DENTAL MATERIALS

1. Dental Ceramics

Ceramic materials are well suited for biomedical applications requiring tissue compatibility, compressive strength, durability, radiopacity, and inertness toward sterilization chemicals and conditions (see CERAMICS). Dental ceramics were first prized as a hygienic alternative to the animal products and human teeth available for denture fabrication during the late 1700s and early 1800s (1). Denture tooth formulations gradually shifted away from the triaxial china compositions from which they originated (kaolin clay, quartz, and feldspar) to become more translucent (higher glass content) materials (2). Today, such glass-matrix ceramics, containing appropriate crystalline fillers and colorants, can richly mimic many of the aesthetic and optical properties of natural teeth (3) (see COLORANTS FOR CERAMICS). As will be discussed, glass-matrix ceramics containing substantial amounts of crystalline fillers and pure polycrystalline ceramics are also being used in dental reconstructions. Limitations to the use of ceramics include design restrictions based upon the sometimes low and variable tensile strengths of ceramic products; susceptibility to stress corrosion, eg, crack extension in the presence of water or other low molecular weight species; and shrinkage during processing. Ceramics have also been associated with high levels of abrasive wear to opposing tooth structure.

The principal use of ceramics in dentistry is for the aesthetic restoration of missing teeth or tooth structure, ie, crowns and bridges (prostheses), primarily as glassy ceramic coatings fused to an underlying cast metal framework (4). Additional aesthetic use is made of ceramics not supported by metal substructures. These uses include single-tooth crowns, ie, restoring all the external surfaces of a tooth; ceramic fillings, eg, inlays and onlays; veneers, ie, replacement of only the visible surface of anterior teeth; denture teeth; and orthodontic brackets. Some semiaesthetic generally more highly crystalline and polycrystalline ceramics are utilized as core materials in place of cast metal substructures and are generally veneered with more aesthetic ceramics. Nonaesthetic dental ceramics include: implants, ie, single-tooth replacements implanted in bone; biologically active ceramics, based upon calcium- and phosphorous-containing minerals or glasses, used as coatings on dental implants or placed into tooth extraction sites and surgery sites to enhance the maintenance or regeneration of bone; dental cements based upon reactions of acids, organic or mineral, with glass or metal oxide powders; and gypsum products. These nonaesthetic uses of ceramics are covered separately.

Ceramic prostheses are generally fabricated from one or two ceramics that derive from three basic categories of material; beneficiated feldspathic minerals, glass–ceramics, and polycrystalline ceramics. Dental fillings and simple prostheses are often fabricated from only one type of ceramic. Prostheses requiring more structural performance are fabricated from two materials, involving an aesthetic outer coating over a stronger ceramic or metal core. More detailed reviews of these materials, their use, and properties are widely available (2,5–7).

1.1. Feldspathic Matrix Ceramics.

The majority of aesthetic ceramics are based on mined feldspar minerals such as potassium feldspar, eg, orthoclase [12251-44-4] and microcline [12251-43-3], $K_2O \cdot Al_2O_3 \cdot 6SiO_2$; sodium feldspar, eg, albite [12244-10-9], $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$; and nepheline syenite [37244-96-5], which contains ~50% albite, 25% nepheline, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, and 25% microcline. These feldspars are processed to remove iron-bearing impurities, melted with various additives, quenched in water, and ground to yield powders (frits) of alkali-modified aluminosilicate glasses containing little or no crystalline filler (8,9) (see also GLASS).

Natural tooth colors are developed in these formulations by the addition of color frits, ie, vitreous powders to which colored and/or opaquing pigments (qv) have been added. Because aluminosilicate glasses are very aggressive solvents at elevated temperatures, pigments must have inertness toward dissolution as well as color stability at elevated temperatures. Crystalline minerals in the spinel family have been found to be successful pigments (5). Spinels have the general formula $MO \cdot M'_2O_3$ where the divalent metal, M, can be Mg, Fe, Cu, Zn, Ni, Co, or Mn; and the trivalent metal, M′, can be Al, Fe, Mn, Ga, or Cr. Particles of metal oxides may also be used as color pigments, eg, the oxides of Ni, Ti, Co, Cu, Cr, Mn, or Sn (10).

Additional raw materials, such as kaolin clay [1332-58-7] and quartz [14808-60-7], may be used as processing aids for factory-based processing, eg, of denture teeth. Kaolin clays form plastic masses useful for molding operations, add Al^{3+} to the glass composition, and aid in sintering because of extremely fine particle size. Quartz can contribute to the shape–stability of vitreous bodies during firing by decreasing flow, as well as add certain aesthetic qualities.

Most ceramics designed to be fused to metals are derived from either high potassium feldspars, or from compositions to which potassium oxide [12136-45-7], K_2O, has been added to above ~11 mol%. This places these ceramics into a phase region from which feldspars melt incongruently to form leucite [1302-34-7], $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, plus liquid (11). Leucite has a high thermal expansion coefficient and undergoes a displacive transformation, tetragonal to cubic, during heating. This raises the effective coefficient of thermal expansion of the leucite-filled glass from ~7 ppm to a range compatible with that of cast dental alloys, 12–15 ppm (12,13).

1.2. Processing.

Traditional ceramic dental restorations are custom fabricated by skilled technicians in specially equipped laboratories. Processing generally involves formation of powder–water slurries that are incrementally built up in layers of varying color and translucency using brushes or spatulas. Consolidation of the greenware is achieved by a combination of vibration and wicking away excess water. Sintering, or thermal fusion of the particles, is generally performed at 800–920°C under vacuum conditions of ~3.3 kPa (25 Torr) using heating rates in the range of 40–60°C (min and hold times of 0.5–10 min at the maximum temperature. Shrinkage of up to 20% by volume can be associated with the sintering process.

Computer-aided design and manufacturing (CAD/CAM) fabrication of customized dental restorations has become a viable option (14). Restorations are machined from standardized blocks of completely sintered and internally colored ceramic, either feldspathic or glass–ceramic (15,16). Feldspathic blocks for CAD/CAM processing are formed using extrusion molding of powders utilizing organic binders, as opposed to kaolin clays prior to sintering.

Transfer molding, or hot pressing, is also used as a technique to form ceramic fillings and crowns from both feldspathic compositions and glass-ceramics (see below) (17). Mold-making usually follows traditional dental lost-wax techniques used for investment casting. Finished ceramic parts are fabricated by pressing filled-glass compositions, designed to have appropriate viscosities and chemical stability at elevated (1100°C) temperatures, into phosphate-bonded molds (17).

1.3. Strengthening.

Strengthening methods for ceramic restorations involve structural approaches, eg, the veneering of metal or high strength ceramic cores, as well as microstructural alterations and surface treatments of the ceramic. Microstructural alteration generally involves increasing the volume fraction of crystalline material in the glass, either by direct addition or by devitrification (ceramming). Surface treatments are used to develop compressive stresses on exterior surfaces by either thermal or chemical routes.

The addition of alumina [1344-28-1], Al_2O_3, to a feldspathic dental glass results in a strengthened ceramic material commonly known as aluminous porcelain (18). The alumina acts as a dispersion strengthening phase. It also decreases the translucency of the sintered filled glass as a result of differences in refractive index between alumina and feldspathic glasses, and the development of residual porosity. Traditional dental laboratory processing techniques and optical property considerations limit the particle size (90%>10 μm) and weight (40–50 wt%) of Al_2O_3 used. A much more highly loaded (>70 wt%), dispersion strengthened, alumina-filled ceramic has been developed for use as a core material (19). In this technique, a much finer alumina (80% >2 μm) is slip-cast onto a refractory material and initially sintered into a highly porous form. A high index of refraction (lanthanum modified) feldspathic glass is infiltrated into the porous alumina preform, yielding a translucent composite ceramic having strength properties approaching that of polycrystalline alumina (see COMPOSITE MATERIALS, CERAMIC-MATRIX).

Leucite has been used for dispersion strengthening both in products provided as powders to be processed via traditional water–slurry techniques and in formulations for high temperature transfer molding (17,20). Because of its index of refraction, leucite is aesthetically superior to alumina as a filler for feldspathic glasses, but it is not superior as a dispersion strengthening filler. Leucite generally is introduced into dental ceramics via nucleation and growth processes from high potassium-content aluminosilicate glasses.

Ion-exchange approaches and thermal tempering have been evaluated for strengthening dental ceramics (21,22). Both of these approaches are aimed at placing external surfaces of dental ceramic restoration in compression. Only ion exchange is promoted commercially and is not in extensive use.

1.4. Dental Glass–Ceramics.

Glass–ceramics (qv) are highly crystalline ceramics having some residual glass matrix prepared by the controlled crystallization of glasses (23). Crystalline phase(s) are formed from elements within the parent glasses by subjecting them to carefully regulated thermal treatments, called ceramming. Generally, ceramming treatments involve separate control, at two different temperatures, over both the nucleation and growth stages of crystallization within the glass.

Glass-ceramics have been developed for restorative dentistry based on four different crystalline phases, ie, tetrasilicic fluoromica, $KMg_{2.5}Si_4O_{10}F_2$, β-quartz crystals, leucite, and lithium disilicate (17,24–26). Fluoromica develop with a plate-like morphology having a relatively low energy cleavage path along their basal plane. These tendencies towards basal-plane cleavage and the interlocking of crystals at high volume fraction provide an effective strengthening mechanism (27). Fluoromica crystals and the residual glass matrix have relatively similar indices of refraction.

The β-quartz solid solution phase is precipitated from a lithium aluminosilicate glass. This ceramming step must be carefully controlled in order to avoid conversion of the β-quartz to β-spodumene, which would rapidly opacify the ceramic. Internal coloration is achieved by interactions between Ce and Ti species in the residual glass. One aesthetic leucite-containing glass-ceramic is manufactured from a glass melt (composition in wt%) of 63% SiO_2, 17.7% Al_2O_3, 11.2% K_2O, 4.6% Na_2O, 0.6% B_2O_3 , 0.4% CeO_2, 1.6% CaO, 0.7% BaO, and 0.2% TiO_2 (17). The lithium disilicate material is reported to have significantly higher fracture toughness than the other glass-ceramics available for dentistry (26).

1.5. Processing. Glass-ceramics are formable into complex shapes while still in the glassy state and essentially retain their finished dimensions during ceramming. Glass for the fluoromica-containing ceramic is cast into a phosphate-bonded refractory mold using a special high temperature centrifugal casting machine at temperatures between 1350 and 1365°C (24). Following formation, the glass castings are cerammed at a temperature of 1070°C for 6 h. Colored feldspathic glasses are fired in very thin external layers in order to develop proper dental aesthetics.

Glass of the β-quartz-containing ceramic is melted at 1600°C and pressure cast, using metal molds, into a variety of small shapes suitable for insertion into teeth being filled with polymer-based restorative materials. Appropriate tooth color, index of refraction, and improved physical properties are developed during a ceramming treatment (25). The surface of the glass ceramic parts is treated using an organofunctional silane to enhance bonding between the glass-ceramic and restorative dental resins.

Parent glass for one leucite-containing glass-ceramic is melted at 1450°C, cast as simple-shaped billets, and cerammed by the manufacturer (17). The precerammed billets, already having appropriate tooth color, are loaded into a dedicated high temperature press and transfer molded at 1100°C into phosphate-bonded molds. This same approach and equipment is used for the lithium disilicate glass-ceramic (26).

1.6. Polycrystalline Dental Ceramics. Pure polycrystalline ceramics were not widely used in dentistry until computer-based systems became available enabling the “net shape” fabrication of prostheses, compensating for the shrinkage inherent during the sintering of such structural ceramics. Such ceramics include alumina and transformation toughened zirconia, in which the tetragonal zirconia (high temperature) phase has been stabilized at room temperature with the addition of yttria or ceria (2–3%). Dental prostheses are custom devices, each one unique, and are required to fit prepared tooth structure to within certain tolerances (eg, 20–30 μm over 10 mm to 30 mm). Three-dimensional (3D) data sets captured from replicas of patients by tactile or optical scanning are used to make oversized greenware of well-controlled ceramic powders having predictable shrinkage (∼30 vol%). One such system for the fabrication of alumina core structures for single tooth crowns creates an enlarged replica of the prepared tooth that is used for dry pressing of alumina powders (28). Another approach has been used for fabrication of both single and multitooth core structures of toughened zirconia, in which partially sintered powder blocks (some shrinkage having already occurred) are machined into greenware that is enlarged slightly for the anticipated final sintering shrinkage (∼20 vol%) (29,30). These ceramics generally have higher strengths two or more times that of vitreous porcelains.

2. Dental Cements

Dental cements are composites, ie, they have a continuous or matrix phase linked to a discontinuous or reinforcing phase by an interphase. Based on their chemistry, dental cements can be divided into acid–base cements, acrylic or resin cements, and resin-modified acid–base cements, ie, hybrid cement composites. Acid–base cements are either aqueous-based cements or nonaqueous-based cements, although small amounts of water or protic agents are essential to the acid–base setting mechanism of the latter. Acrylic cements are resin-based composites modified for cement applications. The monomer(s) used in these cements can be simply methyl methacrylate [80-62-6] or various types of multifunctional monomers, eg, BIS–GMA [1565-94-2], triethylene glycol dimethacrylate, [2351-42-0]. The setting mechanism is by free-radical addition polymerization, either chemical, photochemical, or a combination of the two. The hybrid cement composites include a vinyl resin system as well as the usual acid–base components of the cement. They have a dual, ie, ionic and free radical, setting mechanism.

Although used in relatively small quantities, dental cements are essential in a number of dental applications as temporary, intermediate and, in some cases, more permanent restoratives; cavity liners and bases; luting agents to bond preformed restorations and orthodontic devices; pulp capping agents and endodontic sealers; components in periodontal dressings; and impression pastes. Because this wide range of dental uses makes it virtually impossible for one type of cement to have all the necessary properties demanded, tailored dental cements exist to meet certain specific objectives. Generally, cements are sought that excel in strength, oral environmental resistance, durability, adhesiveness, and biocompatibility.

The oldest acid–base cements, ie, zinc phosphate, and zinc oxide eugenol (ZOE), utilize zinc oxide as the principal base component and orthophosphoric acid or eugenol as the acid component, respectfully. As seen in Table 1, acid–base cements represent an important category of dental cements, although resin-modified glass–ionomers and new types of resin cements are replacing the former types in many dental applications. Research is focused on the

Table 1. **Classification and Composition of Aqueous Dental Cements**

	Components		Set cement		
Dental cement	Aqueous acid	Powder base	Material[a]	Amorphous matrix	Uses
zinc phosphate	orthophosphoric acid (Al^{3+} and Zn^{2+})[b]	calcined zinc oxide, calcined magnesiumoxide[c]	oxides	phosphate	luting agent, base
zinc polycarboxylate	poly(alkenoic acids)[d]	zinc oxide and magnesium oxide[e] or stannic oxide	oxides	polycarboxylate	adhesive liner, base, luting agent
glass–ionomer	poly(alkenoic acid)	ion leachable calcium alumino–fluoro-silicate glasses	glass	polycarboxylate	adhesion base, liner luting agent, sealant core buildup materials, sealants
metal-modified	poly(alkenoic acid)	calcium alumino–fluorosilicate glass containing fused particulate metal	metallized glass	polycarboxylate	restorative for cervical lesions,
resin-modified	monomer system[f], components of initiator system	poly(alkenoic acid), calcium alumino–fluorosilicate glass, component of initiator system	glass	polycarboxylate	

[a] Partially reacted and unreacted in an amorphous matrix.

[b] Minor amounts of these ions.

[c] Present in lesser amounts.

[d] For example, poly(acrylic acid).

[e] For example, 9:1.

[f] For example, 2-hydroxyethyl methacrylate.

improvement of the polyelectrolyte cements, eg, glass–ionomer, and the development of durable, nonshrinking resin or polymer-based adhesive materials with improved biocompatibility.

2.1. Aqueous-Based Cements. *Zinc Phosphate Cements.* Zinc phosphate cements are the oldest of the aqueous-based cements (see Table 1) and are still used in a wide range of applications; eg, cavity bases, temporary restoratives, and for the fixation of inlays, crowns, fixed partial dentures (bridges), posts, facings, and orthodontic bands.

In contrast to glass–ionomer cements, zinc phosphate cements are neither as sensitive to the gain or loss of water during setting nor adhesive to tooth structure. Retention is done by mechanically interlocking the irregularities of surfaces being cemented. The setting times in the mouth are 3–11 min, typically 7–8 min. Dimensional change upon setting may be <0.1% shrinkage, if the mass is protected from water loss, and the compressive strength at 24 h is 88–143 MPa (13,000–20,700 psi). The solubility of the set cement in distilled water is generally from 0.1–0.2% for specimens exposed for 7 days.

The powder consists of calcined zinc oxide [1314-13-7] and magnesium oxide [1314-13-2] in a ratio of ~9:1. The liquids are usually concentrated (45–63 wt%) phosphoric acid solutions buffered by aluminum salts and, in some instances, by both aluminum and zinc salts (see PHOSPHORIC ACIDS AND PHOSPHATES) (31). The compounds formed by reaction of the powder and liquid are predominately noncrystalline phosphates of zinc [7779-90-0], magnesium [7757-86-0], and aluminum [7784-30-7] (32–34). The set cement consists of unreacted cores of powder particles bound together in a generally structureless gel matrix of phosphates of zinc, magnesium, and aluminum. The proportion of unused powder particles and phosphate matrix in the set cement varies with the amount of powder incorporated into a given amount of liquid to produce the optimum consistency for the specific use. The set cement, having a minimum amount of gel matrix and maximum amount of particles, has the best physical properties for use in the mouth.

Except for the little used silicate cements, which use calcium aluminofluorosilicate glasses in place of zinc oxide–magnesium oxide base powder, modifications of the zinc phosphate cement have been minimal (35). A novel modification of the zinc phosphate cement is the inclusion of phosphate-based organic polymers in the formulation, which improves both its strength and adhesion to dentin (36). The most important classes of new acid–base cements are those based on poly(alkenoic acids), ie, the polycarboxylate cements, the glass–ionomer cements, and the resin-modified glass–ionomer cements (see IONOMERS).

Recently introduced to the dental profession, mineral trioxide aggregate is a cement product, approved in 1998 by the U.S. Food and Drug Administration (FDA) with indications for use in the practice of surgical and nonsurgical endodontics as a root-end filling material and for root perforation repair, apexification, and pulp capping procedures (37,38). Mineral trioxide aggregate powder consists of fine hydrophilic particles composed of tricalcium silicate, tricalcium aluminate, tricalcium oxide, and silicate oxide (38,39). The powder is similar to Portland cement except bismuth oxide powder has been added to provide radiopacity (38). Small amounts of mineral oxides added to the powder are responsible for the chemical and physical properties of the set cement.

Mineral trioxide aggregate was divided into specific phases: calcium oxide, which appears crystalline, and calcium phosphate, which has an amorphous appearance (38).

When the powder is mixed with sterile water the resultant colloidal gel has a grainy consistency that solidifies into a hard mass in 3 h. The compressive strength of mineral trioxide aggregate set cement is 40–60 MPa (5800–8700 psi) (38). Radiopacity for mineral trioxide aggregate is equivalent to 7 mm of aluminum (38). The pH of the mixture right after mixing with water is 10.2 and rises to 12.5 after 3 h and then remains constant. This high pH value could impart some antimicrobial activity (40), although other reports demonstrated that calcium hydroxide showed superior antimicrobial activity (41). A tight seal is an important factor for endodontic success of root-end fillings, and mineral trioxide reportedly leaked significantly less than more commonly used root-end filling materials (amalgam and ethoxybenzoic acid/zinc oxide-based cements) and showed better marginal adaptation (42,43).

Since the main ions in the powder are calcium and phosphorous, also found in the mineral, hydroxyapatite that composes teeth and bones, biocompatibility would be expected (44). The cytotoxicity was measured using human periodontal ligament fibroblasts and the mineral trioxide aggregate was significantly less toxic than more commonly used root-end filling materials (45). Mineral trioxide aggregate stimulated cytokine production in human osteoblasts and provided a biologically active substrate for bone cells (46,47). Subcutaneous implantation produced a severe initial reaction that subsided to moderate with the passage of time (48). When used as a direct dental pulp capping material, mineral trioxide aggregate demonstrated the ability to stimulate the healing process with complete tubular dentin bridge formation and no pulpal inflammation after histological examination (49). Because mineral trioxide aggregate is osteoconductive (48), it may have potential use in patients who suffer from bone loss due to periodontal disease (37).

2.2. Polycarboxylate Cements. Polycarboxylate cements (50,51) are made by mixing a zinc oxide-based powder and an aqueous solution of poly (acrylic acid) [9003-01-4] or similar polyacid (see ACRYLIC ACID). The biological effects of these cements on soft and mineralized tissues are mild (52). The effect on the pulp is similar to that of the zinc eugenolate cements (53). This type of cement seems to have overall excellent biocompatibility (35). When freshly mixed, the carboxylic acid groups convert to carboxylates, which seems to signify chemical adhesion mainly via the calcium of the hydroxyapatite phase of tooth structure (52,54–59). The adhesion to dentin is reduced because there is less mineral available in this substrate, but bonding can be enhanced by the use of mineralizing solutions (55–58). Polycarboxylate cement also adheres to stainless steel and clean alloys based on multivalent metals, but not to dental porcelain, resin-based materials, or gold alloys (35,60). It has been shown that basic calcium phosphate powders, eg, tetracalcium phosphate [1306-01-0], $Ca_4(PO_4)_2O$, can be substituted for zinc oxide to form strong, hydrolytically stable cements from aqueous solution of polyacids (61,62).

The compressive strength of polycarboxylate cements at cementing consistency is 55–85 MPa (8000–12,000 psi). Typical diametral tensile strength ranges from 8 to 12 MPa (1160 to 1740 psi). The solubility and disintegration in distilled water after 7 days at 37°C is 0.04–0.08 mass%, and is not reflected in clinical performance.

The powder contains zinc and magnesium oxide (56), and the liquid contains an aqueous solution of an acrylic polycarboxylic acid. Water settable cements have been formulated by inclusion of the solid polyacid in the powdered base component. The set cement mainly consists of partially reacted and unreacted zinc oxides in an amorphous polycarboxylate matrix (34,35). (see POLYMERIC MATERIALS).

2.3. Glass–Ionomer Cement. The glass–ionomer polyelectrolyte system was developed primarily as a restorative for anterior teeth and erosion cavities; a luting cement; a cavity liner; a base; and a pit, and fissure sealant (34,63–68).

The glass–ionomer cement has some translucency in contrast to that of the opaque polycarboxylate cement. The setting time is ~2–4 min. Compressive strength in 24 h is 154–175 MPa, and diametral tensile strength is 7–19 MPa (1000–2700 psi). Solubility in distilled water after 7 days is 0.44%. Glass–ionomers used as restoratives are available in several tooth colored shades. They lack the strength necessary and wear resistance for stress-bearing restorations, but the fluoride from the aluminofluorosilicate glass is slowly released from the filling, possibly inhibiting recurrent caries (69).

Glass–ionomer cement is based on the reaction between calcium aluminofluorosilicate glass powders and aqueous solutions of polymers and copolymers of acrylic acid. Setting modifiers are included to improve working and hardening characteristics (70–72). Tartaric acid [87-69-4] is particularly effective in both prolonging the working time and sharpening the setting time (72). Water settable versions of this cement also are available (73).

These poly(alkenoic acid) based cements are relatively high modulus cements that adhere to enamel and to dentin with minimal surface preparation, and are rapidly replacing the more traditional dental cements in many applications. As with the zinc polycarboxylate cements, adhesive strength to enamel is higher than to dentin, presumably because of the lower mineral content of the latter. But, the cement is weakly adhesive to either substrate because of the low tensile, shear, and flexural strength inherent in this brittle material (74–77). Using a sandwich or laminate technique, the glass–ionomer cement has been successfully used to bond composite resin restorations to dentin (78–80).

Excessive hydration, during early stages of the setting reaction, adversely affects the properties of the glass–ionomer cement. Faster setting cements have been developed in an attempt to correct this deficiency. Moreover, the hardened cement has a propensity to dehydration, even after 6 months; proper maintenance of a water balance is critical not only during the initial setting but also during maturation of the cement. A tendency toward brittle, even catastrophic failure, and severe erosion under acidic conditions are the main deficiencies of this cement (81). The introduction of light cured glass–ionomer cements has eliminated the need for protection against water gain or loss during setting and alleviated the erosion problem.

One approach for ameliorating the highly brittle nature of these cements has involved the use of tougher, more ductile fillers (82,83). Another approach for improving the overall properties of traditional glass–ionomer cements involves the development of hybrid cement-composites and resin-modified cements (84–88).

2.4. Metal-Modified Glass–Ionomer Cements.

In an attempt to improve the physical strength of the material, metal-modified glass–ionomer cements were developed from metallized glass powders called cermets (89,90), or by mixing amalgam alloy powder with the glass powder component of the cement. These metal modified glass–ionomer cements exhibit improved abrasive wear, but the overall strength properties and tendency to brittle failure are not significantly improved.

The glass–cermet cements contain a base powder of modified leachable glass, eg, calcium aluminofluorosilicate prepared by the sintering of soft ductile metals, eg, silver or gold, onto ion leachable particulate glass (83,91). The polyacid components, the chemistry of setting, and most mechanical properties are the same as for conventional glass–ionomers. Compared to conventional glass–ionomer cements, the silver cermet cement shows enhanced resistance to abrasive wear (92). Originally designed as a replacement for amalgam fillings, the cermet cements lack the strength, toughness, and durability of this metallic restorative. The silver cermet cement is recommended as a core buildup material

2.5. Resin-Modified Glass–Ionomer Cements.

Resin-modified glass–ionomer cements are based on poly(alkeonic acid) systems that have been modified to contain vinyl polymerizable groups and/or compatible monomers (84–88,93). The mechanism of setting involves both free radical vinyl addition polymerization as well as the ionic acid-base reactions of the conventional glass–ionomers (64–68,73).

Resin-modified glass–ionomer lining and restorative materials add a multifunctional acidic monomer to the poly(acrylic acid) [9003-01-4] liquid component of the system. Once the glass powder and liquid are mixed, setting can proceed by the acid–glass–ionomer reaction or the added monomer can be polymerized by a free-radical mechanism to rapidly fix the material in place (94,95). The cured material still retains the fluoride releasing capabilities of a glass–ionomer.

Polymer-modified glass–ionomers also have been prepared and involved only acid–base setting mechanisms (87). A related cement contains both compatible polymerizable monomer systems and polymers along with the conventional glass–ionomer ingredients (87). These hybrid cements have mechanical properties similar to those of conventional glass–ionomer cements, but because of their tougher nature are less likely to undergo catastrophic failure. The curing methods could be chemical, visible light or a combination of the two. (96)

Polymeric Calcium Phosphate Cements.

Aqueous solutions of polymers such as poly(acrylic acid), poly(vinyl alcohol), gelatin, etc, and/or autopolymerizable monomer systems, eg, 2-hydroxyethyl methacrylate, glycerol dimethacrylate, calcium dimethacrylate, etc, have been used as liquid vehicles (61,62,97) for the self-setting calcium phosphate cement derived from tetracalcium phosphate and dicalcium phosphate [7757-93-9].

2.6. Nonaqueous-Based Cements.

For many years, dentistry utilized a number of nonaqueous products based on the interaction of phenolic chelating agents and similar compounds and a metal oxide or salt (see Table 2). The most exploited system, dating back to 1884, has been the zinc oxide–eugenol cement. Many modifications and improvements have been suggested, such as the use of

Table 2. **Classification and Composition of Nonaqueous Dental Cements**

	Components		Set cement		
Dental cement	Liquid	Powder base	Material	Matrix	Uses
zinc oxide–eugenol (ZOE)	eugenol	zinc oxide[a]	zinc oxide[b]	zinc eugenolate	temporary luting and filling material; pulp capping; periodontal packs
2-thoxybenzoic acid (EBA)–eugenol	2-ethoxybenzoic acid, eugenol	zinc oxide[a]	zinc oxide[b]	complex zinc eugenolate–EBA	linear and base, temporary filling; temporary cementation
calcium chelate cement	phenolic esters of salicylate acid	calcium hydroxide plus fillers	calcium hydroxide[c]	calcium salicylate	liner and base
resin cements	acrylic monomers[d]	polymeric and/or mineral fillers		reinforced acrylic polymeric	cementation sealants

[a] Reinforced cements contain other fillings that may be reactive.

[b] Partially and unreacted; also other mineral or polymeric fillers present.

[c] Partially reacted; and/or fillers present.

[d] Newer types employ surface active resins.

rosin (98), hydrogenated rosin (99), polymers such as polystyrene (73), and various accelerating systems (100,101). In 1955, a critical study of the basic reaction showed that zinc oxide forms chelate compounds with many materials that have a structure similar to eugenol (102), ie, a methoxy group ortho to a phenolic hydroxyl group. Carboxylic acids and nonphenolic chelating agents also have been investigated as the acid component of several noneugenol cements (103).

2.7. Zinc Oxide–Eugenol Cements. Zinc oxide–eugenol cements have many uses in dentistry. The admixture of powdered zinc oxide [1314-13-2] and liquid eugenol [97-53-0], $C_{10}H_{12}O_2$, forms a bland, easily mixed paste having excellent working time but slow-setting characteristics. Accelerators can be added to the cement to decrease the set time. Compositions of the basic oxide–eugenol cement can be easily adjusted to serve a variety of dental needs. Some of these compositions are of a cementing nature, but many are useful in other applications, eg, impression pastes and surgical packs. Other uses of the zinc oxide–eugenol cements include temporary fillings, root canal fillings, linings for deep-seated cavities under restorations, the cementing of temporary or semipermanent acrylic crown forms or splinted crowns on prepared tooth stumps, and sealing-in treatments.

Suitably formulated, zinc oxide–eugenol cements can be designed having viscosities from thin fluid mixes to heavy puttylike masses. The setting times can be varied from minutes to several hours. Crushing strengths of up to 34 MPa (4930 psi) have been reported after 24 h. The degree of hardness or plasticity of the final set mass can vary from a hard friable mass to a hard strong mass to a soft gummy mass, according to the conditions required. The cements show excellent dimensional stability upon aging. Shrinkages as low as 0.2% have been measured after 48 h. Long-term disintegration (20–22 wk) measurements on conventional zinc oxide–eugenol materials indicate a continual leaching of the eugenol. This loss of eugenol leads to a matrix breakdown and a marked reduction in mechanical properties. Reinforcing agents have been used to enhance mechanical properties (104,105).

The cementing applications employ a variety of products compounded either as powder–liquid two-part formulations, or as two-part paste-type products. The zinc oxide portion of the formula may contain modifying agents to improve the physical properties of the set paste, or to act as accelerating agents to control the setting rate of the mix. Accelerators, such as zinc acetate [557-34-6] and zinc stearate [557-05-1], and reinforcing agents, eg, rosin [8050-09-7], polymerized rosin, hydrogenated rosin, polymers, calcium phosphate [7758-23-8], magnesium oxide [1309-48-4], quartz [14808-60-7], and aluminum oxide [1344-28-1] (106), have been used in the basic cement formulations. Many other additives, including medicinal ones, have also been employed (107).

The eugenol portion of the formula may consist of eugenol alone or may be compounded into a viscous fluid by the addition of various additives. The addition of rosin; polymerized rosin; hydrogenated rosin; plasticizing oils, eg, olive oil; accelerators or retarders; medicinal additives; and other modifiers serve to extend the usefulness of the basic system.

Zinc Oxide–Eugenol Impression Pastes. These two-paste systems are usually supplied in collapsible tubes; one tube contains the white zinc oxide and the other contains the brown eugenol. Approximately equal amounts of the two pastes are mixed to form a smooth, homogeneous mass. The impression paste is spread thinly over the surface of a custom-made tray. The coated tray is positioned in the mouth and held motionless until the paste mix hardens, ~2–5 min. The fluid consistency of the impression paste allows the wash to faithfully copy the finest detail of mucosal surface contours. Impression pastes can have differing characteristics of mix consistency, setting rate, and set-paste hardness. Hard- and soft-setting pastes are recognized in the American Dental Association (ADA) specifications.

The zinc oxide–eugenol impression pastes produce a rigid impression with good accuracy and good reproduction of surface detail. They have sufficient resistance so that borders can be built up if the tray is slightly deficient in any area. They set to a cement-like hardness, and the resulting impression can be taken in and out of the mouth repeatedly, giving an opportunity to test for stability and tissue adaptation. In addition, they register detail well, and are quite stable dimensionally.

The compositions of zinc oxide–eugenol impression pastes are similar to those of the zinc oxide–eugenol cements (107). Variations in specific characteristics are achieved by the proportions of the ingredients (108). Properties vary in commercial products (109). The modifications of the zinc oxide–eugenol system intended for bite-registration pastes may include agents to increase the body or thixotropic character of the unset mix to improve the handling and utility for this specialized use.

Zinc oxide–eugenol impression pastes are used primarily as corrective washes over compound impressions, as veneer impressions, as temporary liners or stabilizers in base-plates and dentures, and as bite-registration pastes for recording occlusal relationships in inlay, crown, and bridge techniques.

The test methods for zinc oxide impression pastes are outlined in ADA specification No. 16 and Federal specification U-I-500.

Surgical Pastes. Zinc oxide–eugenol pastes having essentially the same formulation as impression pastes are used as dressing for gingival protection and healing following periodontal surgery. These pastes have delayed setting times, are less brittle and are weaker after hardening than the impression pastes.

Some mouth tissues are sensitive to eugenol, and a chronic gastric disturbance may occur in some patients after wearing a surgical pack for 2–3 weeks. A noneugenol material similar to zinc oxide–eugenol can be formed by a reaction between zinc oxide and some carboxylic acids. Carboxylic acids, such as *o*-ethoxybenzoic acid, have been employed in the development of noneugenol cements. Bactericides and other medicines can be added without interfering with the reaction. Because of the ascendency of elastomeric impression materials, research in the zinc oxide–eugenol impression paste has been minimal (110). There is no specification for the surgical paste.

2.8. Zinc Oxide–Eugenol(2-Ethoxybenzoic Acid (EBA) Cements. In an attempt to develop an improved ZOE cement, the reaction of zinc and other oxides with other liquid chelating agents as well as carboxylic acids has been investigated. The only ones of commercial importance have been those based on 2-ethoxybenzoic acid [134-112] and eugenol, ie, EBA cements (106,111–113). Composition parameters are critical in maximizing strength properties and minimizing solubility.

This type of cement has been further improved by the substitution of *n*-hexyl vanillate [84375-71-3] and similar esters of vanillic acid [121-34-6] and/or syringic acid [530-57-4] for eugenol (114–116). These substituted cements are strong, resistant to dissolution, and, unlike ZOE and EBA cements, do not inhibit the polymerization of resin-base materials. Noneugenol cements based on the acid–base reaction of zinc and similar oxides with carboxylic acids have been investigated, and several promising types have been developed based on dimer and trimer acids (103).

2.9. Calcium Chelates (Salicylates). Several successful dental cements that use the formation of a calcium chelate system (117) were developed based on the reaction of calcium hydroxide [1305-62-0] and various phenolic esters of salicylic acid [69-72-7]. The calcium salicylate [824-35-1] system offers certain advantages over the more widely used zinc oxide–eugenol system. These products are completely bland, antibacterial (118), facilitate the formation of reparative dentin, and do not retard the free-radical polymerization reaction of acrylic monomer systems. The principal deficiencies of this type of cement are its relatively high solubility, relatively low strength, and low modulus. Less soluble and higher strength calcium-based cements based on dimer and trimer acid have been reported (103).

The formulation of calcium chelate materials is based upon the formation of a low-solubility chelate between calcium hydroxide and a salicylate. Dycal utilizes the reaction product of a polyhydric compound and salicylic acid. Other salicylic acid esters can be similarly used. Vehicles used to carry the calcium hydroxide, extenders, and fillers may include mineral oil, *N*-ethyl-*p*-toluenesulfonamide [80-39-7], and polymeric fluids. The filler additions may include titanium dioxide [13463-67-7], zinc oxide, silica [7631-86-9], calcium sulfate, and barium sulfate [7727-43-7]. Zinc oxide and barium sulfate are useful as X-ray opacifying agents to ensure a density greater than that of normal tooth structure. Resins, rosin, and limed rosins may serve as modifiers of the physical characteristics in both the unset and set states.

The physical characteristics of the calcium salicylate system compare favorably with those of the zinc oxide–eugenol products. The setting times are subject to modification over a wide range. However, they are somewhat more critical to control than those of the zinc oxide–eugenol system owing to the greater solubility of calcium hydroxide as compared with that of zinc oxide. Compressive strengths in excess of 14 MPa (2030 psi) have been obtained in 24 h. The set product may be formulated to have a hard, brittle, resinous fracture or may be modified to a tough, strong, semiplastic mass. The dimensional stability within a 48-h period varies somewhat with the basic system. Shrinkages of only 0.2% in 48 h have been obtained, but 0.4% may be reached in some compositions. Solubilities, when tested according to ADA specification No. 8 for zinc phosphate cements, range from <1 to 14% for the formulations based on polyhydric esters of salicylic acid. The calcium salicylate cements are not retarders for the free radical polymerization of resin-based materials, eg, composites. A visible light activated calcium hydroxide cement (119,120) has been developed.

Calcium hydroxide has been recognized as a desirable lining for deep-seated cavity preparations involving pulp exposures, or near exposures. It stimulates the formation of secondary dentin that forms a natural pulp-protecting wall. Water slurries or mucilage suspensions of calcium hydroxide provides the therapeutic benefits of the material but with no mechanical strength. Cements of hard-setting calcium hydroxide-containing compositions compare favorably with the better qualities of zinc oxide–eugenol cements. The former provide both the therapeutic values of calcium hydroxide and the structurally strong bases needed for permanent restorations of metal, porcelain, or plastic.

The calcium chelate cements are limited to the use of a cavity liner. They may be placed directly over an exposed tooth pulp to protect the pulp and stimulate the growth of secondary dentin, or used as a therapeutic insulating liner under permanent restorations. The high alkalinity and high solubility of these materials prohibits use in close proximity to soft tissues or in contact with oral fluids.

The chelated calcium cementing materials are supplied as two-part paste products. In use, equal parts of the two pastes are thoroughly mixed together to give a fluid mass that can be applied without pressure over an exposed tooth pulp or in a deep-seated cavity. Under the influence of the oral temperature and humidity, the fluid mass sets to a hard, strong, therapeutic protective seal.

2.10. Resin Cements. Early resin cements formed by free radical polymerization, available since 1952, were based primarily on poly(methyl methacrylate) [9011-14-7] and its monomer (121). Relatively rapid setting times, high polymerization shrinkage, and difficulty of removing excess hardened cement from the interproximal spaces and from beneath free gingival margins are principal deficiencies of this type of resin cement (see METHACRYLIC POLYMERS). More recent resin cements are based on high molecular weight, fluid, di- and multifunctional methacrylates, some containing relatively high loadings of fillers, such as fine glass powders.

Resin cements have excellent aesthetic qualities and are essentially insoluble in mouth fluids. Compressive strength is low, but can be increased by the addition of fillers. They have no inherent adhesion to the tooth unless used with resin bonding agents. Retention is dependent on mechanical locking when the cement flows into irregularities on the surfaces of the substances being cemented.

Resin cement materials are provided as a two-part powder–liquid product. The powder consists largely of poly(methyl methacrylate) to which various fillers (qv) may be added. These include calcium carbonate [471-34-1], silica [7631-86-9], barium carbonate [513-77-9], and calcium tungstate [7790-75-2]. An organic peroxide, eg, benzoyl peroxide, capable of generating free radicals is also present (see INITIATORS; PEROXIDES AND PEROXIDE COMPOUNDS, ORGANIC PEROXIDES).

The liquid is basically a methacrylate monomer having a suitable inhibitor to ensure adequate shelf life. *N,N*; Dimethyl-*p*-toluidine [99-97-8] is probably the most common polymerization accelerator although *N,N*-bis(2-hydroxyethyl)-*p*-toluidine and/or a sulfinate salt, eg, sodium *p*-toluene sulfinate [873-55-2], also may be used.

Fluid, free-radical polymerizable resin-based cements based on the use of cross-linking monomer systems, eg, BIS–GMA and urethane dimethacrylates, having small particulate fillers, yield strong, insoluble materials suitable for cementation applications, eg, crowns, bridges, and composites. Bonding is by penetration into etched or roughened surfaces of the substrate. The use of surface active monomers, such as are being used in dentin adhesive systems, eg, 4-methacryl-ethyloxy trimellitic anhydride (4META), have been successfully used in resin cement formulations.

Visible light activated resin compositions containing calcium hydroxide have been made available as cavity lining materials (120) for pulp capping and pulpotomy, and may offer in other applications an alternative to the calcium salicylate type cements.

3. Dental Plasters

Gypsum is widely distributed naturally as calcium sulfate dihydrate [10101-41-4], $CaSO_4 \cdot 2H_2O$. When partially calcined, the hemihydrate, $CaSO_4 \cdot 1/2H_2O$, is formed (see CALCIUM COMPOUNDS–CALCIUM SULFATES). Gypsum has been used in one form since 1756 for making dental casts, and in another form since 1844 for dental impressions (121).

Plaster is the rehydrated calcined gypsum. The ADA classifies five types of dental plaster according to the physical properties: type I, impression plaster; type II, model plaster; type III, dental stone; type IV, high strength dental

Table 3. **Compressive Strength of Dental Plasters, Investments**

Materials	Compressive strength, MPa[a,b]	ISO standard no.
	Plasters	
impression	4.0[c]–8.0[d]	6873
model	9.0[c]	6873
dental stone	20[c]	6873
high-strength dental stone	35[c]	6873
	Investments	
inlay and crown[e]	2.3 (1.7)	7490
partial denture[e]	5.8 (3.3)	7490
phosphate-bonded[f,g]	3.0	7490
ethyl silicate-bonded[f]	1.5	proposed
	Dies	
gypsum refractory	13.0	proposed
phosphate refractory	13.0	proposed

[a] To convert MPA to psi, multiply by 145.

[b] Value given is at room temperature. Value in parenthesis is at casting temperature.

[c] Value given is minimum value.

[d] Value given is minimum value.

[e] Low temperature casting investments.

[f] High temperature casting investments.

[g] Ref. 102.

stone; and type V, high strength, high expansion dental stone. These different types are the result of various calcining methods (122).

Although plaster has been a very successful and serviceable material, it is seriously lacking in hardness, edge strength, chip resistance, abrasion resistance, and strength to fulfill many needs of dentistry. Some of these requirements have been partially filled by the development of the types III and IV plasters. Table 3 lists the compression strength of dental plasters.

To form plaster, gypsum is ground and subjected to temperatures of 110–120°C in open kettles to drive off part of the water of crystallization. The crystals thus formed are large and porous and are the types I and II plasters. These crystals require a 2:1 powder/gauging water ratio for proper consistency. Type I, impression plaster, and type II, model plaster, differ in additives that control working and setting times. When gypsum is formed these crystals form the stronger type III plaster commonly called dental stone, and require 28–35 mL of water for 100 g of powder. Type IV, high strength dental stone is formed by calcining gypsum in a 30% solution of calcium chloride. The crystals resulting from this process are slightly larger and denser than the type II crystals and require even less gauging water (20–22 mL/100 g of powder). Type V dental stone has gypsum that is formed by a process similar to that for the type IV stone, with the use of calcium chloride. Additives, such as fillers and surface tension reducing chemicals, result in higher setting expansion and higher strength. Hence, less gauging water is required, ie, only 18–20 mL/100 g is needed.

Although gypsum products develop a linear expansion during hardening, the true volume of the final dihydrate is ~7% less than (123,124) the total volume of the hemihydrate plus the water required for the chemical conversion of the hemihydrate to hydrate. In order to produce a pourable consistency, an excess of water is always used. As the gypsum crystals grow in the form of needle-like projections from each center of crystallization, these growing spiny shapes floating in an excess of water push themselves apart from each other. Voids form between the growing crystals that ultimately interlock to make the mass rigid and hard. Setting expansion is a result of this apparent increase in volume owing to the formation of voids.

As a result of the linear expansion, the reduced volume of the dihydrate, and the evaporation of excess water, the percentage of void spaces in plaster is ~45%, in stone 15%, and in improved stone 10%. Thus, the additional amount of water required for plaster contributes to the volume but not to the strength of the hardened material (125).

Each 100 g of calcined gypsum theoretically requires only 18.6 mL of water to complete the chemical reaction from the hemihydrate to the dihydrate. Any amount of water >18.6 mL/100 g of powder is excess and reduces the strength of the hardened plaster. When a mixture of the hemihydrate and water hardens, linear expansion takes place. This expansion may amount to as much as 0.5% for plaster. Dental stones also expand on setting, but the amount is significantly less than that permitted in plaster, ie, 0.2% for type III, 0.1% for type IV, and 0.3% for type V.

3.1. Impression Plasters. Impression plasters are prepared by mixing with water. Types I and II plasters are weaker than dental stone (types III and IV) because of particle morphology and void content. There are two factors that contribute to the weakness of plaster compared to that of dental stone. First, the porosity of the particles makes it necessary to use more water for a mix, and second, the irregular shapes of the particles prevent them from fitting together tightly. Thus, for equally pourable consistencies, less gypsum per unit volume is present in plaster than in dental stone, and the plaster is considerably weaker.

Impression plasters are formulated to produce a thin, fluid slurry when mixed with the proper amount of water. A satisfactory impression plaster should have a setting time of 4 ± 1.5 min; fineness, ie, 98% should pass a number 100 sieve (~0.15 mm), and 90% pass a number 200 sieve (~0.07 mm); setting expansion at 2 h should be <0.15%; the compressive strength at 1 h should be 5.9 ± 2MPa (855.5 ± 290 psi); and testing consistency as determined by the diameter of the slump in the consistence test should be 90 ± 3 mm.

Impression plasters are manufactured from the finest finishing plasters, selected for color and purity. Setting time accelerators, setting expansion control agents, fillers, flavors, colors, or other special modifying agents may be added, eg, starch, to cause disintegration of the plaster impression when it is boiled.

Impression plasters are used to obtain an impression (or negative) of the hard and soft tissues of the mouth. The plaster slurry is placed in a tray, inserted into the mouth, pressed in place against the area in question, and held still until it hardens.

3.2. Model Plasters. Model plaster should have a setting time of ~10 min. The fineness of the powder should be such that 98% passes a number 100 sieve (~0.15 mm) and 90% passes a number 200 sieve (~0.07 mm). Setting expansion should be <0.30%, compressive strength at the end of 1 h should be a minimum of 8.8 MPa (1276 psi), and the consistency should form a disk during the slump test of 30 ± 2-mm diameter.

Model plasters are manufactured from select finishing plasters with special emphasis on a clean, white color. Setting-time control agents, setting-expansion control additives, fillers, and pigments may be added.

After it is mixed in water, model plaster is poured into an impression (negative) to produce a cast (positive) or oral structure. This plaster cast is produced chiefly for study or record purposes, ie, successive casts allow an orthodontist to follow and demonstrate the results of corrective treatment. Additional uses for model plaster include the making of study casts and denture repair casts; mounting interarch registration assemblies on articulators; flasking dentures during processing; and for a variety of other applications where strength and abrasion resistance are not of prime importance.

3.3. Dental Stones.

Dental stones, produced from gypsum, are sold as dry powders in sealed containers. They are prepared for use by mixing with water, in proportions recommended by the manufacturer.

Dental stone is generally used at a water/powder volume ratio of ~30 parts water to 100 parts of stone. The mix is not easily poured, but can flow readily under mechanical vibration. The physical property requirements include a setting time of 10 ± 3 min; fineness of powder, where 98% should pass a number 100 sieve (~0.15 mm) and 90% pass a number 200 sieve (~0.07 mm); linear setting expansion at 2 h of <0.20%; compressive strength at 1 h of 20.6 MPa (2987 psi); and consistency such that the slump test disk is 30 ± 2-mm diameter.

Setting-time control agents, setting-expansion control agents, fillers, colors, or other modifying additions may be added. Calcium sulfate dihydrate and sodium chloride [7647-14-5] are effective accelerators. Potassium sulfate [7778-80-5] and sodium potassium tartrate [304-59-6] accelerate the setting rate and decrease the setting expansion. Borax [1303-96-4], potassium carbonate [584-08-7], sodium carbonate [497-19-8], and sodium citrate [68-04-2] are all effective retarders and reduce the setting expansion.

Type III dental stones are used for casts requiring higher compressive strength and abrasion resistance than casts formed using the type II plaster. These dental casts are used for the processing of denture-base materials.

3.4. High Strength Dental Stone.

This dental stone is often referred to as improved dental stone. The crystals are of a cubic or rectangular shape and show a reduction in cracking and porosity. These changes in crystals reduce the amount of water required to wet the powder and produce a workable consistency, ie, 20–22 parts water per 100 parts powder.

Mixes of improved dental stone (type IV) using 22 parts of water to 100 parts of powder produce a mass that is not fluid and pourable but can be easily vibrated into place. The physical properties of the improved dental stone include a setting time 10 ± 3 min, fineness of powder such that 98% passes a 100 sieve (~0.15 mm) and 90% passes a 200 sieve (~0.07 mm); setting expansion at 2 h limited to a max of 0.10%; compressive strength at 1 h of at least 34.3 MPa (4974 psi); and a disk formed in the slump test for consistency of a 30 ± 2 mm diameter.

Type IV dental stones are used to make casts for a single tooth, for crown or inlay work, and for a complete dental arch.

3.5. High Strength, High Expansion Dental Stone. Type V dental stone is used for making dies employed in the fabrication of wax patterns for prostheses cast in non-noble dental alloys. Non-noble dental alloys generally solidify at higher temperatures than the high noble and noble metal alloys and have more shrinkage as they cool to room temperature. The higher expansion of type V dental stone provides a larger die and, as a result, a larger pattern that compensates for the greater shrinkage of the casting. Type V stone is a possible choice whenever compensation for more shrinkage of a prosthetic or other material, such as a duplicating material or impression material, is needed. The setting time is 12 ± 4 min; the compressive strength must be no lower than 48 MPa (6960 psi); and the setting expansion must lie between 0.10 and 0.30%.

Dental plasters are generally white in color, while dental stones are colored to differentiate them.

4. Dental Investments

Dental investments are comprised of refractory materials capable of withstanding elevated temperatures. They are used as casting investments and model investments. The compressive strengths, according to International Standards, of the investments and die materials are shown in Table 3.

4.1. Casting Investments. Casting investments are used to form molds into which molten metal may be cast. The cavity for receiving the metal is formed by the lost wax process. The composition of investments used for alloys cast from low (1100°C) temperatures are different from those used for alloys cast from higher (1300°C) temperatures.

A casting investment must provide sufficient expansion to compensate for shrinkage (up to 0.4%) of the wax (or plastic) pattern during its fabrication, and shrinkage (1.2–2.0%) of the cast alloys resulting from solidification and cooling. The higher the solidification temperature of an alloy the greater is its casting shrinkage.

The compensating expansion of a dental investment may be separated into two types, setting and thermal. Setting expansion includes expansion or dimensional change from the curing of the investment, and expansion from excessive water in contact with the investment after its original mixing with recommended water (126,127). This water may be added by either immersion of the mixed investment in a water bath or as an excess of water from a presoaked porous ceramic liner, called a casting ring that is placed between the mixture and a metal cylinder container. Thermal expansion is caused by the expansion of the set investment during heating through a wax burnout process and by changes of some component(s) of the investment to lower density phases at the elevated temperatures (128).

4.2. Investments for Low-Temperature ($T \leq 1100°C$) Casting Alloys. Low temperature casting alloys are usually comprised of gold, silver, and copper and are used for inlays, crowns, and fixed partial dentures. At the temperature tested, the compressive strengths specified for inlay or partial denture investments are adequate to prevent fracture during handling and in casting. The strength may vary at casting temperature. The strengths of gypsum-bonded investments at high temperatures vary with the additive used to reduce shrinkage during heating (129). The type of binder also influences the effect of the temperature on strength. Table 3 presents the mechanical property limits defined by International Organization for Standardization (ISO) standards for casting investment for low temperature dental casting alloys (130).

These investments consist of a binder of calcined gypsum, ie, calcium sulfate hemihydrate [10034-76-1], $CaSO_4 \cdot ½H_2O$; to which is added silica and modifying agents such as finely ground gypsum, soluble sulfates, and chlorides, ie, accelerators of setting; and low solubility salts, ie, retarders of setting (131). The refractory base consists of the silica in some crystalline form; quartz [14808-60-7] and crystobalite are the main constituents. Quartz is found in great abundance in nature, but crystobalite is prepared commercially by calcining selected quartz at 1500°C. Investments containing crystobalite undergo expansion at lower ($T < 600°C$) temperatures and also, to a greater extent, at higher temperatures than those containing only quartz. Some of the investments used for casting cobalt–chromium–nickel alloys that solidify at a temperature of ~1300°C also have a gypsum binder. In order to reduce oxidation of these alloys the investments contain carbon [14762-74-4] or colloidal copper [7440-50-8] to produce a reducing atmosphere in the mold (132); this is particularly useful if some previously formed metallic parts are embedded in the investment and are carried through the burnout process.

Gypsum decomposes rapidly, especially in the presence of carbon, at temperatures required for casting many of the cobalt–chromium alloys (132). Accordingly, investments for use with type II cobalt–chromium alloys that have solidifying temperatures ~1300°C must have a binder other than gypsum. Organic and inorganic silicates (133,134) as well as some phosphates (135,136) are used. These types of investments are also recommended for use with high fusing gold and other alloys to which porcelain is fused; and for use with alloys offered as substitutes for the gold alloys. Trapped air between the investment and wax pattern may be a problem, even with the use of a wetting agent and vacuum investing (137). Although the phosphate investments are preferred for high melting gold alloys, they are suitable for low melting gold alloys.

A number of modifiers are employed to prevent most of the shrinkage of gypsum when it is heated > 300°C. Among these are boric acid (138) and sodium and other chlorides (139,140). A review of the development and composition of some investments is given (141).

The minimum total expansion must be 1.5% for casting of inlays and crowns and 1.3% for partial denture gold alloy casting (142).

4.3. Investments for High-Temperature Casting Alloys. These investments are used for alloys that require high (1300°C) casting temperatures. The alloys vary greatly in nobility. Some are rich in gold and/or palladium, and others are predominately cobalt, nickel, and chromium. Some of these alloys are used for crowns and fixed partial dentures with porcelain veneers fused to the metal; others are used for removable partial denture frameworks. The noble-based alloys for fixed partial dentures require casting temperatures in the neighborhood of 1300°C, and phosphate bonded investments are used. The cobalt, nickel, and chromium alloys require casting temperatures of ~1400–1500°C, and investments that use ethyl silicate or stabilized silica solutions are used.

Phosphate-Bonded Investments. These are available with two components, a powder and a liquid that react when mixed together. The powder consists of refractory materials that control the thermal expansion, eg, silica glass, quartz, crystobalite; setting reaction, eg, magnesium oxide [14762-74-4]; and resistance to reaction with the molten metal, eg, carbon, silica, and other metal oxides. The liquid is a colloidal suspension of silica that provides some green strength and thermal expansion. During the burnout process the silica provides strength through the formation of silicophosphates. The binder is formed from the reaction of monoammonium phosphate [7722-76-1], $NH_4H_2PO_4$, and calcined magnesia, MgO, in the presence of water.

$$NH_4H_2PO_4 + MgO + 5H_2O \longrightarrow NH_4MgPO_46H_2O$$

External measurements indicate that the setting expansion is ~0.4%. A water bath technique adds another 0.6–0.8% expansion when 100% colloidal silica is used.

The thermal expansion of the investments can vary from 0.8% using 50% colloidal silica solution to 1.2% with undiluted colloidal silica solution. In the green state the modulus of rupture is 0.1–0.5 MPa (14.5–72.5 psi) and ~0.8 MPa (116 psi) fired strength. Firing beyond 900°C results in a decrease in strength due to chemical breakdown of the investment.

Ethyl Silicate-Bonded Investments. These investments are mixtures of powder and liquid. The powder consists of refractory particles of silica glass, crystobalite, and other metal oxides plus magnesium oxide. The liquid is a hydrated silica, tetrasilicic acid [10193-36-9], $Si\,[OH]_4$, that is supplied in a stabilized form; it can be developed by mixing ethyl silicate [78-10-4], denatured ethyl alcohol [64-17-5], and hydrochloric acid [7647-01-0]. The binding of the powder is accomplished by the formation of a silica gel according to the reaction:

$$m\mathrm{Si[OH]}_4 \xrightarrow{\mathrm{MgO}} (\mathrm{SiO}_2)_m + 2m\mathrm{H}_2\mathrm{O}$$

Expansion results entirely from heating; there is no setting expansion. In fact, a setting contraction of 0.3–0.4% occurs. The thermal expansion can be controlled to 1.7–2.1% up to 1150°C. A heat soak can produce an additional 0.1–0.2% within ½h. These investments have very low green strength; models made of them require dipping into a resin that strengthens them for handling. No standard for strength exists yet for these investments. The investments are highly permeable in the as-fired state, and castings of good surface finish, dental accuracy, and fit can be achieved. Fine-grained surface coatings applied to models and patterns produce even smoother surfaces.

4.4. Model Investments. Model investments are materials used for noncasting operations in the fabrication of dental protheses. They differ from casting investments in various ways depending on the prosthetic device being constructed. For low temperature operations, such as soldering, gypsum is used; phosphate-bonded materials are employed for higher solder temperatures or for the fabrication of porcelain veneers.

4.5. Soldering (Brazing) Investments. These are either gypsum or phosphate bonded. They are used to hold the metal components of a prosthesis together while they are joined or repaired via a soldering or brazing process (see SOLDERS AND BRAZING ALLOYS). The goal is to restrict motion between the parts being joined. Soldering investments differ from casting investments primarily through avoidance of ingredients, such as crystoballite, that cause expansion. The soldering investments contain higher percentages of quartz and other inorganic oxides of metals, such as zirconium [1314-23-4] and titanium [1317-70-0], as refractory components.

4.6. Veneering Investments. These are phosphate bonded and contain finely ground quartz, zirconium oxide, and/or titanium oxide to produce highly refractory, low expansion dies of fine detail. The dies are formed within impressions taken of teeth that the dentist has prepared in anticipation of covering the front surface with an aesthetic ceramic veneer. Porcelain or ceramic powders are shaped to detail on the dies and these are fired at high (~1000°C) temperatures to produce the veneers. The veneers are then cemented to the front surface of the previously prepared teeth.

4.7. Investment Casting Rings and Liners. Casting rings and ring liners are needed prior to investing a wax pattern. Casting rings are cylindrical tubes that mold and retain the casting investment. Ring liners are paper or fabric sheets adapted to the inside of the rings to allow the investment to expand within the ring.

4.8. Casting Rings. Three types of castings rings commonly used are metal, split, and disposable rings. Metal rings are the most popular because they can be reused. The rings are available in many sizes and are usually manufactured from stainless steel. Metal rings can be used with most investments, but a liner must be included to allow for expansion. Split rings allow for maximum expansion of investment needed for some alloys. Split rings are made of plastic, stainless steel, or nickel-based alloys and do not need liners. They are available in many sizes. Disposable rings, like split rings, achieve maximum expansion and do not need liners. Most disposable rings are composed of heavy paper and can be cut to different sizes.

4.9. Ring Liners. Liners are either cellulose, which readily absorbs water, or ceramic, which does not absorb water or investment liquid (143). Both are available in many sizes. Ceramic liners are made from fibers of alumino-silicate glass derived from kaolin. The principal components in the glass are alumina, 47–65 wt%, and silica, 35–50 wt%. Ceramic liners are highly heat resistant to 1300°C. Reports suggest that the fiber from ceramic ring liners may be a possible health risk (144).

Cellulose liner material absorbs water and needs to be wet for at least 30 s prior to investing to prevent liquid from being extracted from the investment. The cellulose liner burns when heated in air and is eliminated completely from the mold at burnout temperatures of 700°C (143). To ensure retention of the mold within the casting ring, a cellulose liner should be kept short of each end. For gypsum investments, a liner that is 2 mm shorter than the height of the ring should is often used.

Modern liners are all asbestos free because of the health risk associated with asbestos (qv).

5. Dental Waxes

Waxes and wax composition, ie, pattern, impression, and processing waxes, have been important in the dental profession for many years (145). Most dental waxes find application within the oral cavity during some phase of their use.

Wax cylinders 6.0 mm thick by 10.0 mm in diameter are prepared by a controlled technique, ie, ADA specification No. 4, para. 4.3.1.1. Typical flow curves are shown in Figure 1.

Flow characteristics at 37°C of a ternary wax mixture of spermaceti [8002-23-1], paraffin [8002-74-2], and ceresin [8001-75-0] are shown in Figure 2 (146). A mixture having composition of 60 wt% paraffin 124, 20 wt% spermaceti, and 20 wt% ceresin is sometimes referred to as the Iowa impression wax (127). It has a melting point of 48.5°C, and a flow of 78.6% at 30°C, 95.4% at 37°C, 96.9% at 40°C, and 97.6% at 45°C.

5.1. Pattern Waxes. The pattern waxes, ie, inlay casting, base-plate, and sheet and shape waxes, are used to construct the prototype or pattern from which a finished dental restoration is produced.

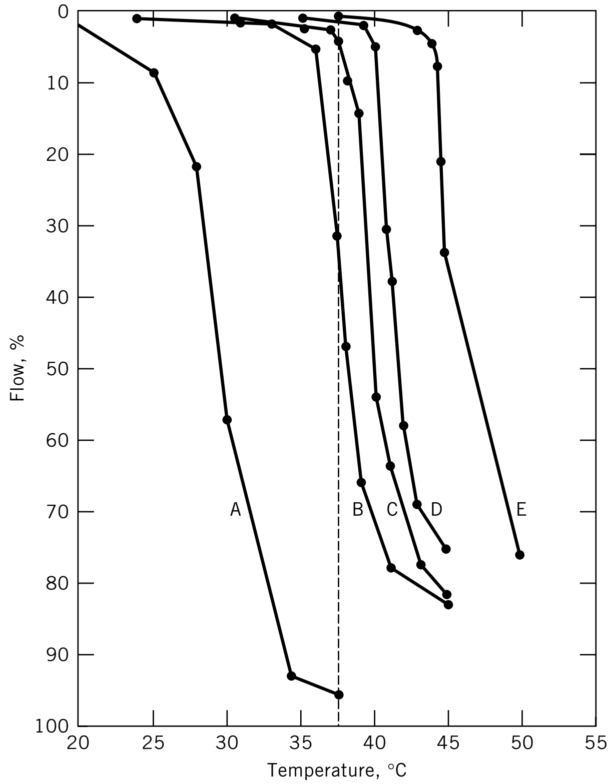

Fig. 1. ADA flow curves of dental waxes. A, impression waxes; B, sheet wax; C, indirect-inlay wax; D, direct-inlay wax; E, base-plate wax. The dashed vertical line represents the temperature (37°C) of the average human mouth.

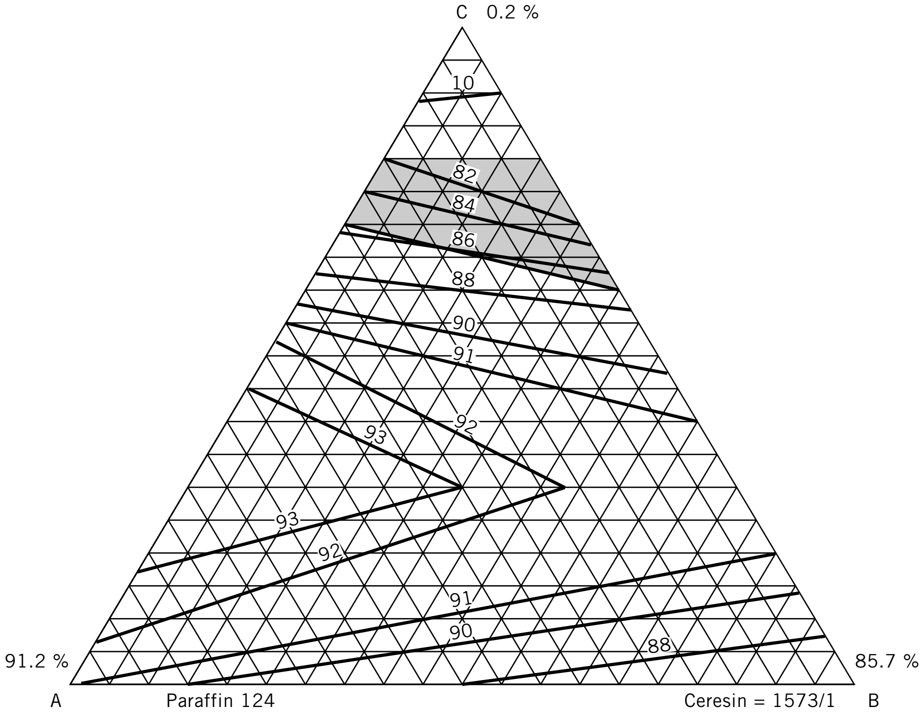

Fig. 2. Flow diagram of ternary wax mixtures of (A) Cornelius paraffin 124, 91.2% flow; (B) Ross ceresin, 1573–1 85.7% flow; and °C) Stevenson spermaceti, 0.2% flow, at 37°C. Numbers in the diagram represent percent flow; the dotted area shows where the waxes are not soluble in each other in the solid state.

5.2. Inlay Casting Waxes.

The three types of inlay casting waxes, ie, types A, B, and C, are used to produce wax patterns for the lost wax casting process in the production of cast gold inlays, crowns, and bridges. Some inlay wax is also used to produce patterns for acrylic restorations.

Type A waxes are hard waxes used when an extra hard wax is preferred by the dentist in making patterns in the mouth. Type B waxes are medium waxes used by most dentists to make patterns in the mouth. Type C waxes are soft waxes used for making patterns outside the mouth. The practice of making wax patterns inside the mouth is not the most common method used, as most patterns are fabricated on stone cast reproductions of the cavity preparation.

The exact formulations for inlay casting waxes are considered trade secrets, and little has been published on the subject. A binary mixture of 65–75 wt% paraffin wax (60–63°C) and a microcrystalline wax having a melting point >60°C has been suggested (147). This produces a mixture having a solid–solid transition point at ~37°C with little plastic deformation (1–3%) at 37°C and a desirable plasticity at 45°C (73–77%) (148).

Inlay waxes are generally dark blue, green, black, or purple; however, inlay waxes for acrylic work are uncolored and are a natural ivory. The waxes are generally produced in stick form, ~75 mm long and 6.5 mm across; the cross section may be round or hexagonal.

5.3. Base-Plate Waxes.

Base-plate waxes are used to substitute for, or be used in conjunction with, a base plate to form a pattern for the production of complete or partial dentures and certain orthodontic appliances to be molded of acrylic resin, modified vinyl resins, or other denture-base polymers.

Base-plate waxes are formulated for specific uses or working conditions into types I, II, and III. Consequently, the flow requirements differ. Type I waxes are soft waxes for building contours and veneers, type II waxes are medium waxes used for pattern production in the mouth in temperate weather, and type III waxes are hard waxes used for production in the mouth in hot weather. At 37°C, type I waxes have a 45–85% flow; at 45°C, type II waxes have a 50–90% flow and type III waxes have a 5–50% flow.

The linear thermal expansion of base-plate waxes should not exceed 0.8% at 25–40°C. It is desirable to invest any waxed-up case as soon after waxing is completed as possible. This minimizes changes in articulation owing to tooth shift, and changes in palatal thickness owing to lifting of the palatal section by wax shrinkage caused by variations in room temperature or by the release of stress.

Base-plate wax compositions are generally regarded as trade secrets. A substantial percentage of paraffin is usually present, probably 50–80 wt%. Beeswax [8012-89-3], carnauba wax [8015-86-9], ceresin, microcrystalline waxes, Acrawax C (Glyco Products Co. Inc.), mastic gum, rosin [8050-09-7], and synthetic resins may make up the balance of the formulation. Base-plate waxes are generally sold in sheet form ~1.3 mm thick, 75 mm wide, and 140 mm long.

5.4. Sheet and Shape Waxes.

Sheet and shape waxes are used to produce patterns from which complete or partial dentures are cast of gold or base metal alloys. They are used to fabricate the restoration prototype directly upon a refractory investment cast.

The flow of sheet and shape wax is much higher than that of inlay wax and base-plate wax, reflecting increased pliability, ductility, and plasticity. At 35°C these waxes should have a flow of 10% max, and at 38°C a flow of 60% min. At 23 ± 1°C they should not fracture when bent double.

The compositions of sheet and shape waxes are also trade secrets. However, they are blends of various proportions of paraffin, microcrystalline waxes, carnauba wax, ceresin, beeswax, gum dammar, mastic gum, and possibly other resins. Sheet waxes are marketed in square sheets ~80 × 90 mm. Various thicknesses are available from 32 gauge (0.5 mm) to 14 gauge (1.63 mm).

Shape wax is similar in composition and properties to the nontacky sheet waxes. It is processed into preformed shapes or definite shape and gauge to facilitate the waxing-up of partial-denture patterns. The shapes and sizes conform to those most needed for lingual bars, palatal bars, clasps, saddle construction, retainers, etc. The available sizes and shapes include rounds from 10 gauge (2.0 mm) to 20 gauge (0.84 mm), half-rounds from 6 gauge (3.36 mm) to 14 gauge (1.63 mm), and half-pear shapes of 6 gauge (3.36 mm). The pieces are usually cut ~10 cm long.

5.5. Impression Waxes.

Impression waxes include those waxes used to obtain a negative cast of the mouth structure (impression waxes), waxes used to establish tooth articulation (bite-registration waxes), and waxes used to detect tooth interference and high spots or improper fit of denture bases (disclosing waxes). They must be plastic and moldable at mouth temperatures, and chill

Table 4. **Flow Properties of Impression Waxes**

Impression wax	Flow, %	Temperature, °C
grade 1	5	37.5
grade 2	79	37.5
grade 3	28	30.0
grade 4	75	30.0

to a still nonplastic mass upon cooling within a few degrees below mouth temperature.

Impression waxes, used for negative casts of mouth structures, are generally considered to be soft, low melting, plastic waxes used as the last wash on an impression to obtain fine detail of the oral structures. However, complete wax-impression techniques are available that involve the use of hard, high melting, rigid base waxes, with successively softer wax additions to build a complete impression. The last low melting wax gives the final detail without thermally destroying the higher softening waxes of the base impression.

Table 4 lists flow properties of a set of impression waxes the exact compositions of which are trade secrets. The materials that have been identified in the compositions are paraffin, ceresin, vegetable waxes, rosin, mastic gum, and spermaceti.

Bite-registration waxes are used to establish the occlusion or horizontal relationship of the lower jaw to the upper jaw when there are opposing teeth present. Bite waxes may have a flow of 84% at 30°C. They are generally compounded from high flow, low melting paraffins, microcrystalline waxes, and resins.

Disclosing waxes, or pressure indicating pastes, are used in fitting a dental appliance to establish the location and extent of high spots or pressure areas, as on impressions and complete dentures. They are very soft, salve-like compositions that are painted onto the tissue side of an impression or denture. When the wax-coated denture is seated in the mouth, the soft paste is forced out of the areas showing hard contact between the denture and the mucous membrane. These areas on the denture can be easily marked and material removed from the denture to relieve the premature or hard contact.

Disclosing waxes include soft paraffins, petrolatums, coconut oil, zinc oxide, titanium dioxide, and suitable dyes.

5.6. Processing Waxes.

The extensive amount of handwork and craftsmanship necessary in the fabrication of most dental restorations and appliances has created a need for several types of wax compositions. These are known as boxing, sticky, utility, or study waxes.

Boxing wax, as the name implies, was developed to box impressions, ie, to construct a retaining ring of wax around an impression to confine the plaster or stone when the cast is poured. These waxes may have melting points of 65.5–71.1°C, and a flow of 60–80% at 37.5°C. Boxing waxes are generally formulated from various microcrystalline waxes to give the desired tackiness and pliability. Various resinous additions may also be made to increase strength and tackiness.

Sticky waxes are used as thermoplastic cements. The broken pieces of a plaster impression are reassembled and held in position with sticky wax. Broken denture bases may be held in proper alignment for repair. Orthodontic appliances may be assembled with a sticky wax prior to investing and soldering. Plaster splints may be sealed to stone models in the production of porcelain or resin facings. Thus, sticky wax is useful in almost any operation where it is desired to position and hold several small pieces in a temporary relationship.

Sticky waxes are generally composed of resins and wax. A high resin content gives viscosity to the melt, a long plastic range, and a brittle fracture when cooled. No modern formulas are available, but the older recipes usually had rosin, beeswax, and gum dammar as the essential constituents.

Utility waxes are waxes of many uses. They are generally useful for sealing, filling, contouring, building up areas, positioning, and many other functional purposes. Their compositions, considered trade secrets, are probably microcrystalline waxes or blends of beeswax, petrolatum, and rosin.

Study waxes, ie, waxes for carving, are useful in the study and modeling of tooth forms and the teaching of anatomical detail. Carving wax compositions include paraffin, ceresin, ozokerite, carnauba wax, montan waxes, and Acrawax C. Fillers and pigments may be added.

5.7. Wax Manufacture. Wax compositions for dental usage are usually compounded in simple melting and blending equipment. The melting is done with the least destruction of the wax properties. Direct-fired equipment can be used, but jacketed melting kettles reduce the chance of localized overheating, ie, control of temperatures and heat distribution is desired. Some compositions may require a carbon dioxide or other protective cover to minimize oxidation. Foaming or swelling of the batch in the kettle may occur on melting from thermal expansion of the waxes and resins, raw materials that contain water, volatilization, or low boiling constituents.

Agitation of the wax melt facilitates heat transfer, reduces localized overheating, and increases the melting rates. Over agitation should be avoided to minimize oxidation of the materials. The melting and processing of waxes should be done as quickly as possible and at the minimum temperature compatible with the process to avoid the loss of volatile constituents, degradation of the materials, and oxidation changes. A cover of inert gas may be used to protect susceptible compositions from excessive oxidation.

Wax compositions are processed into rods, sheets, cakes, and special forms by a variety of processes. Casting, roll forming, and extrusion, by mechanical or hydraulic piston-type extruders or by continuous screw extrusion, are operations in practice. Stamping, roll cutting, or molding are also employed.

The applicable specifications for each type of wax are listed below (149).

Wax type	Specification
dental inlay casting	ADA no. 4
base plate	ADA no. 24
impression	
bite registration	
disclosing	
boxing	Federal U-W-138
sticky	Federal U-W-149
utility	Federal U-W-156
sheet and shape	Federal U-W-140

6. Dental Alloys and Metals

The chemical and physical properties of some metals and alloys, such as hardness, strength, stiffness, toughness, corrosion resistance, and biocompatibility have provided materials capable of withstanding the most severe demands of restorative dentistry, namely, the harsh corrosive environment of the mouth and high stresses on the small cross-sectional areas of teeth. Metallurgical and dental sciences have given dentistry many excellent alloys for restorative dentistry, prosthetic dentistry, orthodontics, and dental techniques. These alloys include amalgams; base metal alloys such as cobalt–chromium casting alloys (for partial dentures), chromium-containing casting alloys (for crowns and bridges), and titanium alloys (for implants, partial dentures, crowns, and bridges); gold and gold alloys, ie, foil, crystal powder, Au–Ca alloy combinations for direct filling and wrought alloys; platinum and platinum alloys; solders, ie, gold solders, silver solders, and special solders; and electrodeposited metals such as copper and silver. An excellent review on metals and alloys in dentistry is available (150).

6.1. Amalgams. The earliest recorded use of amalgam as a dental restorative material was in 1528 (151). Since then amalgam has achieved the status of one of dentistry's main restorative materials. Modern amalgams remain plastic at room and mouth temperatures for several minutes after preparation, allowing them to be compacted into the prepared cavity; they then harden quickly with very small dimensional change. Their proven ability to function adequately and preserve existing dentition is remarkable considering the dental requirements.

Dental amalgam is a novel alloy. Within a few seconds of the start of trituration, the alloy and mercury [7439-97-6] must amalgamate to a smooth plastic mass. Within 3–5 min it must set to a carvable mass and remain so for 15 min. Within 2 h it must develop sufficient strength, hardness, and toughness to resist mild biting and chewing forces. It should not tarnish or corrode in the mouth, nor react to produce toxic or soluble salts, and must maintain its color. Most present-day amalgams can be produced to meet a considerable degree of these formidable requirements.

The mercury content in dental amalgam is generally restricted to a mass fraction of $\sim$50% or less. Excessive mercury in the final restoration results in a low strength amalgam with poor creep resistance, excessive setting expansion, and poor corrosion resistance. Properly proportioned, mixed, and processed amalgams will have compressive strengths in the range of 210–345 MPa (30,000–50,000 psi) in 24 h. Tensile strengths are 48–55 MPa (7000–8000 psi). The linear setting expansion from 5 min after the end of trituration to 24 h should fall within 0 ± 20 μm/cm. Creep-test cylinders (8×4 mm, after aging for 1 week at 20°C) shortened from 0.9% strain to 8.0% strain after being subjected to a static load of 36 MPa (5200 psi) for 4 h (152). Attempts to relate either the dimensional change (on setting) or other mechanical properties to clinical behavior have not been very successful, but it has been shown that the creep rate is important in predicting the marginal fracture of amalgam restorations (153).

6.2. Composition. The composition of powdered alloys used in preparing dental amalgams usually includes mass fractions of 66.7–75.5% silver;

25.3–27.0% tin; 0.0–6.0% copper; and 0–1.9% zinc. These are commonly referred to as conventional alloys, and the amalgams made from them are conventional amalgams. This composition range was in use for almost a century until two Canadian researchers designed an alloy consisting of a mixture of two powders; one having the customary flakes of the aforementioned composition range and the other, spherical shapes of a silver–copper eutectic, ie, 72% Ag, 28% Cu (154). The ratio of the customary powder to the spherical one was ~2:1 by mass, giving an approximate composition (mass fractions) of 70% silver, 18% tin, 11% copper, and 1% zinc. Amalgams made with this powder mix have high compressive strengths and low creep, have better clinical performance than conventional amalgams (155), and are sometimes called dispersed amalgams.

Other powders, made from alloys of uniform composition, appeared on the market with approximately the same overall composition but with a high compressive strength of 462 MPa (67,000 psi), high tensile strength of 55 MPa (8000 psi), and low creep (0.2% strain) when compared to the amalgams made from the mixture of powdered alloys (156). Other alloys having copper content higher than a mass fraction of 18% were subsequently developed. The range of composition (mass fractions) of some of these alloys is 42.2–70.3% silver, 17.7–30.0% tin, 12.0–27.8% copper, and 0–0.3% zinc. In addition, one of the powdered alloys contained 3.4% indium and one contained 0.5% palladium.

The copper-rich amalgams have performed well in clinical trials in which they were compared with alloys having lower copper content. An improved marginal stability was observed, which may be associated with a longer clinical lifetime (157). These amalgams have also been called non γ_2 amalgams, where γ_2 refers to the compound $Sn_{7-8}Hg$.

The complete role of each of the metals in dental amalgams is not fully understood. It is generally agreed that when the conventional powdered alloy is triturated with mercury, the gamma and beta phases of the silver–tin system are attacked by the mercury and that principally Ag_2Hg_3 (γ_1) [12249-78-4] and $Sn_{7-8}Hg$ (γ_2) are formed. These phases form a matrix that binds the remaining unreacted part of the original powder particles together. Usually the less the matrix, the better the values of the pertinent physical properties.

One of the serious defects of the conventional amalgams is the corrosion of the $Sn_{7-8}Hg$ phase, which is normally absent or, if it forms, mostly disappears in amalgams with the increased copper content; hence, the term non-γ_2 amalgams. The phases present in two conventional amalgams used in clinical testing (56,58,62) are

Phase name	Designation	Principal component	CAS Registry number
Ag–Sn	γ	Ag_3Sn	[12041-38-2]
Ag–Hg	γ_1	$Ag_{22}SnHg_{27}$	[69484-15-7]
Sn–Hg	γ_2	Sn_8Hg	[11092-12-9]
Cu–Sn	ε	Cu_3Sn	[12019-61-2]

In the dispersed-phase amalgam an additional phase of a eutectic of the Ag–Cu system and a reaction ring (zone) of Cu_6Sn_5 [12019-69-1] around the residual silver alloy particles has been detected. If a mass fraction of 10% gold is added to conventional alloys at the expense of the silver content, non γ_2 amalgams are formed (158). Other elements, such as manganese and palladium, are also effective in eliminating the tin–mercury compound.

The phases and their proportions present in hardened amalgam are controlled by many factors. The composition of the alloy; the size, shape, and size distribution of the particles; the thermal history of the cast ingot and the comminuted alloy; and the surface treatment of the particles are some of the factors for which the manufacturer is responsible. The tooth cavity preparation and the mixing, compacting, and finishing techniques of the dentist can make the difference between satisfactory and unsatisfactory restorations, even with the best of alloys. A minimal amount of residual mercury and porosity are needed to obtain the most serviceable restorations (159).

Amalgam restorations are prepared by mixing a powdered alloy with mercury to form a plastic moldable mass that is packed or condensed into the prepared cavity. The cavity is designed to provide mechanical retention, maximum marginal mass, support to absorb the functional stresses transmitted through the restoration, and maximum protection to the remaining tooth structure. The restoration reestablishes the normal tooth anatomical form and function.

Amalgams have shown some sensitivity to manipulation variables. The general procedure conforms to the following outline. First, the alloy powder and mercury are proportioned by weight. Next, the amalgam must be condensed properly in the prepared, clean, and dry cavity. In general, the maximum effective load tolerated by the patient should be used on a condenser of optimum size, to remove as much mercury from the mass as possible. The amalgam must be carved to the contour of the lost tooth tissue it is replacing.

Final polishing should be delayed for at least 24 h after placing the restoration. Amalgam restorations should not be subjected to biting or chewing forces for at least 2 h (preferably 6 h) after insertion to avoid fracture of the restoration. A smooth, well-polished amalgam restoration retains its color and appearance much better than a poorly finished one. Roughness promotes plaque adherence, discoloration, and corrosion.

Generally, the newer amalgams having the higher copper content have better values for the properties of interest than the so-called conventional amalgams. The high copper content (non γ_2) amalgams have less creep, higher compressive strength, lower tensile strength, better marginal integrity in restorations, less discoloration, and are more corrosion resistant.

6.3. Manufacturing.

In the general manufacturing processes used to produce alloy powders for dental amalgams, metals of the required purity are melted together in their proper proportions under nonoxidizing conditions. Either atomization is used to produce spherical particles or ingots are cast and cooled at a rate that produces some Widmanstätten structure, a geometrical pattern caused by the formation of a new phase along certain crystallographic planes of the parent solid solution. An ingot may be given a homogenization heat treatment at 400°C, and the ingots are reduced to filings by machining on a lathe or a cutter. Iron particles (from the machining operations) are removed magnetically and the filings may be ground to reduce their size. Undesirable particle sizes are screened out to the desired gap-graded sizes. The particles are given a heat treatment at 60–100°C for 1–6 h to preage the metal, ie, remove the cold-work effects, and reduce the rate of amalgamation and setting, and the particles may be acid-cleaned to remove any oxide film and other contaminants, washed, and dried.

6.4. Gallium-Based Alloys. Gallium-based alloys has been introduced commercially as substitutes for dental amalgam, but problems with high levels of corrosion and latent expansion have prevented their continued use as a direct filling material.

6.5. Gold and Gold Alloys. Gold foil, crystal powder, a gold–calcium alloy, and combinations thereof in the noncohesive states are used in dentistry as direct-filling materials; an adsorbed layer of ammonia renders the gold noncohesive for packaging, and heating returns it to a cohesive state for use. Gold alloys are used for cast restorations and prosthetic devices. Wrought gold alloys are used for wire clasps and fabricated orthodontic appliances (see GOLD AND GOLD COMPOUNDS).

Gold and gold alloys serve the needs of dentistry better than any other metals or alloy systems. Gold alloys have a broad range of working characteristics and physical properties, coupled with excellent resistance to tarnish and corrosion in the mouth.

Pure or alloyed, eg, Au–Ca, gold is used as a direct filling material in restorative dentistry as foil (~0.635 μm thick), also available as a gold–platinum laminated foil containing up to 40% platinum; and powdered pure gold. Gold, in either of these forms, welds to itself at room temperature when condensed by force. Certain other metals have this characteristic, but the difficulty of achieving and maintaining a sufficient degree of surface purity makes adequate welds difficult to obtain. A gold restoration, foil or other type, of pure or alloyed gold, or both, is relatively weak, soft, and malleable. The cohesive characteristic of the gold foil is partially lost with time as the metal is contaminated by exposure to the atmosphere. The cohesive characteristic is restored, immediately before use, by heating in a clean flame to rid the surface of contaminating substances, including sorbed gases. The gold restoration is produced by malleting or condensing the clean metal into the clean, dry cavity preparation. Hardness of the final restoration exceeds the hardness of cast pure gold, owing to the cold working. The hardness approaches that of 22 kt gold.

6.6. Gold Casting and Wrought Alloys. Gold alloys useful in dentistry may contain gold, silver, platinum, palladium, iridium, indium, copper, nickel, tin, iron, and zinc. Other metals occasionally are found in minor amounts. The effect of each of the constituents is empirical, but some observations have been made.

Gold [7440-57-5], Au, is the principal constituent of gold-colored alloys. It contributes gold color; increases the specific gravity; raises the melting point, if that of the alloy is below that of gold; and increases ductility, malleability, corrosion, and stain resistance. Gold produces heat-treatable compositions with copper, platinum, and zinc. It is useful in mass fractions of 25–100%.

Copper [7440-50-8], Cu, produces a reddish color and reduces the melting point of the alloy. It produces heat-treatable compositions with gold, platinum, and palladium that result in increased hardness, strength, and generally improved physical properties. The tarnish resistance of the alloy is usually decreased. The gold–copper, Au–Cu, system is the fundamental system of many dental gold alloys. Copper has a useful mass fraction range of 0–20%.

Silver [7440-22-4], Ag, alters the color of binary gold–silver alloys to green-gold and, as the percentage of silver increases, to a silver-colored alloy. In gold–silver alloys containing copper and platinum, silver improves the color of the alloy. Silver also improves ductility and exerts an influence upon the rate and intensity of response to heat treatment. Excessive silver content may cause alloys to absorb a large volume of oxygen while molten. Upon solidification of the alloy this absorbed gas may be released and cause spitting or gas inclusions in the metal. This problem is seldom evident within the mass fraction range of 0–20% silver.

Platinum [7440-06-4], Pt, detracts from the gold color, producing an undesirable grayish-red color; increased platinum produces a platinum-colored alloy. Platinum increases strength, proportional limit, and solidification temperatures; reduces grain size; and produces a heat-treatable alloy with gold. It has a useful mass fraction range of 0–18%.

Palladium [7440-05-3], Pd, produces a large color change, ie, mass fractions of 5–6% may produce a white alloy. It rapidly raises the melting point; increases hardness, tensile strength, and proportional limit of gold–copper–silver alloys; and slightly lowers tarnish resistance. Palladium absorbs large volumes of oxygen and hydrogen when molten, which may cause inclusions in the alloy from oxidized elements, and upon solidification renders a casting porous or defective due to the expulsion of those gases.

Zinc [7440-66-6], Zn, whitens gold alloys, but not rapidly. It lowers the melting point rapidly with increased additions, increases the hardness of gold alloys, increases strength and elastic limit slightly, reduces surface tension, and protects other elements from oxidation. The useful amount is generally <1%, and when present in high percentage, zinc embrittles gold alloys.

Iridium [7439-88-5], Ir, and rhodium [7440-16-6], Rh, individually increase corrosion resistance, hardness, and strength of platinum alloys. They can be used to reduce grain size (160).

Indium [7440-74-6], In, is sometimes used as a scavenger of oxygen. It promotes uniform grain size and casting fluidity.

Iron [7439-89-6], Fe, is used to produce age-hardening in Au–Pd–Pt alloys at temperatures involved in ceramo–metallic techniques (161).

Tin [7440-31-5], Sn, is used up to a mass fraction of 4.6% to aid in porcelain fused to metal processes and to decrease the melting point of gold solders.

Lead, Pb, and mercury, Hg, are contaminants.

6.7. Gold Alloys, Cast Types.

Four types of gold alloys have been recognized for cast dental restorations (Table 5). They provide desired material for specific uses. The appropriate specifications for these alloys is ANSI/ADA specification No. 5.

Type I, soft alloys (20–22-kt golds), are used for inlays of simpler nonstress-bearing types. Type I gold alloys can be burnished, and are not heat

Table 5. **Mechanical Properties of Cast Gold Alloys**[a]

Gold cast	Yield strength[b], MPa[c]	Minimum elongation, %	Vickers hardness, HV
type I	140 max	18	50–90
type II	140–200	18	40–120
type III	200–340	12	120–150
type IV[d]	340 min (500)	10 (2)	150[e]

[a] Values given for annealed specimens, 0.1% offset.
[b] Minimum–maximum values.
[c] To convert MPa to psi, multiply by 145.
[d] Maximum value for the hardened state given in parentheses.
[e] Minimum value, 300 HV has been reported.

treatable. They are composed essentially of gold–silver–copper with minor modifying additions, eg, zinc.

Type II, medium-hard alloys, are harder, stronger, and have lower elongation than type I alloys. They are used for moderate stress application, eg, three-quarter crowns, abutments, pontics, full crowns, and saddles. The type II gold alloys are difficult to burnish, and can usually be heat treated.

Type III, hard alloys, are the hardest, strongest, and least ductile of the inlay casting alloys. Their use is indicated for restorations required to resist large forces such as three-quarter crowns, abutments, pontics, supports for appliances, and precision-fitting inlays. These alloys cannot be burnished, and heat treatment improves all their physical properties, except ductility, which is greatly decreased.

Type IV, extra hard (partial denture) alloys, are indicated where high strength, hardness, and stiffness are required. They are harder, stronger, and less ductile than the type III alloys. These partial-denture alloys are used for cast removable partial dentures, precision-cast fixed bridges, certain three-quarter crowns, saddles, bars, arches, and clasps.

Casting gold alloy should be meltable in an air–gas flame, meltable and castable without much change in composition, very fluid when melted with low surface tension, and not absorb gases or oxidize excessively in the molten state. The total shrinkage, from the beginning of solidification to room temperature, should be small. Casting gold alloy should have pleasing, acceptable color, and physical properties, ie, hardness, tensile strength, elastic limit, and fatigue resistance, adequate for the intended use. These physical properties should respond to heat treatment. Finally, casting gold alloy should show resistance to all corrosion or tarnish in the mouth (162) and should be passive (163).

Table 6 gives the range of compositions of the four types of dental gold casting alloys, using both yellow and white golds. Compositional requirements have been removed and replaced by biological testing according to ANSI/ADA specification No. 41. The composition requirements listed are those prior to 1988. In addition to the elements listed, In, Ni, Sn, Ir, and Co have been used as modifying metals.

Table 6. **Compositions of Cast Dental Gold Alloys, wt %**[a]

Type	Characteristic	Au	Ag	Cu	Pd	Pt	Zn
		Yellow golds					
I	soft	79–92.5	3–12	2–4.5	0.5[b]	0.5[b]	0.5[b]
II	medium	75–78	12–14.5	7–10	1–4	1	0.5
III	hard	62–78	8–26	8–11	2–4[b]	3	1
IV	extra hard[c]	60–71.5	4.5–20	11–16	5[b]	8.5[b]	1–2
		White golds					
III	hard	65–70	7–12	6–10	10–12	4	1–2
IV	extra hard[c,d]	60–65	10–15	9–12	6–10	4.8	1–2
IV	extra hard[c,e]	23–30	25–30	20–25	15–20	3–7	0.5–1.5

[a] Table adapted from Ref. 164.
[b] Value given is maximum value.
[c] Used for partial dentures.
[d] Yellowish white.
[e] Very white.

Table 7 gives the composition of gold alloys available for commercial use. The average coefficient of thermal expansion for the first six alloys listed is $(14-15) \times 10^{-6}/°\mathrm{C}$ from room temperature to $\sim 1000°\mathrm{C}$; two opaque porcelains used with them have thermal coefficients of expansion of 6.45 and $7.88 \times 10^{-6}/°\mathrm{C}$ from room temperature to 820°C (91). The HV values of these alloys are 109–193, and the tensile strengths are 464–509 MPa ($67-74 \times 10^3$ psi). For the last four alloys in Table 7, the HV values are 102–216, and the tensile strengths are 358–662 MPa ($52-96 \times 10^3$ psi), depending on thermal history.

Gold Alloys, Wrought Type. Two types of wrought gold alloys were formerly recognized by the ADA specification No. 7 for the fabrication of orthodontic and prosthetic dental appliances, ie, type I, high noble metal alloys, and type II, low noble metal alloys (gold color). Alloys of this type are seldom used in the United States; they have been replaced by stainless steels and nickel–titanium alloys.

Table 7. **Composition of Gold-Based Alloys Used in Ceramo–Metallic Prostheses, wt %**

Trade name	Au	Ag	Pt	Pd	In	Other
Amator[a]	82.6	2.4	12.4	0.8		1.8 Zn
Amator 2[a]	82.0	2.5	11.9	1.8	1.8	
Ceramco[a]	87.7	1.0	6.1	4.6	0.6	
Degudent[a]	84.8	1.3	7.9	4.6	1.25	0.15 Ir
Herador[a]	83.2		15.6		0.9	0.3 Ir
V4[a]	81.5	2.7	11.7	2.3	1.8	3.0 Ir
Ceramco[b]	87.5	0.9	4.2	6.7		0.3 Fe, 0.4 Sn
Ceramco “O”[b]	87.1	1.3	4.6	6.5		0.3 Fe, 0.2 Sn
Cameo[b]	51.5	12.1		29.5	6.8	
Vivostar[c]	54.2	15.7	1	25.4		4.6 Sn

[a] Ref. 165.
[b] Ref. 166.
[c] Ref. 167.

6.8. Platinum and Platinum Alloys. Platinum has excellent resistance to strong acids and, at elevated temperatures, to oxidation. Under reducing conditions at high temperatures it must be protected from low fusing elements or their oxides. Easily reduced metals at high temperatures may form low fusing alloys with platinum.

Carbon or silicon may produce brittleness and loss of useful properties. Caustic alkalies and many alkaline earth salts or hydroxides may attack platinum at elevated temperatures.

Platinum, a bluish-white metal, is soft, tough, ductile, and malleable. It has a melting point of 1773–C. The coefficient of thermal expansion is $9 \times 10^{-6}/^{\circ}C$.

Platinum has many uses in dentistry. Pure platinum foil serves as the matrix in the construction of fused-porcelain restorations. Platinum foil may be laminated with gold foil for cold-welded foil restorations. Platinum wire has found use as retention posts and pins in crown and bridge restorations. Heating elements and thermocouples in high fusing porcelain furnaces are usually made of platinum or its alloys (see PLATINUM-GROUP METALS, COMPOUNDS).

Platinum, as an alloying element, is used in many dental casting golds (Tables 6 and 7) to improve hardness and elastic qualities. Platinum in combination with palladium and iridium has limited use for dental pins and wires.

6.9. Palladium and Palladium Alloys. Palladium is not used in the pure state in dentistry. However, it is a useful component of many gold casting alloys, as shown in Tables 6 and 7.

Alloys based on Ag–Pd have been used for a number of years and are available from most gold alloy manufacturers (168). The palladium content is a mass fraction of 22–50%; silver content is from 35 to 66%. Minor amounts of Zn, In, or Sn are often present to increase fluidity. Both In and Sn form intermetallic compounds with both Pd and Ag and, therefore, some of the commercial alloys are susceptible to age hardening (169). These alloys are somewhat difficult to fabricate and require meticulous processing. They may also produce a greenish discoloration when they are fused with porcelain veneers. Nevertheless, clinical experience generally has been satisfactory.

6.10. Base-Metal Alloys. Base-metal casting alloys are inferior to gold-based casting alloys in some dental applications but are superior in others. Gold-based alloys are preferred for inlay, crown and bridge castings because the wax pattern can be reproduced more accurately in the casting. Gold alloys are lower melting and easier to use; restorations can be fabricated conveniently. Up to the 1980s, the noble metal alloys seemed superior for use with dental porcelains. However, base-metal alloys and low noble alloys have made inroads into dentistry at the expense of the noble metal alloys. Base-metal alloys containing sufficient chromium to make them passive have essentially displaced gold-based alloys in the casting of skeletons for partial dentures (170–173). Most partial dentures are fabricated in commercial dental laboratories from cobalt–chromium, Co–Cr, nickel–chromium, Ni–Cr, or Ni–Cr–Co alloys (Table 8). Some inlays, crowns, or bridges are made of non-noble alloys. Wrought stainless steels of the 18Cr–8Ni type are used infrequently as denture bases but have supplanted gold alloys in orthodontic appliances for preventing and correcting malocclusion and associated dental and facial disharmonies. Chromium-containing alloys and titanium-based alloys are the only base metal alloys that can be

Table 8. **Composition of Base-Metal Alloys for Removable Partial Dentures,**[a]**%**

Trade name	Co	Cr	Ni	Mo	Fe	Mn	Si	C	Other
JD	67.0	26.0	0.5	5.0	1.0	1.0			
Vitallium[b]	62.5	30.0		5.0	1.0	0.5	0.5	0.5	
Platinore[b]	60.7	26.7	2.7	5.8	2.6	0.5	0.6	0.3	0.3 W, 0.1 Pt
Niranium N/N[b]	64.7	27.5		5.4	0.4	0.5	1.0	0.4	
Ticonium hard	8.0	16.0	63.0	5.0		3.5			3.0 Al, 1.4 Be
Durallium LG	55.0	27.0	14.0		2.0	1.0	1.0		
Crutanium[c,d]		5–15	5–15	0.3	1.0	4–10			
A[e]	43.5	21.6	20.1	7.0	0.25	3.0	0.35	0.05	3.5 Cu, 0.9 Be
C[e]		13.0	68	4.5	2.5				1 Ti, 6 Al, 2 Nb
E[e]	52.0	26.1	14.2	4.0	1.2	0.7	0.58	0.22	

[a] These alloys have a minimum yield strength (0.1% offset) of 500 MPa (73,000 psi), a minimum modulus of elasticity of 172 MPa (25,000 psi), and a minimum 1.5% elongation.

[b] Ref. 174.

[c] Refs. 175 and 176.

[d] Balance of alloy is Co.

[e] Ref. 177.

used with dental techniques and have almost no tarnish or corrosion in the mouth.

6.11. Cobalt–Chromium Alloys. Co–Cr and Ni–Cr alloys are used predominately for the casting of removable partial dentures; fixed partial dentures (bridges), and crowns. Because of high hardness, corrosion resistance, and wear resistance, cobalt–chromium alloys are used for bite adjustments and as serrated inserts in plastic teeth used in full dentures. These alloys are well tolerated by the body and also are used for dental implants and orthopedic implant alloys.

Removable partial dentures are partial dentures that restore function, maintain surrounding dentition in a stable state, and are removable. They require no (or minimal) dental surgery on neighboring teeth, as opposed to the removal of sound, healthy enamel for the insertion of fixed partial dentures (FPDs). They often are a less aesthetically pleasing restoration than FPDs coupled with the nuisance of removing them at night and a psychologically less satisfying lack-of-permanency.

ANSI/ADA specification No. 14 provides a requirement for removable partial dentures of a combined minimum mass fraction of 85% of chromium, cobalt, and nickel or, for alloys failing to meet that minimum, at least a mass fraction of 20% chromium. Biocompatibility is demonstrated by passing the pertinent criteria of ANSI/ADA specification No. 41, Recommended Standard Practices for Biological Evaluation of Dental Materials.

Because Co–Cr alloys are difficult to adjust and grind, they find limited use in fixed partial dentures, crowns, or inlays. ANSI/ADA specification No. 38 covers alloys used in conjunction with dental porcelains.

The use of Co–Cr alloys is attributed to their light weight, low cost, stiffness, and general passivity (see CHROMIUM AND CHROMIUM ALLOYS). The high temperatures necessary for proper casting fluidity precludes their use in

Table 9. **Comparison of Cast Dental Alloys**

Alloys	Linear casting shrinkage, %[a]	Density, g/cm^3	Modulus of elasticity, MPa[b]
cast gold	1.2	17–18	95,000
cobalt–chromium	2.3[c]	8–9	216,000
titanium alloys	1.7–2.0	4.5	117,000

[a] Values affected by size and shape of casting. No fixed value for metals.

[b] To convert MPa to psi, multiply by 145.

[c] Ref. 158.

gypsum-bonded investments; silicate or phosphate-bonded investments had to be developed. Special materials and techniques have evolved to fabricate restorations from the cobalt–chromium alloys, and have essentially restricted the use of these alloys to commercial dental laboratories. Some progress has been made in the development of alloys with lower melting ranges that can be cast in the gypsum-bonded investments using the customary techniques.

Table 9 lists select properties of Co–Cr alloys. It is generally conceded that the casting shrinkage of the cobalt–chromium alloys is greater than that of the gold alloys. The lower density of the base metal alloys provides a weight advantage over the higher density gold alloys in certain types of bulky restorations. Cobalt–chromium alloys have Knoop hardnesses of 310–415.

6.12. Nickel–Chromium Alloys. Because gold is so expensive, there was an intensive development in the 1970s and 1980s of alloys based mostly on nickel–chromium with as many as eight modifying elements. Nickel–chromium alloys cannot be cast as easily or as accurately as gold-based alloys, nor can they be fabricated as easily by soldering. A modification of the manufacturer's techniques, ie, using hand instead of mechanical spatulation of the investments, a dry asbestos liner in the casting ring, and hygroscopic expansion, was shown in one study to produce oversize crown castings (0.00–0.45%) (179). Castings made by the manufacturers were consistently undersize −0.04 to −0.18%.

The Ni–Cr alloys primarily contain nickel with a mass fraction of 12% or more of chromium. They are used mainly for the casting of fixed partial dentures (bridges), crowns, or inlays, either with or without aesthetic porcelain or plastic veneers (Table 10). However, some of them are used for removable partial dentures.

No data are available on casting shrinkage, but in alloys having the same approximate nickel and chromium contents, pattern makers usually make allowances for roughly 3% linear casting shrinkage.

Because the melting temperature range of Ni–Cr alloy is 1220–1345°C, it is necessary to heat the investment molds to 800–935°C. The castings should not be pickled in acid because of their high nickel content and should be cleaned by sandblasting. The alloys are generally hard and are difficult to finish and to abrade for clinical adjustment in the mouth.

There is no meaningful correlation between laboratory corrosion tests and clinical performance, but high *in vitro* corrosion rates on several high nickel dental prosthetic alloys (183), together with the prevalence of allergy to nickel caused by plated jewelry, gives cause for caution.

Table 10. **Composition of Base-Metal Alloys for Crowns and Bridges**[a]**,%**

Trade name	Ni	Cr	Fe	Al	Mo	Si	Mn	Co	Other
Rexillium III	76.0	13.0		3.0	6.0			0.4	1.8 Be
Nobil Ceram[b]	80.75	12.58		3.42	1.53		0.13		0.37 Be, 0.15 Cu
Qualimet[b]	78.51	19.47	0.43	0.21		1.10			
Wiron S[b]	68.96	16.54	0.37	4.15	5.10	0.83	3.05	0.42	
Microbond NP2	66.0	13.0	5.0		7.0	0.75	0.1		
Neydium[c]	79.0	11.0	0.05	1.8	3.6	1.1			3.2 Pd
Ceramalloy[c]	70.0	20.0	0.2		5.6	3.96		0.22	0.02 Ti, 0.09 C
Ticon[d]	70.0	16.0	0.8	3.0	4.1	0.5	3.9	0.9	0.03 C
Microbond NP[d]	76.0	13.8		3.0		5.0	1.1	0.1	

[a] ANSI/ADA specification no. 38 requires a minimum yield strength (0.2% offset) of 250 MPa (36,000 psi) and a minimum elongation of 2% for ceramo–metallic alloys.

[b] Ref. 180. Elements checked but not found: Zn, Cd, In, Bi, Sb, As, Ti, Ga, Ge, Pb, V, W, Nb, and Ta.

[c] Ref. 181.

[d] Ref. 182.

6.13. Titanium-Based Casting and Wrought Alloys. Titanium-based alloys offer an attractive alternative to gold alloys and to the base-metal alloys that contain nickel or chromium. On a volume basis the cost of titanium is roughly comparable to that of the chromium-containing alloys, but the price of titanium tends to be more stable because its ores are abundant and widely distributed (see TITANIUM AND TITANIUM ALLOYS).

Many of the technical problems of fabrication that formerly inhibited the use of titanium alloys in dental castings (184–186) have been effectively solved, and titanium castings may now be obtained for virtually any type of dental appliance at prices that are increasingly competitive. Special induction or electric arc furnaces are necessary for casting titanium alloys. This specialized equipment has, until now, been available in only a limited number of commercial dental laboratories. However, the relatively high price of this equipment, attributed to development costs, is expected to decline significantly; this should help to improve the general availability of cast titanium appliances.

The property most frequently cited in connection with the use of Ti dental or medical appliances is titanium's unique biocompatibility. This helps practitioners avoid occasional allergic reactions that occur with nickel or chromium alloys, and removes concerns about the toxic or carcinogenic potential of appliances that contain nickel, chromium, or beryllium. Wrought alloys of titanium are used for orthodontic wires because of their unique elastic properties, and are used to fabricate most dental implants.

Arc-melted titanium has excellent fluidity and lends itself readily to the creation of thin margins. Sprues must be carefully placed and abundant venting provided, however, to avoid holes and porosity in the casting. The detection of defects by radiography is facilitated by the low density of titanium, and conventional dental X-ray units may be used in many cases.

The relatively high casting temperatures of titanium-based alloys and the chemical reactivity of molten titanium would seem to indicate the use of special investments based on magnesia or zirconia, but more recent experience indicates that certain commercial phosphate-bonded investments produce satisfactory results (187–189). Some progress has been made in producing titanium alloys with lower melting ranges that can be cast in gypsum-bonded investments (190). It now appears that ANSI/ADA specification for dental casting alloys can apply to the titanium-based alloys, but there are some areas that still require clarification.

Titanium castings may be soldered and welded using appropriate techniques. The relatively high electrical resistivity of this metal combined with its relatively low thermal conductivity permits heat to be effectively focused where it is needed rather than spread out into adjoining areas. Electrical spot welding is used to join portions of the castings, eg, as in the construction of bridges (see WELDING). The spot welding can be done intraorally without damage to adjoining tissues (191,192) because the tissues do not experience high temperatures. Intraoral spot welding should not be attempted on metals other than titanium because metals that have a higher thermal conductivity than titanium may conduct excessive heat to the tissues.

6.14. Properties. The casting shrinkage of titanium alloys is comparable, but not identical, to that of chromium-containing alloys, and greater than that of gold alloys (Table 5). The ability of commercially pure titanium to be cast in relatively thin sections, together with its low density, permits light-weight appliances in bulky restorations.

The Vickers hardness of Ti alloys is strongly dependent on the presence of elements such as oxygen, nitrogen, and carbon that dissolve in hot or molten titanium through contact with residual air molecules or with the surface of refractory molds. A relatively thin (100–250 μm) surface layer is often observed on cast surfaces (193,194) having high Vickers hardness values, ie, >350, often associated with brittleness in Ti alloys. The outer portions of this surface layer, which possess the highest hardness values, are ordinarily removed by normal grinding and polishing operations performed on the castings. Below this surface layer, typical Vickers hardness values of 130–180 commonly are observed. Under optimum conditions, castings of commercially pure titanium show yield strengths of 400–500 MPa and ultimate strengths of 490–650 MPa with elongations of 20–30%. Yield strengths and tensile strengths are increased by the presence of dissolved elements.

Titanium should be melted and cast under carefully controlled and optimum conditions. The higher elongation values of titanium castings reflect the superior ductility of titanium. Ductile clasp arms of titanium castings can withstand relatively large bending adjustments without fracture.

The stiffness of pure titanium can be increased slightly by alloying; alloys such as Ti-6Al-4V may be specified for partial dentures requiring additional rigidity. Titanium appliances do not tarnish or corrode in the mouth, have no metallic taste, and are easy to clean. The relatively low thermal conductivity of titanium (relatively close to that of tooth enamel) gives these appliances a seemingly natural feel in the mouth and minimizes thermal sensitivity (195).

6.15. Composition. Acceptable composition limits for titanium dental castings have not yet been established, but current practice favors the use of commercially pure or unalloyed titanium. Unalloyed titanium is sold in four grades of purity with grade 1 being the purest and grade 4 the least pure.

ASTM specifications govern the maximum allowable content of certain critical elements in each grade. Oxygen is by far the most critical solute element in determining the properties of titanium because of its tendency to produce brittleness. Hardness is a sensitive indicator of the oxygen content of titanium, and limitations on maximum hardness are likely to be part of any future specification.

A need for room temperature ductility motivates the choice of pure titanium rather than a titanium alloy. In appliances requiring greater rigidity or strength, a certain amount of ductility may be sacrificed for extra strength, and a titanium alloy, such as Ti-6Al-4V, may be more suitable.

Oxygen, nitrogen, and carbon promote brittle behavior in all titanium alloys, and it is important to control the cumulative effect of these three elements during casting operations.

6.16. Uses. The use of titanium alloys for cast partial dentures offers light weight, low cost, good ductility, adequate stiffness, chemical passivity toward foods and oral fluids, and biocompatibility with the oral tissues.

Casting of Ti alloys for crowns and bridges is done in investment molds that have been allowed to cool almost to room temperatures after firing. The castings are cleaned in electrolytic solutions or in special chemical polishing solutions that impart a bright smooth surface finish to the casting (196,197).

Special low fusing porcelain veneers are applied to pure (unalloyed) titanium dental castings. It is important that firing be done either in a vacuum or inert atmosphere to protect the metal surface from excessive oxidation. The strength of the metal–ceramic bond is apparently adequate although the bonding is thought to involve primarily a mechanical rather than a chemical component.

6.17. Nickel-Titanium Alloys. Nickel–titanium alloys are used in dentistry primarily as orthodontic wire and for root canal preparation instruments. The alloy is commonly referred to as Nitinol and the two primary uses take advantage of two differing and unique properties of this alloy, shape memory and superelasticity. The metal is a simple alloy of nickel and titanium with approximate mass fractions of 50% of each of these metals. Slight adjustments in the ratio of these two components can result in large changes in the properties of the alloy. The alloy is generally classified by the temperature at which it undergoes transformation from an austenitic crystal structure to martensite. This temperature is referred to as the Active Austenite Finish Temperature (Active A_f).

Shape memory is the ability of the alloy to recover its starting shape upon heating above the transformation temperature. When in its martensitic form, nickel–titanium can be easily bent or shaped. When heated through its transformation temperature, it reverts back to its austenitic form and recovers its original shape. This recovery can produce force used to orthodontically move teeth and can occur over a very narrow range of temperature change.

The most common form of nickel–titanium used in dentistry is orthodontic wire, which was introduced in the early 1970s (198–200) Nickel–titanium orthodontic wires take advantage of the shape memory properties of the alloy. Wire alloys are chosen with Active A_f temperatures just at or slightly below physiologic temperature (37°C). Preformed arch wires of martensitic alloy are selected that have a conformation that matches the desired dental arch shape. This wire is then bent to conform to the existing shape of the dental arch and placed into the orthodontic brackets. Body heat then forces the alloy to transform to its original austenitic shape and this shape change, or shape memory produces the stress required to induce orthodontic tooth movement. The degree of stress can be controlled by the wire size, amount of movement on transformation, and the Active A_f temperature of the alloy (201).

The second most common use of nickel–titanium in dentistry is for endodontic cutting instruments. These instruments are mechanically or manually driven files and reamers used to shape and enlarge the pulp canal in tooth roots (202). These instruments take advantage of the second unique property of nickel–titanium alloys, superelasticity.

Superelasticity is the ability of an alloy to undergo stress-induced transformation from an austenitic crystal structure to martensitic. This transformation occurs above the normal temperature where martensite exists in the alloy and it immediately reverts back into the undeformed austenitic form of the alloy. This ability results in very high levels of flexibility, kink resistance, and gives the metal a unique springiness or rubber-like elasticity.

Endodontic files and reamers undergo a high degree of torsional and flexural deformation and are often strained beyond yield or subject to fatigue failure. Nickel–titanium instruments are fabricated from alloys where the Active A_f is $\sim$20°C. The superelastic properties can occur over a temperature window well above body temperature (37°C) allowing the instruments to bend to conform to the tight curves of the canals, yet return to their original shape when removed from the canal. These instruments can undergo much more deformation and cyclic strain than conventional stainless steel instruments (203). The instruments are manufactured by grinding or shaping nickel–titanium wire to the correct degree of taper and to the desired cross-section for cutting.

Nickel–titanium has also been used as a dental casting alloy (204), as a reinforcing post in root canal treated teeth (205), and as a root canal filling material (206), but none of these are common dental uses.

6.18. Stainless Steels (Iron-Based Alloys). The great abundance of iron and the numerous corrosion resistant iron-based alloys, such as stainless steels, have limited uses as restorative dental materials. Dental restorative alloys evolved from gold casting alloys, entrenching the gold casting technology as a preferred method of fabrication of prostheses. The strength and performance requirements for cast alloy prostheses led to the use of alloys, other than stainless steels, from the 1930–1970s as more desirable, functional replacements for more expensive gold alloys. The iron-based casting alloys of that time did not provide the needed corrosion resistance, especially against pitting and crevice corrosion, casting ease, compatibility with dental porcelains, high temperature oxidation resistance, and surface appearance as did the cobalt–chromium and nickel–chromium alloys.

Today, stainless steels find their primary use in wrought form for temporary applications such as orthodontic wires, brackets, and temporary crowns. The temporary crowns are obtained in preformed sizes/shapes and then are trimmed by the dentist with shears to fit over prepared teeth that are awaiting the fabrication of permanent cast crowns.

Orthodontic wires and brackets owe their strength to work hardening during their formation, contrary to the heat treatment process used for wrought gold alloy wires. The 18–8 stainless steels are the most commonly used alloys; their strength, ductility, and elastic modulus are generally higher than the wrought gold alloys. Because the strength achieved by work hardening is lost during the application of heat from a torch, stainless steel orthodontic appliances must be carefully soldered to limit the amount and extent of heat applied along the appliance.

The 18–8 stainless steels contain mass fractions of 17–19% chromium, 7–9% nickel, 0.08–0.2% carbon, 0.75% silicon [7440-21-3] (max), and 0.60% manganese [7439-96-5] (max). Other alloys used for orthodontic wires and brackets contain mass fractions of 80% Ni–20% Cr alloy; 40% Co, 20% Cr, 15% Ni, and 7% Mo alloy; and nickel–titanium alloy, ie, mass fractions 55% Ni, 1.5% Co, and the balance Ti.

6.19. Aluminum. Aluminum [7429-90-5] and aluminum alloys play a limited role in dental applications. Aluminum is used to make lightweight impression trays, articulator facebows, and radiograph alignment holders. Soft aluminum is used as preformed temporary crowns where shaping and bending can be easily done at chairside. An aluminum-containing alloy, consisting of approximate mass fractions of 12% aluminum, 80% copper, 5% iron, 3% nickel, and the remaining magnesium having trace amounts of silica, silver, and chromium, has been used as a low cost crown and bridge casting alloy in some foreign countries, but has not seen extensive utilization in the United States (207).

6.20. Electrodeposited Metals. Electrodeposited, electroplated, or electroformed metals are used to produce an accurate metal-clad die, or cast, from a compound polysulfide rubber, or silicone rubber impression (see ELECTROPLATING). Copper and silver are used to give accurate dies and casts with an improved working surface having strength, abrasion resistance, and chip resistance. The acidic copper sulfate plating bath has been more compatible with the compound and silicone rubber impressions than with the polysulfide, eg, Thiokol, rubber impressions. The impression surfaces are rendered conductive by a coating of powdered graphite, powdered metallic copper, or powdered metallic silver. Control of plating bath composition, careful application of the conductive layer to the impression surface, cleanliness, current densities, and other factors are essential to achieving consistent and successful results. Usually, 12–18 h is required to produce a satisfactory metal deposit of 25–30 μm thickness. The metal shell obtained must be filled or reinforced with some solid base to prevent distortion or collapse. Artificial stone or self-curing resins may be used for this purpose, before the metal shell is removed from the impression.

The metal-plating baths used are acidic copper sulfate and alkaline silver cyanide. Acid contamination in the alkaline silver cyanide bath will release extremely poisonous hydrogen cyanide gas. For this reason, the two plating setups should be isolated from each other. Both plating baths should be well ventilated and covered when not in use to reduce evaporation losses and contamination.

Copper-plating bath compositions of various types have been used. A typical bath formulation consists of 200-g copper sulfate crystals, 30-mL conc. sulfuric acid, 2-mL phenylsulfonic acid, and 1000-mL distilled water. A pure copper anode may be used; a copper anode containing a trace of phosphorus reduces sludge accumulation in the plating bath.

Silver-plating bath compositions are somewhat variable; a typical composition contains 36-g silver cyanide, 60-g potassium cyanide, 45-g potassium carbonate, and 1000-mL distilled water. A pure silver anode is required (208).

6.21. Solders and Fluxes. Dental solders, like all dental alloys, must be biologically tolerated in the oral environment. They are specifically designed or employed for the purpose of fusing two pieces of dental alloy through the use of intermediate low temperature filler metal.

There are several types of joining processes that involve the use of molten filler metal and the temperatures employed in the joining operations, ie, soldering, welding, and brazing distinguish them. Alloys used in soldering have the lowest melting points, with liquidus temperatures $<427^\circ$C. Brazing alloys have liquidus temperatures $>427^\circ$C, and welding alloys have temperatures close to those of the metal pieces to be joined. The soldering process involves the use of solders and fluxes. Solders are materials that fuse and join two dental alloys together. Fluxes coat the surfaces of alloys to be joined in order to produce clean metal surfaces at the temperatures of joining. This enables the molten solder to fuse with those surfaces.

6.22. Solders. Modern dental solders are made from mostly corrosion-resistant, nontoxic metals. Minimal quantities of tin and other elements are often added. Each solder is used for specific applications (209–217); typical compositions and properties of solders used in dentistry are presented in Table 11. Most of the ingredients in solders are resistant to corrosion, and alloying them with other ingredients render the alloy safe for use in appliances placed in the oral environment. Silver solders corrode, but are used only for temporary appliances. Available products do not contain cadmium, although cadmium was an ingredient of some silver solders up to ~1980.

Gold, platinum, palladium, and silver are the principal components of most of the solders used for joining both noble and base metal alloys. Some solders for base metal alloys also contain nickel, chromium, and/or cobalt as primary ingredients.

A satisfactory solder must not corrode or tarnish in the mouth fluids, ie, it must be sufficiently noble in composition, and its composition must be such that its solution potential approximates that of the metal upon which it is used. A solder's fusion temperature must be lower (by at least 100°C) than that of the alloy upon which it is employed so that the alloy is not fused during soldering. In the case of wires, the solder's melting temperature must be less than the recrystallization temperature of the metal.

Solders should flow promptly and smoothly over the surfaces of the parts to be joined. This property depends on the surface tension, viscosity, and adhesive properties of the molten solder. Finally, the color of a solder should match that of the metal employed, and its physical properties should be at least as good as those of the metal in order for the joint not to be a source of weakness (170).

6.23. Fluxes. Fluxes, composed mostly of salts or oxides of metals, serve to protect underlying metal from the air. This prevents the formation of surface oxides that impede fusion and the formation of a strong solder joint. Fluxes may also act to selectively leach elements from the surface of the underlying metal. The result is a surface free of obstacles to fusion, and of a composition readily wetted by the solder.

Table 11. **Dental Solder Compositions and Applications**[a]

Solder type	Compositional range, wt %									Temperature ranges °C
	Au	Ag	Cu	Zn	Pd	Ni	Cr	Co	Sn	
low karat	45	25–35	15–20	0–9					0–1	691–816
general purpose	50–75	10–25	10–22	4–8		0–6			0–2	724–835
high karat	80	3–10	8–12	0–1	0–8				0–1	746–871
nonprecious alloy	30–40				30–40	25–40	0–20			≥1150
						70–85[b,c]		10–15		
						60–90[c]	3–30	3–30		
						15–25	5–30	40–60		
silver		42–67	15–40	7–20		0–3				~607–688
porcelain–gold	60–90	10–30	5–10	1–3	5–10	0–1			1–2	≥1065

[a] Manufacturers of these include: J. F. Jelenko Co., Armonk, N.Y.; Austenal Dental Products, Chicago; Ivoclar North America, Amherst, N.Y.; J. M. Ney, Bloomfield, Conn.; Johnson & Johnson Dental Products Co., East Windsor, N.J.; Unitek Co., Monrovia, Calif.; and Masel Orthodontics, Bristol, Pa.

[b] Also contains 5–10% Fe.

[c] Also contains 0–3% Al.

Fluxes also contain agents that facilitate application, such as petroleum jelly or alcohol. These burn or evaporate at elevated temperatures before the soldering temperature is attained, leaving behind a uniform coating of flux. Fluxes become molten before the joining temperature is reached. The molten flux flows or spreads to form a continuous coating over the surfaces to which they have been applied.

6.24. Uses. Dental solders and fluxes are used to join orthodontic wires, fasten attachments to partial dentures, repair castings units, and join crown and bridge units either before or after the application of porcelain. They may also be used to repair fixed and removable dental appliances.

A solder and its flux are designed to function as a system for joining specific alloys. The first step in any soldering operation is to make certain that the flux and solder used are those recommended for the alloy to be joined. Next, the pieces to be joined must be thoroughly cleaned. Abrasive blasting or grinding with a sandpaper disk are two common techniques. Once the surfaces have been cleaned, they should be aligned using an acceptable procedure such as an occlusal index. The adjoining parts should be contoured to provide only a small gap between the surfaces to be joined. A space of $\sim$0.1 mm is desirable. Alignment of the parts on dies or with clamps, followed by stabilization with soldering investment, is appropriate. Flux should then be applied liberally to the surfaces. In cases involving deep or inaccessible joints, a thin coating of flux should be applied before the alignment process. Fluxing agents frequently tend to flow beyond the areas intended for joining, causing the solder to fill or obliterate carefully developed contours in cast restorations. The use of an antiflux such as graphite from a soft lead pencil or jeweler's rouge, softened by solvents such as heptane, can contain the flow of the flux and solder. These materials are applied on the surfaces on which no solder is desired.

Heat is applied with a torch or by placing the appliance into a furnace after the proper surfaces have been coated with flux. It is important to heat the parts slowly and uniformly to prevent warpage or inaccuracy in the alignment of the parts. If a torch is used, a slightly reducing or neutral brush flame is usually employed. It is applied to bulky regions near the surfaces to be joined, but not directly to them. The flame should consist of a sharply defined blue inner cone and a long diffuse outer region. Heat is applied gently to prevent excessive bubbling of the flux while water and other agents, such as petroleum jelly, are being eliminated. As the temperature increases, the flux melts and flows over the entire surface to be joined. The temperature should be raised until the solder flows when it is touched to the surfaces at the thicker section. The solder should flow freely to the thinner areas and wet both surfaces throughout the joint. After the solder has been applied, the flame is removed and the soldered appliance is allowed to cool under ambient conditions well below the solidification temperature. It may then be cooled more rapidly to near room temperature. The cooling rate should be chosen according to a predetermined plan to develop either a softened or hardened appliance. The appliance is then removed from the fixture and thoroughly cleaned. The cleaning methods used may include a combination of abrasive blasting, soaking in hot water or mild acidic solution, wire brushing, or abrasion with a sandpaper disk. Manufacturer's directions should be followed. Care must be taken to remove the flux as most fluxes contain chemicals or compounds that could interfere with subsequent operations such as veneering with porcelain. Flux that remains on bridgework that is yet to receive porcelain can cause bubbles and discoloration in the porcelain. The porcelain–metal bond may also be affected. The remaining flux may also promote corrosion at the joint.

The same general procedures of heating and cooling are followed in the case of soldering in a furnace, except that a piece of solder can be laid on the junction prior to insertion in the furnace. The solder melts and flows if the upper furnace temperature is properly set. The temperature should be set at $\sim$14–28°C (25–50°F) above the liquidus temperature of the solder or at the manufacturer's recommended soldering temperature.

6.25. Nonconventional Solder Systems. Nonconventional solder systems are developed for use with newer alloys, especially base metal alloys. They are few in number and will probably remain the exception rather than the rule. Some new solder systems consist of metallic particles either pressed to form a rod or suspended in a paste flux. The metallic composition is close to that of the alloy to be joined. If the particles are nonhomogeneous, the solder has particles with melting points lower and higher than that of the alloy. For nonhomogeneous solders, once the flame has been placed on the parts to be joined and the soldering material, it should not be removed until the flow process is completed.

7. Polymeric Dental Materials

7.1. Acrylic Resins. The first synthetic polymer denture material, used throughout much of the twentieth century, was based on the discovery of vulcanized rubber in 1839. Other polymers explored for denture and other dental uses have included celluloid, phenol–formaldehyde resins, and vinyl chloride copolymers. Polystyrene, polycarbonates, polyurethanes, and acrylic resins have also been used for dental polymers. Because of the unique combination of properties, eg, aesthetics and ease of fabrication, acrylic resins based on methyl methacrylate and its polymer and/or copolymers have received the most attention since their introduction in 1937. However, deficiencies include excessive polymerization shrinkage and poor abrasion resistance. Polymers used in dental application should have minimal dimensional changes and stress development during and subsequent to polymerization (218); excellent chemical, physical, and color stability; processability; and biocompatibility and the ability to blend with contiguous tissues.

7.2. Denture Bases. Prosthodontics is involved with materials and techniques for the replacement of missing oral and extraoral maxillofacial tissues. A large part of prosthodontics involves replacing the teeth of edentulous patients, eg, making dentures.

Dentures require accurate fit, reasonable chewing efficiency, and lifelike appearance (219). The chewing efficiency of artificial dentures is one-sixth that of natural dentition (220). Acrylic resins are generally used as powder–liquid formulations for denture base, bone cement, and related applications. Polymerization is achieved by using thermal initiators; photochemically using photoactive initiators and/or sensitizers and either ultraviolet (uv) or visible light irradiation; and at ambient temperatures using chemical initiator–activator systems.

Heat-Cured Resins. For optimum comfort and to impede further loss of chewing efficiency, close adaptation of the denture base to contiguous oral tissues is required, which necessitates custom-made appliances. Nearly all dentures are made of acrylic resins. A wax pattern is used to form a custom denture base in which the denture teeth are embedded. A plaster or dental-stone investment split mold of this wax denture base and teeth is prepared. The wax portion is removed and the surface of the resulting mold cavity is painted with a separating medium, usually an aqueous solution of alginate, to aid in the removal of the cured acrylic from the plaster mold.

A compression-molding process unique to dentistry is used to process the denture base. A monomer–polymer dough or slurry consisting, by volume, of two to three parts polymer beads and one part monomer is packed by pressure into the plaster mold that also contains exactly positioned teeth. The monomer consists of methyl methacrylate (MMA) inhibited by an inhibitor, eg, 4-methoxyphenol [150-76-5] or 2,6-di-*tert*-butyl-4-methylphenol [128-37-0] (BHT); small amounts of plasticizers; and other acrylic monomers, eg, 1–5% of a cross-linking monomer such as ethylene dimethacrylate [97-90-5] or allyl methacrylate [96-05-9]. The solid portion contains suspension-polymerized methyl methacrylate (PMMA) [80-62-6] or methyl acrylate [96-33-3], modified by comonomers such as ethyl [97-63-2], butyl methacrylate [97-88-1], or ethyl acrylate [140-88-5] to increase solubility of acrylic polymeric powders in the monomer and also to control the properties (toughness) of the final prosthetic device; 0.5–1% benzoyl peroxide [94-36-0]; and pigments, dyes, and opacifiers. Particle size and molecular weight distribution of the resin beads control the monomer solubility and the working consistency of the dough mixture. Traces of suspension agent remaining in the beads, eg, poly(acrylic acid) or soluble starch, may prevent wetting of the beads by the monomer. The polymer beads in the dough may contain enough residual benzoyl peroxide to make further addition of this initiator unnecessary. The molecular mass of a typical MMA–PMMA heat-cured acrylic dough can be as high as 1,000,000. Cross-linking agents result in network polymers having improved physical properties.

Most acrylic dentures are fabricated from heat-cured bases. The polymerization rate increases with temperature and is directly proportional to the square root of the concentration of the initiator, eg, benzoyl peroxide. A customary thermal curing cycle for the MMA–PMMA dough is 90 min at 65°C, followed by heating to 100°C for 60 min or processing for 9 h at 74°C in a water bath. The curing cycle generates enough free radicals to give a denture that shows minimum porosity and is fully cured in the thick portions as well as in the thin palate areas. After cooling, the mold assembly in air, the denture is separated from the investing material, trimmed, and polished. Small amounts of red fibrous materials and highly cross-linked, oversized beads of varying translucency often are added to simulate the appearance of oral soft tissue (gingiva). Another mode of thermal curing involves the use of microwave techniques (see MICROWAVE TECHNOLOGY). Whereas microwave processing can significantly reduce the curing cycle, care must be exercised to minimize the introduction of porosity in the denture (221–224).

Ambient Temperature Polymerization (Self-Cure). Polymerization at room temperature is feasible using a suitable redox initiator–accelerator system, ie, 0.3–0.8 wt% of a tertiary aromatic amine accelerator such as *N,N*-(2-hydroxyethyl)-*p*-toluidine [3077-12-1] is added to the monomer, which is slurried with PMMA containing ∼0.2–2% by mass benzoyl peroxide. Rate and degree of polymerization depend on the type and concentration of initiator and accelerator, the particle size, and the nature of the polymer. Processing by compression molding is very similar to the procedure for heat-cured materials. However, because of the relatively short working time of self-curing resins, the number of dentures that can be cured simultaneously using a freshly mixed monomer–polymer dough is limited.

The temperature rise resulting from the exothermic polymerization reaction depends on the initiator system, the amount of dough used, and the type and concentration of monomer in the mixture. Temperatures within the bulk portions of the denture are higher than those at the surface. The resulting polymer is not porous because no excessive evaporation of monomer occurs. Most of the polymerization takes place within 30 min, but postcuring can continue for hours. The denture flask is therefore held under pressure for 2–3 h or longer to ensure a maximum degree of polymerization. Self-curing material usually contains 3–5% by mass of free monomer compared with only 0.2–0.5% found in heat-cured denture base. Excessive amounts of monomer in the finished denture adversely affect its properties. Amine–peroxide cured materials are subject to yellowing due to the presence of the amine accelerator, and have poorer color stability on aging than heat-cured or peroxide–sulfinate cured products; stabilizers and uv absorbers can ameliorate this color instability (see UV STABILIZERS) (225). The main advantage of self-curing resins is their high dimensional accuracy, which results from the lower curing temperature; this alleviates the stresses associated with heat cure. The difference in the thermal expansion of the denture resin and the plaster mold may result in dimensional changes when the mold is subjected to wide temperature ranges during processing. Self-cured dentures have better dimensional accuracy (226,227), but heat-cured dentures are also clinically acceptable.

Fluid or Pour-Type Resins. Fluid or pour-type resins are modified acrylic systems that can be cured chemically. A fine-particle-size polymer powder consisting mostly of high molecular weight material is preferred to prevent a rapid increase in viscosity during mixing and pouring. Polymerization occurs in flexible agar, alginate, or soft gypsum molds. The fluid resin is mixed and poured into the mold through sprues and cured in a pressurized flask at ambient temperatures for 30 min. This technique simplifies the laboratory procedure and reduces costs (228). However, extensive shrinkage of the resin tends to pull the posterior teeth from the resilient mold and out of the occlusal pattern; flow of the fluid resin over the necks of the anterior teeth is incomplete and bonding to cross-linked plastic teeth is inadequate (229). The technique can be improved by treating the denture teeth with a 50:50 mixture of dichloromethane [75-09-2] and MMA by mass (230). With proper precaution and careful attention to detail, clinically acceptable dentures can be obtained with this technique.

Injection-Molding Resins. In this technique, a special flask is equipped with an injection chamber and sprues to connect the chamber with the mold cavity (231). The mold space is filled by injecting the softened resin under pressure. Upon cooling, the thermoplastic resin solidifies in the mold. The mold is filled automatically, provided the correct pressure is maintained. The more elaborate and costly injection-molding equipment is suitable for large-scale dental laboratories. A variety of thermoplastic materials, such as PMMA, vinyl–acrylic copolymers, polystyrene, polycarbonates, and polysulfones, are processed by this method (see POLYMERS CONTAINING SULFUR, POLYSULFONES; STYRENE PLASTICS; VINYL POLYMERS). Because of inferior wetting, the strength of the denture base bond to synthetic teeth is less than that obtained with a heat-cured dough system.

Light-Cured Resins. An alternate technique employs light curing of a premixed polymer dough (232,233). The molds selected for the arch-form teeth are based, in part, on the arch sizes of natural human dentition. The teeth and denture base are brought together in a specially designed instrument and processed directly on the cast for a few minutes by high intensity visible light in a special curing unit. The denture-base monomer system uses a nonvolatile multifunctional acrylic resin without MMA that forms an interpenetrating polymer network with the polymeric powder component of the dough. The uncured resin includes a photoinitiator system, such as a camphorquinone–tertiary amine system. Dual cure systems also have been developed eliminating the laborious and time-consuming steps associated with heat-cured molding techniques. The properties of the cured material are similar to material cured at ambient temperatures or by heat. The technique is cost-effective and reduces the number of patient visits. It is especially useful in the construction of partial dentures and in repair and rebasing procedures.

Properties of Denture Base Materials. Physical properties of acrylic denture base materials are given in Table 12 (234). Mechanical properties of denture bases can vary considerably, and depend on composition, mode of polymerization, and degree of interaction with the oral environment, especially water sorption.

Self-curing resins have lower strength and stiffness, but the same elastic modulus as heat-cured materials. Polymerization shrinkage of the MMA–PMMA and similar systems is ~6%. Clinically, a linear shrinkage of ~0.5% across the posterior part occurs upon normal denture processing. The water sorption of the acrylic material in the mouth partially compensates for this shrinkage. The net linear shrinkage of 0.3–0.4% is clinically insignificant because

Table 12. **Physical Properties of Denture-Base Resins**

Property	Poly(methyl methacrylate)	Vinyl–acrylics
tensile strength, MPa[a]	48–62	51
compressive strength, MPa[a]	75	61–75
elongation, %	1–2	7–10
elastic modulus, MPa[a]	3.8×10^3	2.3×10^3
impact strength,N · m	1050	3150
transverse strength, MPa[a]	41–55	41–55
flexural strength, MPa[a]	83–117	69–110
Knoop hardness	16–22	14–20
thermal coefficient expansion,$^\circ C^{-1}$	81×10^{-6}	71×10^{-6}
heat-distortion temp, °C	160–195	130–170
polymerization shrinkage, %	6	6
24-h water sorption	0.3–0.4	0.07–0.04

[a] To convert MPa to psi, multiply by 145.

the tissue on which the denture rests adjusts to such changes (231). Some dental resins contain copolymers of 2-hydroxyethyl methacrylate. Such resins impart increased wettability, but high water sorption lowers the dimensional stability. The thermal expansion of denture base resin can be reduced by the addition of fillers. The resulting dentures have higher impact strength, but reduced polishability. They tend to stain and foul because food particles, debris, and bacteria can penetrate into surface irregularities and voids.

Radiopaque materials are used to determine the location of aspirated dentures and fragments (235,236). Opacifying additives include barium sulfate, barium fluoride, barium or bismuth compounds or bismuth-containing glasses, and brominated organic monomers and polymers. The incorporation of these additives into the resin base or tooth can adversely affect physical properties. Radiopaque materials meeting the requirement for ANSI/ADA specifications for denture-base polymers have been described (237).

High impact strength, increased hardness, lower thermal expansion, and high fatigue strength are also important properties required of denture base materials. To address these deficiencies, a number of nonacrylic and acrylic polymers have been investigated for dentures-base applications.

Vulcanized rubber, phenol–formaldehyde, and cellulose nitrate resins preceded the use of acrylic polymers in prosthetics. Epoxy resins were found unsatisfactory clinically because of handling and curing problems and their dimensional and color instability. Vinyl–acrylics, polystyrene, polycarbonates, and polysulfones can be injection-molded to yield dentures with outstanding toughness, high fatigue strength, and low water sorption. Polycarbonates excel in impact strength, but processing requires high temperature and the use of porcelain teeth, which leads to crazing in the polymer around the necks of the teeth because of differences in thermal contraction rates.

Acrylics processed by compression-molding techniques give dentures as satisfactory and dimensionally stable as the estimated 5% of the dentures made with special resins and elaborate processing equipment (238). Promising fiber-reinforced dentures, eg, with organic fibers such as polyethylene, have been reported (239–242).

Requirements for heat- and cold-curing denture base resins prepared from powder–liquids, gels, preopolymerized blanks, and fluid resins composed of acrylic, vinyl, and polystyrene polymers are given in ANSI/ADA specification No. 12 for denture-base polymers. Vinyl resins are used primarily for appliances used in patients having allergic responses to methacrylates.

Special-Purpose Resins, Repair Resins. Fractured acrylic dentures can be repaired with materials similar in composition to cold-cured denture resins. These materials generally cure more rapidly because of the relative simple manipulations involved. The process is quick and there is little dimensional change, but the strength of the repaired denture may be only one-half that of the original appliance (243). Test methods and requirements of these materials are given in ANSI/ADA specification No. 13 for denture cold-curing repair resins.

7.3. Denture Reliners. A denture can be readapted to the changing contours of soft tissue by relining it with rigid or resilient materials. A model of the soft mouth tissues can be used or a relining resin placed directly on the denture. The latter technique has gained considerable clinical acceptance. Some of these materials generate enough heat during polymerization to injure oral tissues. The resins usually contain plasticizers or low molecular weight polymers to facilitate seating of the denture. Even the hard, cold-curing reliners that fulfill the requirements of the respective specification are considered only temporary expedients.

Resilient Liners. Resilient liners reduce the impact of the hard denture bases on soft oral tissues. They are designed to absorb some of the energy produced by masticatory forces that would otherwise be transmitted through the denture to the soft basal tissue. The liners should adhere to but not impair the denture base. Other critical properties include total recovery from deformation, retention of mechanical properties, good wettability, minimal absorption of fluids, nonsupport of bacterial or fungal growth, and ease of cleaning. At present, no material fulfills all of these requirements.

Resilient liner materials are generally supplied as powders, liquids, or ready-to-use sheets. The commercial materials currently available are plasticized acrylics or silicones (see SILICON COMPOUNDS, SILICONES). The acrylics contain higher molecular weight acrylate, methacrylate polymers, or MMA copolymers with ethyl, *n*-propyl, or *n*-butyl methacrylate, and a liquid that may contain ethanol, ethyl acetate, an aromatic plasticizer, and a monomer. The glass temperature of the cured material should be below mouth temperature. Soft acrylics adhere well to dentures, have poor elasticity, and harden upon aging owing to loss of plasticizer (244–247). Reliners with hydrophilic groups are usually based on 2-hydroxyethyl methacrylate and its polymer and copolymers (245). The cured resin softens and swells when placed in water, which may cause undesirable changes in the contours of tissue-bearing surfaces.

Silicone (siloxane) reliners are supplied as either a one-component system that cures in the presence of moisture or heat, or a two-component system containing base and catalyst. Both types adhere poorly to denture base and cannot be polished satisfactorily. Some silicones support propagation of bacteria such as *Candida albicans*. Acrylic-based silioxane monomers and resins have been proposed for overcoming these deficiencies (241).

Soft reliners can weaken the strength of the heat-cured resin, because they reduce the thickness of the denture base and allow the diffusion of the monomer or solvent from the reliner into the base. Relined dentures stain readily and are difficult to clean. A polyphosphazine fluoroelastomer has also been developed in an attempt to overcome the deficiencies of available liners (248).

7.4. Tissue Conditioners. Tissue conditioners are gels designed to alleviate the discomfort from soft-tissue injury, eg, extractions. Under a load, they exhibit viscous flow, forming a soft cushion between the hard denture and the oral tissues. The polymer in tissue conditioners is often the same as that used for resilient liners. The liquid is a plasticizer containing an alcohol of low volatility (249,250).

The alcohol swells the poly(ethyl methacrylate) beads, rapidly promoting diffusion of the plasticizer into the polymer. As a result of the polymer-chain entanglement, a gel is formed. The conditioner is applied to the denture and provides a cushioning effect; alcohol and plasticizer are slowly leached out, and the material becomes rigid. To ensure resiliency, the conditioner must be replaced after a few days. Some materials exhibit high flow over a short period compared with others with low initial flow; the latter remain active longer.

7.5. Crown and Bridge Resins.

These materials, based on methyl methacrylate, higher molecular weight methacrylates, and the epimine resin system, are used as interim tooth coverage during fabrication of permanent prostheses. They are used to maintain the correct biting relationship, stop teeth drifting, and protect the prepared tooth against pulpal irritation and fracture. The epimine resin system requires cationic polymerization rather than free radical polymerization common to acrylic materials (241,251).

Resins are also used for permanent tooth-colored veneers on fixed prostheses, ie, crown and bridges. Compositions for this application include acrylics, vinyl–acrylics, and dimethacrylates, as well as silica- or quartz-microfilled composites. The resins are placed on the metallic substrates of the prostheses and cured by heat or light. These resins are inexpensive, easy to fabricate, and can be matched to the color of tooth structure. These types of acrylic facings do not chemically adhere to the metals and are retained only by curing the resin into mechanical undercuts designed into the metal substrate. They have relatively low mechanical strength and color stability, and poor abrasion and stain resistance; they also deform more under the stress of mastication than porcelain veneers or facings.

7.6. Plastic Teeth.

Excessive wear, crazing, and blanching of the early acrylic teeth, first introduced in the 1930s, has been overcome by better methods of molding and improved cross-linking. Usually more cross-linking agent is employed in acrylic teeth than in denture-base resin. Residual emulsifier and stabilizers employed in the suspension polymerization of the resin are completely removed. Plastic teeth are manufactured by an injection- or transfer-molding process. To fabricate cross-linked anterior teeth, the labial portion of the front veneer of the tooth is made first and partially cross-linked. Then the mold is packed with a dough of a monomer–polymer mixture containing less cross-linking agent. The assembly is cured to give the tooth a solvent-resistant facing. The backside of the tooth, which is only lightly cross-linked, is receptive to the monomer of the denture-base gel, and a strong union results. Both particle size and molecular weight of the polymer, as well as residual resin initiator content, must be carefully controlled; the rheology of the monomer/polymer mix and cure parameters affect the molding process.

In addition to acrylics, vinyl resins, polycarbonates, and polysulfones have been suggested for molded teeth. Newer compositions contain very finely dispersed spheres such as pyrogenic silica as reinforcing fillers, ie, microfillers; a urethane dimethacrylate resin (252); nonfilled highly cross-linked copolymers with interpenetrating networks; and a layered tooth with an exterior containing a BIS–GMA-type resin and silica filler. Pigments impart a natural appearance. The fluorescence of human teeth under uv light is simulated by the incorporation of additives, and a more natural appearance is obtained by painting on stains and striations.

Acrylic teeth have a compressive strength of $\sim$76 MPa (11,020 psi) and a Knoop hardness of 18–20 KHN. These values are lower than those of alloys used for dentures and those of human enamel or dentin. Acrylic teeth have a more natural appearance and are more fracture resistant than porcelain teeth because of their higher impact strength. The low modulus of elasticity reduces the clicking often experienced by porcelain denture wearers. A chemical bond between tooth and resin base is obtained during processing by heat curing. Acrylic teeth have less resistance to cold flow and higher water sorption than porcelain teeth. Bonding of plastic teeth to self-curing resins is poorer than to heat-curing denture base, but can be improved by treatment with a 50:50 mixture of dichloromethane and MMA (230). The deficiencies of plastic teeth are their relatively high wear rate and ultimate loss of occlusal relationship. Plastic teeth exhibit less wear than the supporting structure of the denture prosthesis.

7.7. Mouth Protectors. The widespread use of protective mouth guards in contact sports has greatly reduced the incidence of orofacial injuries (253,254). Guards are produced from ready-made stock or are custom-fabricated. Natural rubber, poly(vinyl chloride), poly(vinyl acetate-*co*-ethylene), polyurethane, and silicone elastomers are the materials of choice. Custom guards are fabricated from poly(vinyl acetate- *co*-ethylene) blanks, soft acrylic dough, liquid rubber latex, polyurethane, and laminated thermoplastic (255,256). Ready-made protectors are often poorly fitting, leading to discomfort, gagging, and interference with speech. Properly fabricated mouth protectors are dimensionably stable and acceptable to the wearer. In addition, these materials are often used in night-guard appliances to protect the occlusal surfaces of teeth against bruxism.

7.8. Maxillofacial Prosthetic Materials. Extraoral or external maxillofacial prosthetics (EMFP) is the science of using polymeric biomaterials for the restoration of missing and/or defective facial tissues. The synthesis of materials that can be easily fabricated into lifelike facial devices has long challenged researchers. Ideally, maxillofacial polymeric materials should mimic as closely as possible the mechanical, physical, chemical, and aesthetic properties of the natural tissues they replace. Mechanically, these materials should combine toughness, strength, and durability with pliability, resiliency, and softness. These materials also are required to exhibit an elastic modulus and compliance that matches that of facial tissues over a relatively wide range of ambient temperatures, eg, −20 to 45°C. Other important mechanical properties that have been difficult to achieve are tear and abrasion resistance and adequate adhesion to contiguous tissues via surgical adhesives. Maxillofacial polymers should be biocompatible, dimensionally stable, physically and chemically inert, color stable, translucent, and solvent and stain resistant, eg, have low water uptake and be relatively unaffected by contact with food, oils, dust, detergents, and other cleansing agents. They also should blend with contiguous tissues in appearance, be able to be colored and textured, exhibit low thermal conductivity, and be easily fabricated and repaired with minimal contraction on processing.

Maxillofacial polymers include the chlorinated polyethylenes, poly (ether-urethanes), polysiloxanes (see ELASTOMERS), and conventional acrylic polymers. These are all deficient in a number of critical performance and processing characteristics. It is generally agreed that there is a need for improved maxillofacial polymers that can be conveniently fabricated into a variety of prostheses (248,257,258). For hard tissue applications (eg, craniofacial repair) PMMA remains the most widely used material. Recent studies have shown the potential for materials based on apatitic calcium phosphates reinforced with biodegradable polymers such as poly (lactide-glycolide) (259,260).

7.9. Other Uses.

Patterns for gold-inlay castings can be prepared from acrylic plastics. The finished casting is not superior to casting produced from a wax pattern, however, and the technique has not aroused much interest. Epoxy die materials are used for the fabrication of cast prostheses in some commercial dental laboratories. Cold-curing plastics are used in making contoured impression trays. These resins contain substantial quantities of fillers that increase the rigidity of the materials after setting. Occlusal night guards are made from PMMA or another thermoplastic to protect teeth against excessive grinding. Orthodontics makes extensive use of plastics in retainers, splints, temporary space maintainers, and bite plates (261).

7.10. Elastomer Impression Materials.

Dentistry requires impression materials that are easily handled and accurately register or reproduce the dimensions, surface details, and interrelationship of hard and soft oral tissues. Flexible, elastomeric materials are especially needed to register intraoral tooth structures that have undercuts. The flexibility of these elastomers allows their facile removal from undercut areas while their elasticity restores them to their original shape and size.

An elastic impression material must be easily and quickly prepared; set quickly to an elastic mass in the mouth; not be harmful or cause discomfort to the oral tissues; and flow to all areas without the need of excessive force. It also must copy detail accurately; possess sufficient strength, toughness, and elasticity to resist permanent deformation when removed from the mouth; not adversely affect the set properties of the cast material; be capable of being manipulated within a temperature range tolerated by the oral tissues; and have sufficient viscosity to remain in a tray.

Impression materials based on natural polymers, eg, reversible hydrocolloids (agar), irreversible hydrocolloids (alginates), combinations of agar/alginate, and, to a lesser extent, zinc oxide–eugenol cements, are still employed. However, the growing use of elastic impression materials by the dental profession has spurred a continuous search for better elastomers. The agar- and alginate-based products fulfill a basic need, but owing to their dimensional instability with any loss or gain of water, improved systems have been sought. The primary emphasis has been in the development of nonaqueous elastomeric impression materials.

7.11. Aqueous Impression Materials Reversible Hydrocolloids (Agar).

The agar-based impression materials are thermally reversible, aqueous gels (262,263) that become viscous fluids in boiling water and set to an elastic gel when cooled <35°C. The popularity of agar-based impression materials has diminished with the introduction of elastic impression materials such as alginate-based, polysulfide, silicone, and polyether impression materials, but agar [9002-18-0] materials are still used in substantial quantities.

Impressions of inlay and crown preparations, and all gingival areas, are best obtained by filling the preparation or gingival area with impression material injected from a hypodermic syringe. This eliminates trapping air in the corners and recesses and gives a more faithful reproduction without nodules or other imperfections.

The agar-based impression materials are used extensively for duplicating casts. Frequently, it is desired to retain the original model for reference and do the actual work on a duplicate cast. Partial-denture fabrication requires that the original stone cast be duplicated in an investment. For duplicating, the agar-based impression material is usually diluted with water, boiled, cooled to the desired temperature, and carefully poured over the model to be duplicated.

The characteristics that make agar good for impression compositions include unusually good elastic behavior and hysteresis between its liquefying and gelation temperatures. Agar sols liquefy at 70–100°C. On cooling, they form a solid gel at 30–50°C. The delay in gelling brings the temperature within a range tolerated in the mouth. Another useful characteristic is the dimensional stability of the material during gelation, cooling, and storage as long as the water content remains constant.

Agar-based impression materials must have a compressive strength of at least 0.2 MPa (29 psi). They should have a strain in compression of 4–20% in stresses of 9.8–98 kPa (1.4–14.2 psi) per specification test method, and should not have a permanent deformation exceeding 3% after 12% strain is applied for 30 s.

Agar, a sulfuric acid ester of a galactan complex, is the basic ingredient for agar-based impression. About 6–12% agar is generally used with a 75–85% water content. Fillers may include zinc oxide and clays. Small percentages of boron compounds increase the viscosity, strength, toughness, and resiliency of the composition. Borax, calcium metaborate [13701-64-9], and organic borate compounds have been used; waxes or fatty acids plus emulsifying agents may be present; plaster-accelerating agents are frequently added and may include potassium sulfate, magnesium sulfate [7487-88-9], and zinc sulfate [7733-02-0]. Such additions can be kept to a minimum if the cold-water-soluble salts and organic contaminants are washed from the agar before compounding. Agents for pH control and fibrous reinforcements have been included in formulations. Agar impression materials must be formulated to remain stable in storage. They should be free of salts or additives that crystallize and salt out, degrade the complex agar molecule, or induce syneresis in the agar gel. Any syneresis destroys the dimensional accuracy of the composition.

Alginate-Based Irreversible Hydrocolloids. Alginate impression materials are supplied as a dry powder. When the correct proportions of the powder and water are mixed, a viscous but slightly fluid mass is formed. The gel formation is based upon the conversion of soluble salts, usually potassium or sodium salts of alginic acid [9005-32-7], to insoluble salts of alginic acid, usually calcium alginate [9005-35-0]. Improvements in available alginate products, convenience of use, and a cost advantage have contributed to their increased growth and popularity.

The technique of preparing an alginate impression material requires only the mixing of measured amounts of the powder and water. The paste is placed in a suitable prepared tray and seated over the area of which an impression is desired. Within 1–4 min the material sets to a strong, tough elastic gel. The impression is unseated by a quick, deft movement to minimize tearing or distortion of the impression. The precautions required to stabilize the water content of the alginate impression materials are the same as those described for the agar impression material. The casts should be poured immediately. Most modern alginates do not require treatment in a fixing solution before pouring the cast.

Alginate impression materials are chemically reactive mixtures. All factors that influence reaction rates are, therefore, important in the use of these materials, ie, correct proportioning; temperature of the water, powder, and mixing equipment; and spatulation rate and duration.

Alginate impression materials must have a compressive strength of at least 0.34 MPa (49 psi) 8 min after the start of the mix; at least 3.5 min of this time interval should be in storage at $37 \pm 1^{\circ}$C. They should have a strain in compression of 4–20% between stresses of 9.8–98 kPa (1.42–14.2 psi) per specification method and they should not have a permanent deformation exceeding 3% after a 12% strain is applied for 30 s.

Alginate impression materials are usually the potassium or sodium salts of alginic acid. These commercially available materials have various degrees of polymerization, controlled pH ranges, and particle sizes. Alginic acid is derived from specific varieties of kelp, a marine plant. It is a high molecular weight linear polymer of anhydro-β-D-mannuronic acid [1986-14-7].

The cold-water-soluble alginates, ie, ammonium, sodium, or potassium, must be precipitated as insoluble alginate salts to be useful as impression materials. The precipitating compounds can be any salt of a divalent-metal ion where rate of availability for precipitation can be controlled. Calcium sulfate [7778-18-9] (264), in its dihydrate form, has been used most frequently. Lead silicate [11120-22-2] (265) and chromic sulfate [10101-53-8] (266) had been used and may still find limited use; however, their use is contraindicated because of their toxicity. Retardation of the precipitation reaction, to give useful working time, is generally accomplished by the introduction of phosphate compounds; disodium phosphate [7558-79-4], trisodium phosphate [7601-54-9], alkali metal polyphosphates, tetrasodium pyrophosphate [7722-88-5], and sodium hexametaphosphate [10124-56-8] are typical retarders. It is desirable to have the precipitation of the insoluble alginate completed as rapidly as possible, after an adequate working time. The addition of accelerating materials promotes a fast snap over. Aluminum, sodium, potassium, zinc, manganese, and magnesium fluorosilicates are helpful. The inclusion of suitable filler gives bulk to the dry powder, and blends and controls the viscosity and body of the mixed material. Calcium carbonate, magnesium oxide, zinc oxide, diatomaceous earth [7631-86-9], or other types of silica fillers may be used.

7.12. Nonaqueous Impression Materials. *Polysulfide Impression Materials.* In 1953, the first nonaqueous, elastic dental impression material based on the room temperature conversion of a liquid polymer, a polyfunctional mercaptan (polysulfide), to a strong, tough, dimensionally accurate elastomer, was introduced. The conversion of the liquid polymer to an elastic solid has been achieved in most products by lead peroxide [1309-60-0]. Significant improvements in strength, toughness, and especially dimensional stability of the set polysulfide elastomers over the aqueous elastic impression materials made these materials popular.

The materials are available in three basic grades, ie, light-bodied or syringe, regular, and heavy-bodied types. The products are supplied as a two-part paste system, usually packaged in collapsible tubes. The polysulfide-containing base and the setting-agent paste, usually lead peroxide, are mixed together in approximately equal amounts to give a homogeneous, streak-free mass, which is transferred to a tray of adhesive-coated metal or of custom-made acrylic resin. The filled tray is then placed over the area of interest and held motionless until the rubber has set, usually within 5–10 min.

The polysulfide impression materials can be formulated to have a wide range of physical and chemical characteristics by modifying the base (polysulfide portion), and/or the initiator system. Further changes may be obtained by varying the proportion of the base to the catalyst in the final mix. Characteristics varied by these mechanisms include viscosity control from thin fluid mixes to heavy thixotropic mixes, setting-time control, and control of the set-rubber hardness from a Shore A Durometer scale of 20–60. Variations in strength, toughness, and elasticity can also be achieved.

The shrinkage on conversion from the fluid state to the elastic solid state has been reported in the range of 0.03% in 24 h for one composition. Generally, the shrinkage in 24 h is 0.15% for most products. The strain in compression, 9.8–98 kPa (1.42–14.21 psi), varies from 7 to 15%. The permanent deformation, after 12% strain is applied for 30 s, varies from 4 to 6.5%. The better polysulfide compositions, if properly packaged, remain workable and useful for many years.

The liquid polysulfide polymers, as manufactured, are slightly acidic. In this condition they are very stable. In an alkaline, oxidizing medium they polymerize rapidly. Heat, moisture, and an alkaline environment accelerate the reaction. Stearic acid [57-11-4], oleic acid [112-80-1], lead stearate [7428-48-0], and aluminum stearate [637-12-7] are active retarders. The polymerization kinetics and rheological behavior of the polysulfides have been studied (267–269).

The polysulfide rubbers are capable of being electroplated by a special technique. Either copper or silver can be used, but the alkaline silver cyanide plating system gives more reliable results.

The polysulfide base material contains 50–80% by mass of the polyfunctional mercaptan, which is a clear, amber, syrupy liquid polymer with a viscosity at 25°C of 35,000 Pa · s (= cP), an average molar mass of 4000, a pH range of 6–8, and a mild, characteristic mercaptan odor. Fillers are added to extend, reinforce, harden, and color the base. They may include silica, calcium sulfate, zinc oxide, zinc sulfide [1314-98-3], alumina, titanium dioxide [13463-67-7], and calcium carbonate. The high shear strength of the liquid polymer makes the compositions difficult to mix. The addition of limited amounts of diluents improves the mix without reducing the set-rubber characteristics unduly, eg, dibutyl phthalate [84-74-2], tricresyl phosphate [1330-78-5], and tributyl citrate [77-94-1].

A number of modifying agents are desirable. Sulfur, in minor amounts, is a powerful activator. Stearic acid and oleic acid may be used as retarding agents. Additions of acid must be carefully selected because strong acid attacks the methylenedioxy linkages and degrades the polymer. Buffering agents for pH control and perfumes for odor masking also are used frequently.

The second catalyst paste of the two-paste product is a curing agent. A wide variety of materials convert the liquid polysulfide polymers to elastomeric products. Alkali salts, sulfur, metallic oxides, metallic peroxides, organic peroxides, and many metal–organic salts, ie, paint driers, are all potential curing agents.

Many curing systems bring about a liquid–solid conversion of the polysulfide polymers. Most curing agents produce an initial solid mass characterized by a high degree of plasticity and poor elasticity. The development of elastic properties is so slow that the materials are not suitable for the accurate reproduction of undercut areas found in oral structures.

Only three types of systems have found application in dentistry. Lead peroxide is the curing agent most frequently used for the polysulfide polymers that serve as dental impression materials. Lead peroxide converts the liquid polymer to elastic solid within a time short enough for oral applications.

The curing paste is usually dark brown owing to the high concentration (20–78% by mass) of lead peroxide. An organic peroxide curing system offers curing pastes in yellow and red that produce lighter shades of set-rubber colors, but inferior dimensional stabilities, while $CuOH_2$ yields a pastel green material with dimensional stability equal to that of the lead peroxide material. Suitable vehicles may be selected from the materials listed as diluents for the base. Suitable fillers also may constitute part of the curing paste formula. Buffering agents, thixotropic additives, and other modifiers may be added.

Condensation Silicones. Odor, color, and stickiness of the polysulfide rubbers have deterred universal acceptance. The development of room temperature vulcanizing (RTV) silicone rubbers, or siloxanes, has made another acceptable elastomeric system available to dentistry. Materials have a shelf life of 2 years or longer, and the setting reaction is completely free from the gas evolution that plagued the earlier versions of these materials. The silicone impression materials have not produced the variety of products that are found with the polysulfide rubbers. Some product individuality has been evident in the initiator systems, but the differences from product to product are less than for the polysulfides.

The silicone bases have a mild, pleasant odor, and are generally white, although some manufacturers add a pink pigment. The materials are nontacky and can be wiped away from instruments, hands, etc, at any stage of the mix or set. The silicones offer a selection of setting rates and mix viscosities. Regardless of base viscosity, the set rubbers are about the same hardness, ie, a Shore A Durometer value of ∼55. The linear shrinkage upon curing exceeds that of the mercaptan rubbers and is in the range of 0.2% in 24 h. The strain in compression, 9.8–98 kPa (1.42–14.21 psi), is 8.8–34%. The permanent deformation, after 12% strain is applied for 30 s, is 1.45%.

Both the silicone base and the catalyst compositions are moisture sensitive and subject to deterioration when exposed to the atmosphere. Condensation silicone materials are based on hydroxyl-terminated polydimethylsiloxane and are made in the form of two paste or paste–liquid catalyst systems.

Polydimethylsiloxane is of moderately high molecular weight. The silicone is a viscous liquid. Colloidal silica or micronized metal oxides, 5–10-μm particle size, are added to prepare a paste that is mixed with a tetraalkyl silicate containing 50% by mass ethoxy groups, eg, commonly tetraethyl orthosilicate, and 1–2% by mass of an organic tin activator. This type of catalyst has a limited shelf life because of oxidation.

In the presence of the organic silicate, the heavy-metal salts trigger the chain extension and cross-linking reactions that lead to silicone rubber and volatile ethanol as a by-product. Useful metal soaps include stannous octanoate [1912-83-0], zinc octanoate [557-09-5], dibutyltin dilaurate [77-58-7], and dibutyltin diacetate [1067-33-0]. The reactivity of the different salts varies considerably. Stannous octanoate effects a cure in 0.5–2 min; zinc octanoate may require

24–96 h; the dibutyltin dilaurate, 10–20 min. Heat and moisture accelerate the curing rate, but to a lesser degree than in the case of the polysulfide rubbers.

Addition Silicones. Perhaps the most important development in the area of elastic impression materials has been the addition siloxane (or silicone) system. Several reviews have been published on the materials (270,271).

Addition siloxanes are the kind most frequently used in the dental clinic and are supplied as a two-paste system. One paste contains a low molecular weight silicone with terminal vinyl groups and reinforcing filler, and the other consists of a hydrogen-terminated siloxane oligomer, filler, and chloroplatinic acid catalyst. On mixing, the catalyzed the vinyl-hydrogen addition reaction results in a cross-linked elastomer. Hydroxyl-containing silicones evolve hydrogen in the setting reaction. Some formulations contain palladium to absorb this gas. Addition silicones have the best elastic properties and lowest dimensional change on setting of all elastomeric impression materials.

The silicone impression materials are very compatible with gypsum products, give casts having excellent hard surfaces, and can be electroplated with either copper or silver. However, the acidic copper sulfate bath gives more acceptable results.

The technique of making a silicone rubber impression is similar to that employed for the polysulfide rubber impressions. The materials are available in four viscosities, low, medium, high, and very high. The products are supplied as two-part products. The silicone bases are viscous fluids and may be packaged in collapsible metal tubes, cartridges with mixing tips for injection or in jars for the very high viscosity material. The catalysts are either liquid or paste products; the liquids are packaged in plastic bottles or collapsible metal tubes. Further reduction in technique sensitivity has been achieved by the use of dual-injectable, automatic mixing syringes. The impression procedures are similar to those given for the polysulfide impression materials.

Polyether Impression Materials. A polyether-base polymer elastomeric impression material was introduced in 1964 (272,273). This material is related to the epimine resin and cured by the reaction between aziridine (cyclic imine) rings, which are at the ends of branched polyether molecules. The main chain is probably an ethylene oxide–tetrahydrofuran copolymer [27637-03-2]. Setting is by cross-linking brought about by an aromatic sulfonate ester catalyst (274,275) that produces cross-linking by cationic polymerization via the opening of the cyclic imine end groups. These polyethers are supplied as two pastes. Just as with the rubber and silicone light-body materials, one mix is used in the syringe, and the remainder in the tray. Setting time for these materials is relatively short, eg, <2.5 min.

To improve the rheological properties and extend the very short working time, a simple polyester is included as thinner. Mixing is easy, and dimensional change in air is <0.1% over several hours. Elastic recovery and reproduction of detail are excellent. The elastomeric cyclic imine impression materials have a higher modulus of elasticity than the condensation silicone or polysulfide rubbers, but are more difficult to remove from the mouth. The materials have relatively low tear strength and an equilibrium water sorption of 14% by mass; thus, polyether impression materials tear readily. Because of their poor dimensional stability in water, they should be stored in a dry environment.

A novel impression material that has a polyether backbone with urethane–acrylic end groups and that cures free radically by visible light irradiation has been developed (276).

7.13. Restoratives. Polymer resins were introduced as tooth restorative materials in the early 1940s. These materials can be classified as unfilled tooth restorative resins, composite or filled restorative resins, and pit and fissure sealants.

7.14. Unfilled Tooth Restorative Resins. Unfilled resins were some of the first polymer materials introduced to repair defects in anterior teeth where aesthetics were of concern. They have been completely replaced by the filled composite resins that have overcome the problems of poor color stability, low physical strength, high volume shrinkage, high thermal expansion, and low abrasion resistance commonly associated with unfilled resins.

7.15. Resin Composite Restorative Materials. Improvements in the properties of resin-based restoratives have been brought about primarily by the addition of reinforcing silane-treated silica fillers to unfilled resins. These modifications have made resin composites the most popular aesthetic filling material used today. Research has at extended the use of composite restoratives to the posterior teeth as alternatives to amalgam restorations. Techniques are now available that permit resin composite inlays to be fabricated by a laboratory technician, and then adhesively cemented into the tooth cavity by the dentist.

The addition reaction product, Bis–GMA, of bisphenol A [80-05-07] and glycidyl methacrylate [106-91-2] can be a compromise between epoxy and methacrylate monomers (277). Thus, Bis–GMA polymerizes through the free-radical induced covalent bonding of methacrylate groups rather than by ionic opening of the oxirane (epoxide) ring of epoxy resins (278). Mineral fillers, coated with a silane coupling agent, which bond the powdered silica-type fillers chemically to the resin matrix, are incorporated into Bis–GMA monomer diluted with other methacrylate monomers to make it less viscous (277). A second base monomer commonly used to make composites is UDMA, a urethane dimethacrylate derived from the reaction of 2-hydroxyethyl methacrylate and aliphatic diisocyanate [69766-88-7].

Composite resins can be cured using a variety of methods. Intraoral curing can be done by chemical means, where amine–peroxide initiators are blended by mixing two components to start the free-radical reaction. By contrast, single paste systems can be formulated with photoinitiators, eg, camphorquinone-tertiary amines, and then cured by exposure to visible light irradiation (400–500 nm) spectrum (279). In contrast to chemically activated composites, single paste, light cured composites have virtually an unlimited amount of working time. Single pastes activated by uv light were previously used in some early materials but are no longer employed for direct restorations (280). Laboratory curing of indirect restorations can be done by the above methods as well as the additional application of heat and pressure (281,282).

Thus composites can be dispensed as paste systems in one or two parts. Visible light initiated composites are systems containing one paste that can be directly placed into a cavity and cured by proper light exposure. Generally, clinical curing can be accomplished in under 1 min, depending on the size and complexity of the restoration and the power output of the light source. Chemically cured systems are supplied as two-paste systems where the two parts are hand mixed before placing the paste into the cavity. Polymerization occurs in 3–5 min from mixing. There also are dual-cure systems, supplied as two pastes that are mixed, placed, and can be cured with light in under 1 min; if not exposed to a curing light, these will chemically cure in 5–9 min. Ingredient lists of typical composites are available (283).

The combination of a high molecular weight monomer, BIS–GMA, in the resin matrix with a bonded filler reduces the total polymerization shrinkage of composites to 1.5–6 vol% (284). In addition, the coefficients of thermal expansion have been reduced and strength and durability enhanced by the addition of the inorganic fillers (284). Fillers can be composed of particulate quartz and silica glass, colloidal silica, and/or ceramic particles that are chemically bonded to the methacrylate resin using the silane coupling agent 3-methacryloxypropyltrimethoxysilane [2530-85-0]. Filler particles made from barium-, strontium-, or zirconium-containing glasses, can be used to increase the radiopacity of the composite. Filler particles range in size from <1 μm to ~ 10 μm in diameter. Composites formed only from submicrometer-sized particles are generally classified as microfills. Composites formed from a blend of two filler types, eg, colloidal (submicrometer-size) silica plus small-sized radiopaque macrofillers, with particle sizes ranging from 1 to 10 μm, are classified as hybrids. Composites formulated from only macrofillers larger than ~ 3 μm are generally classified as macrofills. Fillers of various shapes (glass fibers or spherical glasses) are also used in composites. A new class of composite, characterized by a continuous distribution of particles of one composition, has been introduced. Filler loading levels as high as 60% by weight for microfills to near 88% by weight for hybrids and macrofills are feasible (285). ADA specification No. 27 and ISO specification 4049 are for direct filling resins.

7.16. Pit and Fissure Sealants. The BIS–GMA or urethane dimethacrylate portion of the composite restorative material has been further diluted with methyl methacrylate monomer or other low viscosity monomers and used to seal developmental pits and fissures on natural tooth enamel. These naturally occurring pits and fissures are very prone to decay soon after the teeth erupt. Sealing can be accomplished by properly acid etching the enamel within and surrounding these pits and fissures and flowing the low viscosity resin onto the etched surface and polymerizing it. The resin flows into the porosities created by etching and polymerizes by light or chemical initiators to form an impervious barrier that has proven to be clinically effective in reducing the decay rate on these vulnerable surfaces (286–290). As a means of strengthening the sealants, the resins may be lightly filled. Pit and fissure resins are covered by ADA specification No. 39.

Compomers. These restorative materials are poly(acid) modified resin composites. The resin phase consists of conventional dental resins with small amounts of acidic monomers or oligomers, usually of the carboxylic acid type. The filler systems of these composites are designed to contain ion-leachable glasses similar to those in glass ionomer cements. The rationale is to improve adhesion of the polymeric material to tooth structure without the use of an intermediary bonding system. Some contain water and are called hydromers and others have no water present and are called compomers. Polymerization of the monomer system occurs by the free-radical polymerization and acid–base reaction between the leachable ion and the carboxylic acid groups. Filler content may include strontiumfluoroaluminum silicate glasses and provide fluoride release (291,292).

Bioactive Polymeric Composites. Amorphous calcium phosphate (ACP), a plausible precursor in the formation of biological hydroxyapatite, exhibits high solubility in aqueous environments and undergoes relatively facile conversion to hydroxyapatite. These properties make ACP an interesting candidate as a bioactive filler phase for polymeric composites. Potentially bioactive composites based on ACP and utilizing photocurable dental monomer systems to provide the matrix phase have recently been developed. Many of these composites, especially those formulated with 2-hydroxyethyl methacrylate, have demonstrated sustained release of calcium and phosphate ions into simulated saliva milieus. A wide variety of polymeric ACP composites with remineralizing capabilities can be fabricated from both biostable and biodegradable resins and polymers. Potential dental applications include protective liners, bases, prophylactic sealants, and/or remineralizing adhesives. These therapeutic materials, in appropriate formulations, eg, with biodegradable matrices, also should provide osteoconductive environments for healing defective bone as well as tooth structures (293).

7.17. Adhesives. The fundamentals of adhesion have an important role in modern restorative dentistry (see ADHESIVES). The retention of restorative materials to tooth structure, in addition to holding the restoration to the teeth, seals the interface between the tooth and restorative material. Maintenance of this seal reduces pulpal irritation and the potential for marginal discoloration and recurrent decay. The application of high performance adhesives reduces the need for mechanically retentive cavity designs, thereby minimizing removal of healthy tooth structure. Adhesion also plays an important role in holding prosthetic materials to one another. Polymer adhesive materials can be classified as composite or filled resin cements, porcelain or ceramic coupling agents, metal coupling agents, or enamel and dentin adhesives (294).

7.18. Composite or Filled Resin Cements. Composite resin cements are similar to restorative composites. They are used to adhesively retain crowns, bridges, orthodontic appliances, and other intraoral prostheses to hard tooth structure. The resin cements are similar to the microfil classification of composites, generally with a slightly lower filler level, ie, $\sim$50% by mass. The lower filler loading allows these materials to be used in thin films as cements and luting agents. Curing can be by light, chemical, or dual initiating systems. These cements are usually used in conjunction with a dentin and enamel adhesive, metal coupler, and/or porcelain or ceramic coupling agent to effectively laminate the prosthesis to the tooth structure.

7.19. Porcelain or Ceramic Coupling Agents. Dental porcelains or ceramics are commonly employed as aesthetic restorative materials. Restorations fabricated from these materials can be adhesively retained on tooth structure or metallic prostheses using the proper combination of couplers and adhesives. Repair of fractured or damaged porcelain restorations can be made using composite restorative materials in conjunction with these coupling agents. Adhesion to the porcelain or ceramic surface is achieved through an organofunctional silane, 3-methacryloxypropyltrimethoxysilane [2530-85-0] (295,296). The silane is applied as a dilute solution that is supplied as either a single-component prehydrolyzed system or a two-component unhydrolyzed system that must be mixed to achieve hydrolysis prior to application. Porcelain or ceramic is usually etched with hydrofluoric acid or air abraded and painted with the silane coupling agent. The silane interacts with the porcelain or ceramic surface and chemically copolymerizes with the composite cement used to lute it to the tooth or prosthesis (297).

7.20. Metal Coupling Agents. Metal prostheses can also be bonded to tooth structure or other restorative materials using composite cements with the proper metal conditioning and coupling agents. Metal conditioning can consist of etching the metal surface chemically or electrolytically, air abrading the surface, or electroplating. Etching is done to achieve a micromechanical surface profile that dental polymers can flow into and mechanically interlock to the surface (298,299). Air abrading with an aluminum oxide abrasive increases surface roughness and area, and provides for a clean oxide formation on exposure to air (300). Electroplating is generally reserved for highly noble alloys that do not readily form oxide layers. Brush plating can be done after air abrading to electrodeposit a thin layer of oxide forming metal, such as tin, on the noble metal surface (301).

Once a metal surface has been conditioned by one of the above methods, a coupling agent composed of a bifunctional acid–methacrylate monomer, similar to those used in dentin adhesives, is applied. This coupling material is usually supplied as a solvent solution that is painted over the conditioned metal surface. The acidic functional group, eg, carboxylic or phosphate, of the coupling molecule interacts with the metal oxide surface while the methacrylate functional group of the molecule copolymerizes with the resin cement or restorative material placed over it (302,303).

7.21. Enamel and Dentin Adhesives. Tooth enamel and dentin are heterogeneous tissues. Enamel, much less heterogeneous than dentin, has an extremely highly inorganic content (96% hydroxyapatite mineral). The much more heterogeneous dentin has a lower apatitic content (60% mineral by mass) and a higher organic content (mainly type I collagen), and water content is relatively high. The microstructure of the two tissues is also very different; enamel is very dense, while dentin is a porous tubular structure and the tubules increase in diameter as they approach the pulp. Simultaneous adhesion to both structures is very difficult but makes up the basis for conservative restoration of diseased tooth structure.

Like metal and porcelain, enamel and dentin must be conditioned prior to application of an adhesive. Conditioning treatments enhance adhesion by cleansing the surface or selectively removing some of the organic or inorganic portions of the dental tissue and surface cutting debris. Enamel is usually conditioned by etching with some form of acid. Acid etching increases the surface area and roughness, and reduces the surface energy to permit the adhesive resin to wet the enamel and form microscopic tags or projections into the surface irregularities for mechanical retention (304). Acid etchants for enamel are usually supplied as concentrated solutions either gelled or in liquid form. The most common is 37 or 40% phosphoric acid that is applied to the enamel surface for 15 s and then rinsed off with water. Excess water is removed from the surface before application of a resin, eg, BIS–GMA or urethane dimethacrylate based resins (305).

Adhesion to dentin also requires conditioning of the surface. Dentin is most often etched with an acidic or chelating agent prior to the application of an adhesive monomer. The acidic conditioner can be supplied as a liquid or a gel form of several acids, ie, phosphoric, nitric, and maleic. Bifunctional monomers with acidic pendant groups such as a carboxylate or phosphate may be considered self-etching primers. The etching procedure removes the surface-altered layer created during cutting or instrumentation of the cavity, and dissolves the mineral matrix from around the collagen fiber network to expose a fiber-rich demineralized zone. This fiber-rich demineralized zone is then infiltrated with an adhesive resin that polymerizes around the collagen fibers, thereby mechanically retaining the adhesive to the surface (306). The polymerized resin-infiltrated demineralized fiber zone is called the *hybrid layer*. Self-etching primers are increasingly being used because they simplify the adhesion bonding process by combining surface conditioning and activation in one step. Self-etching primers address the problem of over etching the dentin surface because, in contrast to conventional conditioners, the reduced acidity of self-etching primers provides a less aggressive attack of the tooth substrate.

Effective dentin adhesion is dependent upon proper wetting of the demineralized collagen-rich zone by the adhesive monomer system. Wetting can be promoted through the use of multifunctional surface-active coupling agents that adsorb onto the surface of the dentin. These coupling agents are usually monomers with surface active groups such as carboxylic, phosphoric, or hydroxy groups that adsorb to the surface; a portion of the molecule that does not adsorb presents a surface that is more easily wetted by the methacrylate restorative material placed over it. An example of a surface active monomer for dentin is *N*-(2-hydroxy-3-methacryloxypropyl)-*N*-phenylglycine [4896-81-5] (NPG–GMA) (307,308). Many surface-active molecules are available for dentin adhesion and most are associated with a high degree of hydrophilicity, because of the adsorbing acid group. They also contain a methacrylate-polymerizing group that covalently bonds to the subsequently applied restorative resin by a free-radical mechanism. These adhesive monomers are supplied as solvent solutions, or mixtures of monomers that are painted over the conditioned dentin surface. Another type of surface-active agent is the aryl tertiary amine, *N*-phenyliminodiacetic acid (PIDAA), which acts to promote adhesion to dentin by surface conditioning, priming, and activation of free-radical polymerization of adhesive monomers (309,310). (PIDAA is suitable for use in self-etching primer adhesive systems.) The adhesive film can be polymerized using light, chemical, or dual initiator systems similar to those used in the restorative polymers.

Polyalkenoic Adhesive Cements. An aqueous-based polymer adhesive is the zinc polycarboxylate cement system that offers good adhesion under moist conditions (311). This cement system contains a powder consisting of 90–95% zinc oxide [1314-13-2] and some magnesium oxide powder that is mixed with an aqueous poly(alkenoic acid), such as poly(acrylic acid) [9003-01-4] or an acrylic acid–itaconic acid copolymer. The setting mechanism results from the neutralization of the polycarboxylic acid with metal oxides, as well as the stiffening of the polymeric network by ionic interactions between carboxylate groups primarily with zinc ions and by the reinforcing action of excess metal oxides (312). The aqueous polyacid interacts with the Ca^{2+} of the apatitic mineral of the tooth structure to form ionized carboxylic acid groups (313). The adhesion of the cement arises from the etching of the tooth surface by the acid, providing mechanical interlocking, and by the formation of ionic bonds between the calcium and carboxylate ions at the tooth–cement interface. The cement adheres well to tooth structure and many metals with minimal substrate surface preparation, but does not bond to porcelain or dental restorative resins.

An adhesive material similar to the polycarboxylate cement is the glass–ionomer cement. This material is available as a luting cement, restorative material, or cavity lining material. Restorative and lining ionomers are fast setting while luting cements have slower setting times and smaller filler particles. The system contains an ion-leachable powder of calcium fluoroaluminosilicate glass that is mixed with an aqeous solution of a poly(alkenoic acid), eg, acrylic acid–itaconic acid copolymer. The setting mechanism occurs primarily in two stages. The faster reaction is the result of partial dissolution of the glass powder by the acid, with the leached calcium ions forming a calcium polysalt matrix. A slower reaction involves the leached aluminum ion from the glass, with the acid forming an aluminum polysalt structure in the matrix. The fully set cement is a composite of unreacted glass particles bound within a matrix of silica gel and calcium and aluminum polysalts (314–316). Adhesion of the cement to tooth structure is by acid etching of the surface and by ionic interaction of the poly(acid) with the Ca^{2+} ions of the tooth mineral. The cement adheres to tooth structure and many metals, but does not bond well to porcelains. Dental restorative resins can be bonded to glass–ionomer by acid etching the ionomer surface and then using an enamel adhesive (317). Resin-modified glass ionomers based on the use of water compatible monomers, oligomers or polymers also have been developed. The curing methods could be chemical, visible light, or a combination of the two (318). In addition to being weakly to moderately adhesive, glass ionomer cements and resin-modified glass ionomers release fluoride (319,320), which may adsorbed onto the tooth structure surrounding the cement to provide an anticaries effect. This phenomenon is important in clinically managing the high caries risk patient.

8. Abrasives

Dental abrasives range in fineness from those that do not damage tooth structure to those that cut tooth enamel. Abrasive particles should be irregular and jagged so that they always present a sharp edge, and should be harder than the material abraded. Another property of an abrasive is its impact strength, ie, if the particle shatters on impact it is ineffective; if it never fractures, the edge becomes dull. Other desirable characteristics include the ability to resist wear and solvation.

It is essential to select the appropriate abrasive for specific purposes. For example, levigated alumina imparts a high polish to metal without removing much metal, but if used on tooth, an excessive amount of tooth tissue will be removed without obtaining the desired polish. The term polishing usually denotes the gradual reduction in the size of surface irregularities or scratches by using successively finer abrasive. The final abrasive should leave a mirror-like high luster.

Dental abrasives can be classified either according to their use or according to the degree of their ability to abrade (see DENTIFRICES). The use classification, adopted for the ADA specification No. 37 for powdered dental abrasive materials, is based on removal of stain from natural teeth or on restorations of all types. Silica, calcium carbonate, calcium pyrophosphate, and tin oxide described below are most often used in dentifrices while the other more aggressive abrasives are used by the dentist for cleaning and polishing. Several abrasives are used in dentistry in a variety of grit sizes and shapes.

8.1. Aluminum Oxide. Emery [57407-26-8] is a natural oxide of aluminum with various impurities. One of these impurities, iron oxide, also acts as an abrasive. Pure aluminum oxide is made from bauxite [1318-16-7] and has partially replaced emery.

8.2. Silicates. Garnet [12178-41-5] is any one of many siliceous combinations with aluminum, cobalt, magnesium, iron or manganese, or both. Garnet for dental use is usually coated on paper with glue and formed in disks and strips. Pumice is of volcanic origin. Kieselguhr is the siliceous remains of minute aquatic plants known as diatoms. Its common name is diatomaceous earth, and in a coarser form it is used as filler in many materials. The finer particles are excellent mild abrasive and polishing agents.

Tripoli is a mild abrasive and polishing agent from porous rocks near Tripoli.

Rouge is a fine red powder of ferric oxide [1309-37-1] (Fe_2O_3). It is usually used in the cake form but is also impregnated in paper or cloth known as crocus cloth.

Tin oxide is a pure white powder. Mixed with water, glycerol, or alcohol into a paste, it is used for polishing teeth and metallic restorations.

Chalk is a calcium carbonate prepared by precipitation. It is used in many polishing compounds including dentifrices.

Calcium pyrophosphate is an insoluble powder that is a mild abrasive. It is currently used as a toothpaste abrasive and the standard to which other abrasives are compared.

Sand and other forms of quartz are used as a powder in sandblasting. If a gentler abrasive material is wanted, powdered walnut shells are often used.

Carbides and diamond [7782-40-3] are imbedded as small particles in a binder and are used to cut tooth structure. Diamond chips are the hardest and most effective abrasive for tooth enamel.

Zirconium silicate [10101-52-7] is a polishing agent with the unique characteristic of gradually reducing its abrasive capability during use. Its high coarseness when first applied permits it to cut rapidly.

9. Therapeutic Dental Materials

9.1. Fluorides. Most worldwide reductions in dental decay can be ascribed to fluoride incorporation into drinking water, dentifrices, and mouth rinses. Numerous mechanisms have been described by which fluoride exerts a beneficial effect. Fluoride either reacts with tooth enamel to reduce its susceptibility to dissolution in bacterial acids or interferes with the production of acid by bacterial within dental plaque. The multiple modes of action with fluoride may account for its remarkable effectiveness at concentrations far below those necessary with most therapeutic materials. Fluoride release from restorative dental materials follows the same basic pattern. Fluoride is released in an initial short burst after placement of the material, and decreases rapidly to a low level of constant release. The constant low level release has been postulated to provide tooth protection by incorporation into tooth mineral.

9.2. Composite Resins. Many composite restorative resins have incorporated fluoride into the filler particles. One commonly used material, yttrium trifluoride [13709-49-4], is incorporated as a radiopaque filler to aid in radiographic diagnosis, and is also responsible for slow release of fluoride from the composites (321). This same effect is achieved with barium–alumina–fluoro–silicate glass filler in composite filling and lining materials. Sodium fluoride [7681-49-4] has also been used in composites by incorporating it into the resin matrix material where it provides long-term low level release (322–324).

9.3. Glass-Ionomers. Glass–ionomers show fluoride release at levels that are usually higher than those found in composite materials. The fluoride is found within the aluminosilicate glass, which is melted with fluoride fluxes and ground to form powder filler. The fluoride is added as calcium fluoride [7789-75-5], aluminum fluoride [15098-87-0], and sodium fluoride [7681-49-4] in a combined proportion of ~20% by weight in the final powder (325,326).

9.4. Other Fluoride Containing Materials. Many forms of fluoride are used strictly as preventive or therapeutic materials. Varnishes containing sodium fluoride are available to place in a cavity prior to filling (327). These varnishes can also be applied as protective agents on tooth crown and root surfaces. Cavity rinses containing stannous fluoride [7783-47-3] and/or acidulated phosphate fluoride are applied topically to a cavity just before filling. The largest groups of therapeutic fluorides are the topical formulations used for treatment of both primary and permanent teeth. These materials are topically applied to tooth surfaces as gels or rinses. The current (1992) ADA accepted materials have fluoride present as 1.23% acidulated phosphate-fluoride, 2% sodium fluoride, or 8% stannous fluoride (328). Prescription fluoride supplements are supplied as rinses, drops, and tablets containing sodium fluoride or acidulated phosphate fluoride in varying doses (329). These are used as both topical treatments and dietary supplements. Fluoride is also available at varying concentrations in many over-the-counter mouth rinses, toothpastes, and chewable vitamins. The most common and widespread form of fluoride is that contained in drinking water supplies. Fluoride is found endogenously in most water supplies at widely varying concentrations. High concentrations of fluoride in water are associated with mottling or staining of enamel, while low levels have been shown to produce no adverse effects (330). Many centralized water systems are currently supplemented to a level of 0.7–1.2 ppm fluoride; this has demonstrated a 30–40% reduction in dental decay (329–331).

9.5. Chlorhexidine Gluconate. Chlorhexidine gluconate [18472-51-0] (1,1′-hexamethylene bis[5-(*p*-chlorophenyl) biguanide] di-D-gluconate) is used as an antimicrobial against both aerobic and anaerobic bacteria in the oral cavity. It is used as a therapeutic supplement in the treatment of gingivitis, periodontal disease, and dental caries. A mouth rinse form is available as a 0.12 wt% aq solution (329).

10. Calcium Phosphate Materials

10.1. Hydroxyapatite. The mineral of teeth and bone comprises impure forms of hydroxyapatite (HA) [1306-06-5], $Ca_{10}(PO_4)_6(OH)_2$. Because of its excellent biocompatibility, synthetic HA, in ceramic forms, has been used clinically for filling bony defects since the mid-1970s. Dense and porous types of ceramic HA are available. Dense HA ceramics are made by compressing calcium phosphate solids from a very fine powder form, known as the green state, into a pellet that is then subjected to a heat treatment that causes the powder particles to fuse together by means of solid-state diffusion (331). Porous HA ceramics are derived from certain species of coral in the genus *Protes* that have regularly patterned 200-μm diameter pores. Processes have been developed to convert the calcium carbonate [471-34-1], $CaCO_3$, in the coral to HA while conserving the macroporous structure (332). Porous ceramic HA permits bone ingrowth if the pores have minimum diameter of 100 μm. Interconnecting pores of 40–100 μm are necessary for the development of functioning haversian systems (333). Neither the dense nor the porous HA undergo significant resorption or degradations *in vivo* (334). Several reviews (335–337) provide a thorough survey of the literature concerning the use of both types of ceramic HA for filling periodontal defects or for the augmentation of alveolar ridges that have resorbed due to aging or disease.

10.2. Other Ceramic Calcium Phosphate Materials. Other ceramic calcium phosphate materials for repairing bony defect include β-tricalcium phosphate (β-TCP) [7758-87-4], $\beta\text{-}Ca_3(PO_4)$, and biphasic calcium phosphate (BCP) ceramics that consist of both β-TCP and HA. Unlike ceramic HA, β-TCP resorbs in the tissue (334). The *in vivo* dissolution of BCP ceramic implants was shown (337) to increase with increasing β-TCP/HA ratio in the implants. Both β-TCP and BCP can lead to new bone growth to various extents depending on the applications and the type of materials used (334,337).

10.3. Calcium Phosphate Cements. Self-setting calcium phosphate cements have been a subject of considerable interest in recent years. Materials that are totally biocompatible and also harden like cement at the site of application are highly desirable in a wide range of biomedical applications. Data in the literature (338) show that cementation can occur in mixtures containing a variety of calcium phosphate compounds. The products formed in these systems included a dibasic calcium phosphate known as dicalcium phosphate dihydrate (DCPD) [7789-77-7], $CaHPO_4 \cdot 2H_2O$ (339), octacalcium phosphate (OCP), $Ca_8H_2(PO_4)_6 \cdot 10H_2O$ (340), and HA (341).

The cement system that uses either tetracalcium phosphate [1306-01-0], $Ca_4(PO_4)_2O$, and dicalcium phosphate anhydrous (DCPA) [7757-93-9], $CaHPO_4$, or TTCP and DCPD (300), as the starting ingredients has been studied quite extensively. This cement forms HA with a stoichiometric Ca/P ratio of 1.67; the pH of the cement is at or near the physiological pH (342). These probably contribute to the cement's high biocompatibility and excellent *in vivo* characteristics (343,344). When implanted in bone, the cement resorbs slowly and is replaced by new bone tissue without loss of volume (345). This cement has a compressive strength of over 70 MPa (10,150 psi) (301), making it acceptable for repairing bony defects in most nonload-bearing skeletal sites. The cement has been evaluated for a number of dental and medical applications including root canal filling (346,347), alveolar bone implant (348), frontal sinus obliteration (349), and cranioplasty (350).

11. Dental Implants

The use of dental implants is increasing due to improved success rates and is considered a predictable procedure (351,352). The use of implants in dentistry to replace missing teeth is widespread and may now be considered a standard treatment option. Implants may be used to replace a single tooth or multiple teeth. This success relies on the discovery of Prof. P-I Brånemark that living bone cells have an affinity for titanium oxides on the surface of the implant. Brånemark termed the phenomenon osseointegration, defined as bone-to-implant contact on a microscopic level with no intervening connective tissue (353,354). The majority of implants placed today are artificial tooth root analogs made of titanium or titanium alloy. Success criteria for dental implants include: implant immobility, absence of a radiolucency between bone and implant, no progressive bone loss, and no other adverse symptoms (355) such as pain and infection. The 1988 National Institutes of Health Consensus Development Conference on Dental Implants (356) provided a review of the history and status on dental implants. Reports indicated then that the use of better materials and technology had resulted in an improved implant–bone interface responsible for a higher success rate for dental implants. A number of present day implants have means for mechanical fixation such as grooved and porous surfaces. In 1986, based on these factors, a success rate of 85% after 5 years and 80% after 10 years was expected (357); this was a 10% increase over a 1979 expectation. In 2002, expected success rates continue to increase. Success rates in the anterior mandible can reach 95% or greater. Success rates are reported to vary between the various regions of the oral cavity. The highest success rate is usually achieved in the anterior mandible while the lowest success in the posterior maxillae. Currently, dental implants can be expected to function for 12 years or more (358).

Titanium continues to be the most popular material for dental implants (359). Various surface treatments and coatings have been developed to attempt to improve the adaptation or attachment of the bone to the implant surface.

11.1. Regulation. Dental implants are regulated by the FDA. All dental implants fall into the FDA class III, which covers devices that are life sustaining, life supporting, or are implanted into the body and have the potential to cause unreasonable risk, illness, or injury. Because dental implants are "preamendments" (pre-1976) devices, they are cleared under the 510(k) premarket notification (clearance) program, rather than the more difficult Premarket Approval process used for most Class III devices. There are at least 80 companies that have FDA marketing clearance for specific dental implants, based on substantial equivalency to implants marketed prior to 1976.

11.2. Requirements. Requirements for dental implant materials are similar to those for orthopedic uses. The first requirement is that the material used in the implant must be biocompatible and not cause any adverse reaction in the body. The material must be able to withstand the environment of the body, and not degrade and be unable to perform the intended function.

There are a number of designs for dental implants. The patient must have bone of sufficient quality and volume to accommodate the design of the implant used. Other factors that can affect the success of dental implants are oral hygiene, personal habits, such as smoking, and overall health.

The American Society for Testing and Materials (ASTM) F4 Committee on Medical Materials and Devices has developed specifications for chemical composition and mechanical properties of materials used for dental implants and for test methods used for their evaluation. Standard test methods also are available from ASTM, 1916 Race Street, Philadelphia. Also, implant manufacturers have interest in compliance with the ISO standards of quality assurance, ISO 9001 and ISO 9002. These are models of quality assurance in design, development, production, installation, and servicing (352). Such standards provide a means of evaluation and validation that the manufacturer meets stated claims. ISO Technical Committee 106/Subcommittee 8 is in the process of developing international standards for implant testing, bioevaluation, and labeling. The accuracy of castings used to attach prosthetic devices to the implants is important and standards to define this would be useful.

11.3. Materials. Currently, titanium, either commercially pure or a Ti-6 Al-4 V alloy, is the most widely used metal for implants. Materials used as dental implants throughout history include natural teeth from man, animal teeth, ivory, wood, plastic, vitreous carbon, alumina, and various metals including gold, aluminum, 316L stainless steel, cobalt–chromium–molybdenum alloys, titanium and Ti-6 Al-4 V alloy. The cobalt–chromium–molybdenum was used for many years and still is used for casting individual implants and for some of the blade implants. Ceramic materials including hydroxyapatite, high density alumina, and single-crystal sapphire (alpha alumina) also have been studied and/or used as dental implants. Implant coating and surface treatments include machined surfaces, textured surfaces, HA coated, titanium plasma-sprayed, particulate-blasted (aluminum oxide, tricalcium phosphate, or titanium dioxide) or treated with leaching agents (352). The goal of implant surface treatments is to increase the implant surface area and to enhance cellular activity for improved bone-to-implant contact (352,360,361).

Hydroxyapaite, the mineral constituent of bone, is applied to the surfaces of many dental implants for the purpose of increasing initial bone growth. However, titanium and its alloy, Ti-6Al-4V, are biocompatible and have osseointegrated as successfully as dental implants without the hydroxyapatite coating.

Surface preparation of the dental implant prior to implantation will have an effect on corrosion behavior, initial metal ion release, and interface tissue response (363). The titanium and titanium alloy dental implants presently in use have many configurations designed to facilitate bone ingrowth including cylinders with holes, screw threaded surfaces, porous surfaces, and other types of roughened surfaces. The body geometry of endosseous implants is generally cylindrical in shape (352). The implant body also may be solid or hollow. There may be a presence or absence of threads, depending on whether the implant is designed to be screwed to place or press-fit. Threaded implants are available and characterized as straight, tapered, ovoid or expanding. Thread patterns vary widely and include broad macrothreads, threads that induce self-tapping or microthreads. The shape of press-fit implants could vary from straight-walled cylinders to tapered or conical forms. Methods used to produce porous surfaces include arc plasma spraying of metal (titanium) onto the implant and the sintering of spheres to the implant surface.

In addition to the body shape of the implant and surface treatment, the implant can also be classified by the implant–abutment interface. In general the connection is either internal or external. Antirotational geometric features of the connection include the cone screw, the cone hexagonagonal, the cylinder hex, the Morse taper, the spline, and the internal spline (352).

11.4. Types of Dental Implants. Indications for a specific type of implant are based primarily on the amount of bone available to support the implant. Also to be considered is the implant proven most successful. Three types of implants are discussed here.

11.5. Endosseous. The implants that are anchored in the bone are commonly referred to as being osseointegrated, and are the most successful implants. Endosseous implant types are root form (cylinder, screw, cone; blade-form, and ramus frame). The root form, which can be a hollow cylinder, a screw, or a blade, has been the most successful, and currently is the most widely used. One technique is to use a two-stage surgery to submerge the implant in the alveolar ridge and cover it with mucosal tissue. The implant could be a screw type that has a healing-screw in the top. At the second stage after healing has occurred, the healing screw is removed, and the part intended to support and connect to the prosthetic component is screwed into the space vacated by removal of the healing screw. This procedure results in the implant being well covered with bone, and prevents the growth of the epithelium down the sides of the implant and subsequent mobility of the implant. The modern screw-type implant has a 95% success rate in the anterior mandible over a period of >10 years (354). Similar success rates have been reported in the maxilla (358,363).

A relative recent development is an evolving change in the clinical protocol. The most widely used clinical protocol for root form implants was introduced in the United States in the early 1980s. The protocol called for a two-stage surgical technique. The implants were placed in the bone during the first stage surgery and covered by mucosa and allowed to heal for 3–4 months in the mandible and 4–6 months in the maxillae. The implants were uncovered at the second stage surgery and if osseointegrated, they were used to support a prosthesis. A newer protocol allows a one-stage surgery with immediate loading of the implants with an interim prosthesis (364–366).

11.6. Subperiosteal. The subperiosteal implants are placed on the residual bony ridge and are not osseointegrated. This implant is most commonly used in the mandible but sometimes is used in the maxilla. Subperiosteal implants have been installed since the 1940s (357) and have a reported success rate after 5 years of 50–60%. A success rate of >90% for 5 years and 50% for

15 years also has been quoted (367). Subperiosteal implants are fabricated by custom casting a framework to fit each individual mandible or maxilla. The use of subperiosteal implants has declined significantly in recent years, primarily due to the simpler surgical procedures required for placement of titanium root form implants, their high success rates and the wide availability of prefabricated titanium implants and prosthetic components.

11.7. Transosteal and Staple Implants. Implants of this design generally consist of a plate attached to the inferior border of the anterior mandible and posts attached to that plate. The posts are intended to go through the mandible and are intended to support a denture. The mandibular bone staple plate has replaced the transosteal pin. In 1985, a success rate of 93% after 5 years was reported (368). The use of this design of implant has also decreased as the popularity of the root form implants has increased.

Certain commercial materials and equipment may be identified in this article for adequate definition of subject matter. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, or that the material or equipment is necessarily the best available for the purpose.

BIBLIOGRAPHY

"Dental Materials" in *ECT* 1st ed., Vol. 4, pp. 894–928, by F. H. Freeman, Kerr Manufacturing Co.; in *ECT* 2nd ed., Vol. 6, pp. 777–847, by F. H. Freeman, Kerr Manufacturing Co.; in *ECT* 3rd ed., Vol. 7, pp. 461–521, by G. C. Paffenbarger and N. W. Rupp, American Dental Association Health Foundation, Research Unit, National Bureau of Standards.; in *ECT* 4th ed., Vol. 7, pp. 946–1022, by, John A. Tesk, Joseph M. Antonucci, Clifton M. Carey, Fred C. Eichmiller, J. Robert Kelly, Nelson W. Rupp, Richard W. Waterstrat, Anna C. Fraker, Lawrence C. Chow, Laurie A. George, Gary E. Schumacher, Jeffrey W. Stansbury, and Edward E. Parry, National Institute of Standards and Technology (NIST).; "Dental Materials", in *ECT* (online), posting date: December 4, 2000, by John A. Tesk, Joseph M. Antonucci, Clifton M. Carey, Fred C. Eichmiller, J. Robert Kelly, Nelson W. Rupp, Richard W. Waterstrat, Anna C. Fraker, Lawrence C. Chow, Laurie A. George, Gary E. Schumacher, Jeffrey W. Stansbury, and Edward E. Parry, National Institute of Standards and Technology (NIST).

CITED PUBLICATIONS

1. M. E. Ring, *Dentistry, an Illustrated History*, Abrams, New York, 1985, pp. 160–81, 193–211.
2. J. R. Kelly, *Ann. Rev. Mater. Sci.* **27**, 443 (1997).
3. F. J. J. Clarke, in J. W. McLean, ed., *Dental Ceramics: Proceedings of the First International Symposium on Ceramics*, Quintessence Publishing Co., Chicago, Ill., 1983, p. 441.
4. G. J. Christensen, *J. Prosthet. Dent.* **56**, 1 (1986).
5. I. L. Denry, *Crit. Rev. Oral Biol. Med.* **7**, 134 (1996).
6. J. Tinschert and co-workers, *J. Dent.* **28**, 529 (2000).
7. J. L. Drummond and co-workers, *Dent. Mater.* **16**, 226 (2000).
8. D. W. Jones, *Dent. Clin. North Am.* **29**, 621 (1985).

9. D. E. Southan, in J. A. von Fraunhofer, ed., *Scientific Aspects of Dental Materials*, Butterworths, London, 1975, p. 277.
10. W. J. O'Brien, *Dental Materials: Properties and Selection*, Quintessence Publishing Co., Chicago, Ill., 1989, p. 397.
11. B. O. Mysen, *Structure and Properties of Silicate Melts*, Elsevier, Amsterdam, The Netherlands, 1988, p. 99.
12. J. R. Mackert, in J. D. Preston, ed., *Perspectives in Dental Ceramics: Proceeding of the Fourth International Symposium on Ceramics*, Quintessence Publishing Co., Chicago, Ill., 1988, p. 53.
13. U.S. Pat. 3,052,983 (Sept. 11, 1962), M. Weinstein and A. B. Weinstein (to Permadent Manufacturing Co.).
14. W. H. Mörmann, M. Brandestini, and F. Lutz, *J. Am. Dent. Assoc.* **120**(6), 517 (1990).
15. D. G. Grossman, in W. H. Mörmann, ed., *International Symposium on Computer Restorations*, Quintessence Publishing Co., Berlin, 1991, p. 103.
16. J. R. Kelly and co-workers, in W. H. Mörmann, ed., *International Symposium on Computer Restorations*, Quintessence Publishing Co., Berlin, 1991, p. 253.
17. J. K. Dong and co-workers, *Int. J. Prosth.* **5**(1), 9 (1992).
18. J. W. McLean and T. H. Hughes, *Br. Dent. J.* **119**, 251 (1965).
19. V. Piddock and A. J. E. Qualtrough, *J. Dent.* **18**, 227 (1990).
20. R. R. Seghi, T. Daher, and A. Caputo, *Dent. Mater.* **6**, 181 (1990).
21. D. E. Southan, *Aust. Dent. J.* **15**, 507 (1970).
22. K. J. Anusavice, C. Shen, and R. B. Lee, *J. Dent. Res.* **71**, 1134 (1992).
23. P. W. McMillan, *Glass Ceramics*, 2nd ed., Academic Press, London, 1979, p. 1.
24. D. G. Grossman, *Dent. Clin. North Am.* **29**, 725 (1985).
25. L. A. George, F. C. Eichmiller, and R. L. Bowen, *Ceram. Bull.* **71**, 1073 (1992).
26. W. Hoeland and co-workers, *J. Biomed. Mater. Res.* **53**, 297 (2000).
27. D. G. Grossman, *J. Am. Ceram. Soc.* **55**, 446 (1972).
28. M. Andersson and co-workers, *Quintessence Int.* **29**, 285 (1998).
29. F. Filser and co-workers, *Int. J. Comput. Dent.* **4**, 89 (2001).
30. D. Suttor and co-workers, *Int. J. Comput. Dent.* **4**, 195 (2001).
31. G. C. Paffenbarger, W. T. Sweeney, and A. A. Issacs, *J. Am. Dent. Assoc.* **20**, 1960 (1933).
32. G. E. Servais and L. Cartz, *J. Dent. Res.* **50**, 613 (1971).
33. S. Crisp, M. A. Jennings, and A. D. Wilson, *J. Oral Rehab.* **5**, 139 (1978).
34. A. D. Wilson, *Chem. Soc. Rev.* **7**, 265 (1978).
35. D. C. Smith, R. D. Norman, and M. L. Swartz, *Restorative Dental Materials; An Overview*, Vol. 1, Quintessence Publishing Co., London, 1985, pp. 35–39.
36. K. DeGroot and co-workers, *J. Dent. Res.* **59**, 1493 (1980).
37. R. S. Schwartz, M. Mauger, D. J. Clement, and W. A. Walker, *J. Am. Dent. Assoc.* **130**, 967 (1999).
38. M. Torabinejad, C. U. Hong, F. McDonald, and R. R. Pitt Ford, *J. Endod.* **21**, 349 (1995).
39. R. Roda, *Pract. Proced. Aesthet. Dent.* **13**, 467 (2001).
40. M. Torabinjead, C. U. Hong, T. R. Pitt Ford, and J. D. Kettering, *J. Endod.* **21**, 403 (1995).
41. C. Estrela, L. L. Bammann, C. R. Estrela, R. S. Silva, and J. D. Pecora, *Braz. Dent. J.* **11**, 3 (2000).
42. S. J. Lee, M. Monsef, and M. Torabinejad, *J. Endod.* **19**, 541 (1993).
43. M. Torabinejad, P. W. Smith, J. D. Kettering, and T. R. Pitt Ford, *J. Endod.* **21**, 295 (1995).
44. W. Geurtsen, *Aust. Endod. J.* **27**, 12 (2001).
45. K. Keiser, C. C. Johnson, and D. A. Tipton, *J. Endod.* **26**, 288 (2000).
46. E. T. Koh, M. Torabinejad, T. R. Pitt Ford, K. Brady, and F. McDonald, *J. Biomed. Mater. Res.* **37**, 432 (1997).

47. T. Koh, F. McDonald, T. R. Pitt Ford, and M. Torabinejad, *J. Endod.* **24**, 543 (1998).
48. T. R. Moretton, C. E. Brown, Jr., J. J. Legan, and A. H. Kafrawy, *J. Biomed. Mater. Res.* **52**, 528 (2000).
49. I. M. Faraco, Jr., and R. Holland, *Dent Traumatol.* **17**, 163 (2001).
50. D. C. Smith, *Br. Dent. J.* **124**, 381 (1968).
51. U.S. Pat. 3,655,605 (Apr. 11, 1972), D. C. Smith (to National Research Development Corp.).
52. D. C. Smith, *J. Can. Dent. Assoc.* **37**, 22 (1971).
53. G. S. Beagrie, J. H. P. Main, and D. C. Smith, *Br. Dent. J.* **132**, 351 (1972).
54. D. R. Beech, *Archs. Oral. Biol.* **17**, 907 (1972).
55. D. R. Beech, *Br. Dent. J.* **135**, 442 (1973).
56. D. R. Beech, A. Solomon, and R. Bernier, *Dent. Mater.* **1**, 154 (1985).
57. B. E. Causton, *J. Dent. Res.* **58**, 1383 (1979).
58. B. E. Causton, *Biocompatibility of Dental Materials*, Vol. 2, CRC Press, Inc. Boca Raton, Fla., 1982, Chapt. 7.
59. M. A. Monharram and co-workers, *J. Mater. Sci.* **21**, 1681 (1980).
60. T. Nasu, *J. Biomed. Mater. Res.* **20**, 347 (1986).
61. K. Miyazaki and co-workers, *J. Dent. Res.* **69**, 367 (1990).
62. Y. Matsuya and co-workers, *J. Dent. Res.* **71**, 141 (1992).
63. A. D. Wilson and B. E. Kent, *Br. Dent. J.* **132**, 133 (1972).
64. A. D. Wilson and H. J. Prosser, *Biocompatibility of Dental Materials*, Vol. 3, CRC Press, Inc., Boca Raton, Fla., 1982, Chapt. 3.
65. A. W. G. Walls, *J. Dent.* **14**, 231 (1986).
66. A. D. Wilson and J. W. McLean, *Glass-Ionomer Cement*, Quintessence Publishing Co., Chicago, Ill., 1988.
67. J. W. McLean, *Br. Dent. J.* **164**, 293 (1988).
68. G. J. Mount, *The Clinician's Handbook*, Martin Dunitz, London, 1989.
69. A. Maldonado, M. L. Swarz, and R. W. Phillips, *J. Am. Dent. Assoc.* **96**, 785 (1978).
70. S. Crisp, B. G. Lewis, and A. D. Wilson, *J. Dent.* **7**, 304 (1979).
71. R. G. Mill and A. D. Wilson, *J. Dent. Res.* **67**, 1446 (1988).
72. J. W. Nicholson and co-workers, *J. Dent. Res.* **67**, 1451 (1988).
73. J. W. McLean, A. D. Wilson, and H. J. Prosser, *J. Prosthet. Dent.* **52**, 175 (1984).
74. P. Hotz and co-workers, *Br. Dent. J.* **141**, 41 (1977).
75. D. P. Powis and co-workers, *J. Dent. Res.* **61**, 1416 (1982).
76. B. L. Dahl and G. Oilo, *Dent. Mater.* **2**, 17 (1986).
77. Y. E. Y. Aboush and C. B. G. Jenkins, *J. Dent.* **15**, 147 (1986).
78. J. W. McLean and co-workers, *Br. Dent. J.* **158**, 410 (1985).
79. F. I. Magnum, E. A. Berry, and U. K. Parikh, *J. Am. Dent. Assoc.* **120**, 535 (1990).
80. J. E. Rusz and co-workers, *Dent. Mater.* **8**, 31 (1992).
81. J. E. McKinney, J. M. Antonucci, and N. W. Rupp, *J. Dent. Res.* **66**, 1134 (1987).
82. H. J. Prosser, D. R. Powis, and A. D. Wilson, *J. Dent. Res.* **65**, 146 (1986).
83. J. W. McLean and O. Gasser, *Quintessence Int.* **16**, 333 (1985).
84. J. E. McKinney and J. M. Antonucci, *J. Dent. Res.* **66**, (1980).
85. J. M. Antonucci, J. E. McKinney, and J. W. Stansbury, *Trans. 13th Ann. Mtg. Soc. Biomater.*, 1987, p. 225.
86. J. M. Antonucci, *Trends Tech.* 5, 4 (1988).
87. J. M. Antonucci and J. W. Stansbury, *J. Dent. Res.* **68**, 251 (1989).
88. R. S. Mathis and J. L. Ferracane, *Dent. Mater.* **5**, 355 (1989).
89. J. W. McLean, *J. Am. Dent. Assoc.* **120**, 43 (1990).
90. J. J. Simmons, *J. Am. Dent. Assoc.* **120**, 49 (1990).
91. U.S. Pat. 4,527,979 (July 9, 1985), J. W. McLeonard and O. Gasser (to ESPE, Fabrik Pharmazeutischer Praeparate, GmbH).
92. J. E. McKinney, J. M. Antonucci, and N. W. Rupp, *J. Dent. Res.* **67**, 83 (1988).

93. S. B. Mitra, *J. Dent. Res.* **70**, 72 and 75 (1991).
94. S. B. Mitra, *J. Dent. Res.* **70**, 72 (1991).
95. *Ibid.* **70**, 75 (1991).
96. L. Linden, in J. C. Salmone, ed., *Polymeric Materials Encyclopedia*, 1996, p. 1854.
97. A. Sugawara and co-workers, *J. Nihon Sch. Dent.* **31**, 372 (1989).
98. G. V. Balck, *Operative Dentistry*, Vol. 3, 7th ed., Medico Dental Publishing Co., Chicago, Ill., 1936, p. 233.
99. D. A. Wallace and H. C. Hanson, *J. Am. Dent. Assoc.* **26**, 1536 (1939).
100. W. Harvey and W. J. Pitch, *Br. Dent. J.* **80**, 1 (1946).
101. E. J. Molnar and E. W. Skinner, *J. Am. Dent. Assoc.* **29**, 744 (1942).
102. H. I. Copeland and co-workers, *J. Dent. Res.* **34**, 740 (1955).
103. J. M. Antonucci and co-workers, *2nd World Congress on Biomaterials, Trans. 10th Ann. Mtg. Soc. Biomater*, 1984, p. 137.
104. M. D. Jendresen, M. L. Swartz, and R. D. Norman, *J. Prosth. Dent.* **21**, 176 (1969).
105. M. D. Jendresen and R. W. Phillips, *J. Prosth. Dent.* **21**, 300 (1969).
106. G. M. Brauer, R. McLaughlin, and E. Huget, *J. Dent. Res.* **47**, 622 (1968).
107. A. D. Wilson, in J. A. von Fraunhoffer, ed., *Scientific Aspects of Dental Materials*, Butterworths, London, 1975, Chapts. 4 and 5.
108. D. F. Vieira, *J. Prosthet. Dent.* **9**, 70 (1959).
109. M. T. Tyas and H. J. Wilson, *Br. Dent. J.* **129**, 461 (1970).
110. S. Olson, B. Bergman, and M. Bergman, *Swed. Dent. J.* **6**, 177 (1982).
111. G. M. Brauer, E. E. White, and M. G. Mashonas, *J. Dent. Res.* **37**, 547 (1958).
112. G. M. Brauer, L. Simon, and L. Sangermono, *J. Dent. Res.* **41**, 1096 (1962).
113. S. Civjan and G. M. Brauer, *J. Dent. Res.* **43**, 281 (1964).
114. G. M. Brauer and J. W. Stansbury, *J. Dent. Res.* **63**, 137 (1984); *Ibid.* **63**, 1315 (1984).
115. J. W. Stansbury and G. M. Brauer, *J. Biomed. Mater. Res.* **19**, 715 (1985).
116. G. M. Brauer, J. W. Stansbury, and D. Flowers, *Dent. Mater.* **2**, 21 (1986).
117. U.S. Pat. 3,047,408 (July 31, 1962), E. W. Dougherty (to L. D. Caulk Co.).
118. F. J. Fisher, *Br. Dent. J.* **143**, 231 F(1977).
119. W. L. Lang, *J. Dent. Res.* **65**, 175 (1986).
120. N. S. Seale and H. R. Stanley, *J. Dent. Res.* **65**, 772 (1986).
121. P. J. Schouboe, G. C. Paffenbarger, and W. T. Sweeney, *J. Am. Dent. Assoc.* **52**, 584 (1956).
122. C. L. Hadden, *Chem. Ind.* **21**, 190 (1944).
123. *Dental Phosphate-Bonded Casting Investments, International Standard ISO 9694*, American National Standards Institute, New York.
124. D. B. Mahler and K. Asgarzadeh, *J. Dent. Res.* **32**, 354 (1953).
125. K. D. Jorgensen, *Odontol. Tidskr.* **61**, 305 (1953).
126. C. W. Fairhurst, *J. Dent. Res.* **39**, 812 (1960).
127. *Guide to Dental Materials and Devices*, 8th ed., American Dental Assoc., Chicago, Ill., 1976–1978, p. 110.
128. D. B. Mahler and A. B. Ady, *J. Dent. Res.* **39**, 578.
129. R. H. Volland and G. C. Paffenbarger, *J. Am. Dent. Assoc.* **19**, 185 (1932).
130. R. Earnshaw, *Aust. Dent. J.* **14**, 264 (1969).
131. *Guide to Dental Materials and Devices*, 8th ed., American Dental Assoc., Chicago, Ill., 1976–1978, p. 112.
132. R. Earnshaw, in W. J. O'Brian, ed., *Dental Materials, Properties and Selection*, Quintessence Publishing Co., Chicago, Ill., 1989.
133. W. J. O'Brien and J. P. Nielsen, *J. Dent. Res.* **38**, 541 (1959).
134. U.S. Pat. 1,909,008 (May 16, 1933), C. H. Prange (to Austenal Laboratories, Inc.).
135. C. P. Mabie, *J. Dent. Res.* **52**, 758 (1973).
136. U.S. Pat. 2,222,781 (Nov. 26, 1940), T. E. Moore (to Ransom and Randolph Co.).

137. C. P. Mabie, *J. Dent. Res.* **52**, 96 (1973).
138. R. J. Schnell, G. Mumford, and R. W. Phillips, *J. Prosthet. Dent.* **13**, 324 (1963).
139. U.S. Pat. 1,708,436 (Apr. 9, 1929), L. J. Weinstein.
140. U.S. Pat. 1,924,874 (Aug. 29, 1933), T. E. Moore (to Ransom and Randolph Co.).
141. N. O. Taylor, G. C. Paffenbarger, and W. T. Sweeney, *J. Am. Dent. Assoc.* **17**, 2266 (1930).
142. J. S. Shell, *Dent. Surv.* **36**, 616, 770.
143. *Dental Gypsum-Bonded Casting Investments for Gold Alloys, International Standard ISO 7490*, American National Standards Institute, New York.
144. R. Earnshaw, *J. Dent. Res.* **67**, 1366 (1988).
145. D. R. Davis, *J. Prosthet. Dent.* **57**, 362 (1987).
146. L. Forsten, *Scand. J. Dent. Res.* **98**(2), 179 (1990).
147. M. Ohashi and G. C. Paffenbarger, *J. Nihon Univ. Sch. Dent.* **11**, 109 (1969).
148. L. C. Dirksen, *J. Am. Dent. Assoc.* **26**, 273 (1939).
149. J. W. McCrorie, *Br. Dent. J.* **132**, 189 (1972).
150. J. F. Bates and A. G. Knapton, *Int. Metall. Rev.* **22**, 39 (Mar. 1977).
151. P. Reithe, *Tsch. Zahnaertzl. Z.* **21**, 301 (1966).
152. D. B. Mahler and J. van Eysden, *J. Dent. Res.* **48**, 501 (1969).
153. D. B. Mahler and co-workers, *J. Dent. Res.* **49**, 1452 (1970).
154. D. B. K. Innes and W. V. Youdelis, *J. Can. Dent. Assoc.* **29**, 587 (1963).
155. D. B. Mahler, L. G. Terkla, and J. van Eysden, *J. Dent. Res.* **52**, 823 (1973).
156. K. Asgar, *J. Dent. Res.* **53**, special issue, abst. 23 (1974).
157. J. W. Osborne and R. D. Norman, *Dent. Mater.* **6**, 189 (1990).
158. L. B. Johnson, *J. Biomed. Mater. Res.* **4**, 269 (1970).
159. R. Nadal, R. W. Phillips, and M. L. Swartz, *J. Am. Dent. Assoc.* **63**, 488 (1961).
160. J. P. Nielsen and J. T. Tuccillo, *J. Dent. Res.* **45**, 964 (1966).
161. D. L. Smith and co-workers, *J. Dent. Res.* **49**, 283 (1970).
162. S. Civjan and G. M. Brauer, *J. Dent. Res.* **43**, 281 (1964).
163. D. C. Smith, *Br. Dent. J.* **124**, 381 (1968).
164. *Metals Handbook*, 8th ed., American Society for Metals, Metals Park, Ohio, 1961, p. 1189.
165. J. N. Nally, *Int. Dent. J.* **18**, 309 (1968).
166. S. Civjan, D. F. Huget, and J. E. Marsden, *J. Am. Dent. Assoc.* **85**, 1309 (1972).
167. S. Civjan and co-workers, *J. Am. Dent. Assoc.* **90**, 659 (1975).
168. E. F. Huget and S. Civjan, *J. Am. Dent. Assoc.* **89**, 383 (1974).
169. R. W. Phillips, *Skinner's Science of Dental Materials*, 7th ed., W. B. Saunders Co., Philadelphia, 1973, p. 565.
170. R. L. Coleman, *Bur. Stand. U.S. J. Res.* **1**, 867 (1928).
171. U.S. Pat. 1,909,008 (May 16, 1933), C. H. Prange (to Austenal Laboratories, Inc.).
172. U.S. Pat. 1,956,278 (Apr. 24, 1934), R. W. Erdle and C. H. Prange (to Austenal Laboratories, Inc.).
173. U.S. Pat. 1,958,446 (May 15, 1934), C. H. Prange (to Austenal Laboratories, Inc.).
174. H. F. Morris and K. Asgar, *J. Pros. Dent.* **33**, 36 (1975).
175. J. Jahtzen, *Quintessence Int.* **1**, 1 (1970).
176. J. F. Bates and A. G. Knapton, *Int. Metall. Rev.* **22**, 39 (1977).
177. R. W. Phillips, *Skinner's Science of Dental Materials*, 7th ed., W. B. Saunders Co., Philadelphia, 1973, p. 593.
178. R. Earnshaw, *Aust. Dent. J.* **3**, 159 (1958).
179. G. T. Eden and co-workers, *J. Dent. Res.* **56**, special issue, abst. 648 (1977).
180. J. P. Moffa, in T. M. Valega Sr., ed., *Alternatives to Gold Alloys*, conference proceedings, Jan. 24–26, 1977, DHEW publication, Bethesda, Md., (NIH) no. 77–1227, 1977.

181. E. F. Huget, J. M. Vilca, and R. M. Wall, *J. Dent. Res.* **56**, special issue B, abst. 642 (1977).
182. J. F. Bates and A. G. Knapton in Ref. 77.
183. J. P. Moffa and W. A. Jenkins in Ref. 54, p. 652. N. K. Sarkar and E. H. Greener, *Materials Engineering Conference*, Oct. 1973, Chicago, American Society for Metals, Metals Park, Ohio.
184. O. E. Beder and W. J. Ploger, *Oral Surg. Oral Med. and Oral Path.* **12**, 787 (1959).
185. T. M. Valega, Sr. ed., *Alternatives to Gold Alloys*, conference proceedings, Jan. 24–26, 1977, DHEW publication, Bethesda, Md., (NIH) no. 77–1227, 1977, pp. 224–233.
186. K. Ida and co-workers, *Dent. Mater. J.* **1**, 8 (1982).
187. H. J. Mueller, A. A. Giuseppetti, and R. M. Waterstrat, *J. Dent. Res.* **69**, special issue, 2072 (1990).
188. Y. Tamaki and co-workers, *J. Dent. Res.* **70**, special issue, abst. 1755 (1991).
189. R. J. Baez, T. Nonaka, and R. Blackman, *J. Dent. Res.* **70**, special issue, abst. 1757 (1991).
190. A. S. Algabab and co-workers, *Northwestern Dent. Res.* **2**, 21 (1991).
191. A. R. Hruska, *Quintessence Int.* **18**, 683 (1987).
192. A. R. Hruska, *Quintessence Int.* **15**, 198 (1989).
193. F. Watari, *Dent. Mat. J.* **8**, 83 (1989).
194. A. Kuroiwa and co-workers, *Dent. Mat. J.* **9**, 279 (1990).
195. S. P. Thompson and co-workers, *J. Dent. Res.* **71**, special issue, abst. 1418 (1992).
196. N. Morita, *Dent. Mater. J.* **9**, 218 (1990).
197. Y. Tamaki and co-workers, *Dent. Mater. J.* **8**, 103 (1980).
198. G. F. Andreasen and T. B. Hilleman, *J. Am. Dent. Assoc.* **82**, 1373 (1971).
199. G. F. Andreasen and P. R. Brady, *Angle Orthod.* **42**, 172 (1972).
200. S. Civjan, E. F. Huget, and L. B. DeSimon, *J. Dent. Res.* **54**, 89 (1975).
201. G. F. Andreasen and R. E. Morrow, *Am. J. Orthod.* **73**, 142 (1978).
202. W. L. Wildey, E. S. Senia, and S. Montgomery, *Oral Surg. Oral Med. Oral Pathol.* **74**, 499 (1992).
203. J. Camps and W. J. Pertot, *J. Endod.* **20**, 395 (1994).
204. J. Takahashi, M. Okazaki, H. Kimura, and Y. Furuta, *J. Biomed. Mater. Res.* **18**, 427 (1984).
205. K. Hasegawa, *Shika Zairyo Kikai.* **8**, 388 (1989).
206. S. W. Wang, *Zhonghua Kou Qiang Yi Xue Za Zhi.* **29**, 183 (1994).
207. A. H. L. Tjan and co-workers, *J. Prosthet. Dent.* **66**, 157 (1991).
208. Ref. 150, p. 39.
209. *Brazing Manual*, American Welding Society, United Engineering Center, New York, 1955.
210. J. F. Johnston, G. Mumford, and R. W. Dykema, *Modern Practice in Dental Ceramics*, W. B. Saunders Co., Philadelphia, 1967.
211. *Specification B 32-60aT*, ASTM Standards, 1992.
212. *Soldering Manual*, American Welding Society, United Engineering Center, New York, 1959.
213. *Metals Handbook*, 8th ed., American Society of Metals, Metals Park, Ohio, 1961, pp. 1188–1189.
214. R. W. Phillips, *Skinner's Science of Dental Materials*, 7th ed., W. B. Saunders Co., Philadelphia, 1973, Chapts. 31–33.
215. E. M. Wise, *Gold: Recovery, Properties and Applications*, D. Van Nostrand Co., Inc., New York, 1964.
216. T. M. Valega, Sr., ed., in Ref. 185, pp. 224–233.
217. E. H. Stade, M. H. Reisbick, and J. D. Preston, *J. Prosthet. Dent.* **34**, 527 (1975).
218. J. L. Ferracane, *Operative Dent.*, Suppl. **6**, 199 (2001).

219. R. G. Craig, in B. R. Land and C. C. Kelsey, eds, *International Prosthodontics Workshop on Complete Denture Occlusion*, University of Michigan Press, Ann Arbor, Mich., 1973, pp. 205–236.
220. K. K. Kapur and S. D. Somarn, *J. Prosthet. Dent.* **14**, 687 (1964).
221. R. V. Reitz, J. L. Sanders, and B. Levin, *Quintessence Int.* **16**, 547 (1985).
222. J. L. Sanders, B. Levin, and P. V. Reitz, *Quintessence Int.* **18**, 453 (1987).
223. D. A. L. Doori and co-workers, *Dent. Mater.* **4**, 25 (1988).
224. V. T. Truong and F. G. V. Thomas, *Aust. Dent. J.* **33**, 201 (1988).
225. S. Winkler, J. P. Powell, and H. R. Ortman, *Dent. Dig.* **77**, 460 (1971).
226. J. B. Woelfel, G. C. Paffenbarger, and W. T. Sweeney, *J. Am. Dent. Assoc.* **70**, 1170 (1965).
227. W. E. Mowery and co-workers, *J. Am. Dent. Assoc.* **57**, 345 (1958).
228. W. L. Shepard, *J. Prosthet. Dent.* **19**, 561 (1968).
229. J. B. Woelfel, *Dent. Clin. North Am.* **15**, 67 (1971).
230. N. W. Rupp, G. C. Paffenbarger, and R. L. Bowen, *J. Am. Dent. Assoc.* **83**, 601 (1971).
231. J. B. Woelfel, G. C. Paffenbarger, and W. T. Sweeney, *J. Am. Dent. Assoc.* **61**, 413 (1960).
232. *Dentsply TRIAD Denture System, Pamphlet 3542C*, Dentsply Int., York, Pa., 1983.
233. H. Wolfe, *Dent. Tech.* **37**, 6 (1984).
234. J. B. Woelfel, G. C. Paffenbarger, and W. T. Sweeney, *J. Am. Dent. Assoc.* **67**, 489 (1963).
235. H. H. Chandler, R. L. Bowen, and G. C. Paffenbarger, *J. Biomed. Mater. Res.* **5**, 245 (1971).
236. Council on Dental Materials, Instruments, and Equipment, *J. Am. Dent. Assoc.* **102**, 347 (1981).
237. Ref. 235, p. 335.
238. *Dentist's Desk Reference: Materials, Instruments and Equipment*, 1st ed., American Dental Assoc., Chicago, Ill., 1981, p. 97.
239. R. Chapman and co-workers, *IADR Abst.* 959 (1982).
240. M. Braden and co-workers, *Br. Dent. J.* **164**, 109 (1988).
241. M. Braden, *Adv. Dent. Res.* **2**, 93 (1988).
242. S. C. Bayne, *Adv. Dent. Res.* **98**, (1988).
243. J. W. Stamford, C. L. Burns, and G. C. Paffenbarger, *J. Am. Dent. Assoc.* **61**, 307 (1955).
244. P. S. Wright, *J. Dent.* **4**, 247 (1976).
245. W. J. O'Brien, J. Herman, and J. H. Shepherd, *J. Biomed. Mater. Res.* **6**, 15 (1972).
246. J. F. McCabe, *J. Oral Rehab.* **3**, 273 (1976).
247. E. Makila and O. Honka, *J. Oral Rehab.* **6**, 199 (1979).
248. L. Gettleman and co-workers, in *Biomedical Engineering IV: Recent Developments*, Pergamon Press, New York, 1985, pp. 141–144.
249. M. Braden, *J. Dent. Res.* **49**, 145 (1970).
250. M. Braden, in *Scientific Aspects of Dental Materials*, Butterworths, London, 1975, pp. 448–458.
251. *Ibid.*, pp. 439–448.
252. R. J. Michl, *Quintessence Int.* **3**, 29 (1978).
253. J. C. Hickey and co-workers, *J. Am. Dent. Assoc.* **74**, 735 (1967).
254. J. M. Stenger and co-workers, *J. Am. Dent. Assoc.* **69**, 273 (1964).
255. R. E. Going, R. E. Loehman, and M. S. Chan, *J. Am. Dent. Assoc.* **89**, 132 (973).
256. S. J. Chaconas, A. A. Caputo, and N. K. Bakke, *J. Dent. Res.* **63**, 1488 (1984).
257. D. H. Lewis, T. E. Fischer, and A. Koran, *Restorative Dental Materials*, Quintessence Publishing Co., Chicago, Ill., 1985, pp. 214–241.
258. J. M. Antonucci, *Transactions of the Academy of Dental Materials; Proceedings of the Conference on Materials Research in Maxillofacial Prosthetics*, 1992, pp. 136–155.

259. A. S. Von Gonten, J. R. Kelly, and J. M. Antonucci, *J. Mater. Sci: Mater. Med.* **11**, 95 (2000).
260. H. H. K. Xu and J. B. Quinn, *Biomaterials.* **23**, 193 (2002).
261. G. M. Brauer and J. M. Antonucci, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. 4, 2nd ed., Wiley-Interscience, New York, 1986, p. 705.
262. Brit. Pat. 252,112 (May 14, 1925), A. Poller (to DeTrey Bros. Ltd.).
263. U.S. Pat. 1,672,776 (June 5, 1928), A. Poller (to DeTrey Bros. Ltd.).
264. U.S. Pat. 2,249,694 (July 5, 1939), S. W. Wilding (to the Amalgamated Dental Co.).
265. U.S. Pat. 2,434,005 (Jan. 6, 1948), S. E. Noyes.
266. U.S. Pat. 2,454,709 (Nov. 23, 1948), E. J. Molnar (to Montclair Research Corp.).
267. W. D. Cook, *J. Biomed. Mater. Res.* **16**, 315 (1982).
268. *Ibid.*, 331 (1982).
269. *Ibid.*, 345. (1982).
270. *Ibid.*, 711 (1982).
271. R. G. Craig, *Advances in Dental Research*, 1988, pp. 51–64.
272. Fr. Pat. 1,423,660 (Jan. 7, 1966), (to ESPE, Fabrik Pharmazeutischer Praeparate, GmbH).
273. U.S. Pat. 3,453,242 (July 1, 1969), W. Schmitt and R. Purrman (to ESPE, Fabrik Pharmazeutischer Prawparate, GmbH).
274. M. Braden, B. E. Causton, and R. L. Clarke, *J. Dent. Res.* **51**, 889 (1972).
275. R. G. Craig, *J. Am. Dent. Assoc.* **95**, 127 (1977).
276. R. G. Craig and P. H. Hare, *J. Prosthet. Dent.* **63**, 16 (1990).
277. U.S. Pat. 3,066,112 (Nov. 27, 1962), R. L. Bowen (to U.S. Dept. of Commerce).
278. U.S. Pat. 3,179,623 (Apr. 20, 1965), R. L. Bowen (to U.S. Dept. of Commerce).
279. M. L. Swartz, R. W. Phillips, and B. F. Rhodes, *J. Dent. Res.* **61**, 27 (1982).
280. N. O. Salaki and co-workers, *Br. Dent. J.* **146**, 375 (1979).
281. M. Berge, *Dent. Mater.* **5**(2) 77 (1989).
282. S. L. Wendt, Jr., and co-workers, *J. Am. Dent. Assoc.* **120**, 177 (1990).
283. G. M. Brauer, in R. B. Graig, ed., *Polymers in Dentistry, Dental Material Reviews*, University of Michigan School of Dentistry, Ann Arbor, Mich., 1977, p. 49.
284. R. L. Bowen, *J. Am. Dent. Assoc.* **66**, 57 (1963).
285. R. W. Phillips, *Science of Dental Materials*, W. B. Saunders Co., Philadelphia, 1991, pp. 217–235.
286. I. E. Cueto and M. G. Buonocore, *J. Am. Dent. Assoc.* **75**, 121 (1967).
287. M. G. Buonocore, *J. Am. Dent. Assoc.* **82**, 1090 (1971).
288. W. P. Rock, *Br. Dent. J.* **134**, 193 (1973).
289. R. J. McCune and J. F. Cvar, *Int. Assoc. Dent. Res. Program and Abstracts of Papers, Abst. 745*, Chicago, Ill., International Association for Dental Research, Washington, D.C., 1971.
290. R. J. Simonsen, *Quintessence Int.* **20**(2) 75 (1989).
291. P. D. Hammesfahr, *Polymer Preprints.* **38**, 131 (1997).
292. S. B. Mitra, B. Wang, S. M. Rozzi, and T. R. Clark, *Polym. Adv. Technol.* **12**, 380 (2001).
293. D. Skrtic J. M. Antonucci, and E. D. Eanes, *Polym. Adv. Technol.* **12**, 369 (2001).
294. N. Nakabayashi, *Biomedical Applications of Polymeric Materials*, 1993, Chapt. 4, p. 219.
295. E. P. Pleuddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982, pp. 111–139.
296. E. P. Pleuddemann, *J. Adhesion.* **2**, 184 (1970).
297. I. Stengel, D. Nathanson, and C. S. Hsu, *J. Dent. Res.* **66**, 1460 (1987).
298. G. J. Livaditis and V. P. Thompson, *J. Prosthet. Dent.* **47**, 52 (1982).
299. G. J. Livaditis, *J. Prosthet. Dent.* **56**, 181 (1986).
300. W. A. Wiltshire, *Quintessence Dent. Tech.* **10**, 277 (1986).

301. Y. Kondo and co-workers, *Shika Zairyo Kikai* (1), (1989).
302. I. Harashima and co-workers, *Dent. Mater. J.* **7**(2) 141 (1988).
303. L. T. Tenjoma, *Int. J. Prosthodont.* **3**(1) 78 (1990).
304. M. G. Buonocore, *J. Dent. Res.* **34**, 849 (1955).
305. D. H. Anthony, M. S. thesis, University of Michigan School of Dentistry, ann Arbor, Mich., 1961.
306. A. Watanabe and N. Nakabayashi, *Tokyo Ika Shika Daigaku Iyo Kizai Kenkyusho Hokou* **21**, 17 (1987).
307. R. L. Bowen, *J. Dent. Res.* **44**, 895, 903, 906 (1969).
308. D. N. Misra and A. D. Johnston, *J. Biomed. Mater. Res.* **21**, 1329 (1987).
309. G. E. Schumacher, J. M. Antonucc, and P. S. Bennett, *J. Dent. Res.* **76**, 602 (1997).
310. J. E. Code, J. M. Antonucci, P. S. Bennett, and G. E. Schumacher, *Dent. Mater.* **13**, 252 (1997).
311. D. C. Smith, *Br. Dent. J.* **125**, 381 (1968).
312. A. Jurecik and C. W. Fairhurst, *Int. Assoc. Dent. Res., Program and Abstracts of Papers, Abst. 379*, Las Vegas, Nev., International Association for Dental Research, Washington, D.C., 1972.
313. D. R. Beech, *Arch. Oral Biol.* **17**, 907 (1972).
314. S. Crisp and A. D. Wilson, *J. Dent. Res.* **53**, 1408 (1974).
315. S. Crisp, I. W. Pringuer, and A. D. Wilson, *J. Dent. Res.* **53**, 1414 (1974).
316. S. Crisp and A. D. Wilson, *J. Dent. Res.* **53**, 1420 (1974).
317. J. W. McLean and co-workers, *Br. Dent. J.* **158**, 410 (1985).
318. L. Linden, in J. C. Salmone, ed., *Polymeric Materials Encyclopedia*, 1996, p. 1854.
319. S. B. Mitra, *J. Dent. Res.* **70**, 72 (1991).
320. S. B. Mitra, *J. Dent. Res.* **70**, 75 (1991).
321. R. Earnshaw, *Aust. Dent. J.* **3**, 157 (1958).
322. J. Arends and co-workers, *Quintessence Int.* **21**, 541 (1990).
323. M. E. Jensen and co-workers, *Am. J. Dent.* **3**(2), 75 (1990).
324. M. L. Capilouto and co-workers, *Caries Res.* **24**, 6, 441 (1990).
325. K. D. Jorgensen, *Odontol. Tidskr.* **61**, 179 (1953).
326. L. Forsten, *Scand. J. Dent. Res.* **99**(3), 241 (1991).
327. A. Tewari and co-workers, *J. Indian Soc. Pedod. Prev. Dent.* **8**(1), 28 (1991).
328. H. S. Horowitz and co-workers, *J. Public Health Dent.* **51**(1), 20 (1991).
329. *Physicians Desk Reference*, 45th ed., Medical Economics Co. Inc., Oradell, N.J., 1991.
330. Center for Disease Control, *JAMA*, **266**, 1061, 1066 (1991).
331. M. Jarco, *J. Mater. Sci.* **11**, 2027 (1976).
332. R. A. White, J. M. Webber, and E. W. White, *Science.* **176**, 187 (1972).
333. R. E. Holmes and H. K. Hagler, *Plast. Reconstr. Surg.* **81**, 662 (1988).
334. K. de Groot and co-workers, in T. Yamamuro, L. L. Hench, and J. Wilson, eds., *Handbook of Bioactive Ceramics*, Vol. 2, CRC Press Inc., Boca Raton, Fla., 1990, p. 3.
335. R. Z. LeGeros, *Adv. Dent. Res.* **2**, 164 (1988).
336. T. Yamamuro, L. L. Hench, and J. Wilson in Ref. 334.
337. R. Z. LeGeros and G. Daculsi, Ref. 334.
338. L. C. Chow, *J. Ceramic Soc. Jpn.* **99**, 954 (1991).
339. A. A. Mirtchi, L. Lemaitre, and N. Terao, *Biomater.* **10**, 475 (1989).
340. H. Monma, M. Goto, and T. Kohmura, *Gypsum Lime* **188**, 11 (1984).
341. W. E. Brown and L. C. Chow, in P. W. Brown, ed., *Cements Research Progress*, American Ceramics Society, Westerville, Ohio, 1986, p. 352.
342. L. C. Chow and co-workers, *Matl. Res. Symp. Proc.* **179**, 3 (1991).
343. Y. C. Hong and co-workers, *J. Biomed. Matls. Res.* **24**, 485 (1991).
344. P. D. Costantino and co-workers, *Arch. Otolaryngol. Head Neck Surg.* **117**, 379 (1991).
345. C. D. Friedman and co-workers, *Arch. Otolaryngol. Head Neck Surg.* **117**, 385 (1991).

346. A. Sugawara and co-workers, *J. Endodon.* **16**, 162 (1990).
347. Y. C. Hong and co-workers, *J. Biomed. Matls. Res.* **25**, 485 (1991).
348. A. Sugawara and co-workers, *Tokyoto Shika Ishikai Zashi* **38**, 348 (1990).
349. C. D. Friedman and co-workers, *Arch. Otolaryngol. Head Neck Surg.* **117**, 385 (1991).
350. P. D. Constantino, C. D. Friedman, R. Jones, L. C. Chow, and G. A. Sisson, *Plast. Reconstr. Surg.* **90**, 174 (1992).
351. W. C. Jarvis, *Compendium* **18**(7), 687 (1997).
352. P. P. Binon, *Int. J. Oral Maxillofac. Imp.* **15**(1), 76 (2000).
353. P. I. Branemark, *J. Prosthet. Dent.* **50**, 399 (1983).
354. P. Krogh, *J. Dent. Educ.* **52**, 767 (1988).
355. T. Albrektsson, E. Dahl, L. Enhom, and S. Engerall, *J. Periodont.* 287 (May, 1988).
356. National Institutes of Health, Consensus development Conference Statement on Dental Implants, Vol. 7, 1998.
357. T. Albrektsson and co-workers, *Int. J. Oral Maxillofac. Impl.* 1, 11, (1986).
358. C. C. Wyatt and G. A. Zarb, *Int. J. Oral Maxillofac. Impl.* **13**(2), 204 (1998).
359. U. Lekholm, J. Gunne, P. Henry, K. Higuchi, and U. Linden, *Int. J. Oral Maxillofac. Impl.* **14**, 639 (1999).
360. D. M. Brunette, *Int. J. Oral Maxillofac. Impl.* **3**, 231 (1988).
361. K. Kieswetter, Z. Schwark, D. D. Dean, and B. D. Boyan, *Crit. Rev. Oral Biol. Med.* **7**, 329 (1996).
362. A. C. Fraker and co-workers, in M. J. Fagan, Jr., and co-workers, eds., *Implant Prosthodontics: Surgical and Prosthetic Techniques for Dental Implants*, Yearbook Medical Publishers, Littleton, Mass., 1991, pp. 293–304.
363. O. Bahat, *Int. J. Oral Maxillofac Impl.* **15**(5), 646 (2000).
364. W. Becker, B. E. Becker, H. Israelson, J. P. Lucchini, M. Handelsman, W. Ammons, E. Rosenberg, L. Rose, L. M. Tucker, and U. Lekholm, *Int. J. Oral Maxillofac. Impl.* **12**(4), 454 (1997).
365. M. Chiapasco, S. Abati, E. Romeo, and G. Vogel, *Int. J. Oral Maxillofac. Impl.* **16**(4), 537 (2001).
366. I. Ericsson, K. Randow, K. Nilner, and A. Peterson, *Clin. Implant Dent. Relat. Res.*, **2**(2), 70 (2000).
367. L. B. Schulman, NIH Consensus Development Conference Statement on Dental Implants 7, Vol. 43, 1988.
368. D. Adams and D. F. Williams, *A Review of Dental Implants, Dental Update*, Upstate Publications, Ltd., London, 1985, p. 480.

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