### Aim
- To introduce dental materials aspects related to amalgam fillings as used in modern day dental practice

### Objectives
- Definition.
- Compositions.
- Types.
- Applications.

### Definition
- Dental amalgam is produced by mixing liquid mercury with solid particles of an alloy of silver, tin, copper, and sometimes zinc, palladium, indium and selenium.

### Amalgam in dental practices
- Uses:
  - Direct, permanent, posterior restorations
  - Large foundation restorations
  - Cores for crown or fixed partial denture restorations (Nayyar core).
A journey of an amalgam capsule

Amalgam capsule

When activated
Advantages of amalgam
- Easy to insert
- Not overly technique sensitive
- Maintain anatomical form
- Have adequate resistance to fracture
- Prevent marginal leakage after a period of time in the mouth
- Can be used in stress bearing areas
- Have a relatively long service life (>8 years)

Disadvantages
- Not tooth colored
- Relatively brittle
- Subject to corrosion and galvanic action.
- May demonstrate a degree of marginal breakdown
- Do not help retain weakened tooth structure,
- Alleged mercury toxicity, both on personal and environmental level
Composition

- Essential elements of amalgam alloy:
  - Silver (Ag)
  - Tin (Sn)
- Other elements:
  - Copper
  - Zinc
  - Gold
  - Palladium

Role of elements

- **Ag**: Main reactant
- **Sn**: Creates fluidity and solubility
- **Cu**: Reacts with Sn
- **Zn**: To facilitate production of alloy
- **Hg**: Reactant with Ag and Sn

Zinc

- Decolorizer: a scavenger (O2) during melting
  - Formation of oxides
- Can cause an abnormal expansion if the amalgam is condensed in the presence of moisture

Basic reaction

- **Amalgam alloy + Mercury (Hg) → Amalgam**

ANSI/ADA Spec. #1 (ISO 1559) requires that amalgam alloys be predominantly silver (Ag) and tin (Sn).

- **containing Zn > 0.01%**: “Zinc Containing”
- **containing Zn ≤ 0.01%**: “nonzinc”

<table>
<thead>
<tr>
<th>Phases in Amalgam Alloys and Set Dental Amalgam</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>η</td>
<td>Ag3Sn1</td>
</tr>
<tr>
<td>η</td>
<td>Ag3Sn</td>
</tr>
<tr>
<td>η</td>
<td>Ag3Sn2</td>
</tr>
<tr>
<td>η</td>
<td>Ag3Sn (phases)</td>
</tr>
<tr>
<td>η</td>
<td>Ag3Sn6</td>
</tr>
<tr>
<td>η</td>
<td>Ag3Sn10</td>
</tr>
<tr>
<td>Silver copper eutectic</td>
<td>AgCu</td>
</tr>
</tbody>
</table>
Alloy types based of production technique.

- Lathe cut
  Metal ingredients → heated → poured into a mold → ingot (Ag3Sn (γ) + some β, ε, η)
  Ingot → homogenizing anneal
  An annealed ingot of alloy is placed in a machine and is fed into a cutting tool.
  60-120 μm in length, 10-70 μm in width
  Some aging of the alloy is desirable

Homogenizing Anneal

- The ingot is placed in an oven and heated at an elevated temperature (at 400°C) for sufficient time (6-8 hours) to allow diffusion of the atoms to occur and the phases to reach equilibrium.

- Spherical
  Made by melting the desired elements together
  The liquid metal is atomized into fine spherical droplets of metal by being sprayed under high pressure of an inert gas.
  → "Spherical powders" 2-43 μm
  Also have heat treatment and are usually washed with acid.

Spherical

- Admix
  A mix of both lathe cut and spherical
Admix

- Lathe-cut or admixed powders resist condensation better than spherical powders.
- Spherical alloys require less mercury than typical lathe-cut alloys because of the smaller surface area per volume.
- Amalgams with a low mercury content generally have better properties.

Low-copper (Conventional) amalgam alloy
(at least 65 w% Ag, 20 w% Sn, < 5 w% Cu)
- Lathe-cut (regular) powder or spherical particles or mixed
  - Ag-Sn

High-copper amalgam alloy
(460 w% Cu)
- (1) Admixed (Ag-Sn + Ag-Cu)
  - A mixture of irregular and spherical particles of different or same composition
- (2) Unimixed or single composition (Ag-Sn-Cu)
  - All spherical particles

Trituration process

Amalgam alloy is mixed with mercury.

"Amalgamation Process"
- Mercury dissolves the surface of alloy particles to form a composite plastic mass (some new phases form).
- Setting and hardening occur as the liquid mercury is consumed in the formation of new solid phases.

Setting reactions

**Low-Copper Dental Amalgam:**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>High</th>
<th>Residual Alloy</th>
<th>Matrix 1</th>
<th>Matrix 2</th>
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</thead>
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<tr>
<td>Ag-Sn</td>
<td>+ High</td>
<td>–</td>
<td>+ Sn</td>
<td>+ Ag-Sn</td>
</tr>
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**High-Copper Dental Amalgam:**

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Low Cu alloy mixing

- When the solubility is exceeded, crystals of two binary metallic compounds precipitate into the mercury.
  - Ag₂Sn compound ($\gamma_1$) precipitates first.
  - Sn₂Hg compound ($\gamma_2$) precipitates later.
- As the remaining mercury dissolves the alloy particles, $\gamma_1$ and $\gamma_2$ crystals grow.
As the mercury disappears, the amalgam hardens. Particles become covered with newly formed crystals, mostly $\gamma_1$.

- Unconsumed particles (smaller after being partly dissolved) are surrounded and bound together by solid $\gamma_1$ and $\gamma_2$ phases.

A typical low-copper amalgam is a composite in which the unconsumed particles are embedded in $\gamma_1$ and $\gamma_2$ phases.

- Physical properties
  1. $\gamma$ phase $\rightarrow$ strongest; $\gamma_1$ phase $\rightarrow$ weakest
  2. Hardness: $\gamma > \gamma_1 >>> \gamma_2$
  3. $\gamma_2$ $\rightarrow$ poor corrosion resistance

**High Cu Admix alloys**

- Ag dissolves into the Hg from the Ag-Cu alloy particles.
- Both Ag and Sn dissolve into Hg from the Ag-Sn alloy particles. *(same as in low-Cu alloy)*
- Sn in solution diffuses to the surface of Ag-Cu alloy particles and reacts with the Cu to form the $\eta$ phase ($\text{Cu}_2\text{Sn}$) (therefore, the $\text{Sn}_2\text{Hg}$ or $\text{Sn}$ is eliminated).

**Silver-Copper eutectic alloy**

- 71.9 wt% Ag, 28.1 wt% Cu

**High Cu uni compositional alloys**

- Each particle has the same chemical composition.
- Major components: Ag-Cu-Sn
- Phases found in each single-composition alloy particle are $\beta$ ($\text{Ag}_2\text{Sn}$), $\gamma$ ($\text{AgSn}$), and $\epsilon$ ($\text{Cu}_2\text{Sn}$).
- $\eta$ crystals are found as meshes of rod crystals at the surfaces of alloy particles ($\eta'$), as well as dispersed in the matrix.
- Little or none of $\gamma_2$ phase can form.
Properties of dental amalgam

- Dimensional changes:

  ADA spec. #1: amalgam neither contract nor expand more than 20 μm/cm between 5 min and 24 hours after beginning of trituratation.

- Contraction results as the particles dissolve and the Y₁ growers.
- If there is sufficient liquid mercury present to provide a plastic matrix, expansion will occur when Y₁ crystals impinge against one another.
- Zinc-containing amalgam contaminated by moisture during trituratation or condensation → delayed or secondary expansion.
  - Zn + H₂O → H₂ collected within the restoration → creep

- Lower Hg-alloy ratios and higher condensation pressures → less Hg in the mix → contraction
- Longer trituratation times, use of smaller particle size alloys → accelerate setting → contraction.
- Modern amalgams → contraction
  - Hg-alloy ratio
  - Speed of trituratation

Corrosion

- Contraction of amalgam → marginal leakage
- If amalgam expanded during hardening, leakage around the margins of restorations would be eliminated.
- The detrimental effect of shrinkage occurs only when the amalgam mass shrinks > 50 μm. (ADA allows 20 μm/cm shrinkage)

- Order of corrosion resistance (in pure phases)
  - AgHg₂ → Ag₂Sn → Ag₂Cu → Cu₂Sn → Cu₂Sn₃

- In the low-Cu amalgam, the most corroding phase is the Sn₃Hg₂ (11-13% of amalgam mass).
- Corrosion → liberated Hg + Tin oxide or Tin Chloride.
  - Povosity and lower strength

- Gold v.s. amalgam restorations
  - Galvanic corrosion
  - Free mercury can weaken the gold restoration.
- High Hg: alloy ratio → formation of γ, phase → promoting corrosion
- Gold vs. amalgam restorations
  - Galvanic corrosion
  - Free mercury can weaken the gold restoration

- The space between the alloy and the tooth permits the microleakage of electrolyte and a classic concentration cell process results.

- The build-up of corrosion products gradually seals this space, making dental amalgam a self-sealing restoration.
- Most common corrosion products = oxides and chlorides of Sn

### Mechanical properties
- Compressive strength: the most favorable feature of amalgam.
- Amalgam is a viscoelastic material.
  - What does this mean??
- High Cu, unicompartmental has the highest initial and delayed compressive strength
  - What are the advantages??

### Tensile strength
- Only a fraction of compressive strength.
  - What are the implications in cavity design?
- Final tensile strength are the same for different types.
- High Cu alloys attain much higher initial tensile strength.
  - What advantages?

### Transverse strength
- What are the implications for the base materials under the amalgam?
Mercury content
- The strength of an amalgam is a function of the volume fractions of unreacted alloy particles and mercury-containing phases.
- Inadequate Hg \( \rightarrow \) dry, granular mix \( \rightarrow \) a rough, pitted surface \( \rightarrow \) corrosion
- Excess Hg left \( \rightarrow \) reduction in strength

Condensation
- Lathe-cut alloys
  - Greater condensation pressure \( \rightarrow \) higher compressive strength
- Spherical amalgams
  - Lighter condensation pressure \( \rightarrow \) adequate strength
  - Heavy pressure \( \rightarrow \) condenser may punch through the amalgam

Porosity
- Related to the plasticity of the mix
- Increasing condensation pressure \( \rightarrow \) improved adaptation and decreases the number of voids

Amalgam hardening rate
- When will amalgam gain sufficient strength for its function? (chewing, core preparation, ...)
- ADA spec. \( \rightarrow \) min compressive strength 80 MPa at 1 hour
- High-Cu single-composition amalgams may be strong enough shortly after placement to permit amalgam buildups to be prepared for cements.
- Patients should be cautioned not to subject the restoration to high biting stresses for at least 8 hours after placement.

Creep
- Creep rate has been found to correlate with marginal breakdown of conventional low-copper amalgams.
- Higher creep \( \rightarrow \) greater marginal deterioration
- ADA spec. #1: creep rate < 3%
Microstructure v.s. Creep
- Low-Cu
  - Larger γ phase volume fraction → Decrease creep rate
  - Larger γ phase grain size → Decrease creep rate
  - Presence of γ phase → Decrease creep rate
- Single-composition high-Cu amalgam
- η rods limit the deformation of γ phase

Manipulation
- Alloy selection
- Mixing (trituration), high speed
- Effect on creep:
  - 2 to 3 seconds → Undenatured (dry and crumbly) or overmixed (moisty and tends to stick to the capsule)
  - Overtrituration decreases working time, slightly higher contraction
  - Effect on strength
  - Overtrituration increases strengths in both-cut alloys
  - Both over- and undertrituration decrease strengths in spherical alloys and admixed high-Cu alloy
- Effect of creep
  - Overtrituration increases creep
  - Undertrituration decreases creep

Condensation
- The more Hg left in the mass after condensation, the weaker the alloy. → Great condensing force should be used.
- Hand v.s. Mechanical condensation
  - Spherical amalgam → large tip condenser

Finishing amalgam restorations
- Decreases tarnish and corrosion
- Low-Cu amalgam restoration should be left undisturbed for at least 24 hours.
- High-Cu unicompositional amalgams with high early strengths can be finished at the first appointment.

Mercury hazards and waste management
- Is amalgam toxic??!!

Mercury form
- Methyl and ethyl mercury
- Vapour
- Inorganic compounds

The amalgam controversy
An evidence-based analysis
JOHN E. DOOES JADA 2011
Concentration of mercury
- Threshold value of Mercury vapour: 50 µg/m³
- More mercury vapor during removal of amalgam

Historical Problems:
- Tanners
- Thermometer technicians
- High-melt workers
- Minamata Bay, Kyushu, Japan (fish problem)
- Iraq (grain problem)
- Alamogordo, NM (grain problem)

Recent Incidents:
- Sweden (environmental lead problem)
- Michigan (distillation problem by lab tech)

Detection of Hg
- Chemical and Electrochemical Corrosion → NO Hg RELEASED
  a. Low-copper dental amalgam:
     - [Hg] → [Hg] + valence → [Hg-O2] (stable)
     - [Hg] + [Hg] → [Hg2] + [Hg2] (stable)
  b. High-copper dental amalgam:
     - [Cu-Hg] → [Hg] + valence → [Hg-O2] (stable)
     - [Hg] + [Hg] → [Hg2] + [Hg2] (stable)

Dental mercury hygiene recommendations
JADA 2003
- Amalgam contains mercury.
- Some Scandinavian countries have banned the use of amalgam.
- ADA and BDA are against such ban.

GENERAL MERCURY HYGIENE RECOMMENDATIONS
- Training for the staff involved.
- Remove professional clothing before leaving the surgery.
### OFFICE settings
- Well ventilated.
- Use proper work area design to facilitate spill containment and cleanup. Floor coverings should be non-absorbent, seamless and easy to clean.
- Periodically check the dental operatory atmosphere for mercury vapour. This may be done using dosimeter badges or through the use of mercury vapour analyzers for rapid assessment after any mercury spill or cleanup procedure.

### HYGIENE RECOMMENDATIONS DURING PREPARATION AND PLACEMENT OF AMALGAM
- Use only pre-capsulated amalgam alloys.
- Use an amalgamator with a completely enclosed arm.
- If possible, recap single-use capsules after use, store them in a closed container and recycle them.
- Use care when handling amalgam. Avoid skin contact with mercury or freshly mixed amalgam.
- Use high-volume evacuation systems (fitted with traps or filters) when finishing or removing amalgam.

### Mercury spills
- Never use household cleaning products, in particular those containing Ammonia or Chlorine.
- Never use vacuum cleaners.
- Never allow mercury to go down the drain.
- Never use a paint brush to remove mercury

### Amalgam waste management
- [http://www.ada.org/prof/resources/topics/topics_amalgamwaste.pdf](http://www.ada.org/prof/resources/topics/topics_amalgamwaste.pdf)

Information included are required for the purpose of examination.

### Very good luck with your final exams
- "A smooth sea never made a skilled mariner"