

MATERIALS IN DENTISTRY

By Doc. Dr. Ivan M. Malbohan, and Dr. Jan Pláteník

1 Metallic Materials

1.1 Dental Alloys

Pure metals are only infrequently used in dentistry. Occasionally pure gold (**Au**) is used as a high quality, although expensive inlay. **Au** is biologically well tolerated, but too soft material. It is chemically very stable and does not corrode. For the prosthetic purposes, other metals are usually added to gold in order to get an alloy with better properties, especially harder and with higher melting point. Typical gold alloys are composed of **Au-Cu-(Ag)**; or **Au-Pt-Cu-Zn**; or **Au-Pd-Cu**.

The content of **Au** in gold alloys must be at least 65 %; the content of **Ni** must be less than 0.1 %; and **Be**, **Cd** must be less than 0.02 %.

The addition of **Cu** to a gold alloy increases its hardness, but too much of copper leads to corrosion of the alloy in the oral cavity. The hardest and most durable alloys seem to be combinations of **Au**, **Ag**, **Cu**, and **Pt**. Additions of **Sn**, **Zn**, **Fe**, **Ir**, and **Si** improve the melting properties of the alloy.

The main disadvantage of gold alloys in general is the high price.

Alloys with lower **Au** content, such as *Aurose*, *Aurix*, contain between 25 % and 75 % of **Au** and **Pt** metals. Examples are combinations **Ag-Au-Pd-Cu-In**; **Ag-Pd-Cu**; and **Ag-Pd-In-Zn**.

Alloys based on common metals:

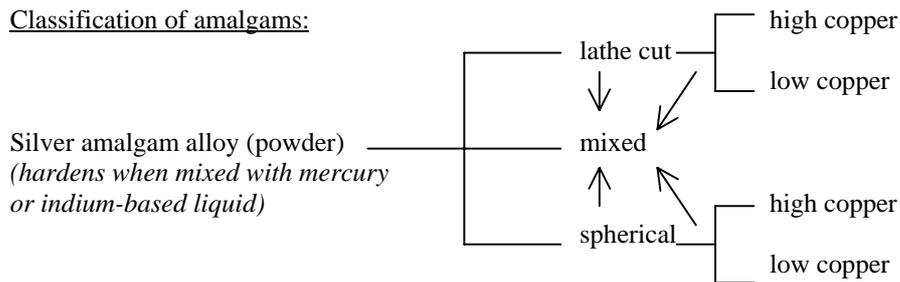
- a) **Co**: e.g. **Co-Cr-Mo-Si-Mn**; **Co-Cr-Mo-W-Si**; **Co-Cr-Mo-Ti**.
Cobalt makes for very hard alloys (!), especially in combination with **Cr**, and **Mn**.
- b) **Ni**: e.g. **Ni-Cr-Mo-Si**.
Nickel is a strong allergen !!! Very high melting point (1400-1600 °C) of nickel alloys causes making an exact casting difficult.
- c) Aluminium bronzes, e.g. **Cu-Al-Ni-Mn-Fe**: display a nice yellow colour, but also an extremely high corrosion in oral cavity. They cause allergic reactions very often!!! Many patients do not tolerate the aluminium bronzes at all !

Metal-ceramic restorative systems:

This type of alloy must have a very high melting point (over 1000 °C), because most of the ceramic materials are fired at 900 °C. An example is **Au-Ag-Pt-Cu** (*SAFIBOND*), or a nickel containing (...less suitable!) alloy *Oralium Ceramic*.

1.2 Dental Amalgams

Amalgam is used in dentistry for more than 150 years (!). It still makes for more than 3/4 of all direct posterior restorations today, because of easy manipulation, relatively low cost, and long clinical service life. Some concern has arisen regarding the toxicity of mercury from both biological and environmental viewpoints; especially in Scandinavia, where it is not allowed in children and pregnant women.

Classification of amalgams:

The dental amalgam consists of **Ag**, **Sn**, **Cu**, and **Hg**. The traditional amalgams, since the end of 19th century (Black, 1895) until 60's those exclusively used, are of the low copper type (70 % **Ag**, 26 % **Sn**, less than 3 % **Cu**). The high copper amalgams, introduced in 1963, contain 40-60 % of **Ag**, 15-30 % of **Sn** and 10-30 % of **Cu** in the powder. The high copper amalgams are clinically superior to the traditional ones in marginal integrity and mechanic resistance.

Amalgamation is quite difficult to describe from the chemical point of view. It starts when the "powder" or "sawdust" is mixed with liquid mercury (**Hg₂**). The process of hardening, "maturation" of amalgam lasts more than 24 hours, but usually after 2 hours the amalgam filling can resist mastication. No free mercury can be present in the mature amalgam. If toxicity of mercury is of concern, the **Hg₂** can be replaced by mixture of gallium (cca 65 %) indium (cca 19 %) and tin (cca 16 %), which is also liquid at the room temperature. Toxicity of mercury can also be reduced by addition of selenium or indium to the powder.

Requirements on dental amalgam composition according to ISO 1559:	
Ag	min. 40 %
Sn	max. 32 %
Cu	max. 30 %
In	max. 5 %
Pd, Pt	max 1 %
Zn	max 2 %
Hg	max 3 %

It is worth noting that there is no reaction between amalgam and the dental tissue, therefore, the amalgam filling must have every time a good retention (!) If not, it will fall out!

2 Non-metallic Materials

2.1 Gypsum Products

Gypsum products are various forms of calcium sulfate, hydrous or anhydrous, prepared by the calcination (prolonged heating below the melting point) of calcium sulfate dihydrate (the plaster stone, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which results in a partial or complete dehydration. The resulting plaster powder (calcium sulfate hemihydrate, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) give after re-mixing with water the plaster used e.g. for models for making dental prostheses.

The gypsum products in general are important accessory materials used in many clinical and especially laboratory procedures. Their appropriate usage contributes to success of these procedures.

Classification of gypsum products according to International Standards Organisation (ISO) 1998:

Type 1: Impression plaster

Type 2: Plaster

Type 3: Stone

Type 4: Stone, high-strength, low-expansion

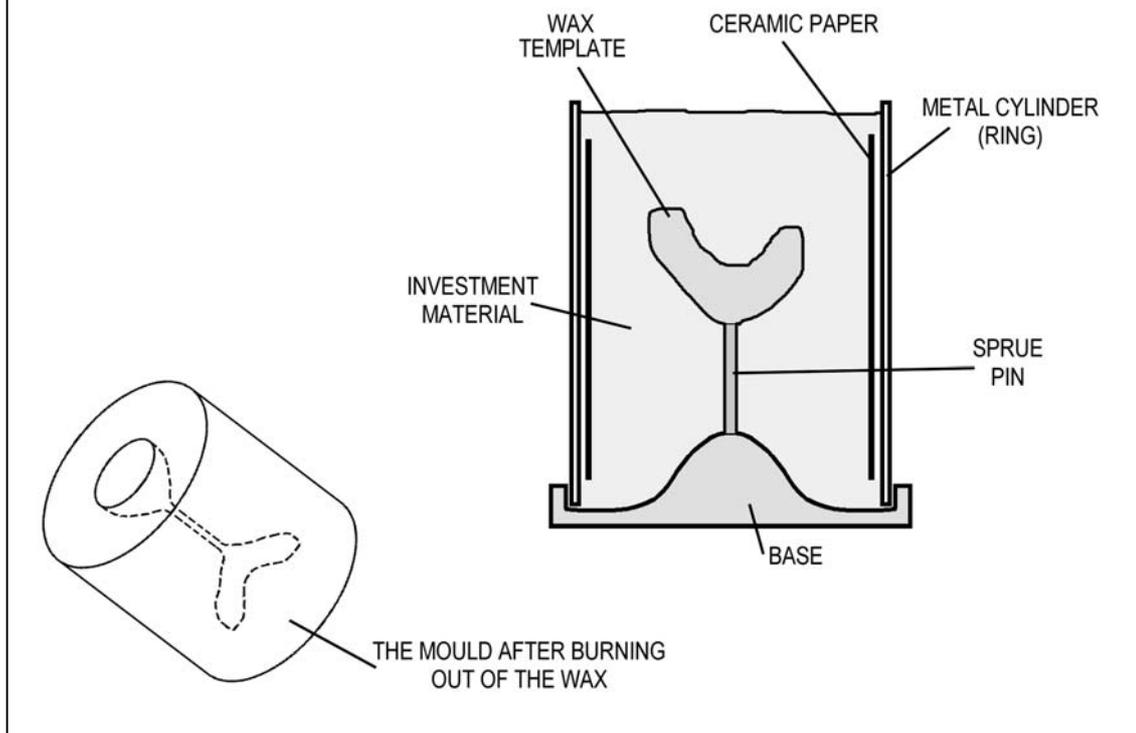
Type 5: Stone, high-strength, high-expansion

Types 1 and 2 are based on ordinary gypsum plaster, while 3, 4, and 5 are based on high-strength gypsum plasters. The type 3 is usually used for preparation of models from imprints; types 4 and 5 are called die stones.

Casting Dental Restorations:

The lost wax casting technique is the one most commonly used.

1. Prepare (rub down) the tooth (or teeth) on which the dental restoration is to be mounted.
2. Make an impression of the prepared tooth.
3. Pour gypsum slurry into the impression to make a positive cast that is an exact replica of the dental arch from which the individual parts (dies) representing the prepared tooth or teeth can be sectioned.
4. Create a wax template of the desired dental restoration.
5. Sprue (fix in space) the wax template (see figure).
6. Invest (embed) the wax template.
7. Remove the wax template by burning the wax out of the investment in a furnace thus making a mould.
8. Force molten metal alloy into the mould and allow to cool down.
9. Remove the secure pin from the casting and clean the cast from the investment substance.
10. Finish and polish the cast on the gypsum die.
11. Cement the finalized dental restoration on the prepared tooth in the patient's mouth.

**High temperature (other than gypsum based investments):**

- 1) Cristobalite is a high expansion form of silica.
- 2) Phosphate-bonded investments: contain silica, primary ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and magnesium oxide (MgO). The setting reaction in aqueous solution is:



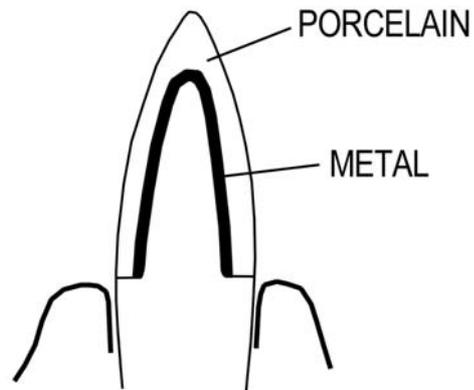
This type of investment material is used for high-melting point gold alloys used with porcelain.

- 3) For the alloy systems not containing noble metals even the phosphate-bonded investment is not heat resistant enough, rather, silicate, zirconate, and various magnesium based investments are employed. Special dental alloys with very high melting point are used for porcelain-fused-to-metal (PFM) fixed partial dentures, because the porcelain must be repeatedly fired in the furnace at high temperature.

2.2 Dental Porcelains (Silicates)

Composition of dental porcelains is usually:

SiO ₂	50-60 %
Al ₂ O ₃	12-16 %
K ₂ O	10-11 %
Na ₂ O	5-8 %
ZrO ₂	0.1-5 %
B ₂ O ₃	0-10 %
Rb ₂ O	0.1 %
SnO ₂	0-15 %
BaO	0-3 %
ZnO	0-0.25 %
CaO	0-2 %
TiO ₂	0-3 %



2.3 Dental Cements

Dental cements are used in very small quantities, but represent the most important materials in clinical dentistry nowadays because of their applications as:

- 1) luting agents to bond preformed restorations and orthodontic attachments on or in the tooth
- 2) cavity liners and bases serving as protection of the dental pulp, foundation and anchor for restorations
- 3) restorative materials.

In the last decades of the 20th century the emphasis has been on materials for luting because of the extensive usage of fixed partial dentures. More recently, with the introduction of glass-ionomer cements, interest in restorative applications has increased substantially.

Such different applications require materials of different physical properties, therefore new international standards (ISO) being developed are based on performance criteria rather than a specific chemical composition.

From the chemical point of view, we can differentiate:

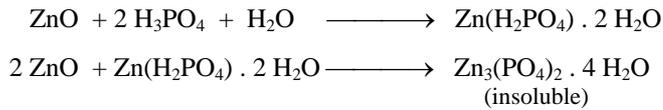
- 1) pure inorganic cements, such as zinc phosphate, zinc silicophosphate
- 2) mixed (organic + inorganic) cements, such as cements based on phenolate (zinc oxide-eugenol, calcium hydroxide salicylate), polycarboxylate (zinc polycarboxylate, glass-ionomer, resin-modified glass-ionomer)
- 3) pure organic cements, such as acrylate, dimethylmethacrylate, adhesive cements

2.3.1 Inorganic dental cements

Zinc phosphate cements have been in use since the beginning of 20th century. They were especially widespread until 70's, when the new sorts of dental cements appeared. The zinc phosphate cements had a broad spectrum of applications, ranging from cementation (luting) of fixed cast alloy, porcelain restoration or orthodontic bands, to their use as a cavity liner or base to protect the pulp from mechanical, thermal or electric irritation.

Composition: zinc phosphate cement is supplied as powder + liquid, which are to be mixed just before use. The powder is mainly zinc oxide with up to 10 % of magnesium oxide. The liquid is an aqueous solution consisting of 45-64 % of H₃PO₄ (phosphoric acid) and 30-55 % of water. The liquid also contains 2-3 % of aluminium (essential for cement-forming reaction) and 0-9 % of zinc (modulator of the reaction allowing adequate working time).

The setting process is essentially an acid-base reaction in which phosphoric acid and zinc oxide give an amorphous salt zinc phosphate:



One serious disadvantage of zinc phosphate cements is a very low pH after their preparation (about 2 !!) resulting in a strong irritation of the dental pulp after application.

Modified zinc phosphate cements for cavity liners with lowered H_3PO_4 (25 %) and higher aluminium content in the liquid and $\text{Ca}(\text{OH})_2$ in the powder can be used to decrease irritation of the pulp. Also, stannous fluoride can be added (up to 10 %) that contributes with an anticariogenic effect. Disadvantage of these modifications is lower strength and higher solubility compared to the ordinary zinc phosphate cement.

Silicophosphate cements have been available for many years as combination of zinc phosphate and silicate cements; their principal applications have encompassed cementation of fixed restorations and orthodontic bands, as well as provisional posterior filling materials.

Composition: the powder consists of a blend of 10-20 % ZnO and silicate glass, usually containing 12-25 % of fluoride. The presence of silicate glass provides a degree of translucency and improved strength; and the possibility of fluoride release makes for an anticariogenic effect. Small amount of silver (Ag) in the powder is supposed to have germicidal (antibacterial) effects. The liquid is again orthophosphoric acid, 45 % water, and 2-5 % aluminium and zinc salts.

Chemistry of setting: again the acid-base reaction resulting in formation of zinc aluminosilicate phosphate gel:



Good translucency makes the silicophosphate cement suitable for cementation of ceramic restorations and orthodontic bands. Another main advantage is low solubility in the environment of oral cavity. The major disadvantage is, similarly to the zinc phosphate cement, a very low pH (1-2 !) upon preparation that causes a strong pulp irritation. The acidity is even greater than in case of the zinc phosphate cement !! It follows that the pulp of vital tooth must always be protected when this sort of cement is to be used !

2.3.2 Organic cements

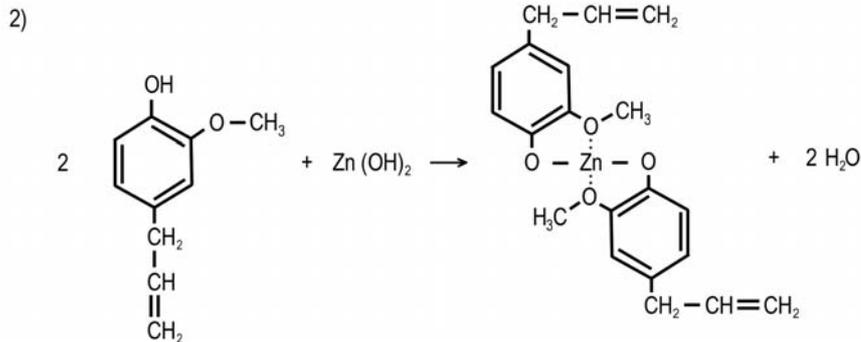
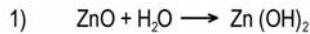
2.3.2.1 Phenolate-based cements

Zinc oxide-eugenol cements come again as powder + liquid. The powder is essentially pure zinc oxide, with less than 1 % of zinc salts acting as accelerators of hardening. The liquid is either pure eugenol, or clove oil. Eugenol is a main constituent of clove oil (85 %).

Chemistry of setting:



The reaction is not fully understood, but the most probable phases are:



The presence of eugenol imparts this sort of cement an anodyne (pain relief) and antibacterial effects, thus protecting the pulp in deep cavities. Zinc oxide eugenol cement is used as a base under amalgam restorations. Its main disadvantage is a low stability in oral environment due to hydrolytic decomposition.

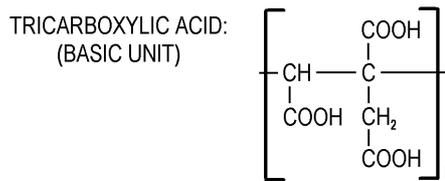
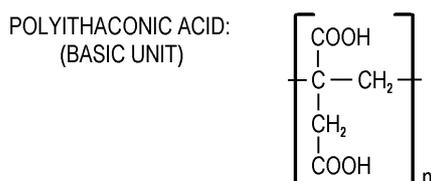
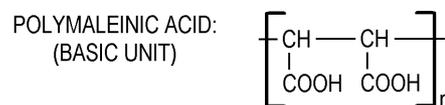
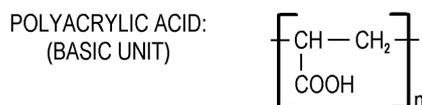
Reinforced zinc oxide-eugenol cements contain in addition to ZnO and eugenol also 10-40 % of natural or synthetic resins in the powder, or also in the liquid. The resin can be pine resin, polymethyl methacrylate, polystyrene or polycarbonate.

Calcium hydroxide-chelate cements. The value of $\text{Ca}(\text{OH})_2$ as a pulp-capping material that facilitates the formation of reparative dentin has long been recognized. Since early 1960's the phenolate type cements based on the hardening reaction between $\text{Ca}(\text{OH})_2$ and salicylate esters have been used. These materials are suitable as a liner in deep cavity preparations. Their chemistry of setting encompasses reaction of calcium and zinc oxides with the salicylate esters that produces a chelate similarly as in case of the zinc oxide-eugenol reaction.

EBA chelate cements. In order to improve the basic ZnO -eugenol system also other liquid chelating agents were tested. The only commercially successful system utilizes ortho-ethoxybenzoic acid (EBA). The powder is ZnO containing 20-30 % aluminium oxide, sometimes with polymeric reinforcing agent such as polymethyl methacrylate. The liquid consists of 50-66 % of the ethoxybenzoic acid with the remainder eugenol. The setting mechanism is similar as in the zinc oxide-eugenol cements.

2.3.2.2 Polycarboxylate-based cements

This type of cement employs instead of phosphoric acid or eugenol in the liquid phase a polycarboxylic acid, for example:



The molecular weight of the polycarboxylate polymer is usually 30,000-50,000. Cement preparation means again mixing of the liquid (polycarboxylate solution) with the zinc oxide powder. The resulting cement has effects on the pulp comparable to the ZnO-eugenol system. The pH rises rapidly to neutrality; and diffusion of the polycarboxylic acid is low due to its high molecular weight.

2.3.2.3 Glass-ionomer cements

These extremely important materials were formulated during 1970's by bringing together the silicate and polyacrylate systems. Combination of an acid-reactive glass powder together with polycarboxylate solution leads to a translucent strong cement that can be used both as luting and filling material.

Applications: glass-ionomer cements are used for cementation of cast alloys and porcelain restorations, orthodontic bands, and as cavity liners and restorative materials, especially for eroded lesions.

Composition and setting: The powder in these materials is finely ground calcium aluminium fluorosilicate glass with particle size around 40 μm for the filling materials and less than 25 μm for the luting ones. The liquid is, similarly as in the zinc oxide-polycarboxylate cements, 50 % aqueous solution of a polycarboxylic acid, containing in addition 5 % tartaric acid.

On mixing, the polycarboxylic acid reacts with the glass leaching Ca^{2+} and Al^{3+} from its surface, which cross-link the polyacid molecules to a gel. The tartaric acid serves as reaction modulator to increase working time.

SiO₂	30.1 %
Al₂O₃	19.9 %
CaF₂	34.5 %
AlF₃	2.6 %
NaF	3.7 %
AlPO₄	10.0 %

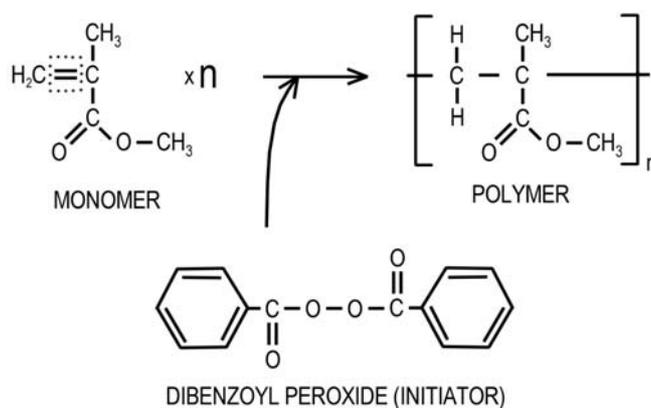
In the new hybrid ionomer cements the mixture includes also polymerizable organic monomers; the setting process then involves a polymerization reaction in addition to the acid-base exchange, improving the cement strength.

2.3.2.4 Polymer-based cements

The majority of materials in this group is represented by

- 1) polymethyl methacrylates (PMMA)
- 2) aromatic dimethacrylates

PMMA: The powder of these materials consists of finely dispersed methyl methacrylate monomer, together with dibenzoyl peroxide as a polymerization initiator. The liquid is a methyl methacrylate monomer containing an amine accelerator. Upon mixing the monomer dissolves and softens the polymer; and concurrently polymerizes through the action of free radicals from the peroxide-amine interaction:



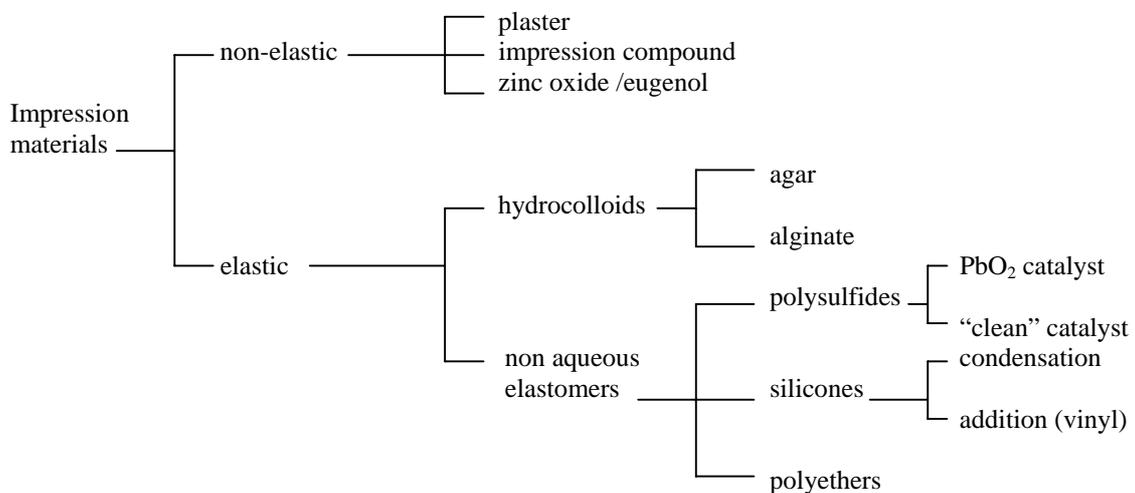
Advantages of PMMA cement are its low solubility, high strength and toughness. On the other hand, the main disadvantage is a strong pulp reaction: the pulp must be always protected.

Dimethacrylate cements are similar to composite restorative materials. According to the mechanism of hardening, we can distinguish a) light-cured, b) chemically-cured, and c) combined (the best).

2.4 Impression Materials

Impression materials are used for making replicas (impressions, imprints) of oral structures. Such materials must be plastic in the time the replica is being made; later a physical or chemical change is required to convert the substance into a solid one that keeps the shape of negative replica of the hard and soft tissues in the mouth. A model material (e.g. gypsum) is then poured into the impression in order to produce a positive replica (model) of the oral tissues of interest.

Classification of impression materials:



The impression compound consists of about 40 % of natural resins, which make the mixture thermoplastic. Shellac is often used; waxes also make for thermoplastic properties; while stearic acid acts as a lubricant and plasticizer. Fillers and inorganic pigments account for approximately 50 % of the formulation. Diatomaceous earth, soapstone and talc are examples of commonly used fillers.

The dental compound is thermoplastic: it is used warm (45 °C) and then cooled to the mouth temperature (37 °C), at which it is fairly rigid. The setting mechanism, then, is a physical rather than chemical reaction. Accordingly, the results are relatively poor.