

STRENGTHENING DENTAL AMALGAMS

A Thesis

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Robert Lawrence Prosis

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The undersigned, appointed by the Dean of the Graduate Faculty, have
examined a thesis entitled

INVESTIGATION OF THE EFFECT OF SURFACE IMPURITIES ON THE
STRENGTH OF DENTAL AMALGAMS

presented by Robert Lawrence Prosis

a candidate for the degree of Master of Science

and hereby certify that in their opinion it is worthy of acceptance.

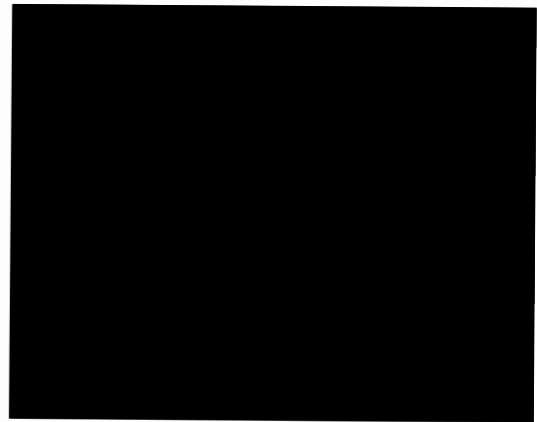


TABLE OF CONTENTS

	Pages
ACKNOWLEDGEMENTS.	i
LIST OF TABLES.	ii
LIST OF ILLUSTRATIONS	iii
LIST OF GRAPHS.	iv
CHAPTER	
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURE	8
General	8
Alloy Preparation	8
Specimen Preparation.	25
Testing Equipment and Procedures.	35
III. EXPERIMENTAL RESULTS	39
IV. DISCUSSION	51
Washing	51
Oxidizing	52
V. SUMMARY.	54
VI. APPENDIX	56
A: Alloy Washing System.	57
B: Oxidation Chamber	60
C: Design of Storage Box	63
D: Design of Spacers	73
VII. REFERENCES	76

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LIST OF TABLES

Table	Page
1. Schedule for Preparation of Capsules Before Trituration.	26
2. Schedule for Preparation of ADA Specimens.	29
3. Carving Test Specimen Preparation Schedule	34
4. Diametral Compression Test Data for Dental Amalgam Subjected to Various Degrees of Ag ₃ Sn Alloy Oxidation.	42
5. Diametral Compression Test Data for Dental Amalgam Subjected to Various Degrees of Ag ₃ Sn Alloy Oxidation.	44
6. Carving Time Data for Dental Amalgam Subjected to Various Degrees of Ag ₃ Sn Alloy Oxidation	45
7. Parts List for Washing System.	59
8. Parts List for Modification of Oxidation Chamber	62
9. Parts List for Storage Box	64

LIST OF ILLUSTRATIONS

Figure	Page
1. External Loading of Dental Amalgam for Marginal Fracture	2
2. Predosed Amalgam Capsule	9
3. Modified Amalgam Capsule	11
4. Filling-Decanting System with Washing Equipment.	13
5. Equipment Needed for Oxidation	16
6. Oxidation Chamber.	17
7. Storage Box.	18
8. Stacked Petri Dishes and Spacers	21
9. Re-weighed Alloy in Capsule, and Steps for Re-assembly of Capsule	23
10. Equipment Used for Re-weighing the Alloy	24
11. ADA Specimen Preparation Equipment	28
12. Preparation of ADA Specimen.	30
13. ADA Standard Die Set	31
14. Carving Specimen Preparation Equipment	33
15. Tensile Stress Distribution in Diametral Compression Specimen	36
16. Washing System for Cleaning Alloy.	57
17. Oxidation Chamber for Oxidizing the Alloy.	60
18. Storage Box for Alloy Transfer	63
19. Spacers Used for Separating Petri Dishes	73

LIST OF GRAPHS

Graph	Page
1. STS vs. Time of Re-oxidation	42
2. STS vs. Oxidation Stage for 4 Second Trituration	46
3. STS vs. Oxidation Stage for 5 Second Trituration	46
4. STS vs. Oxidation Stage for 6 Second Trituration	46
5. STS vs. Oxidation Stage for 7 Second Trituration	46
6. Carving Time vs. Oxidation Stage	47

INVESTIGATION OF THE EFFECT OF SURFACE
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DENTAL AMALGAMS

CHAPTER I

INTRODUCTION

For over 100 years dental restorations have been produced from an alloy containing mercury, silver, tin, and other components in lesser amounts. Early research done by such men as Townsend and Flagg in the last half of the nineteenth century, and Black in 1895 and 1896, contributed greatly to the understanding of the amalgam setting reaction and testing methods. In the last four decades various investigators have done much to further improve the amalgam alloy and refine the techniques of manipulation. These studies have not only described the factors related to the manufacture and production of the amalgam alloy, but also the factors related to mixing, manipulation and compaction. Also studied were factors relating to the basic nature of the reaction between mercury and the silver alloy. Most research in changing the amalgam preparation was done to improve the handling characteristics of the amalgam.

Even with all the improvements designed to benefit the service characteristics of the amalgam, fractures still occur too regularly for satisfactory acceptance of the present amalgam. One investigation of defective dental restorations (Moore and Stewart, 1967)¹⁰ reported that of the amalgam restorations studied, 42% were defective. Twenty-six percent of all restorations studied had fractured in service.

Recent research has shown that tensile stresses and "shock" loading are responsible for the failure of many restorations (Jørgenson, 1965; Mahler, 1958).^{4,9} Amalgams in service are typically thought of as being totally in compression during mastication. This is true for the bulk of the restoration. However, at the amalgam-tooth interface, the outer margins of the amalgam can be considered a geometric wedge. This situation is illustrated in Figure 1.

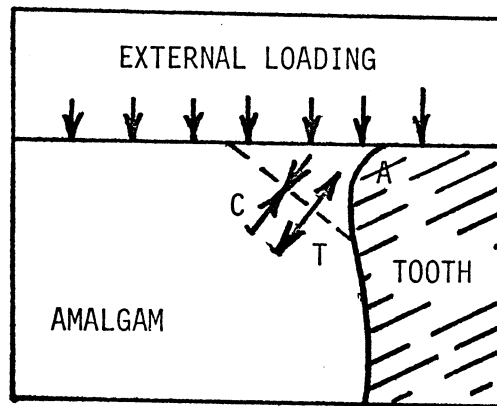


Figure 1. External Loading of Dental Amalgam for Marginal Fracture

Loading of the amalgam produces tensile forces (T) in the external side of the wedge and compressive stresses (C) in the opposite side. Since the top of the tooth (i.e., the enamel) is much stronger than the interior (i.e., the dentin), the amalgam may be thought of as being supported at point A while under load. (The point A, in three dimensions, is actually a ring defined by the amalgam-tooth interface at the surface of the tooth.) The compressive strength to tensile strength ratio for dental amalgams may be as high as 10:1 (Young and Johnson, 1967).¹⁴ When stresses

are asymmetrically compressive, materials fail by a shear mechanism. For the previously described system, the stress level exceeds the tensile strength of the material before the material can fail in shear. This ratio of 10:1 is usually nearer to 3:1 for most multi-phase alloys such as cast iron. This extreme ratio has led many researchers to conclude that many fractures of restorations have been the result of low tensile strengths (Skinner, 1967).¹³

A number of investigators have shown the fracture mode to be typically brittle (Jørgenson, 1965; Asgar and Sutfin, 1965; Young and Johnson, 1967).^{4,2,14} Brittle materials are characterized by little or no local deformation upon fracture. Metallurgical factors having little or no effect on a material's compressive properties may exhibit marked effects on the tensile strengths. Crack propagation is much more pronounced while a material is under tension than while under compression. Voids, interstitial components, and impurities promote tensile crack propagation.

Some researchers (Young and Wilsdorf, 1972)¹⁵ have shown that the tensile strengths of dental amalgams may be increased by merely washing the alloy particles with distilled water before amalgamation. Young and Wilsdorf also cleaned the alloy in a mild acid wash to remove the oxide coating which results from oxidation during manufacture and storage. Test specimens prepared from the "cleaned" alloy exhibited an increased tensile strength and a changed fracture mode. The fracture mode in current amalgams is reported to be intergranular (i.e., the crack propagates along a grain boundary) (Asgar and Sutfin, 1965; Young and Wilsdorf, 1972).^{2,15} The amalgam pre-

pared from cleaned alloy using a 40,000 psi compaction pressure exhibited transgranular failure (i.e., the crack propagated through the grains of the amalgam).

Often tensile strength is reduced while compressive strength remains unaffected. Embrittlement of many multiphase alloys, such as cast iron, is caused by interstitial elements such as hydrogen or oxygen. Another case is sulfur in steel which is known to segregate to form a grain boundary precipitate which embrittles steel at high temperatures. Trace amounts of substitutional impurities result in similar effects for other alloys.

It is not known whether the oxygen impurities are present only on the alloy surface, or if the oxygen diffuses directly into the alloy matrix itself. It is known that oxygen diffuses rapidly through silver at elevated temperatures and that oxygen is soluble in silver. Oxygen dissolved in silver causes embrittlement. On the other hand, a small amount of tin oxide dispersed in tin has a hardening effect. Exactly how the silver-tin alloy behaves cannot be determined from the single characteristics of each component.

Interstitial elements have already been shown to be present in dental amalgam alloys (Ag-Sn) as an oxide coating and perhaps as bulk impurities (Young and Wilsdorf, 1972).¹⁵ Asgar and Sutfin (1965)² have speculated that impurities segregated at grain boundaries in dental amalgams may be the dominant factor in determining the properties of this alloy. Holland (1972)⁷ found that the tensile strength could be increased by mixing the amalgam in argon gas (argon is an inert gas, which does not react readily

with other elements). Thus, there is sufficient evidence to indicate that interstitial impurities may be responsible for the low tensile strengths and for the poor resistance to fracture characteristic of current dental amalgam.

At this point, for simplicity, some terms will be defined. Cleaned amalgam corresponds to amalgam prepared from "cleaned" (i.e., oxide free) alloy; normal amalgam is normal, or "as received," alloy (i.e., alloy oxidation naturally occurring since manufacture); partially oxidized amalgam is an alloy with an oxide thickness less than the normal alloy.

In clinical application the Ag_3Sn alloy and the mercury are triturated (mixed) using a high speed mechanical amalgamator. The resultant amalgam is in a plastic state. The dentist then compacts the amalgam by hand, with a condensing tool, into the prepared cavity in the patients tooth. This process adapts the plastic amalgam mass to the walls of the prepared cavity of the tooth to minimize leakage which could lead to secondary caries (i.e., decay acting at the amalgam-tooth interface). After compaction the dentist sculptures or carves the amalgam to reproduce the proper tooth anatomy.

It was earlier stated that after trituration the resultant amalgam is in a plastic state. The amalgam becomes less plastic as a function of time, eventually reaching its final strength. (See Chapter II for details). There is some point in time, as measured from the start of trituration, at which the amalgam is no longer plastic enough for a dentist to manipulate it. This time is referred to as the setting time or carving time of the amalgam.

Generally, as the final tensile strength of an amalgam is increased, its setting time is decreased (Young and Wilsdorf, 1972)¹⁵. The stronger cleaned amalgam sets up much faster than the weaker normal amalgam. This setting time is too short for the cleaned amalgam to be useable in clinical applications.

It was the project objective, based on the paper by Young and Wilsdorf (1972)¹⁵, to examine amalgam prepared from several different (small to large) alloy surface oxide thicknesses. It was hoped that a significantly large increase in tensile strength, as compared to that of the normal amalgam, would be found, which would give a clinically useable setting time.

If this expected substantial increase in tensile strength did indeed exist, it was the subsidiary objective of this research to subject the data to a statistical optimization analysis. This analysis could hopefully optimize the relationships between trituration time, alloy oxide thickness, and tensile strength, while giving a clinically useable setting time.

It was realized from the start that the standard deviations of the data for tensile strength tests on dental amalgams are on the order of 10-20% of the means. This was demonstrated in the tensile test results obtained by Holland (1972)⁷ and Lewis (1972)⁸ among others.

If small changes in the means between experimental groups (e.g., 10% changes) would be observed, then approximately 50 specimens per group would be needed in order to compare the differences in means at the 95% confidence level. In addition if only 10% changes in tensile strength are achievable the practical clinical significance is questionable. However, if large changes (e.g., 50%), would be

observed, then as few as five specimens per experimental group can be utilized and still achieve meaningful comparisons at the 95% confidence level.

Based on the paper by Young and Wilsdorf (1972)¹⁵, large shifts (e.g. 50%) in the means between experimental groups were anticipated; hence a population of five specimens per sample was chosen for this initial investigation.

In the event that the changes observed in the means between experimental groups would be the same order of magnitude as the standard deviations, statistical optimization of the results methods would be meaningless. Indeed, the variability of procedure among dentists probably precludes the assignment of clinically significant improvement to any increase in strength less than perhaps 30%. Since this was the case, as is reported in Chapter three, no statistical optimization of the results is presented in this thesis.

CHAPTER II

EXPERIMENTAL PROCEDURE

General

The experimental work was divided into four functional areas: alloy preparation, specimen preparation, testing, and data analysis.

Due to the many manipulative variables and to the nature of the investigation (i.e., a study of the effect of surface impurities), special care was required in the alloy washing, specimen preparations and in the handling of the finished specimen. Strict reproduction of the manipulative variables and a high degree of cleanliness was of prime concern. The presence of only the desired surface impurity was essential.

Alloy Preparation

Alloy

It was not the intent of this research program to demonstrate one manufacturer's product superiority over other amalgam types or brands. Only one amalgam brand was used in this research program.

Holland (1972)⁷ outlined certain guide lines, unrelated to the amalgam's tensile or carvability properties which were adhered to in the selection of the amalgam to be used. The guide lines are as follows: (1) the amalgam satisfied American Dental Association (ADA) Specification No. 2 (Guide to Dental Materials and Devices)¹,

(2) the amalgam was of the predosed type (i.e., the premeasured alloy and mercury were separated in opposite ends of a disposable capsule), (3) the capsule could be opened and the contents removed and later be easily replaced, (4) the capsule was constructed of a minimum number of parts and those parts could be opened and manipulated easily.

Pacs* amalgam was selected for use in this series of experiments. Figure 2 shows the assembled capsule on the left and its disassembled components on the right.

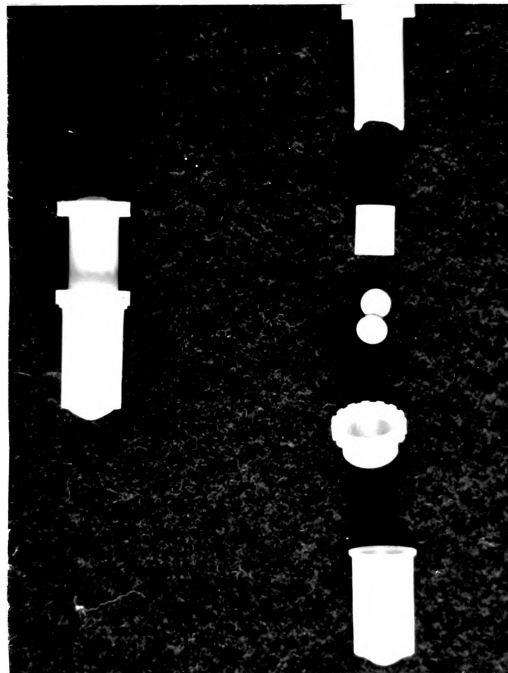


Figure 2. Predosed Amalgam Capsule

*Pacs, Warner-Lambert Pharmaceutical Co., Morris Plains, N.J.

The capsule is divided into upper and lower chambers separated by an encapsulating sleeve with a plastic membrane. The upper chamber contains two alloy pellets made of compressed alloy filings of 390 mg each and a pestle to facilitate in breaking up the pellets upon trituration (mixing). The lower division contains 780 mg of mercury, giving a 1:1 alloy to mercury ratio.

The amalgam is prepared by forcing the top chamber through the membrane of the encapsulating sleeve into the lower chamber. This combines the two chambers and their contents into a unit ready for trituration.

Breaking

As mentioned before, the Pacs amalgam capsules are provided with the silver-tin alloy compressed into two wafers of 390 mg each which are broken apart into their original filings by the pestle upon trituration. For use in this research program (i.e., before the surface impurities could be removed and later added), the wafers had to be broken up before trituration.

This was done by triturating the two pellets with a pestle in a modified capsule without the mercury in a high speed mechanical Silimat amalgamator*, oscillating at approximately 4570 rpm for 15 seconds. The capsule was modified by cutting the shank of the top chamber to approximately 5/16-inch in order to match the length of the encapsulating sleeve containing the membrane. The membrane

*Justi Silimat, A Williams Justi Ivoclar Product, Liechtenstein.

was removed from the encapsulating sleeve and the cut shank and encapsulating sleeve were put together as one unit to form a "cap" for the bottom chamber. A pestle was included to facilitate in breaking up the wafers. Figure 3 shows the modified parts and the assembled modified capsule.

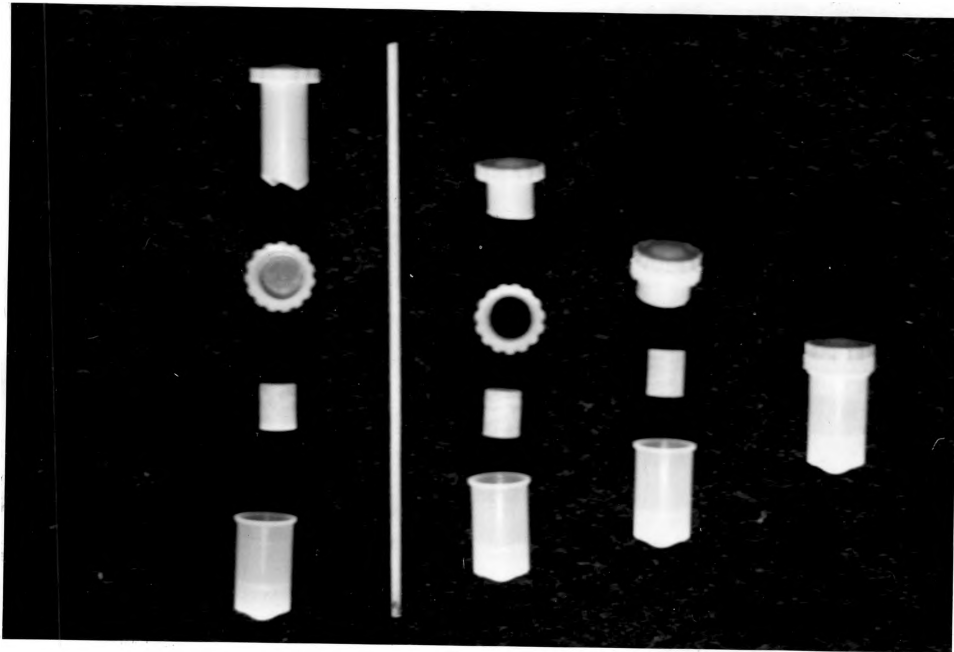


Figure 3. Modified Amalgam Capsule

Immediately after breaking, the alloy was sieved to remove particles larger than 53 microns. Roughly 6.5% of the alloy was larger than 53 microns, while about 3.5% was lost in transfer, giving a useable alloy of approximately 90% of the starting amount. The alloy filings were then stored until needed.

Washing

The surface impurities on the alloy filings were removed by washing the alloy in an acid solution. The alloy was dried under vacuum and stored in argon gas (argon is an inert gas, which does not react readily with other elements) to avoid possible surface re-contamination by air.

The washing procedure used in this research was adapted from Young and Wilsdorf (1972)¹⁵. The only major change was in the amounts of alloy washed.

Equipment and supplies required for the washing of the alloy include distilled water, Hydrochloric acid, 95% ethanol, a 15,000 ml container, a plastic stirrer, a 5 gallon plastic bucket, various assorted articles of glass-ware, and a filling-decanting system.

See Figure 4 for picture and Appendix A for a schematic drawing

The filling-decanting system incorporated a 5 gallon aspirator bottle for dispensing the distilled water using a shut-off valve. The liquid was decanted by a siphon system capable of being primed by tap water without contaminating the washing ingredients. The siphon operates on an 8 foot elevation with a decanting speed of 4,000 ml/minute to 500 ml/minute depending on the size of tubing used and the elevation of the siphon. Care was taken at low liquid levels not to draw off liquid so fast as to disturb the alloy particles resting on the bottom. All ingredients were siphoned into the 5 gallon plastic bucket which was later emptied. Figure 4 shows the filling-decanting system along with the necessary equipment for washing the alloy.



Figure 4. Filling-Decanting System with Washing Equipment

Before washing, the alloy filings were sieved to remove particles larger than 53 microns. A reagent grade 5wt.% hydrochloric acid was used as the washing agent. A ratio of 100 ml acid to 1 ml powdered alloy was used. It was determined that approximately 8 capsules (6.25 g) worth of hard packed alloy equaled 1 ml of powder. At first 5 ml of alloy was washed in a 2,000 ml beaker. After this first washing a larger container became available and the remaining alloy needed for this research was washed all at once in a 15,000 ml glass container measuring 8.25 inches in diameter and 17 inches high. A 37.5 ml (300 capsules) amount of hard packed alloy was washed at once in the 15,000 ml container. The 37.5 ml of alloy was added to 3,750 ml of the acid cleaning solution. The suspension

was vigorously stirred by hand with a plastic stirrer for 3 minutes, then 11,250 ml of distilled water was added to the container. The mixture was then allowed to settle for 30 minutes and the liquid was decanted to about a 1-cm level. The majority of alloy particles had settled to the bottom of the container. The container was immediately re-filled with distilled water and stirred briefly by hand while re-filling before allowing another 15 minutes of settling. Decanting and re-filling were performed two more times making a total of three complete washing cycles. The alloy was then rinsed with 3,750 ml of 95% ethanol, stirred briefly, and allowed to settle for 15 minutes. The ethanol was carefully decanted down to a level where it just covered the alloy to avoid alloy to air contact. The alloy was immediately vacuum dried with a partial backfill of argon at 500 microns pressure to a final vacuum of less than 20 microns. The vacuum chamber was then backfilled with argon so that the alloy never came in contact with air after the washing process.

It should be noted that the cleaning treatment eliminates particles which have not had sufficient time to settle to the bottom of the container before the liquid was decanted. Young and Wilsdorf (1972)¹⁵ used Stoke's Law to determine approximately what amounts and size distributions were eliminated. Such a determination for this research program was not possible. Stoke's Law is valid only for spherical particles and not for the irregular shaped alloy filings used in this research. Based on Young and Wilsdorf's (1972)¹⁵ calculations, it was guessed that particles below 1 micron to 10 microns in size and lesser proportions of larger particles were

eliminated. The effect of the cleaning process was to shift the mean value of the size distribution to a slightly higher particle size. The effect on strength could not be determined since the exact size distributions before and after cleaning were unknown.

The first 5 ml of alloy was washed in a 2,000 ml beaker in the exact same manner as described earlier with the following changes: (1) The first settling time of 30 minutes was only 15 minutes. (2) The final vacuum was only 150 microns.

Oxidizing

After cleaning, some of the alloy was re-oxidized to several different stages to determine the effect of surface impurities (i.e., oxidation) on its tensile strength and carvability. Great care was taken to minimize contamination by impurities other than the desired oxygen. Each container and instrument coming in direct contact with the alloy was kept to the utmost cleanliness. From the time of washing until the start of oxidation, the alloy was never exposed to any airborne impurities. It was always exposed to an argon environment or a vacuum of less than 150 microns. After the period of oxidation, the contaminate was evacuated and the alloy was again subjected to the previous conditions of an inert environment.

The equipment needed for oxidation (see Figure 5) includes a vacuum tight storage box, 2-oz jars, a Scoopula*, a 1/4-inch brush, a thermometer, four 3 1/2-inch petri dishes, a 3 1/2-inch watch glass, a 5-ml graduated cylinder, a pair of tongs, 4 asbestos spacers, an

*Scoopula, Fisher Scientific Company, St. Louis, Mo.

electric furnace, a Variac* autotransformer, and an oxidation chamber. Figure 5 shows the oxidation chamber along with the equipment needed for oxidation of the cleaned alloy



Figure 5. Equipment Needed for Oxidation

The oxidation chamber was a dry box originally designed for use in crystallography work (see Ref. 5 for details). It was easily modified for use as an oxidation chamber (see Figure 6 for a picture and Appendix B for a schematic diagram). The only modifications were: (1) The entrance and amounts of two gases (i.e., argon and oxygen) were able to be controlled accurately, each gas

*Variac Autotransformer, General Radio Co., Concord, Mass.

having a main valve and a low range flow meter for fine adjustments.

Both gases entered the chamber by means of a common purge valve.

(2) A 50-inch mercury manometer was installed to give chamber pressure readings from ± 30 inches Hg with 0.10 inch resolution.

(3) A 1 psi safety release valve was installed. Figure 6 shows the oxidation chamber.

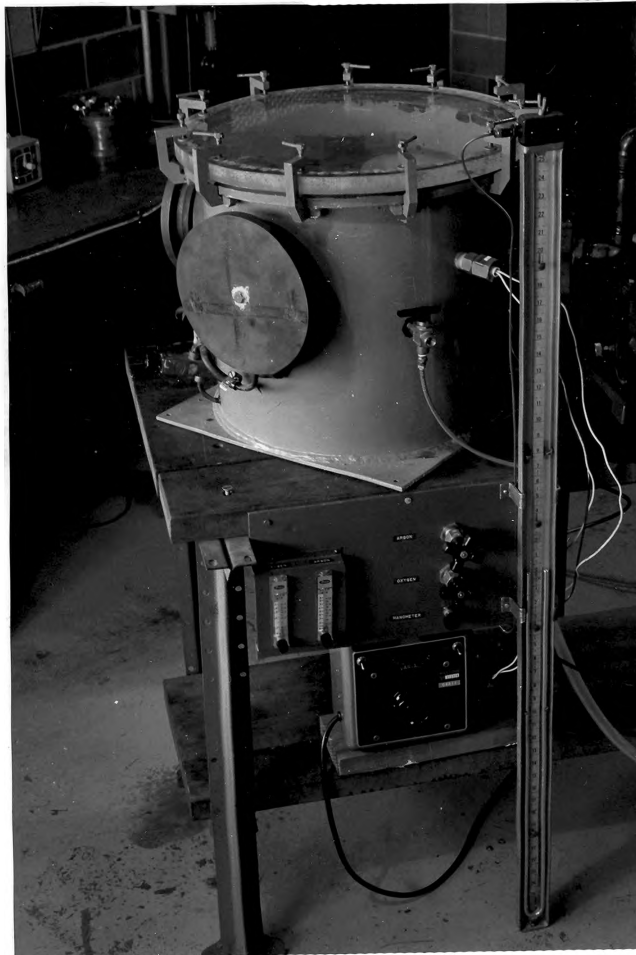


Figure 6. Oxidation Chamber

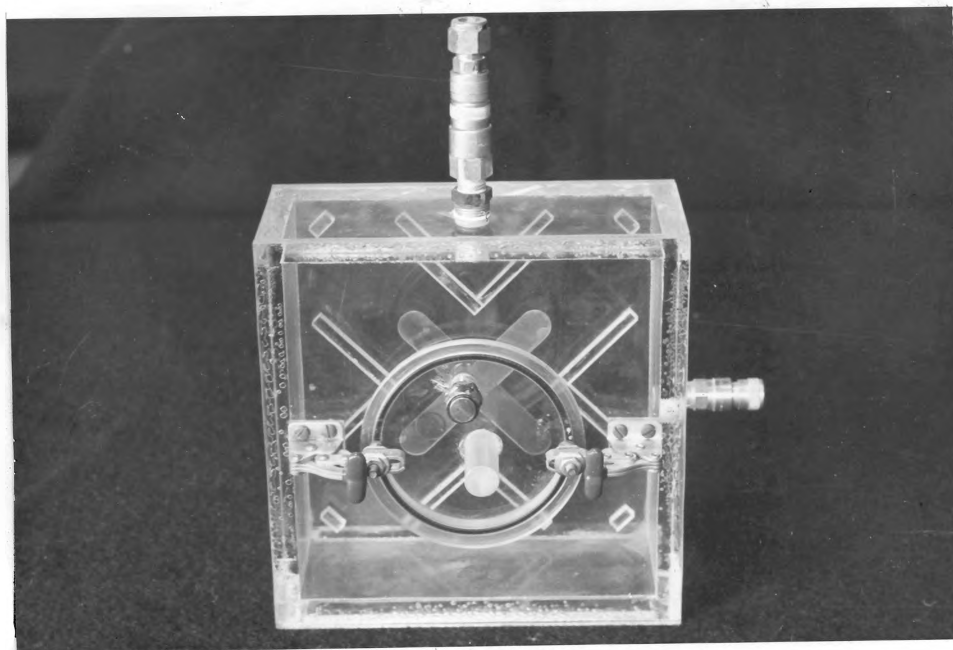


Figure 7. Storage Box

The storage box (see Figure 7) was used to transfer the alloy between the dry box and the oxidation chamber without contamination by air. The alloy is placed inside 2-oz, 2x2 inch glass jars, which are then placed inside the storage box. Up to eight jars may be placed inside at once. The storage box is equipped with two quick-connect female couplings for external vacuum or gas connections, which were not used for such in this research program. Through use of a 1 psi safety release valve, the inside gas was maintained at approximately 1 psi pressure above its surrounding environment as the inside of the drybox or oxidation chamber was

evacuated. However, upon re-pressurizing the surrounding environment, no gas is able to enter the inside of the storage box. Inside the drybox the alloy is placed inside the storage box and is then sealed and removed from the drybox. The storage box is then placed inside the oxidation chamber which is evacuated to 500 microns, back-filled with argon to 20 inches Hg, evacuated again to less than 150 microns, and finally backfilled with argon to give a nearly pure argon environment. The storage box was emptied out, all but approximately 1 psi of its argon environment, while no gas was allowed to enter it. Now that the oxidation chamber environment is inert, the storage box may be pressurized with it. This was done by inserting an open-end male coupling into one of the female quick-connect couplings of the storage box. This permitted the inert outside gas to flow into it. Hence, the alloy was always protected by an inert environment. This method of keeping the alloy protected was used between oxidations and for re-entering the drybox for re-capsuling.

The environment used for oxidizing was composed of 21% oxygen and 79% argon by volume, to correspond to the oxygen content of air, only without other impurities present. This environment was obtained by starting with the oxidation chamber full of argon at atmospheric pressure, decreasing the pressure of argon by 6.0 inches Hg, and subsequent addition of oxygen to achieve atmospheric pressure again. The addition of oxygen took less than 30 seconds. The 4,750 cubic inches inside of the oxidation chamber was considered as an infinite environment for the alloy to oxidize in. No more oxygen was added during oxidation.

The temperature of the oxidation was $250 \pm 5^\circ\text{F}$. The arrival at this value will be explained later. The temperature was maintained inside a 4x4x4 inch electric furnace regulated by a Variac autotransformer. The temperature was measured directly in the furnace by a bi-metallic strip thermometer.

After an inert environment was established inside of the oxidation chamber, the glove ports and the storage box were then opened. The cleaned alloy was then measured out in the 5-ml graduated cylinder using the Scoopula. Approximately 2.5 ml of loose packed alloy filings were placed in each 3 1/2-inch petri dish, or approximately 0.26 ml of loose alloy filings per square inch. It would have been best to agitate the filings to insure uniform oxidation, but a suitable method was not available. It was determined by an optical microscope that the layer was thin enough and there was enough space between filings at 0.26 ml of alloy filings per square inch to insure adequate surface contact by the surrounding gases. Up to 10 ml of loose packed alloy could be oxidized at once.

The petri dishes were then stacked on top of each other, separated by 1/8-inch thick asbestos spacers to give adequate ventilation inside of the preheated furnace (see Figure 8). The top petri dish was covered by a 3 1/2-inch watch glass also separated by a 1/8-inch thick asbestos spacer. The furnace and its contents were always allowed 10 minutes to reach the oxidizing temperature of $250 \pm 5^\circ\text{F}$ before the oxygen was added. Figure 8 shows the stacked petri dishes and spacers.

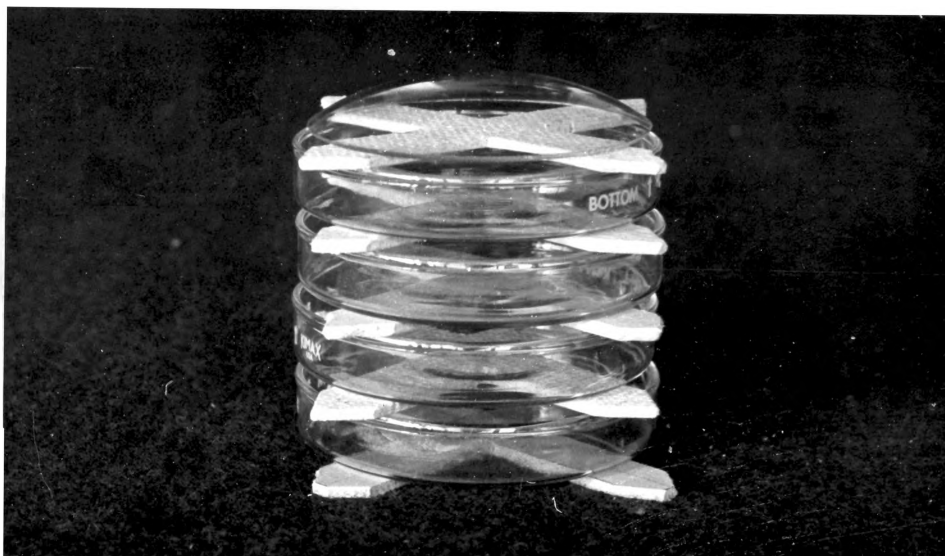


Figure 8. Stacked Petri Dishes and Spacers

After the desired time of oxidation the oxygen-argon environment was evacuated to less than 700 microns. In 5 minutes the chamber could be evacuated to 1.5 inches Hg and in 10 minutes, to less than 1,000 microns. Due to the amount of time required to reach a vacuum of 150 microns, it was decided that a 700 micron oxygen-argon environment would not appreciably further oxidize the alloy at the 90°-100°F temperature outside of the furnace. The explanation for this assumption is as follows: if the environment is considered to behave as a perfect gas, and the temperature and volume remain constant, the effect on the oxidation rate of the

alloy is assumed to be merely a ratio of pressures, (i.e., 700 microns : 760 mm Hg). This ratio turned out to be less than 0.01 of a percent; hence the 700 micron 21% oxygen-79% argon environment had little contaminating effect on the alloy at the 90°-100°F chamber temperature outside of the furnace.

After backfilling with argon, the alloy was removed from the furnace. The 1/4-inch oxhair brush helped facilitate removal of the alloy from the petri dishes into a 2-oz jar which was then labeled and placed inside of the storage box. At this time another 10 ml of alloy could be removed from the storage box and be placed in the furnace as before if desired. The storage box was closed before the next oxidation.

Before the last quantity of alloy was removed from the furnace, the oxidation chamber was evacuated and backfilled in the same manner as earlier described at the start of the first oxidation. This was done to insure a reasonably pure argon environment inside of the storage box for transfer into the drybox for re-capsuling. After the final backfill the alloy inside the furnace was removed and placed inside the storage box which was then sealed. The oxidation chamber was then opened and the sealed storage box was removed and placed inside the antechamber of the drybox. The antechamber was evacuated to 500 microns, backfilled with argon to approximately 20 inches Hg, then evacuated to less than 25 microns, and finally backfilled to atmospheric pressure with argon. The storage box could then be brought into the main chamber of the drybox where it was opened and the alloy removed for re-capsuling.

Re-capsuling

After washing, the cleaned alloy or the re-oxidized alloy, whichever the case might have been, was re-weighed back into cleaned capsules inside the argon drybox. The alloy was weighed directly into a part of the capsule to minimize losses by transfer. This part was the encapsulating sleeve with the plastic membrane intact as described earlier (see Figure 9). Figure 9 shows the re-weighed alloy in the capsule, and the steps required to re-assemble it.

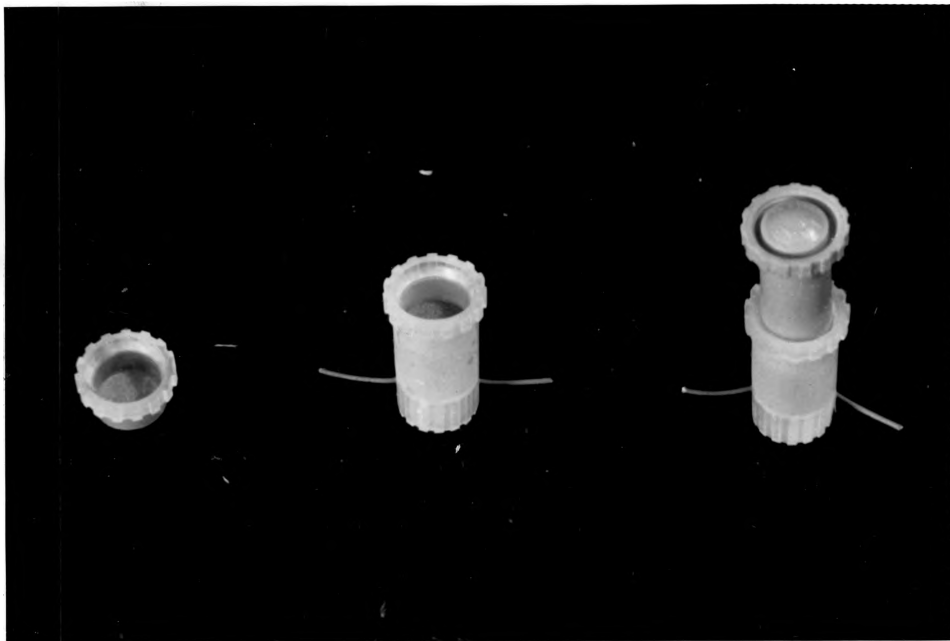


Figure 9. Re-weighed Alloy in Capsule, and Steps for Re-assembly of Capsule

Equipment for re-weighing the alloy included a Scoopula, a vibro-spatula, and a millibalance (see Figure 10). The Mettler LV2 Vibro-Spatula* employs a vibrating spoon capable of dispensing a powdery substance, such as the silver-tin alloy filings, to an accuracy of 0.1 mg. The Cahn Millibalance** is capable of weighing quantities of 0.1 mg with a 10 g tare and a range of 1.250 g. Figure 10 shows the equipment used for weighing out the alloy.

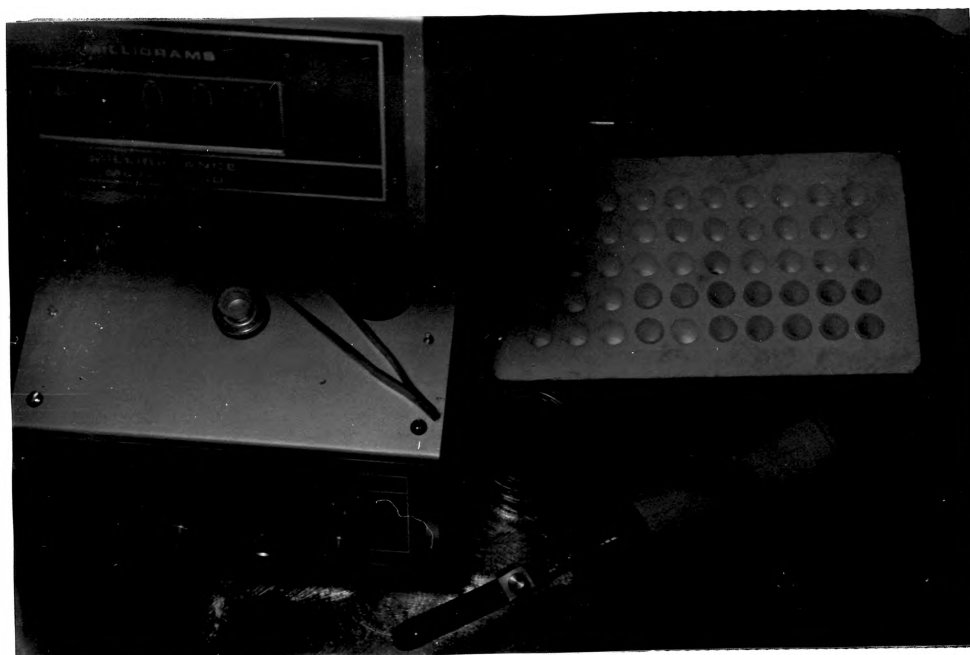


Figure 10. Equipment Used for Re-weighing the Alloy

*Mettler LV2 Vibro-Spatula, Mettler Instruments AG CH-8606,
Greifensee-Zurich, Switzerland

**Cahn Millibalance, Scientific Products, Paramount, Calif.

The alloy was removed from its container in small quantities with the Scoopula and placed in the vibro-spatula for re-weighing. Due to the awkward conditions imposed by the drybox, 780 ± 5 mg was decided to be the amount weighed out. This affected the 1:1 mercury to alloy ratio by only 0.64% at most.

After weighing, the encapsulating sleeve with membrane containing the re-weighed alloy, was placed on to the lower chamber containing the mercury. The upper chamber was then added to form the original predosed capsule as before, with the exception of the pestle being left out (see Figure 9 on page 23).

After re-capsuling, the capsules were individually placed inside air tight film cans. The film cans were then placed inside of glass jars with metal lids containing rubber seals. Up to 12 film cans could be placed in a jar at one time. With this procedure the capsules could be removed from the drybox and stored in open air for long periods of time without contamination by air.

Specimen Preparation

Methods

It has been discovered that amalgam mixed (trituated) in an inert gas (i.e., argon) displays a higher tensile strength than that mixed in open air (see Holland, 1972).⁷ Since this research program was concerned with surface impurity free (cleaned) and designated surface contaminated (oxidized) alloy, all amalgam was mixed in argon. This was done not only for the expected increase in tensile strength, but for protection against unwanted contamination by air born impurities.

Immediately before a group of specimens were made, the lid was removed from the glass jar containing that group of capsules. The air tight film cans containing one capsule each were removed. The capsules were prepared for trituration according to the schedule of events in Table 1. The capsules were mixed (trituated) with a high speed mechanical Silimat amalgamator oscillating at approximately 4570 rpm.

TABLE 1

Schedule for Preparation of Capsules Before Trituration

a. Film can opened and capsule removed	0 sec.
b. Capsule prepared for trituration (<u>i.e.</u> , alloy and mercury combined)	2-4 sec.
c. Capsule placed in Silimat amalgamator	4-7 sec.
d. Start of trituration	10 sec.

Before sample preparation can begin, the effect of the manipulative variables must be considered. The time of trituration is a major factor influencing the properties of the amalgam product. Generally, the longer the time of trituration, the more time the mercury has to react with the alloy resulting in more mercury being retained by the amalgam after compaction. Longer trituration times (4-6 seconds in a high speed amalgamator such as the Silimat model) gives an increase in tensile strength. After a certain length of trituration time the tensile strength starts to decrease again. Also with a longer increase in trituration time, the amalgam becomes increasingly harder to manipulate (i.e., compact, carve, etc.). Most manufacturers give a trituration time that

optimizes strength properties and workability. For the Pacs predosed amalgam, the suggested trituration time was five to six seconds in a high speed mechanical amalgamator such as the Silimat model. For further discussion of trituration, see Holland (1972).⁷

For this research program, four different trituration times were chosen. They are 4, 5, 6, and 7 seconds respectively using the Silimat amalgamator.

Compaction pressure, length of time, and specimen size are other crucial manipulative variables. They will be explained for each test shortly. See Holland (1972)⁷ for further discussion of manipulative variables.

ADA Diametral Compression Specimen Preparation

The American Dental Association precisely describes the dimensions and preparation technique for a standard test specimen in the ADA Specification No. 1 (Guide to Dental Materials and Devices).¹

Equipment required for the ADA preparation include an ADA die and plungers (see Holland, 1972)⁷, a static press capable of developing 2030 psi pressure on the amalgam (see Holland, 1972)⁷, electric timer, amalgamator, a Teflon funnel and plunger, and rubber-tipped tweezers. Figure 11 illustrates the equipment necessary to prepare an ADA specimen.

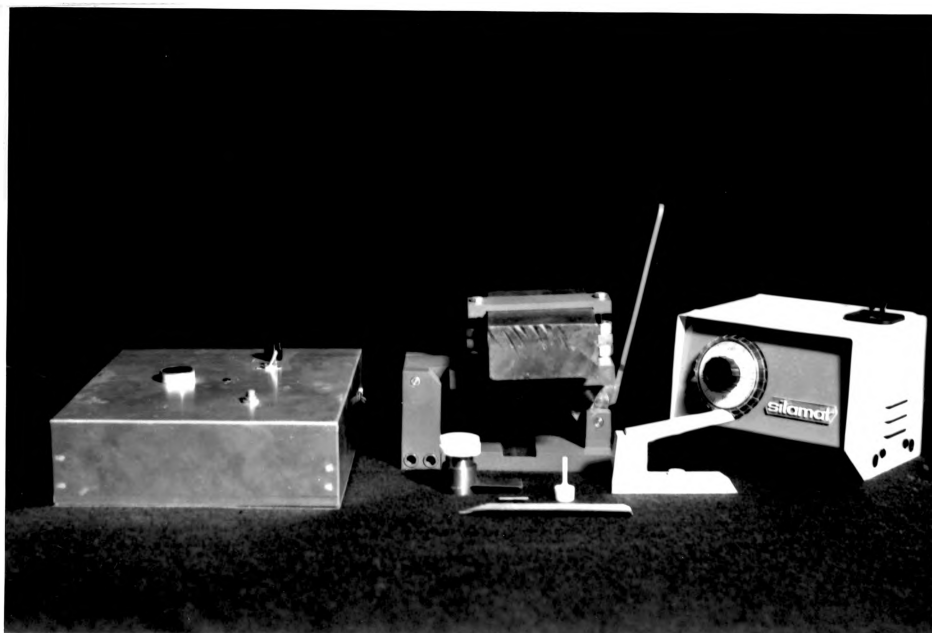


Figure 11. ADA Specimen Preparation Equipment

The electric timer was designed to start and stop the amalgamator with a precisely timed triturations of either 4.00, 5.00, 6.00 and 7.00 seconds. It also signaled (by buzzer) at the end of predetermined intervals corresponding to the beginning and ending of an event described in TABLE 2.

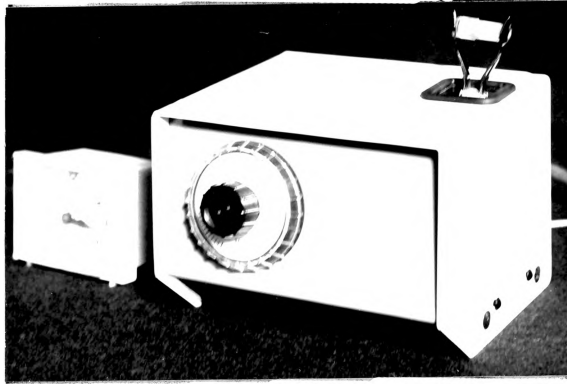
The Teflon funnel and plunger were used to aid the introduction of the amalgam to the die cavity. A rubber tipped tweezer was used to handle the specimens.

The preparation schedule used to produce the ADA specimen was taken from Holland (1972)⁷, and is described in TABLE 2.

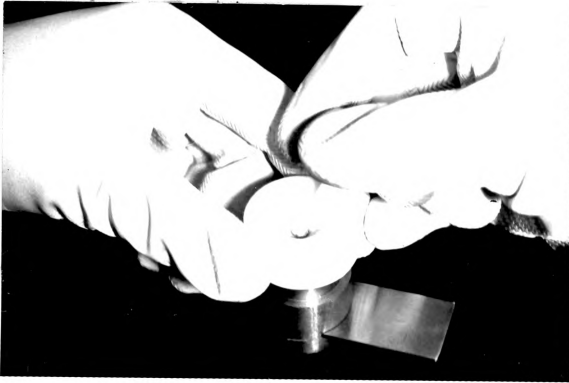
TABLE 2
Schedule for Preparation of ADA Specimens

a. End of trituration (see Figure 12-a)	00 sec.
b. Place triturated mass in mold and apply 2030 psi pressure (see Figure 12-b, c)	30 sec.
c. Release load and remove No. 2 spacer at (see Figure 12-d)	45 sec.
d. Replace load at	50 sec.
e. Release load at	90 sec.
f. Brush away mercury and eject specimen at (see Figure 12-e)	120 sec.

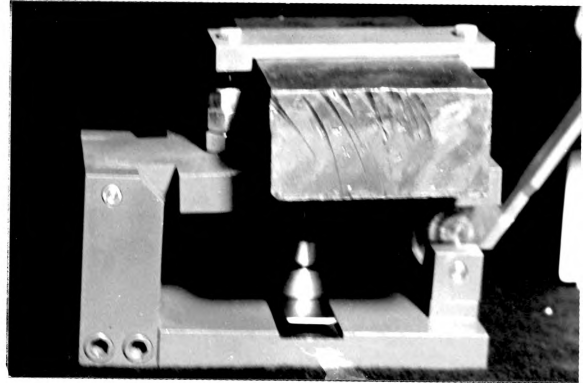
One Pacs capsule produced a cylindrical specimen 4 mm in diameter by approximately 10 mm. In order to obtain consistent lengths, all amalgam must be introduced to the die. The temperature for the preparation was $75 \pm 5^{\circ}\text{F}$ with the relative humidity maintained at $50 \pm 5\%$. The Teflon plunger was used to inject the amalgam in the funnel into the die. The funnel was removed, plunger No. 2 (the longer, top plunger) was placed in the die, and the assembled die set was placed in the static press. Figure 13 (on the second page following) shows the ADA die.



(a) Trituration



(b) Introduction of Amalgam to Die



(c) Application of Pressure



(d) Removal of No. 2 spacer



(e) Ejection of Specimen

Figure 12. Preparation of ADA Specimen

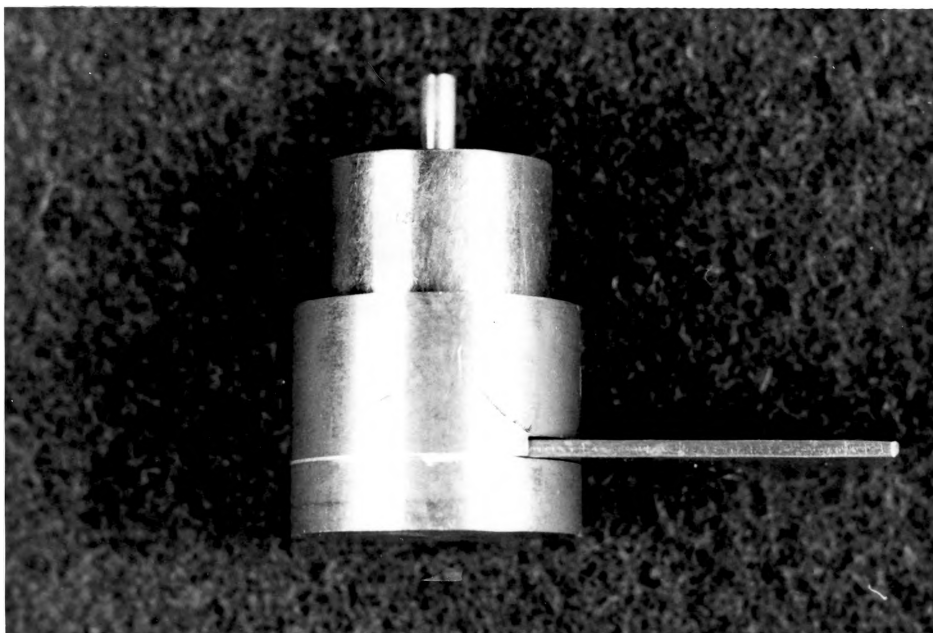


Figure 13. ADA Standard Die Set

The weight of the static press, as shown in Figure 11, was eased on to the plunger to minimize shock loading of the plunger by the static load. The amalgam was handled with rubber tipped tweezers. Gloves were worn during the specimen preparation to minimize moisture contamination of the specimen and of the dies. The sample was discarded if the schedule listed in TABLE 2 was not adhered to exactly.

Carving Test Specimen Preparation

After the amalgam has been condensed into the prepared cavity of a tooth, the dentist carves the restoration to reproduce the

proper tooth anatomy. The amalgam is usually ready for carving soon after the completion of the condensation. However, the carving should not be started until the amalgam is sufficiently hard to offer resistance to the carving instrument. A scraping or "ringing" sound should be heard when it is carved. If the carving is started too soon, the amalgam may be so plastic that it may be pulled away from the margins of the tooth. After a period of time the amalgam becomes too hard for carving. The carving tool no longer shapes the restoration smoothly, it skips or "hops" over the surface. The end of this period of carvability is often referred to as the setting time of the amalgam.

A setting time of 5-8 minutes after the start of trituration is considered by most dentists to be ample time to carve the amalgam. Actual experimental measurement of the setting time is difficult. Some researchers (Nagai, 1968)¹¹ used the Gilmore Needle to determine the setting time. This method employs a known pressure acting through an indenter of given area applied to an uncompressed globe of amalgam. That time, after the start of trituration, at which the amalgam is no longer deformable, is referred to as the setting time. This method was termed undesirable for use in this research program for two reasons: 1) The relationship between fracture strength and carvability was unknown. 2) It does not reproduce the clinical conditions.

Isenoume and Jørgensen (1968)³, attempted to measure the carving time as a function of the amount of material removed by the carving action. They attempted to relate this to the tensile

strength and concluded that an amalgam having a tensile strength of 0.3 kg/mm^2 or greater was no longer carvable. A fair amount of material can still be removed easily after the carving time is up. The carver begins to skip over the surface and pull or "chip" the amalgam out of the surface. This still removes material but the amalgam is no longer carvable according to clinical standards. Also, two different amalgam types with the same setting time may carve differently (i.e., one may carve more brittle in nature or rougher than the other). Hence the amount of material removed as a function of time is not a good indication of the setting time of amalgam.

To best reproduce the clinical conditions, specimens were compacted by a hydraulic press, for a given time and pressure, in a steel die. This prepared specimen was hand-carved by a dentist while remaining inside the steel die.

This same die and press set up was used by Holland (1972)⁷ and Lewis (1972)⁸ for preparation of uniaxial tensile test specimens (see Figure 14). Figure 14 shows the carving specimen preparation equipment.



Figure 14. Carving Specimen Preparation Equipment

Three capsules of amalgam were compacted, all at once, at 5,000 psi pressure for 15 seconds. The resulting specimen measured 5 mm x 40 mm and was 1.07 mm deep. See Holland (1972)⁷ for further information concerning the die, press and specimen. TABLE 3 shows the schedule of events, adapted from Holland's (1972)⁷ tensile test specimen preparation schedule, used in making a carving test specimen.

TABLE 3

Carving Test Specimen Preparation Schedule

a. The first of three capsules is individually removed from its film can and triturated for the designated amount of time in the amalgamator.	00 sec.
b. After each capsule is triturated, its contents are emptied into the die cavity while the next capsule is removed from its film can and mixed.	
c. The three amalgams are crumbled, leveled, and partially compacted in the die with a Scoopula. Care must be taken to compact the amalgam along the ends and sides of the die. The amalgam must be leveled so that it is equally distributed along the die. If it is not, the effective compaction pressures will not be equal across the entire die.	
d. The die cavity is placed in the hydraulic press. The amalgam is subjected to a condensing pressure of 5,000 psi. for 15 seconds with five additional thrusts required to hold the pressure due to the mercury being expressed from the die.	75 sec.
e. After removal from the press, the excess mercury at the surface of the compacted amalgam is brushed away with a cotton swab.	90 sec.

Testing Equipment and Procedures

The time interval from the end of sample preparation until the start of tensile testing is a very important factor in this research. This point is not as important in many alloy systems. It has been demonstrated that the strength properties of amalgam vary directly with the time from preparation to testing. It is generally agreed that the setting strength of amalgam is well developed in 24 hours (Pires, et al., 1969).¹² The strength increases rapidly as a function of time for the first 12 hours; after that the rate of increase declines sharply. After the 24 hour period, the remaining increase is only slight (Nagai, et al., 1968).¹¹ Holland (1972)⁷ and Lewis (1972)⁸ both used a curing time of 24 hours for the time interval between specimen preparation and testing. The 24 hour cure was also selected for use in this research program.

Diametral Compression Test

The diametral compression test is commonly used for testing brittle materials such as concrete. These specimens are usually quite large in comparison to the specimens used in this research. The test is an acceptable method for determining the tensile strength of dental amalgam as described in the ADA Specification No. 1 (Guide to Dental Materials and Devices¹). The small amalgam specimens are subject to different stress distributions and porosity effects than the larger samples for which the test was originally devised. It is doubtful that this test gives a very accurate indication of the

true tensile strength of dental amalgam. However, it may be used as a comparison and an indication of the tensile strength relationship between amalgam specimens, provided that major variables such as composition, compaction pressure and trituration time are not varied dramatically. The following description of the diametral compression test as used in this research is taken from Holland (1972).⁷

The test is performed by placing a cylindrical specimen on its side between two platens which exert compressive forces upon the specimen. The mechanics of the test involve measuring the diameter and length of the amalgam specimen, wrapping the specimen in a double thickness of aluminum foil, and breaking the specimen with a strain rate of 0.02 in./min. on the tensile tester. The tensile tester used was the Tinius-Olsen Universal Testing Machine*. The surface of the specimen is rough and full of tiny pits and voids. The specimen is padded with ductile aluminum foil to rid the effect of these surface inconsistencies on the stress distributions in the material. The result is a more accurate representation of the actual tensile strength of the amalgam. Figure 15 illustrates the tensile stress

Distribution of Tensile Stress

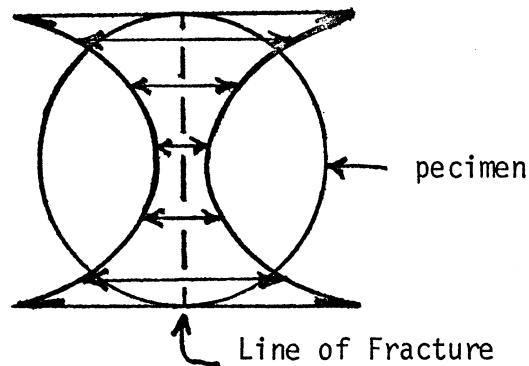


Figure 15. Tensile Stress Distribution in Diametral Compression Specimen

*Tinius-Olsen Testing Machine Company, Willow Grove, PA

distribution on the plane defined by the lines of contact between the specimen and testing platens.

The force (P) at fracture along with the values for the length (L) and diameter (D) of the specimen are substituted into the following equation to determine the tensile strength (this value is termed splitting tensile strength - STS).

$$STS = \frac{2P}{\pi DL}$$

A controversy has arose whether the value obtained from the previous equation is a true tensile strength. See Lewis (1972)⁸, and Holland (1972)⁷, for the details of this controversy and of the diametral compression testing.

Carving Test

The actual clinical carving of the amalgam was done by Dr. Lawrence Hines (D.D.S.) of the V.A. Hospital; Columbia, Missouri. Dr. Hines attempted to find the time at which the amalgam carving could be started, as well as the time at which it was no longer carvable. The following statement describes the criteria used by Dr. Hines in determining the carving period of the amalgam.

After condensation in the hydraulic press and removal of excess mercury with a cotton swab, the carving was started as soon as possible. This time, as measured from the start of trituration, ranged between 1 min. 45 sec., to 2 min. 15 sec. The amalgam was "cut" with a sharp instrument having a flat cutting edge 3.00 mm in width. This instrument was a standard type as used by dentists in practice. The starting carving time was (i.e., START TIME) that time when 1) the material was not so plastic as to be burnished away from the margins of the die, 2) the amalgam offered resistance to the carver,

and 3) a scraping sound was heard. The end of the setting time (i.e., END TIME) was when the amalgam could no longer be "cut" with the sharp carver without undue pressure and fracture of the material. The carving period was defined as the difference between END TIME and START TIME.

CHAPTER III

EXPERIMENTAL RESULTS

As previously stated, the optimization of the relationship of alloy surface impurities to the tensile strength and carvability of dental amalgams was the objective in this investigation.

As discussed in Chapter II, the cleaned alloy was re-oxidized to several different stages. The major variables affecting the oxidation of a metal are the oxygen composition of the environment, the volume of the environment (*i.e.*, the amount of oxygen available), the temperature, the pressure, and the length of time exposed. It was decided to hold all variables constant except for time. The environment was composed of 21% oxygen and 79% argon to correspond to the oxygen content of air. The volume was the 4,750 cubic inches of the oxidation chamber. The pressure was atmospheric, and the temperature was set at $250 \pm 5^{\circ}\text{F}$.

There is a marked visible difference between cleaned and normal (uncleaned) alloy. The cleaned alloy with its surface impurities removed appears more "silvery" or brighter to the naked eye. A simple experiment was performed by exposing some cleaned alloy to room air at approximately 75°F . The purpose was to determine the amount of time it would take for it to compare in appearance to the normal alloy. After 2-4 weeks it had not fully re-oxidized according to visible observations. Because of the time limitations

imposed upon this research program 2-4 weeks was much too long for re-oxidation. A time of 1-3 hours was desired for the maximum re-oxidation of the alloy. The easiest way to speed up the reaction is to increase the temperature. A temperature high enough to considerably speed up the oxidation of the alloy but low enough not to alter any of its metallurgical properties was desired. A simple experiment was performed to determine this temperature. Some cleaned alloy was oxidized in room air at 250-260°F in an electric furnace. The alloy was visibly comparable to the normal uncleaned alloy after 1-2 hours. After 14 hours it was much darker, indicating much oxidation. This procedure was not accurate enough to determine the exact time which the alloy had re-oxidized to a state equal to that of the normal uncleaned alloy. However, $250 \pm 5^\circ\text{F}$ was decided upon to be the oxidation temperature.

It was desirable to examine the properties of several different alloy surface oxidations between the cleaned and normal states. One ml of cleaned loose packed alloy was oxidized at $250 \pm 5^\circ\text{F}$ for 15 minutes in the same manner described in Chapter II using the oxidation chamber. Groups of 30, 45, 60, 75, 90, 105 and 120 minutes were also done. It was decided to use the amalgam's tensile strength, as measured by the diametral compression test, to compare amalgam prepared with the re-oxidized alloy to amalgam prepared with cleaned and normal alloy. The re-oxidized alloy was then re-weighed in the dry-box as described in Chapter II.

A trituration time of 6 seconds was used. All capsules were trituated in argon.

Five specimens, each of cleaned and normal alloy, were prepared and tested as described in Chapter II. Four specimens were made and tested of each re-oxidized group. Due to a slight under-measurement of alloy powder, only four capsules could be prepared from each re-oxidized group. The results of this experiment are shown in TABLE 4 and graphically in GRAPH 1 on the next page.

To insure an accurate representation of this curve, at least 25-50 specimens should have been made for each oxide group; however this experiment was attempted only as a survey of the relationship between STS and alloy oxidation thickness. The following conclusions are drawn from the data as represented in TABLE 4 and GRAPH 1.

1. An oxidation time of 105 sec. at 250°F is sufficient to produce an oxide thickness at least as thick as that of "normal" alloy.
2. The observed shift in mean STS does not exhibit the magnitude (i.e., at least 50%) as anticipated from the work of Young and Wilsdorf (1972).¹⁵

In order to obtain more detailed data with respect to the relationships among trituration time, oxide thickness, STS, and carving time, a second series of experiments were undertaken. The time of oxidation was assumed to be proportional to the amount of oxidation of the alloy (i.e., the longer the time, the greater the amount of oxidation occurring). Oxidation times of 15, 45, 75, and 105 minutes were chosen to represent various degrees of alloy oxidation.

For each group, 15, 45, 75, and 105 minutes respectively, 10 ml of cleaned alloy filings (i.e., approximately 50 capsules) were

TABLE 4

DIAMETRAL COMPRESSION TEST DATA FOR
DENTAL AMALGAM SUBJECTED TO VARIOUS
DEGREES OF Ag_3Sn ALLOY OXIDATION

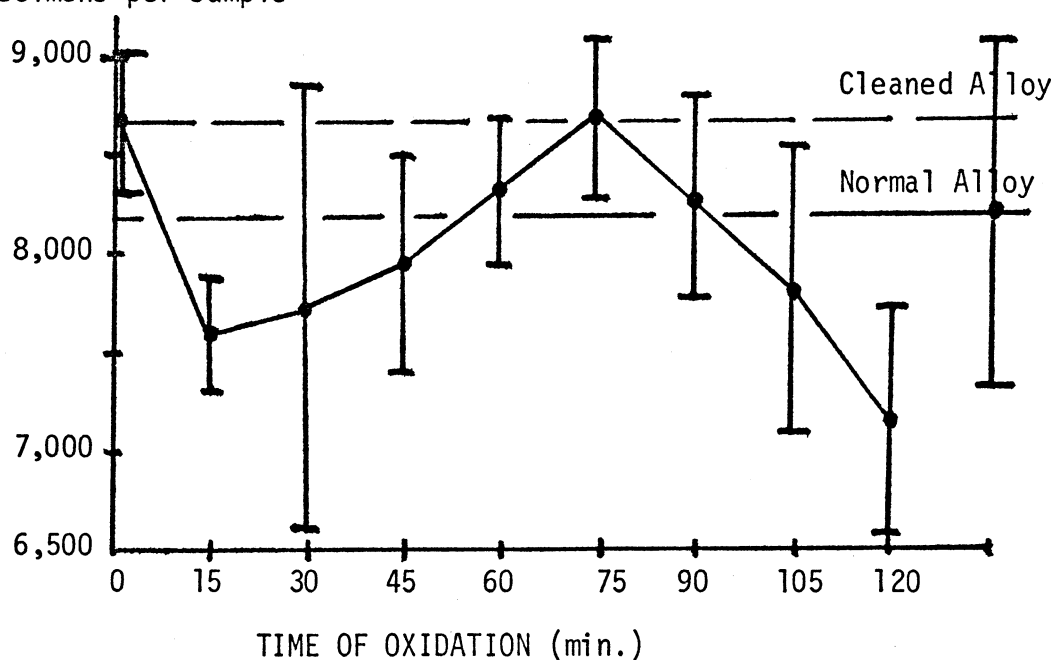
Sample (6 sec. trituration)	Average Tensile Strength (psi.)	Standard Deviation (psi.)	High (psi.)	Low (psi.)
Cleaned*	8668	369	9060	8090
Normal Powdered*	8208	860	9200	6980
15 min.	7598	299	7950	7270
30 min.	7728	1140	9090	6330
45 min.**	7957	558	8560	7460
60 min.	8320	388	8850	7920
75 min.	8693	411	9180	8220
90 min.	8238	499	8750	8240
105 min.	7835	709	8760	7140
120 min.	7147	590	7940	6690

4 specimens per sample otherwise indicated.

* 5 specimens per sample

this data also appears in TABLE 5

** 3 specimens per sample



GRAPH 1. STS vs. Time of Re-oxidation (6 sec. trituration)

oxidized in the oxidation chamber as described in Chapter II. The re-oxidized alloy groups were then taken into the drybox via the storage box for re-capsuling and were then prepared for testing as described in Chapter II.

For each group of alloy (i.e., cleaned, 15, 45, 75, and 105 minute re-oxidized, 5 specimens for the diametral compression test were prepared using 4, 5, 6, and 7 second trituration times respectively, as described in Chapter II. The results are given in TABLE 5 on the following page.

For each group of alloy (i.e., cleaned, 15, 45, 75, and 105 minute re-oxidized) 2 carving test specimens of 3 capsules each were prepared using 4, 5, 6, and 7 second trituration times respectively, as described in Chapter II. The result was eight carving specimens (24 capsules) for each re-oxidized group or 40 carving specimens (120 capsules) total. The results are given in TABLE 6 on page 45.

As stated earlier, the cleaned alloy was re-oxidized in 21% oxygen - 79% argon at $250 \pm 5^{\circ}\text{F}$ for times of 15, 45, 75, and 105 minutes respectively. For ease in discussing the experimental results, these different degrees of oxidation will be named as stages. Stage #0 amalgam will correspond to amalgam prepared with the cleaned alloy; Stage #1 amalgam: 15 minute re-oxidized alloy; Stage #2 amalgam: 45 minute re-oxidized alloy; Stage #3 amalgam: 75 minute re-oxidized alloy; and Stage #4 amalgam: 105 minute re-oxidized alloy.

TABLE 5

DIAMETRAL COMPRESSION TEST DATA FOR DENTAL AMALGAM SUBJECTED TO VARIOUS DEGREES OF Ag ₃ Sn ALLOY OXIDATION					
SAMPLE*		AVERAGE TENSILE STRENGTH (psi.)	STANDARD DEVIATION (psi.)	HIGH	LOW
STATE	TRITURATION TIME (sec.)				
CLEANED	4	7,134	232	7,460	6,790
	5	7,900	525	8,550	7,210
	6	8,668	369	9,060	8,090
	7	8,636	770	9,250	7,380
15 MIN. AT 250°F	4	7,204	1,014	7,600	5,620
	5	7,504	934	8,740	6,340
	6	8,606	713	9,730	7,740
	7	7,954	1,565	9,550	5,880
45 MIN. AT 250°F	4	7,614	640	8,280	6,830
	5	7,698	986	9,280	6,590
	6	8,934	243	9,260	8,580
	7	8,310	563	8,870	7,450
75 MIN. AT 250°F	4	7,852	601	8,370	6,900
	5	7,722	726	8,740	6,960
	6	8,094	596	8,940	7,290
	7	8,244	642	9,070	7,410
105 MIN. AT 250°F	4	7,972	235	8,110	7,730
	5	7,950	609	8,900	7,230
	6	8,862	202	9,220	8,740
	7	8,154	887	9,320	7,160

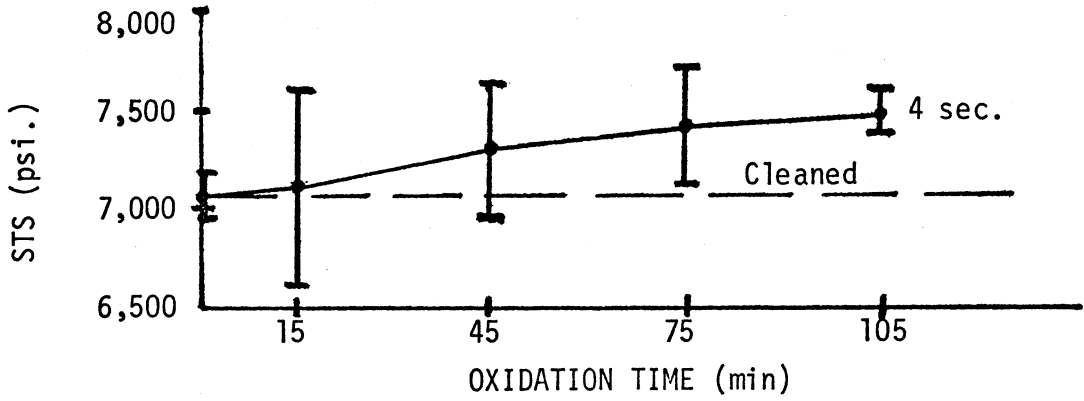
* 5 specimens per sample.

TABLE 6

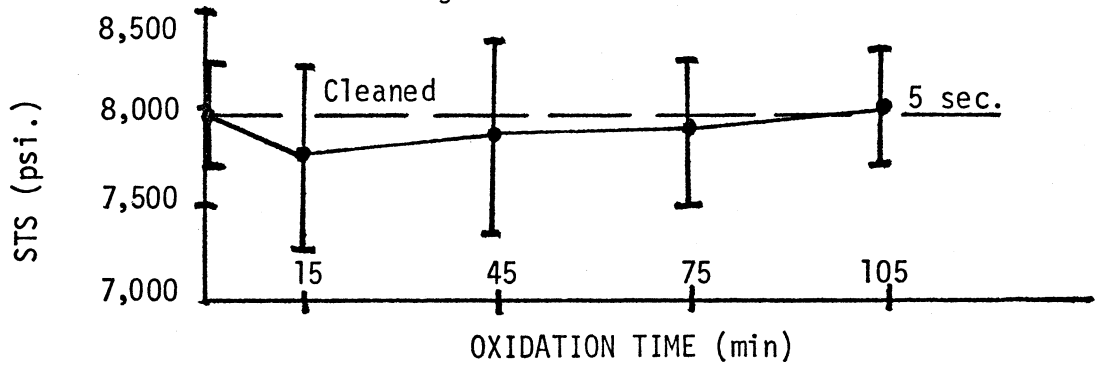
SETTING TIME DATA FOR DENTAL AMALGAM SUBJECTED TO VARIOUS DEGREES OF Ag ₃ Sn ALLOY OXIDATION								
SAMPLE+								
STATE	TRIT. TIME (sec.)	START TIME (min:sec)			END TIME (min:sec)			CARVING PERIOD (min:sec)
		1	2	AVG.	1	2	AVG.	
CLEANED	4	2:20	2:30	2:25	3:50	3:50	3:50	1:25
	5	2:00*	2:30	2:15	4:45	4:15	4:30	2:15
	6	2:25	2:35	2:30	3:25	3:25	3:25	0:55
	7	2:15*	2:15*	2:15	3:05	3:05	3:05	0:50
15 MIN. AT 250°F	4	2:25	2:30	2:28	4:10	4:25	4:18	1:50
	5	2:35	2:45	2:40	4:15	3:40	3:58	1:18
	6	2:20	2:25	2:23	3:25	3:30	3:33	1:10
	7	2:15*	2:15*	2:15	3:25	3:35	3:35	1:10
45 MIN AT 250°F	4	2:20	2:25	2:23	4:45	5:35	5:10	2:47
	5	2:20	2:30	2:25	4:45	4:50	4:48	2:23
	6	2:50	2:20	2:35	4:55	4:00	4:28	1:47
	7	2:30	2:25	2:33	4:05	4:00	4:03	1:30
75 MIN. AT 250°F	4	2:25	2:30	2:28	5:30	5:00	5:15	2:43
	5	3:05	2:45	2:55	5:05	4:25	4:45	1:50
	6	2:30	2:30	2:30	4:25	4:44	4:33	2:33
	7	3:05	2:30	2:43	4:45	5:00	4:53	2:10
105 MIN. AT 250°F	4	3:25	4:30	4:03	6:30	7:30	7:00	2:57
	5	4:15	3:40	3:58	6:35	7:40	7:08	3:10
	6	2:20	2:15	2:18	5:35	5:35	5:35	3:17
	7	2:35	2:40	2:38	5:05	5:05	5:05	2:27

+2 specimens per sample

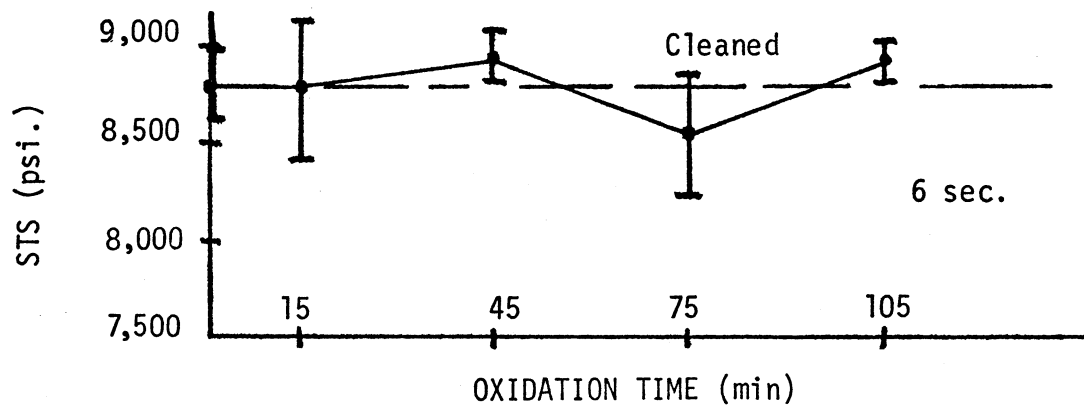
*This time represents the first attempt to carving, which was successful; hence, the true start of carving time is somewhat less than is indicated.



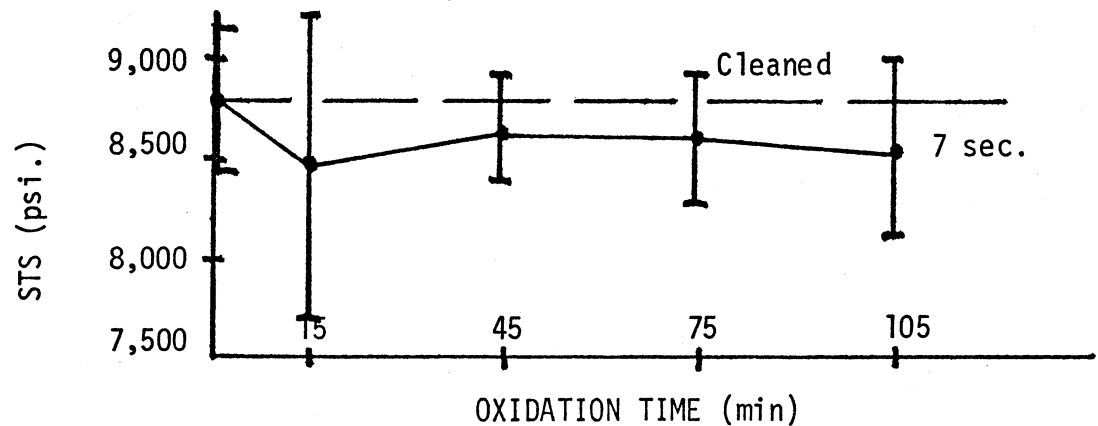
GRAPH 2. STS vs. Oxidation Stage for a 4 Second Trituration



GRAPH 3. STS vs. Oxidation Stage for a 5 Second Trituration

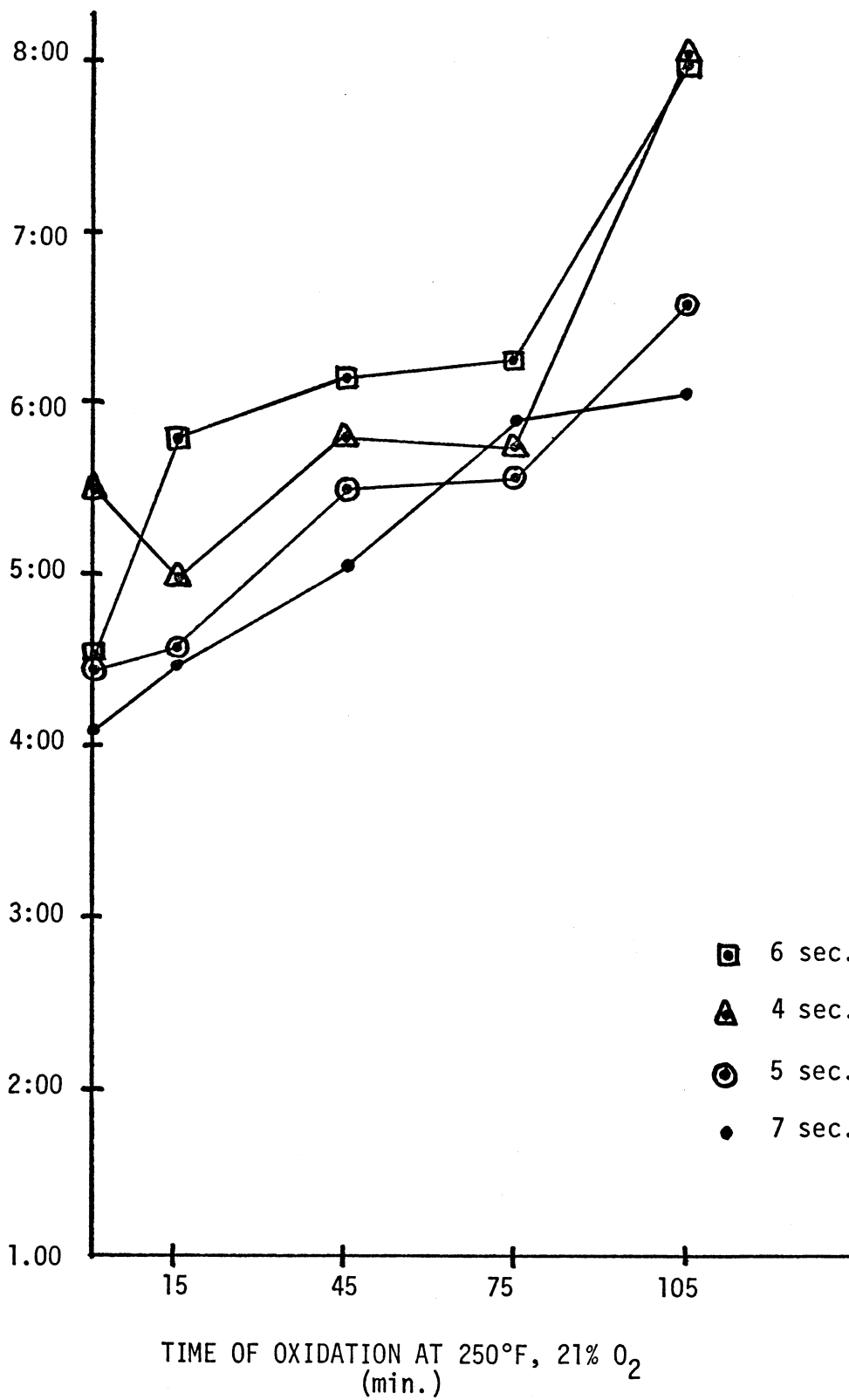


GRAPH 4. STS vs. Oxidation Stage for a 6 Second Trituration



GRAPH 5. STS vs. Oxidation Stage for a 7 Second Trituration

GRAPH OF SETTING
TIME (i.e., END TIME) v.s. OXIDATION



The data exhibits standard deviations as great as the noticeable differences in mean STS values for each oxidation stage. Hence, as is alluded to in the Introduction, no clinical significance can be assigned to the attempt to control oxide thickness. Predictions or conclusions based upon the STS data would be useless. If only the average for each sample was examined no consistent trends can be observed (See GRAPHS 2-5). Also the validity of any trends in GRAPHS 1 to 5 would be questionable due to the small single size and large standard deviations.

If GRAPH 1 is compared to GRAPH 4 (they both are for the same sample conditions), the observed trend in the sample means for each graph differs significantly. This verifies the need for a larger sample population size in order to compare means among the specimen groups in a statistically significant manner.

The large standard deviations are, unfortunately, inherent in the experimental data. Any brittle material will exhibit a large standard deviation due to its inability to relieve internal stresses due to stress risers (i.e., cracks, voids, etc.).

The diametral compression test for determining the amalgam's tensile strength was used by Holland (1972)⁷ and Lewis (1972)⁸. This test was also used in this research program. The test was originally designed for use with relatively large specimens; small specimens were used in this research. The smaller specimen size may account for larger standard deviations because of a lower frequency of occurrence of internal defects (i.e., cracks, voids, etc.). In a large specimen the defects are almost always present and the tensile strength will

therefore be about the same from one specimen to another (i.e., since all have similar defects, they all fracture similarly. The chances of internal defects being present in a smaller specimen are less; hence some specimens may be entirely free of these defects, thus yielding a subsequently larger tensile strength than a specimen containing a defect. Depending on the presence, size, number and location of the defects, a wide range of tensile strength results (i.e., larger standard deviations) are present for similar specimens. It is suggested that the standard deviations for dental amalgams subjected to the diametral compression test are a function of the defect distribution in the specimen.

A different statistical procedure needs to be developed for looking at the STS extrema (maximum). Due to the effect of the defect distribution in the amalgam specimens, the maximum observed values for each sample group is probably statistically more meaningful than the mean of the group.

The carving test data do follow a definite trend. However, the reliability and reproducibility of the test is questionable. It appears that the END TIME (i.e., the setting time) increases as a function of increased alloy oxidation and decreased trituration time. Amalgam prepared from alloy in an advanced oxidized state (Stage #4) set up slower and carve for a longer time than did amalgam prepared from a lesser oxidized state (Stage #1). Also, as the trituration time of the amalgam was increased, the amalgam set up faster and the end of the carving period came sooner (i.e., setting time decreased). This was true for each oxidation Stage. Visual curve fitting for the data points indicated a linear relationship. GRAPH 6 shows setting time plotted against the oxidation Stage for each trituration time.

It may be concluded that the end of the carving period is increased by increased oxidation of the amalgam alloy. The end of the carving period also increases as the trituration time decreases.

CHAPTER IV

DISCUSSION

Previous chapters have dealt with defining the research problem and describing the methods and procedures used in attaining the results of this problem. This section will discuss some influencing factors and their implications on the results.

Washing

As mentioned in Chapter II the alloy fillings were washed in a dilute solution of hydrochloric acid to remove existing surface impurities. They were then rinsed first in distilled water, and finally in ethanol before vacuum drying. Hydrochloric acid was chosen specifically because of its non-oxidizing properties. It could not be certain that the acid removed all surface impurities or if it affected the properties of the alloy itself. It was noticed that cleaned alloy allowed to be in contact with ethanol for 12 hours appeared darker in color than freshly cleaned alloy. This indicates possible re-contamination of the alloy by the ethanol. During the last rinse, the alloy was only in contact with ethanol for 15 minutes before decanting and vacuum drying. This was probably not enough time for any significant re-contamination of the alloy.

One important factor concerning the experimental results was the alloy particle loss upon decanting. The end result was an upward shift of the particle size distribution. Particle size is

a major variable affecting the amalgam tensile and carving properties. The size and amount of alloy particles lost and their effect were not quantitatively determined.

To rid the experimental results of the effects of the washing process (i.e., alloy oxide removal), it would be best to test the amalgam before any alloy surface contamination from the atmosphere could happen. Immediately after production the alloy could be protected by an inert environment until testing.

Oxidizing

As stated in Chapter II, the oxidation temperature of $250 \pm 5^\circ\text{F}$ was chosen to speed up the oxidation process. This temperature was chosen to be low enough as not to alter the metallurgical properties of the alloy. However, there are two metallurgical phenomena present which are always increased with an increase in temperature.

The first of these is the aging process. After the alloy filings are produced, they are aged to relieve the residual stresses present. For example, the filings may be aged for 3 hours at 200°F . The alloy continues to age at a slower rate at room temperature. The 15 - 105 minute exposure at $250 \pm 5^\circ\text{F}$ was certain to have affected the aging process in some way. For the extent of the effect, the initial aging process and the time since production would have to be known for the alloy.

The second metallurgical phenomenon present is that of diffusion. As the alloy oxidizes, the oxygen may: (1) diffuse into the alloy, (2) increase the surface oxide thickness, or (3) a combination of both may be present. One thing is for certain; as the temperature

is increased, the diffusion rate is somewhat higher. Since there is inadequate diffusion information available for the Ag_3Sn alloy, this increase in the diffusion rate could not be calculated. In order to remove any doubt concerned with oxidizing at $250 \pm 5^\circ\text{F}$, the alloy should be oxidized at room temperature.

CHAPTER V

SUMMARY

Moore and Stewart (1967)¹⁰ found that 42% of the amalgam restorations studied were defective. Of these, 26% had fractured in service. Other investigators (Jørgenson, 1965; Mahler, 1958)^{4,9} cited weakness in tensile strength as the principle cause of failure resulting from marginal fracture. The compressive-tensile strength ratio of dental amalgams is uncommonly high. Impurities present in other alloy systems may lower the tensile strengths of the amalgams. However, if the proper amount of impurity is present, it may cause the tensile strength of the alloy to increase. Young and Wilsdorf (1972)¹⁵ determined that the presence of an oxide layer on the amalgam alloy causes a deleterious weakening of the amalgam. Holland (1972)⁷ found that amalgams triturated (mixed) in an inert gas, exhibited higher tensile strengths than those triturated in air. It was also known that amalgam prepared from cleaned alloy was carvable for only a very short time. This made it impractical for clinical application. Hence, the effect of different degrees of alloy oxidation on the amalgam's tensile strength and carvability properties was investigated with the hope of finding some optimum relationship. This research consisted of three processes: removal of the alloy oxidation, re-oxidizing the cleaned alloy, and testing.

The existing surface impurities were removed from the alloy by washing it in a dilute solution of hydrochloric acid. From the

moment of washing until final testing, the alloy was protected from all unwanted contaminates.

The cleaned alloy was then re-oxidized in a predetermined oxygen-argon environment at a given temperature for several different periods of time. The result gave four different stages of oxidation.

The diametral compression test was employed to determine the tensile strength of the amalgam. The determination of the carving time was done by a dentist in an attempt to duplicate the actual clinical condition. Tests were run on the cleaned alloy and four stages of re-oxidized alloy using four different trituration times respectively.

Results indicated that the STS data were inconclusive with regards to observing significant trends due to the unexpectedly low observed changes in mean STS. The large standard deviations (of the same approximate magnitude of the observed changes in average STS), due to the defect distribution in the specimen, made analysis of any consistent trends in mean STS meaningless. Therefore, statistical optimization was not feasible. It was suggested that perhaps a method of statistical analysis examining extrema might give a better representation of the data.

Setting time appeared to be: 1) increased with increased alloy oxidation, 2) increased with decreased trituration time. The setting time was clinically determined by a dentist.

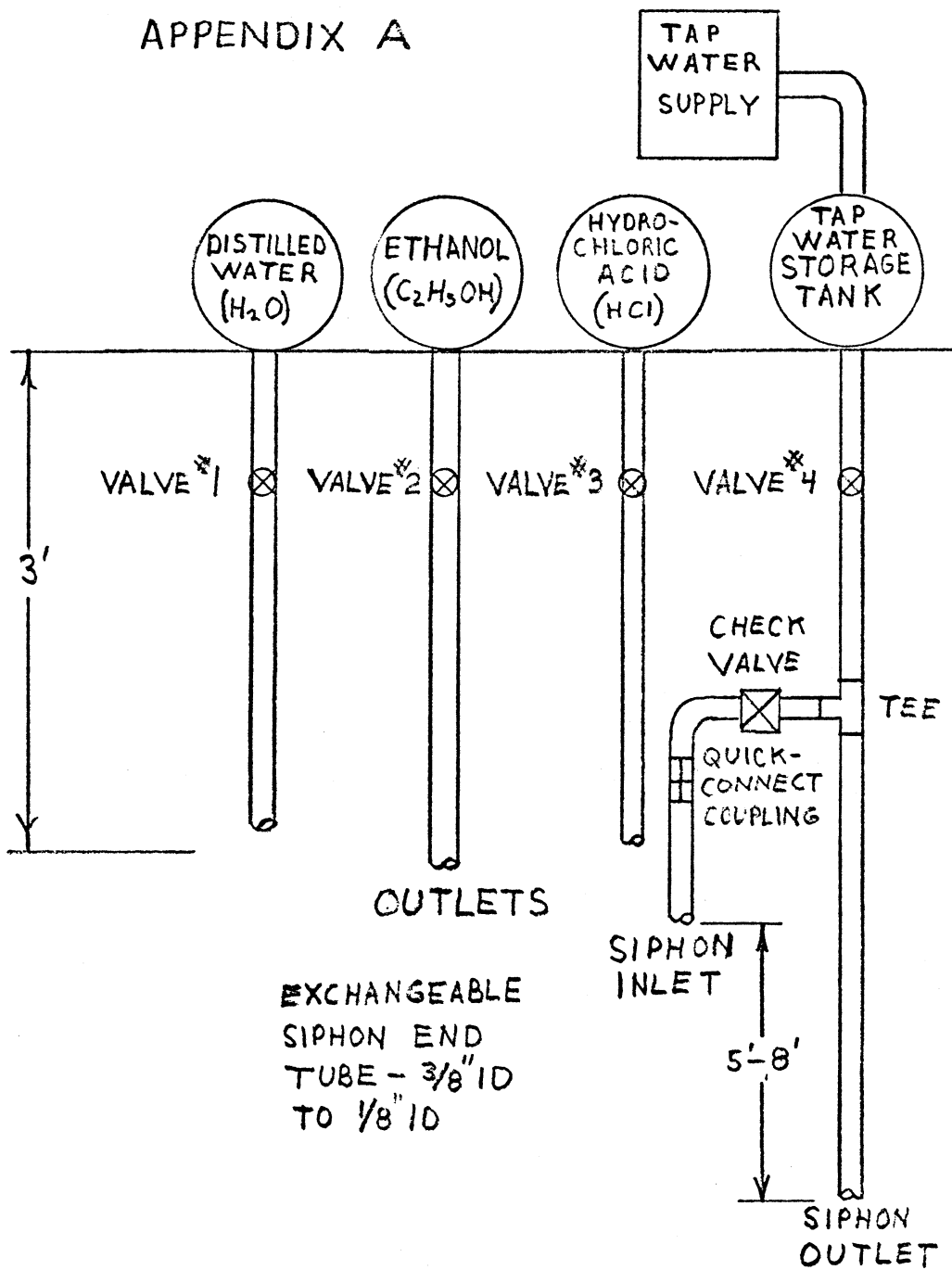
APPENDIX

APPENDIX A
ALLOY WASHING SYSTEM



Figure 16. Washing System for Cleaning the Alloy

APPENDIX A



WASHING SYSTEM SCHEMATIC

PROSISE

12-15-73

TABLE 7
PARTS LIST FOR WASHING SYSTEM

Part Name	No. Req'd	Description
Ethanol Tank*		
Hydrochloric Acid Tank*	3	1-Gal. Polyethylene Aspirator Bottle 3/8"-Tubing
Tap Water Storage Tank*		
Distilled Water Tank*	1	5-Gal. Polyethylene Aspirator Bottle 1/2"-Tubing
Tubing*	25'	3/8"-I.D. Tygon Tubing
Check Valve*	2	Polyethylene Check Valve 3/8"-Tubing
Tee*	1	Polyethylene Tee 3/8"-Tubing
Quick-Connect Coupling*	1	Polyethylene Quick-Connect 3/8"-Tubing
Valve #1 and #2*	2	Polyethylene Needle Valve
Valve #3 and #4	2	Gate Valve, Brass

*These materials were ordered from V.W.R. Scientific; St. Louis, Mo.

APPENDIX B
OXIDATION CHAMBER

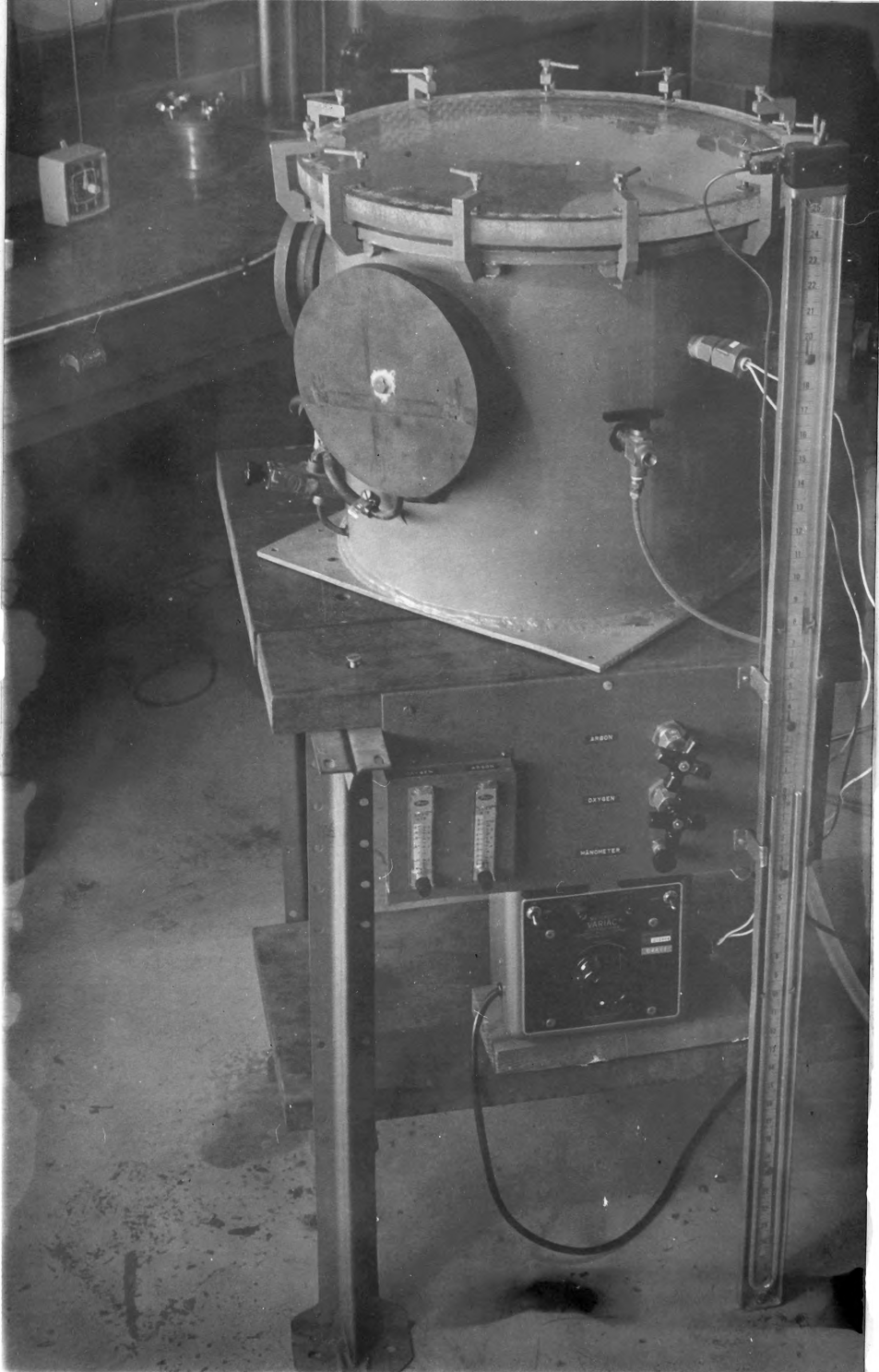


Figure 17. Oxidation Chamber for Oxidizing the Alloy

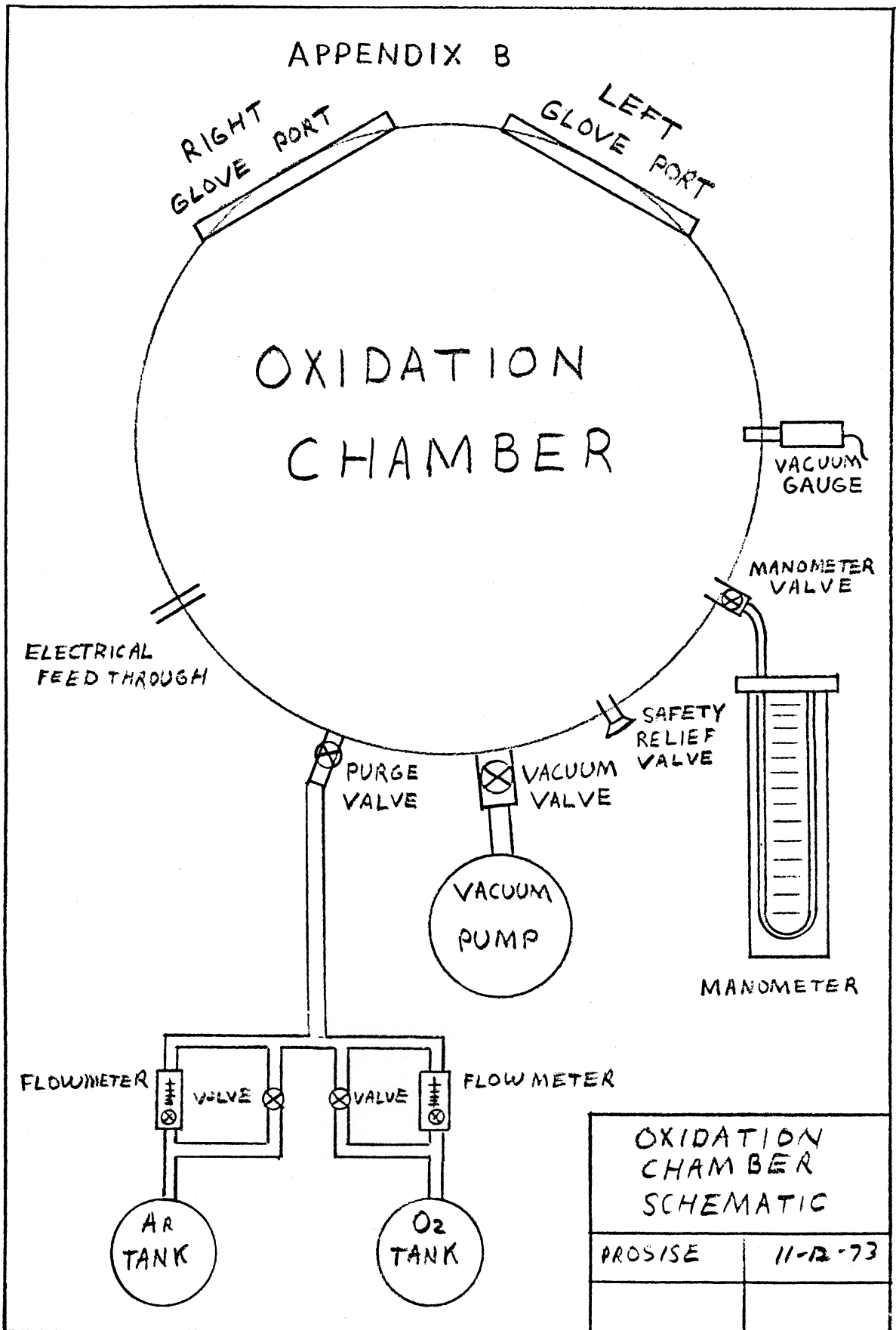


TABLE 8

PARTS LIST FOR MODIFICATION OF OXIDATION CHAMBER

Part Name	No. Req'd.	Specifications
Manometer*	1	50"
Needle Valve**	2	6,000 psi
Flow Meter***	1	RMA1-SSV
	1	RMA2-SSV
Safety Relief Valve****	1	0.5 psi

*50" C. O. Standard Cleanout Manometer, The Meriam Instrument Company; Cleveland, Ohio

**Needle Valve, Marsh Instrument Company; Skokie, Illinois

***Flow Meters, Dwyer Instruments Company; Michigan City, Indiana

****0.5 PSIA Relief Valve, Circle Seal; Anaheim, Calif.

APPENDIX C
DESIGN OF STORAGE BOX

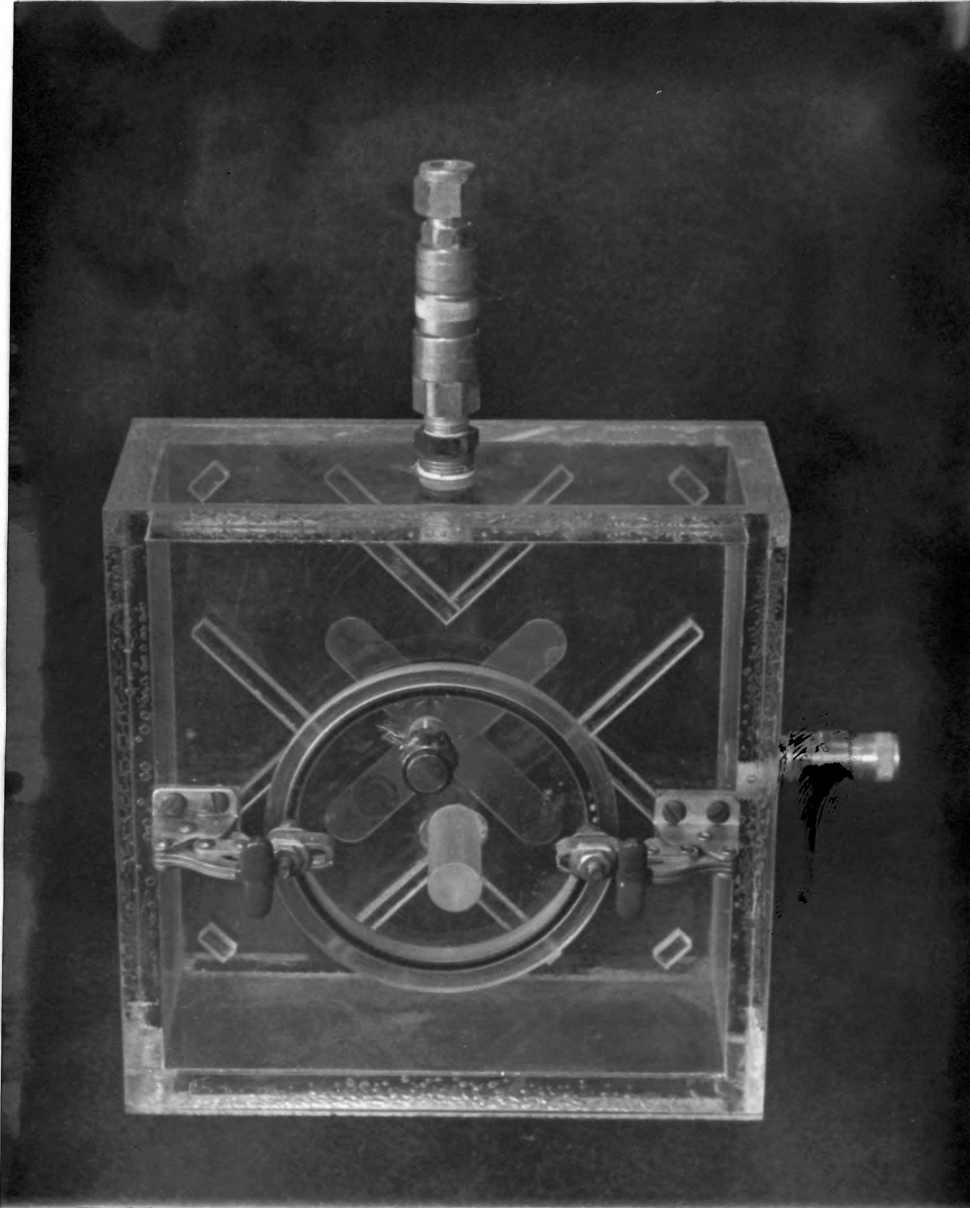


Figure 18. Storage Box for Alloy Transfer

TABLE 9
PARTS LIST FOR STORAGE BOX

Part No.	No. Req'd.	Part Name	Dimensions
101	1	Side Plate	0.50" x 3.00" x 8.00"
102	1	Side Plate	0.50" x 3.00" x 8.00"
103	1	Side Plate	0.50" x 3.00" x 7.00"
104	1	Side Plate	0.50" x 3.00" x 7.00"
105	1	Top Plate	0.50" x 8.00" x 8.00"
106	1	Bottom Plate	0.50" x 8.00" x 8.00"
107	1	Lid	4.25" Dia. x 0.50"
108	1	Handle	0.625" Dia. x 1.625"
109	8	Screws	8-32-UNC x 0.375"
110	1	O-ring	0.125"-3.50" Dia.
111	1	Relief Valve*	0.50 PSIA
112	2	Hold Down Clamps**	
113	1	Quick-Connect Coupling*** (body)	B-3/8QC-100-4
114	1	Quick-Connect Coupling*** (body)	B-1/4QC-100-4
115	1	Quick-Connect Coupling*** (stem)	B-600-3/8QC-200

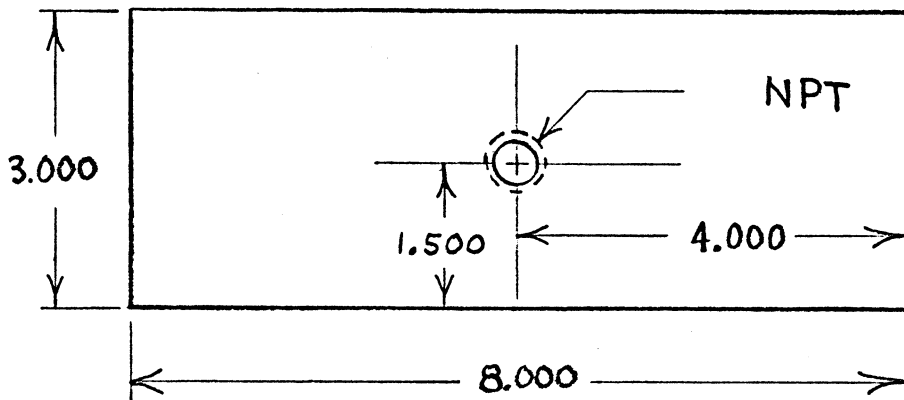
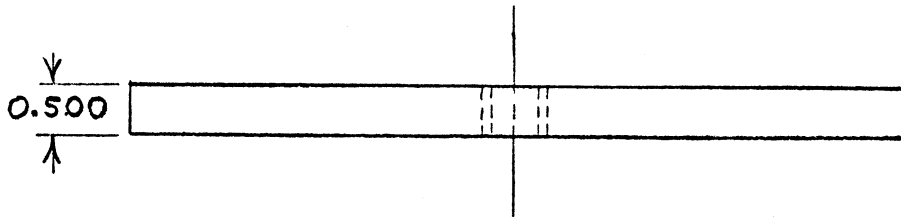
*0.5 PSIA Relief Valve, Circle Seal; Anaheim, Calif.

**De-Sta-Co Model 305 Clamps, De-Sta-Co Division, Dover Corporation; Detroit, Michigan.

***Swagelok Quick-Connects, Crawford Fitting Company; Cleveland, Ohio.

PART NO. 101

1 REQ'D.



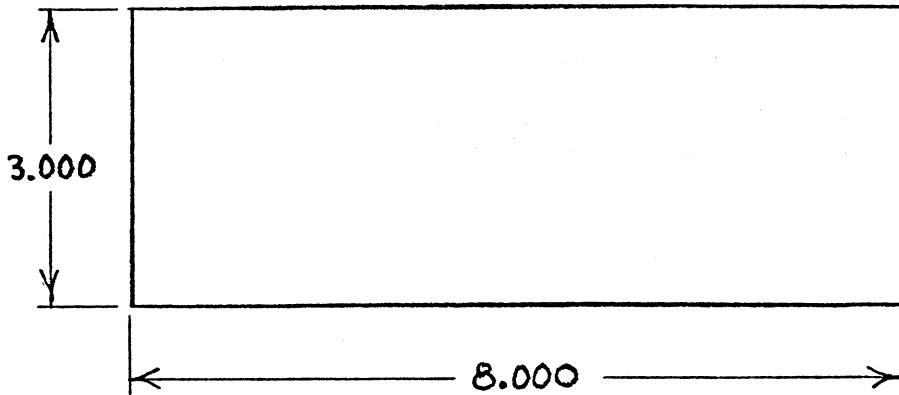
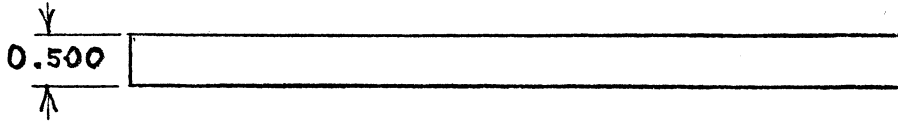
SIDE PLATE

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11-11-73

PART NO. 102

1 REQ'D.

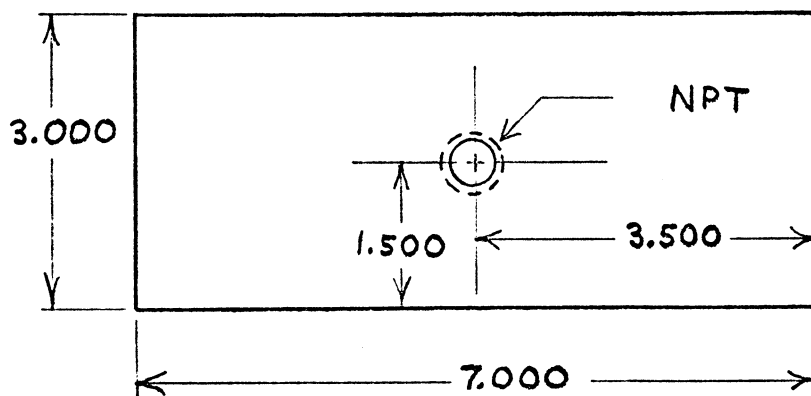
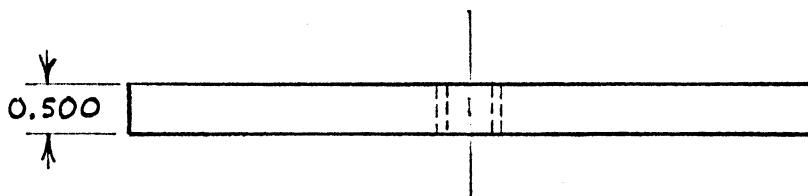


SIDE PLATE

PRO SISE

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PART NO. 103

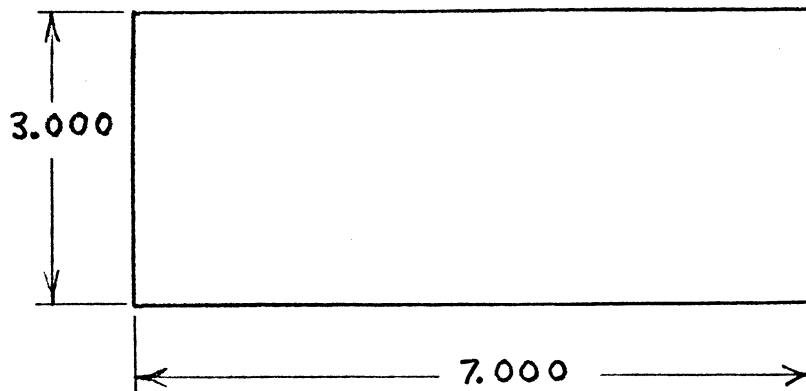
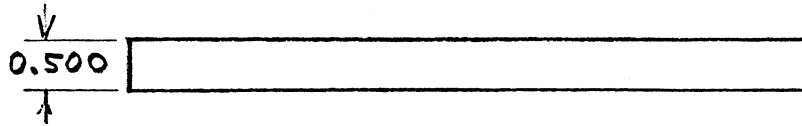
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SIDE PLATE

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PART NO. 104

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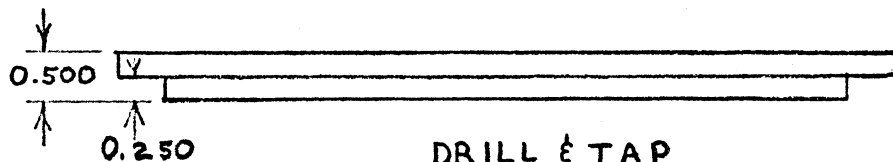
SIDE PLATE

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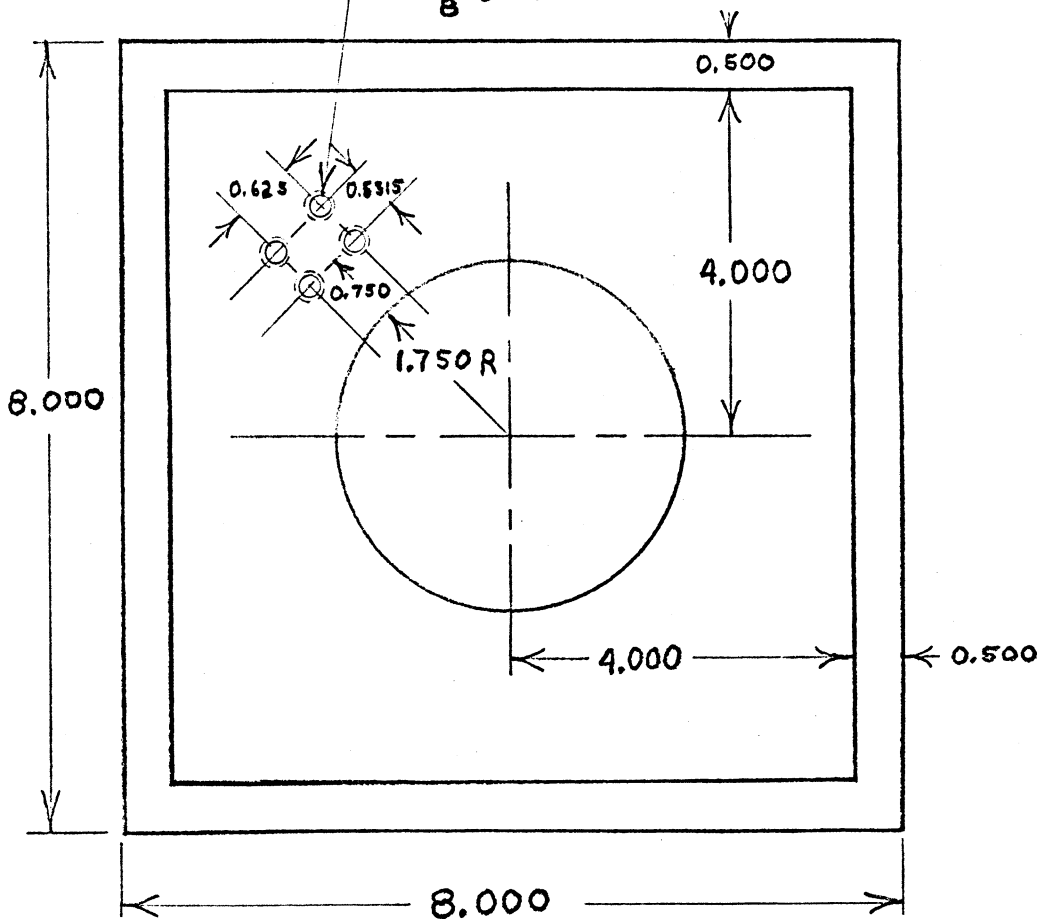
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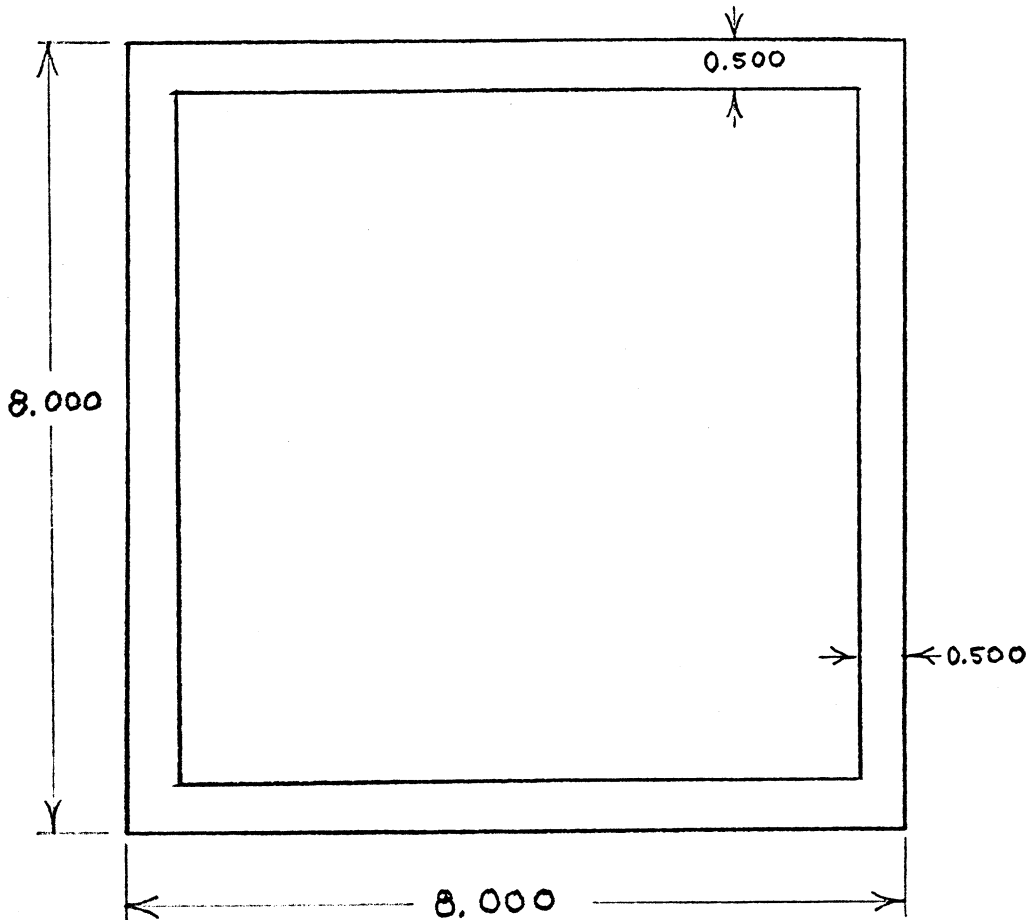
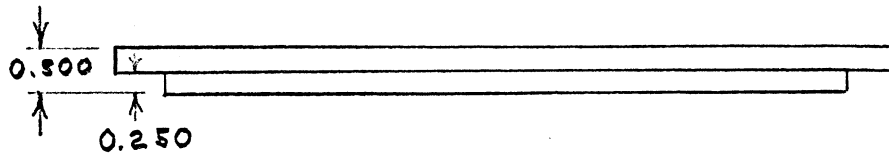


DRILL & TAP
 8-32-UNC
 $\frac{3}{8}$ DEEP



TOP PLATE	
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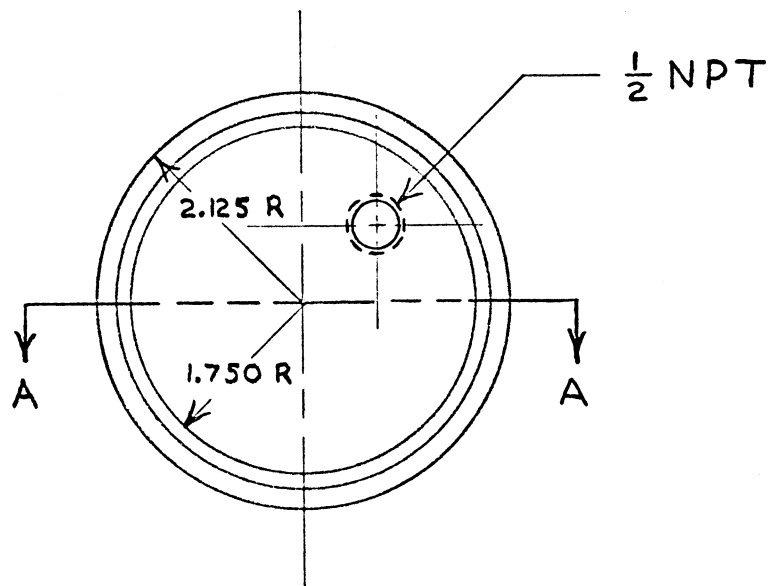
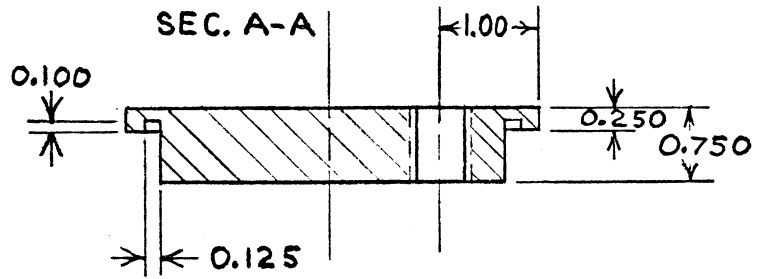
PART NO. 106

1 REQ'D.

BOTTOM PLATE

PROSISE

11-11-73

PART NO. 107 1 REQ'D

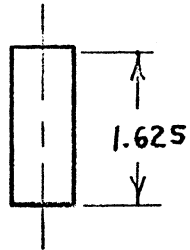
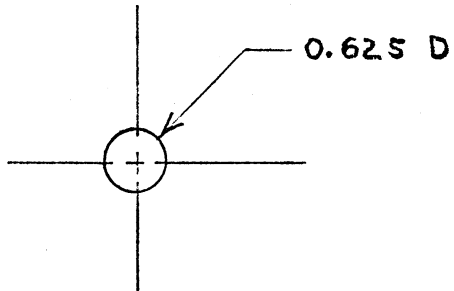
L I D

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11-11-73

PART NO. 108

1 REQ'D.



HANDLE	
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APPENDIX D
DESIGN OF SPACERS

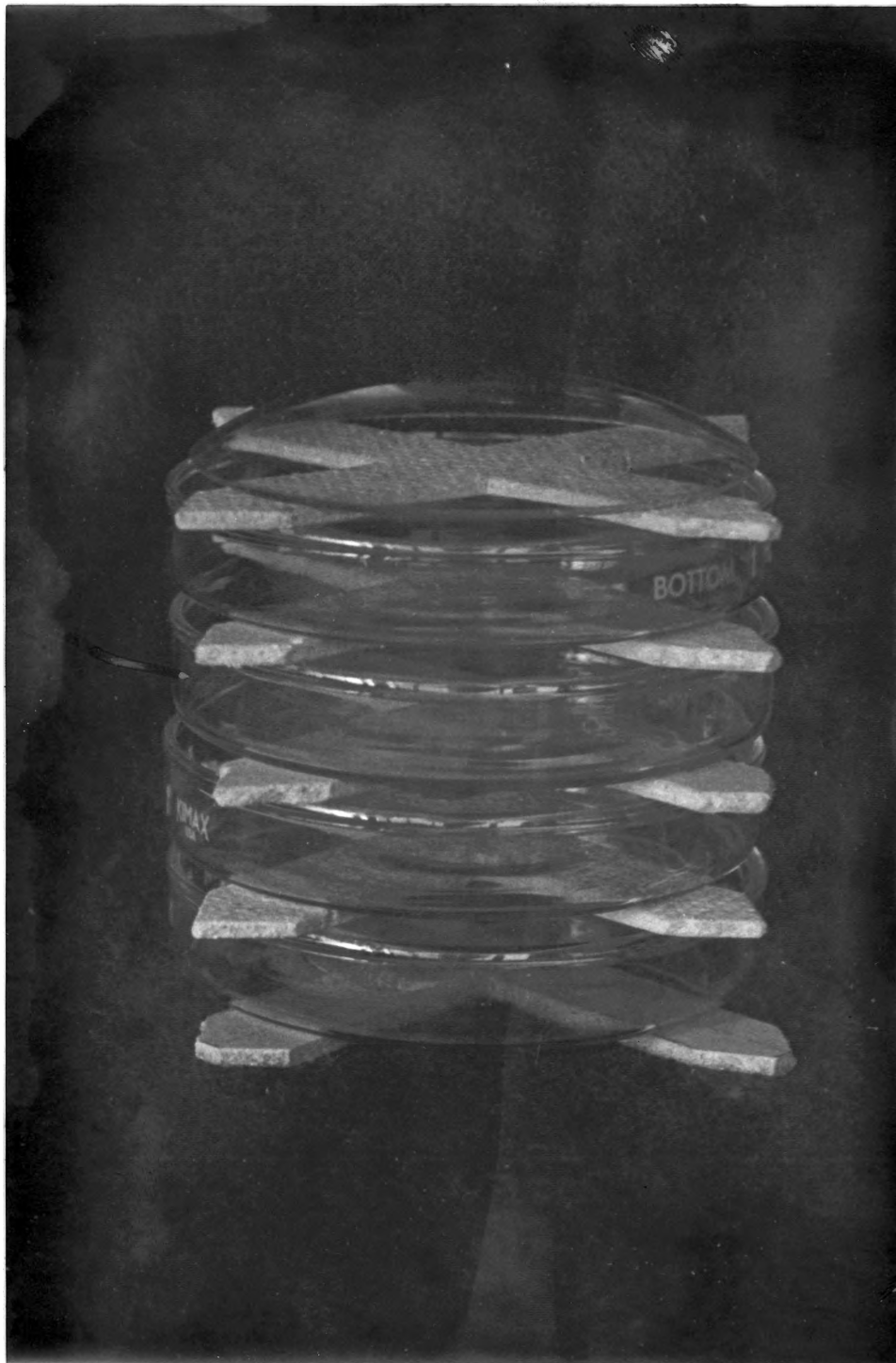
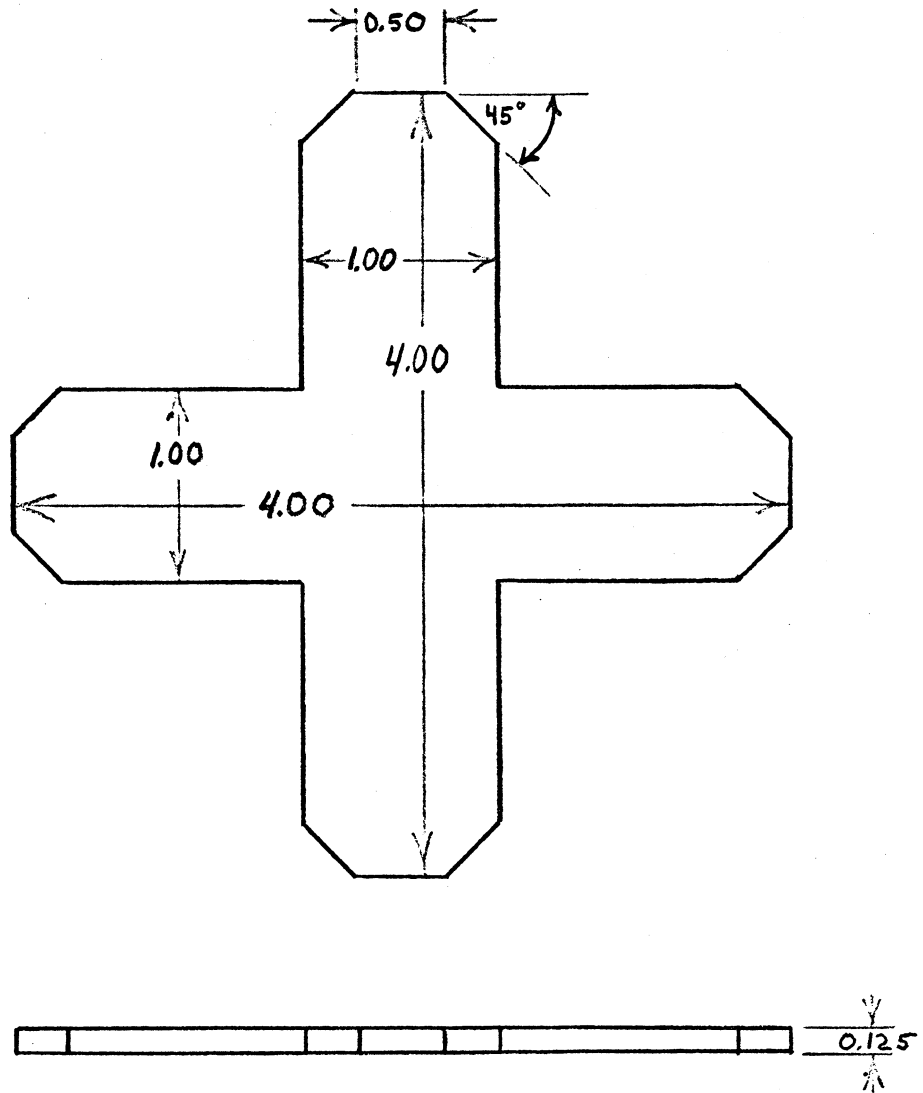


Figure 19. Spacers Used for Separating Petri Dishes

5 REQ'D.



SPACER

PROSISE

11-15-73

1" = 1"

MATERIAL
ASBESTOS

REFERENCES

REFERENCES

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