Indirect procedures in dental materials require that a cast or die be created that duplicates the geometry and dimensions of the oral tissues so that requisite laboratory work can be performed in the construction of a restoration. To capture the intraoral details, an impression material is used. These materials vary in composition and properties and are selected on the basis of relative need for (1) accuracy, (2) dimensional stability, and (3) elasticity.

For example, if you are interested in establishing the occlusal relations of the maxilla and mandible, the requirement for accuracy is relatively low and alginate impressions are perfectly acceptable. However, for capturing the final details of the margin for a crown preparation, accuracy is very important and polyvinylsiloxane is normally used.
PROBLEM ANALYSIS
What are tolerable limits for “error” in indirect procedures?

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Error Limits</th>
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<tbody>
<tr>
<td>a. Impressions</td>
<td>+/- 0</td>
</tr>
<tr>
<td>b. Casts, Dies</td>
<td>+/- 0</td>
</tr>
<tr>
<td>c. Waxing</td>
<td>+/- 0</td>
</tr>
<tr>
<td>d. Investing</td>
<td>+/- 1.5%</td>
</tr>
<tr>
<td>e. Casting</td>
<td>-1.5%</td>
</tr>
<tr>
<td>f. Finishing, Polishing</td>
<td>+/- 0</td>
</tr>
<tr>
<td>g. Cementation</td>
<td>+/- 0</td>
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Prepped Tooth Width

8 mm (=8,000 µm)

8,000 µm x 0.5% = 40 µm = 20 µm/side

Typical clinical error = >100 µm/side

Indirect procedures (inlays, onlays, crowns, bridges, etc.) require a number of steps in the capturing of intraoral information, fabrication of restorations in the laboratory, and cementation of the restorations in place. The steps are summarized in the figure above.

The critical question is “how much error” can be tolerated in the procedure and still produce an acceptable result. The errors are summed from step-to-step and so the overall error can be significantly influenced by a large amount of error in any single step. If impressions are taken correctly and poured at the proper time then very little error is involved. Working casts and dies can be created with almost no error. Waxing is subject to large amounts of potential error due to the inherent instability with small temperature fluctuations and/or stress relaxation during cooling. However, this can be dramatically reduced if waxed patterns are quickly invested. Investment must expand to compensate for casting alloy shrinkage during solidification and cooling. These two steps involve the greatest amount of dimensional change overall. If it is well-matched, then together expansion and contraction will cancel each other out. Finishing and polishing generally involves very little production of error. Cementation accommodates for errors between the preparation size and the casting size.

Generally the total error is expected to be less than 0.5%. If a crown preparation is assumed to be 8 mm (8000 µm) in width, then this amounts to 40 µm of error (or 20 µm per side).
The simplest method of classifying impression materials is by key properties: (A) rigid, [CLICK] (B) water-based, and [CLICK] (C) elastomeric.

Of the rigid types, impression plaster was the first material used for both edentulous and dentulous impressions. However, since it is rigid on setting, it must be carefully fractured (at the cupids and occlusally) to produce pieces that can be removed and then glued back together to create a complete impression. Nowadays, impression plaster is only used for edentulous impressions without undercuts. Impression compound is used for single tooth impressions where there are no undercuts. Zinc oxide eugenol (ZOE) is used for edentulous impressions.

Water-based systems include alginate (irreversible hydrocolloid) and agar-agar (reversible hydrocolloid). Both types of materials are inherently unstable because water is 85% of the composition. They are very easily distorted during syneresis (loss of water to the air or surrounding environment) or inhibition (absorption of water from the air). Alginate is generally wrapped in a wet paper towel to try to control these problems and poured quickly. However, it is still not accurate. It is only acceptable for low resolution applications.

Elastomers are rubbery polymers that are capable of elastic deformation from undercut areas to produce a complete impression for dentate situations. There are four major types (polysulfide, silicone, polyether, and polyvinyl siloxane), but polyether (Pe) and polyvinyl siloxane (PVS) are most often used. Information on all four types will be reviewed but the primary focus will be on Pe and PVS.
Impression materials must have some strength, but generally their design is focused more on accuracy, dimensional stability, and flexibility (or tear resistance).

[CLICK] When impression material comes into contact with soft and hard tissues (which are hydrophilic), it must adapt and flow over these surfaces to capture the fine details of the structure. This is referred to as “accuracy.”

[CLICK] The impression must be “dimensionally stable” so that its specific dimensions are preserved until it can be poured to create a working cast. If it does distort, then the working dies will be the wrong size and/or geometry and produce an ill-fitting restoration. Only small amounts of mis-fit are tolerated and accommodated by the dental cement for attaching the prosthesis to tooth structure.

[CLICK]

[CLICK] Once an impression undergoes a hardening or setting reaction, it must be strong enough to resist tearing during removal (“tear resistance”).

<table>
<thead>
<tr>
<th>Key Properties</th>
<th>Description</th>
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<tbody>
<tr>
<td><strong>Accuracy</strong></td>
<td>ability to replicate the intraoral surface details.</td>
</tr>
<tr>
<td><strong>Dimensional Stability</strong></td>
<td>ability to retain its absolute dimensional size over time.</td>
</tr>
<tr>
<td><strong>Tear Resistance</strong></td>
<td>ability to resist tearing in thin sections (such as through the feather-edged material within the gingival sulcus).</td>
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All "elastic impression materials" have the same general type of formulation. They all have a flexible matrix (the continuous phase) that is filled with extender or filler (the dispersed phase) to minimize the effects of polymerization shrinkage during setting on the overall accuracy and dimensional stability of the system. [CLICK] All setting reactions generate polymerization shrinkage that is approximately 1-4%. [CLICK] The addition of extensive fillers (50-70% by weight) [CLICK] decreases this to tolerable levels of about 0.2 to 0.4%. [CLICK]

Most of the original liquid impression material is a high-molecular weight monomer or pre-polymer that will become reacted and crosslinked with a second moiety. Curing agents are included. Modifiers are used to accelerate the setting reaction, counteract potential side reactions, increase the flexibility, control the taste to the patient, and suitably colorize the material for identification and/or distinction from other materials. Fillers are chosen to be compatible with the resin component (hydrophilic or hydrophobic) but also be as cheap as possible since they are not required for reinforcement. Most elastomeric impression materials have a 12-18 month shelf-life that is extended by storing the materials in the refrigerator. Be careful to check the expiry date so that the material does not needlessly grow too old and have to be discarded.
To minimize any effects of shrinkage, almost all impression materials are supplied as a combination of (1) high viscosity and low viscosity paste-paste materials, or (2) putty-wash option. Usually they are different colors. One of the clinical tricks for minimizing the effect of polymerization shrinkage on impression distortion is to use a low viscosity version (more shrinkage due to less filler) [CLICK] to wet the surfaces of the preparation or areas of interest [CLICK] and then use high viscosity material (low shrinkage but poor flow) [CLICK] to make up most of the bulk of the rest of the impression. [CLICK]

Another feature of most impressions [CLICK] is that the shrinking impression material tends to be distorted toward the impression tray. This ultimately results in an impression that is slightly oversized.

[CLICK] Impression trays may be rigid (metal or custom acrylic) or flexible (plastic). Elastomeric impressions are generally used with either a custom-made acrylic resin tray or a plastic tray with some undercuts or retention holes. To insure a uniform lock of the impression material to the tray, a tray adhesive is often used. [CLICK] It behaves like rubber cement and works best in a thin well-dried layer. [CLICK] The heavy and light-bodied impression material are made of the same polymer matrix and so are well-cured together during the setting reaction. [CLICK] Shrinkage occurs toward the restrained surface (tray) and away from the unrestrained (tooth) surface. [CLICK]
Elastomeric impression materials are 2-component chemically setting materials that are traditionally delivered as two tubes of pastes. The pastes can be mixed together with (1) mixing pads (manually), (2) auto-mixing guns (by manually expressing the two pastes through a Kenics mixing tip), or (3) mixing equipment (electrically driven pumps for proportioning of materials from larger tubes through a Kenics mixing tip).

The type of mixing technology depends on the rheological behavior of the mixture. [CLICK] Materials that are Newtonian or dilatant are actually hard to mix through a mixing tip. [CLICK] Silicone and polysulfide elastomers are examples of those situations, respectively. [CLICK] Therefore, they must be mixed manually on a mixing pad. Materials that are shear-thinning (pseudo-plastic) [CLICK] benefit from high shear in a mixing tip on an auto-mix gun or auto-mix equipment. [CLICK] Polyether and polyvinyl siloxane are examples of materials that are shear-thinning. [CLICK]

A typical Kenics mixing tip is shown above disassembled to reveal a series of connected mixing paddles (alpha-helixes with alternating rotations) that split and fold the mixing stream to produce mixing. A mixing tip with 8 paddles will split and fold the stream of two components 256 times ($2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 = 2$ to the eighth power $= 256$). [CLICK] The entire mixing event occurs in less than 1 second. Material that is left in the mixing tip will set and so the tip must be discarded. However, before the next mixing event, the tip functions as a cap on the dispensing gun.
RAPID removal of an elastomeric impression material leads to the least chance for plastic deformation if the procedure involves rapid elastic deformation. Remove the impression with a SNAP. [CLICK] This creates a rapid loading rate. Remember that all polymers are very STRAIN RATE SENSITIVE. [CLICK] If the stress is applied quickly, then all the energy is stored elastically and the material will not undergo plastic deformation. This is particularly important in the region of the greatest deformations (e.g., the margins) [CLICK] Fast removal rates [CLICK] guarantee that loads (see the blue dotted line) only generate elastic deformations. Slow removal rates [CLICK] would actually cause plastic deformation and distort the impression in critical areas.
You can follow the reaction conversion (see the vertical axis) versus time or the log of time (look at the horizontal axis) of the impression material. Once the reaction is complete [CLICK] the polymerization shrinkage should be complete as well. You will recall that those materials that undergo stepwise polymerizations (polysulfide, silicone, and polyether) are relatively slow. After the impression is removed, these materials are continuing to react, shrink, and thus distort themselves. It is advantageous to pour the impression as soon as is clinically practical. [CLICK] Polyvinylsiloxane is fast because it is a chain reaction polymerization. [CLICK]

Once the impression is clinically set (which corresponds to about 50% or greater reaction conversion), [CLICK] the impression tray can be removed with a SNAP. This procedure helps to force the material to behave elastically. However, some time is required for complete elastic recovery. The rule of thumb is that 20-30 minutes should be permitted before pouring the impression. [CLICK] Thus, for some impression materials (polysulfide, silicone, polyether), you are balancing out the effect of time for elastic recovery and potential problems with continued shrinkage. Stick to the rule-of-thumb of waiting 20-30 minutes. Polyvinylsiloxane, on the other hand, has completed its shrinkage and is stable over time.
Polysulfide rubber (rubber base, mercaptan rubber, or Thiokol rubber) is the first elastomeric rubber to be developed for dentistry. Its origins were right after the second world war when natural rubber was still scarce. It is made predominantly at one plant in Mississippi that produces the material for a wide range of commercial applications, including Thiokol seals for the US Space Shuttle. Some of the noteworthy properties are that the material is brown, stains clothing easily, and produces a strong odor. While the material is cheap, it is not well-accepted by most patients. However, it has been used in dentistry for almost 50 years and still remains popular with the oldest clinicians.

The general composition of polysulfide is a mercapto-functional polymer (see the chemical link within the brackets above) that is crosslinked with sulfur or oxygen from lead peroxide. The material is filled to reduce shrinkage using the least expensive fillers that are available at the time of production (TiO2 or zinc sulfate or lithopone or calcium sulfate dihydrate). The fillers do not matter much. Manufacturers may even change the filler from month-to-month.

The reaction is shown in the figure above. Adjacent sulf-hydryl groups are condensed in the presence of oxygen to eliminate water (which stays inside of the polymer) and produces a sulf-hydryl bridge that connects the molecules. This is a stepwise reaction that is relatively slow, affected by heat, and exothermic.
**POLYSULFIDE RUBBER**
Manipulation and Technique Considerations

a. Two-step techniques recommended: Reduces air entrapment and surface tension effects.
b. Material adversely affected by H₂O, saliva, and blood.
c. Set impression should be removed quickly - do not rock tray.
d. No syneresis or imbibition, but distortion due to continued reaction.
e. Ideally need uniform thickness and at least 2 mm thick for accuracy.
   (1) Adhesive must be thin
   (2) Adhesive must be dry
f. Paste-Paste Mixing Recommendations:
   (1) Dispense pastes at the top of the mixing pad
   (2) Mix pastes with tip of spatula only for 5 seconds
   (3) Transfer mass to fresh surface at center of mixing pad
   (4) Wipe spatula off with paper towel; Strop mass for 15s to constant color
   (5) Load syringe or tray
   (6) Use pad excess to monitor setting time
g. Pouring of models:
   (1) Wait 20-30 minutes before pour for stress relaxation to occur
   (2) RB is non-reactive with model and die materials
   (3) Be careful of glove powder contamination of impression
   (4) RB can be electroplated

Special notes on the techniques for using this material are reported above. Polysulfide is adversely affected by contact with water, saliva, and/or blood and should be carefully washed after removing the impression. It works the best in a custom acrylic impression tray utilizing a tray adhesive. Because it must be mixed manually and is difficult to mix, so a special procedure is recommended. [CLICK] The two pastes are dispensed in equal lengths [CLICK] on a mixing pad and stirred together with the tip of a STIFF mixing spatula. The materials are collected to the center of the pad, stropped vigorously and then used to load the tray and/or light-bodied delivery syringe. [CLICK] It is important to wait 20-30 minutes after tray removal for stress relaxation to occur.
Silicone rubber was first employed as an impression material in the 1960s. At the time, clinicians were using polysulfide or reversible-hydrocolloid for most dental impressions requiring high accuracy. The polymer phase forms in a similar fashion to polysulfide rubber. Polydimethyl siloxane moieties are crosslinked by alkyl orthosilicate molecules. The reaction produces ethanol as a by-product but that does not seem to have detrimental effects on the properties.

This type of silicone rubber is catalyzed with tin octoate. It is medical grade silicone rubber. Commercially available silicone rubber that you might buy in the hardware store is non-medical grade and utilizes dibutyl tin dilaurate catalyst that is extremely toxic. Several years ago there was a case of a man who used non-medical grade to repair the inside of his dishwasher and slowly poisoned he and his family as the material leached catalyst onto their dishes. Be very careful.

Silica is the primary filler.

This is a stepwise reaction that is relatively slow, affected by heat, and exothermic.
SILICONE RUBBER
Manipulation and Technique Considerations

b. Requires mechanical retention or special tray adhesives
c. No syneresis or imbibition, but continued polymerization shrinkage.
d. Better dimensional stability than RHC but more expensive
e. Pouring of models:
   (1) More flexible so more chance for distortion during removal
   (2) Wait 20-30 minutes before pour for stress relaxation to occur

Special notes on the techniques for using this material are reported above. Silicone has a limited shelf-life and is best stored in the refrigerator prior to use. Silica fillers tend to settle out of the material over time. It is important to wait 20-30 minutes after tray removal for stress relaxation to occur.

These materials represented a substantial improvement over polysulfide rubber in terms of having no odor and generally not staining clothing. Other properties were approximately the same to polysulfide.
Polyether rubber was first produced in Europe in the late 1960s. The reaction is shown in the figure above. Amine-terminated polyether moieties are crosslinked in the presence of aromatic sulfonates. These materials are filled with silica to insure their stability. This is a stepwise reaction that is relatively slow, affected by heat, and exothermic.
Special notes on the techniques for using this material are reported above. Polyether produces an excellent impression and has been very popular, especially in Europe.

The material is very stiff. Typically, a plasticizer is provided as a modifier to reduce the stiffness. It is critical to release the hydrostatic seal with tissues before removal with a snap.

Like polysulfide, this material is negatively affected by water, saliva, and/or blood and the impression should be quickly cleaned after removal. It is important to wait 20-30 minutes after tray removal for stress relaxation to occur. Because the material is pseudoplastic, [CLICK] it can be easily mixed with a Kenics mixing tip using an automix gun or machine (like the ESPE PentaMix).
Polyvinylsiloxane (or PVS) is often called ‘viny polysiloxane’ (or VPS) as well. Since it is based on silicone chemistry, it has sometimes been referred to as an addition-silicone. These oligomers are double-bond-functional silicones which become polymerized by free radicals from chloroplatinic acid. The catalyst is consumed as it provides radicals and it generates hydrogen gas as a by-product. The mixture is filled with silica because that is the only thing with the right degree of hydrophilicity to be blended into the resin.

The reaction is shown in the figure above. This is a chain reaction that is very fast, affected by heat, and exothermic.
POLVINYL S ILOXANE
Manipulation and Technique Considerations

a. BEST impression material for dimensional stability:
   Pouring should be delayed at least 4 hours for H2 out-gassing.
   Pouring can be delayed up to 7-to-10 days (or indefinitely).
b. Stiffness makes removal difficult.
c. Most material dispensed using auto-mixing gun and mixing tips

Special notes on the techniques for using this material are reported above. The best feature of polyvinylsiloxane is that the reaction is essentially complete at the time of impression removal so that it is not subject to reaction distortion. One still must wait 20-30 minutes for elastic recovery to occur, but there is no distortion occurring during this waiting period. For all practical purposes, the impression does not need to be poured until it reaches the dental laboratory. Therefore, this is a favorite material for most clinicians.

One of the side-effects of the reaction, is the decomposition of the chloroplatinic acid. This produces small amounts of hydrogen gas. If the impression tray is resting with the impression facing upward, then during the next 3-4 hours small gas bubbles escape from the surface. Do not pour the impression during this time or else the gas will collect at the boundary of the stone and create bubbles. Newer materials include hydrogen-getters (or scavengers) that catch the hydrogen before it can create bubbles at the surfaces.
Before 1996, all four types of elastomers were still prevalent in the US market. Costs of auto-mixing guns, mixing tips, and polymer for PVS and polyether restrained their use in dental practice. [CLICK]

The largest volume of dental material used in any dental practice is impression material. This is a highly competitive market among dental manufacturers, and some companies such as ESPE have made most of their profits on this commodity. For a single procedure (e.g., crown preparation), taking one impression is equivalent in volume to about 40-50 composite restorations. The cost for a single impression can vary from $12 to $18. There have even been calculations of the relative amount of material lost in the mixing tip as a consideration of the overall economics of these procedures.
However, the economics shifted toward PVS and polyether systems as production costs became lower. By 1996, there was relatively rapid discontinuance of polysulfide and condensation silicone use in general practices. Clearly, PVS and Pe systems saved time and more easily produced good impressions. At the same time, dental manufacturers were attempting to produce hydrophilic impression materials. Additives to generate these modifications were much easier to blend with polyvinylsiloxanes.

PVS (or VPS) impression material is now routinely used for just about all crown and bridge needs.
Recall the 3 principal properties of interest for impression materials – (1) accuracy, (2) dimensional stability, and (3) tear resistance. Associated with each of these important properties are several contributing factors that deserve special attention.

**Accuracy** depends on not only the ability of the impression material to wet the surface of hydrophilic tissues, but also on the ability of dental stone to wet the subsequent impression. **Dimensional stability** is a function of several events that can increase or decrease the size of the impression – polymerization shrinkage on setting, thermal shrinkage once the impression is removed from the mouth, loss of volatile components generated by the setting reaction, and/or stress relaxation after setting. **Tear resistance** is improved if the elastomeric impression is more capable of elastic deformation without plastic deformation.

Rankings of examples of water-based gels (RHC = reversible hydrocolloid; ALG = alginate) and elastomeric impression materials (PS = polysulfide, SIL = condensation silicone, PE = polyether, PVS = polyvinyl siloxane) are shown above. While PVS dominates in most categories, it is not excellent in all cases (e.g., wetting by dental stone). In a similar way, despite its relative disuse, PS is intermediate in ranking in many categories, and best in terms of tear resistance.
The graph above is a summary of many different product examples in each of the 4 elastomer categories and it reports the percentage change or shrinkage of the materials [CLICK] at 30 minutes and also at 24 hours. [CLICK] Obviously, waiting longer times allows more potential shrinkage. The mean shrinkages for the 4 elastomer groups [CLICK] is shown as well. The materials reported in this graph represent the market about 10 years ago. The actual shrinkages for polyether and polyvinylsiloxane are actually even smaller for today’s products. Everything we discussed comes down to making sure that the accuracy, dimensional stability, and tear resistance provide a good impression.
Thank you.