challenging application, as molds are made on wet buccal surfaces and as moisture can interfere with the cross-linking reactions) or as intermediates to designing and preparing prototypes before market launch. More recently, bakery forms made from silicone elastomers were commercialised to cast and bake cakes.

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