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BASIC ADHESION MECHANISMS IN THICK AND THIN FILMS

PRRL-74-Cr-29

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character, ink formulation, and circuit manufacturing processes upon film microstructures and, hence, properties of commercial and model thick-film materials. Twenty commercial gold conductors are under initial investigation; preliminary analyses of ten of these inks are presented. Alumina of 96 and 99.5 wt pct purities will be used as substrates in the study of commercial and model inks. Gold metal powders described in this report will be used in the formulation and testing of the model conductor inks. Plans for continuation of the above study and for additional work are outlined.

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PREFACE

This report describes work performed in the Process and Applied Materials Research Laboratory of RCA Laboratories under Contract N00019-74-C-0270.

P. Rappaport is the Laboratory Director and G. L. Schnable is the Project Supervisor and Group Head. J. Willis is the Government Project Monitor.

It is a pleasure to acknowledge the help of a number of individuals who have contributed to this work by the performance of several analytical techniques. Notable are H. H. Whitaker - optical emission spectrometry; E. M. Botnick - solids mass spectrometry; and G. R. Auth and B. J. Seabury - scanning electron microscopy. We also acknowledge the able assistance of E. J. Conlon and W. I. Rogers in the preparation of samples for analysis and in the day-to-day pursuit of the study. G. L. Schnable, J. L. Vossen, and E. J. Conlon aided with reviews of the manuscript.

The continued encouragement and helpful suggestions of G. L. Schnable, and the support of P. Rappaport in this work are much appreciated.

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I. INTRODUCTION

The reliability problems related to metallization systems in thick-film microcircuitry stem in large measure from poor adhesion strength between ceramic substrates and various functional metallizations. Usually these adhesion failures occur at the critical sites of module interconnections or discrete part bonding. Moreover, many of the reliability problems of wire bonds, beam-lead bonds, or soldered interconnections to thick films can be traced to trade-offs between thick-film adhesion and bondability or solderability.

Factors that are known to affect adhesion strength include chemical and mechanical components concomitant with materials selection, process variations, and diverse environmental stresses. More specifically the factors include: a) substrate selection - material type, dimensional control, grain size, surface and bulk composition, porosity, surface topography, and prior substrate process history; b) metallization choice - thick-film molybdenum-manganese, conventional frit-bonded noble metal systems, newer transition metal oxide-noble metal (reactively bonded) systems, or certain frit-bonded base-metal systems, e.g., Cu, Ni; and c) process parameters - including ink deposition, print thickness, drying, peak firing temperature and time, heating and cooling rates, over-coating with resistive and dielectric materials, and exposure to certain chemicals and atmospheres during subsequent processing.

The contract study includes chemical and physical analyses of commercially available aluminum oxide substrates and of both conventional frit-bonded systems and the newer reactively bonded thick-film gold conductor systems. The adhesion strengths of these systems will be carefully determined and analyzed. Formulation and evaluation of model inks will also be a part of the study.

Two concepts, which are indigenous to the plan of the study, are important to understanding why the program is expected to have strong influence in improving both the performance and the reliability of military hybrid packages. First, the study is devoted principally to the material types of both substrates and metallizers that are being used in or are most likely to be used in military hybrid circuitry. Thus, the technologist will not be required to make any translation of esoteric, research-derived principles. Second, the study is directed to increasing the basic understanding of the principles,

factors, and components affecting adhesion. A serious, practical study that leads to the elimination of art and the use of science and understanding to specify materials systems, to control their quality, and to improve processes must lead to a more rapid attainment of built-in reliability.

It is anticipated that the precise elucidation of the basic adhesion mechanisms in this study will result in the design of more rugged metallization-substrate systems and will preclude failures resulting from poor control of materials. Improvements are expected in adhesion strength, bondability, device replacement and repairability, and metallization conductivity. Furthermore, superior test methods for film properties - both destructive and nondestructive - are expected to result from this study. An example of a nondestructive, easily implemented quality control method is the use of crossed-polarized light microscopy, a technique developed in prior studies at RCA, to judge as-fired gold and silver thick-film metallizers. The technique is capable of revealing the amount of glass present on the surface of these metallizers. It has obvious use as a quality control before bonding. Less obviously, we believe that crossed-polarized metallography should be successful in assessing the prior firing history of particular inks to judge their probable adhesion strength nondestructively. We expect that by identifying and optimizing the critical process steps, more consistent and improved metallization properties can be obtained.

II. BACKGROUND

A. THE PROBLEM OF ADHESION

One of the problems in understanding *adhesion* is that the term can have a variety of different meanings. Several committees of the various industrial organizations desiring to improve standardization in hybrid manufacture have drafted or are now seeking definitions of such terminology which may benefit this study[1]. Until their work is further along, however, we must consider the term *adhesion* in its various common usages.

In reference to physically determinable measures of adhesion, perhaps the most precise usage is sometimes termed *adhesion strength in peeling*. It is the stress (force per unit width) required to maintain the continuous detachment of a strip of film from a substrate at a specific detachment rate. Ideally, the film should be no more or less adherent at its edges than anywhere else, and the detachment stress should be strip-width independent.

Another usage of *adhesion*, with at least some quantitative significance, is the *adhesion strength in tension* - defined as the stress (now force per unit area) required to remove a specific area of film when the entire area of the film is pulled in a direction which is perpendicular to the substrate surface.

Both of these definitions for *adhesion* result from specific attempts to quantify adhesion strength; neither approach has proved universally satisfactory. The definitions and much of the discussion that follows are attempts to address the *true adhesion strength*. The reader should understand that the property of *true adhesion strength* should be independent of test sample size, metal film thickness, and the geometry of loading by external forces.

Perhaps the most common usages of the term *adhesion* are in reference to the integrity or delamination of specific objects containing layered structures. Used in this way, *adhesion* is an engineering property - what we here will call *structural adhesion* - and, in contrast to *true adhesion*, is highly dependent on metal film thickness, direction of loading, load bearing area, size of the

1. D. B. Zimmerman, Committee Chairman, ISHM Hybrid Standard Specifications, Draft III, planned for release by Intl. Soc. for Hybrid Microelectronics in October 1974.

film periphery surrounding the load bearing area, and numerous other mechanical features. The general treatment of *structural adhesion* logically falls into the province of mechanical engineering for optimizing the package design. Clearly, proper mechanical design of a package and its components is mandatory to obtain the best package reliability from films with a given *true adhesion strength*. On the other hand, if the *true adhesion strength* is increased, *structural adhesion* can become a much less problematical area.

Despite its acknowledged importance, proper macro-mechanical design will be, in general, outside the scope of the study proposed, but the influence of micro-mechanical structures lies at the heart of this study. The dividing line between micro-structures and small macro-structures is not always a clear one.

B. IMPORTANT ADHESION CHARACTERISTICS IN THIN-FILM AND THICK-FILM METALLIZATION

There are several problems in understanding the adhesion of thick and thin films to ceramic substrates. First, it must be realized that a large thermal expansion mismatch exists between the ceramics and the metals commonly used for conductor films. When metal films are very thin, the lateral expansion mismatch is compensated elastically through a change in film thickness. When the metals are thicker, the above elastic mechanism is precluded, and, when any substantial temperature change is imposed on a system, one of the following must occur: The strain is borne elastically by the entire system, the metal layer may crack, or the metal layer must plastically deform. Of course, different systems behave differently in the face of temperature changes. If the metal is brittle and its elastic limit in tension is exceeded, the metal must either crack (craze) or delaminate from the substrate. Pure metal systems, especially face-centered-cubic conductors - gold, silver, copper, aluminum - are likely to accommodate the thermal expansion mismatch by deforming plastically.

To be useful, a film-substrate combination must have, at a minimum, sufficient adhesion between film and substrate to preclude delamination when acted on by the thermal fluctuations necessary for processing the circuit into a finished, packaged unit. In addition, it must withstand whatever forces are imposed in service by interconnected parts and hardware.

Unfortunately, there are no fully satisfactory ways of measuring adhesion of films to substrates. If such a test existed, it would 1) be useful for a wide range of conductor material types, 2) give quantitative, reproducible data over a wide range of adhesion strengths, 3) not be influenced by the choice of materials required to perform the test, 4) be implemented easily and without operator sensitivity, and 5) allow the measurement of adhesion strengths distinct and apart from other strength parameters such as cohesion strengths. We have, instead of this ideal situation, a large number of semiquantitative tests in use. Many of these are threshold tests; e.g., Scotch tape is pressed down on a film and then jerked upward, after which the film is examined for delamination. If the film has not lifted, we only know that the adhesion strength is above a threshold value - not that the adhesion is necessarily satisfactory. The razor blade scrape test for thin films is better, in that it describes a higher threshold (in thicker thin films), but it suffers even more than the Scotch tape test in being operator-dependent. The well-known duPont soldered-pad wire-pull adhesion test[2] for solderable thick films gives quantitative data up to the point that the substrate breaks, but the number found for adhesion strength is a strong function of the amount and type of solder used, the hardness of the wire, the substrate hold-down fixture, the test operator, and other variables.

A principal difference between thick and thin films is that thin films depend almost entirely on an adhesion-enhancing layer of a chemically active metal deposited directly on the substrate. If foreign material covers the surface, bonding is prevented. For example, oxidation in the thin-film Cr-Cu system has been examined[3]. In this system, bonding is almost entirely chemical. In thick films, on the other hand, bonding can be chemical or mechanical. Although thin films are commonly more adherent than thick films, it is known that when a particular lot of thin-film metallization has adhesion problems, its adhesion strength is often extremely low.

2. L. C. Hoffman, V. L. Bacchetta, and K. W. Frederick, "Adhesion of Platinum-Gold Glaze Conductors," IEEE Trans. Parts, Materials, and Packaging PMP-1, No. 1, s-381 (1965).
3. J. J. O'Neill and J. L. Vossen, "Cr-Cu and Cr-Cu-Cr Thin-Film Metallization," J. Vac. Sci. and Tech. 10, 533 (1973).

Thick films are usually more forgiving in that a small quantity of foreign matter on the substrate may either be included in the glass phase or the metal film, or be burned and driven off in the firing process. Adhesion usually does not suffer drastically unless the retained foreign matter has substantial volume.

If we consider the problem from the point of view of the physical and chemical forces that determine adhesion, we note that there are forces that act to *attach* the film to its substrate and forces that act to *detach* the film from its substrate. If the former are stronger than the latter, the film is said to be adherent. To be more definitive one should refer to attachment forces as "bonding forces." There are basically two types of bonding forces, chemisorption and physisorption; each is further subdividable. Chemisorption processes usually lead to maximum bonding. If there is a chemical reaction between the arriving film material and the substrate, a chemical bond is formed, as shown in Table 1. It should be noted that some intermetallics

Table 1. Bonding Forces Resulting from Chemisorption

| <u>Film Material</u> | <u>Substrate Material</u> | <u>Bond Type</u> | <u>Example</u> |
|---|---------------------------|------------------|------------------------|
| Metal that forms solid solution with metallic "substrate" | Metal | Metal-Metal | Ag-Au W-Mo |
| Metal that form inter-metallic compound(s) with substrate | Metal | Intermetallic | Pt-Si |
| Metal that can chemically reduce compound substrate | Compound | Reactive | Al-SiO ₂ |
| Compound soluble in substrate | Compound | Chemical | Glass-SiO ₂ |

are quite brittle and do not promote bonding; the fraction of chemical reduction that will occur in reactive bonding is dependent upon the free energies of formation of the compound formed by the arriving metal and the substrate material and upon the kinetics of the reaction. Complete reduction rarely occurs, but adequate bonding can result from partial reduction of the substrate. For example, Ta cannot reduce Al₂O₃ to Al metal in thermodynamic

equilibrium, but Ta does adhere very well to Al_2O_3 substrates because partial reduction of the substrate occurs.

Physisorption alone occurs in systems where the conditions in Table 1 are not met. The bonding forces involved (van der Waals and electrostatic) are fairly weak by comparison with those described above. Film-substrate systems that involve only physical bonding (e.g., gold on glass) have few practical uses, though they are of some laboratory significance. The major internal forces acting to detach films from substrates are stresses - internal and interfacial. Interfacial stress is largely due to thermal expansion mismatches between film and substrate. Internal stress has been the subject of numerous experimental investigations, yet its origins are still not well understood. However, it is known that the magnitude of the detachment force resulting from internal stress can be extremely large. For example, Mo films do not adhere to clean Mo substrates if they are evaporated by electron-beam techniques or sputtered at low bias voltages. Films prepared in this way exhibit very large tensile stresses. However, films sputtered at relatively high bias voltages (-125 V) exhibit compressive stress. Films deposited at zero stress or in slight compression by the use of intermediate bias voltage adhere while those that are in substantial tensile stress do not.

C. DEVELOPMENT OF ADHESION IN FIRED THICK-FILM METALLIZERS

1. Frit-bonded Inks

Included for consideration in the category of frit-bonded conductors are all thick-film conductor inks containing a second phase or phases that, through their wetting (fluxing) of the ceramic, achieve the principal bond to the substrate ceramic. Most of these materials are glasses, but certain inks previously studied[4] include bismuth oxide in such high concentrations that the flux probably is not a true glass.

In the works of Skaw* and Hitch[4], the principal components of adhesion in a properly fired thick-film conductor were judged to be both chemical and

4. T. T. Hitch, "Phase Morphology and Adhesion in Thick-Film Conductor Inks," Proc. Intl. Soc. for Hybrid Microelectronics Symposium, p. 7.7.1 (1971).
* E. Skaw, private communication, 1971.

mechanical. Optimum mechanical adhesion was found to occur when the flux phase formed an interlocking structure that bound the metal phase to the ceramic. Two glass phase structures were shown by Hitch[4] to cause good micromechanical adhesion. These were the "fiber" and the "re-entrant" structures. The development of these structures required optimized firing temperatures and times and a sufficient loading of the paste with the glass phase; these conditions were necessary, but not sufficient[4].

Structures with low micromechanical adhesion were also identified. These were 1) the underfired structure - resulting from insufficient time and temperature to allow the flux to wet the ceramic - and 2) the overfired or "scalloped" structure that can result from either insufficient loading of the ink with flux or too much firing time and/or temperature. Overfiring causes any interlocking structures in the flux phase to be destroyed by phase separation in sintering[4].

The chemical aspects of adhesion in thick films improves with the chemical affinity between the flux and metal as well as between the flux and ceramic. Either a more active flux or a more reactive metal should improve the chemical part of the adhesion strength.

2. Reactively Bonded Inks

In the last two years, several thick-film noble-metal conductor inks have been marketed which contain neither glass nor other obvious flux, yet on firing can bond strongly to ceramics. Small quantities of copper oxide, sometimes with minor additions of cadmium oxide, have been identified as the adhesion-producing agent in some of these inks[5]. When the inks are fired onto alumina substrates, adhesion is produced by the formation of compounds such as copper aluminate[6].

A preliminary study indicated that the morphologies formed by the reactively bonding compounds are unlikely to make a significant micromechanical (physical interlocking) contribution to the adhesion strength. The same study showed also that some of the materials fire to form unusually dense, smooth

5. T. T. Hitch, "Adhesion, Phase Morphology, and Bondability of Reactively Bonded and Frit-Bonded Gold and Silver Thick-Film Conductors," J. Electron. Mat. 3, 553 (1974).
6. R. M. Pillar, T. G. Carruthers, and J. Nutting, "Oxide-Oxide Interactions Studied by Transmission Electron Microscopy," J. Mat. Sci. 2, 28 (1967).

highly adherent films that are extremely conductive at low frequencies[5]. Unreported work at RCA further indicates that the materials have unusual potential for use at microwave frequencies. Adherence to 99.5 wt pct alumina and to beryllia is reported to be much higher than the normal frit-bonded thick films[7].

The adhesion mechanism of these materials will be addressed in this investigation. Their compatibility with the more usual thick-film materials and processing also requires definition.

D. PROBLEMS IN ADHESION RESULTING FROM SUBSTRATE SPECIFICATION OR SELECTION

As many have already discovered, changing the thick-film hybrid circuit substrate from the widely used 96 wt pct alumina to 99.5 wt pct alumina or to beryllia without changing processes and/or ink materials can be disastrous. Adhesion of most thick-film conductors on these materials is markedly less than on the 96 wt pct alumina. The two logical reasons given for the employment of 99.5 wt pct alumina and beryllia substrates are improved high-frequency performance and improved thermal conductivity. Better understanding of conductor ink-substrate-process requirements is required for use of high-purity alumina and beryllia substrates. However, if the use of 99.5 wt pct alumina or beryllia substrates is truly required, new conductor materials tailored to these substrates, together with optimized processing, can probably deliver the all-around performance necessary.

By way of example, it is foolish to stipulate a ground surface of less than 5- μ inch center line average (CLA) on the ceramic to obtain good microwave characteristics and then to use an arbitrarily chosen frit-bonded ink. We have shown that frit-bonded inks can produce fiber structures in their nonconductive, glassy phase which give the assembly an effective ceramic surface roughness estimated at 300- μ inches[4].

Specification for substrate materials must be derived to preclude the substrate vendor from: 1) making intentional process changes without warning or 2) operating with insufficient process control. However, the designation of exactly what properties are most desirable in a substrate must be made. The studies of this contract will contribute to understanding in this area.

7. B. R. Smith and R. L. Dietz, "An Innovation in Gold Paste," Proc. Intl. Soc. for Hybrid Microelectronics Symposium, p. 2.A.5.1 (1972).

E. SOME CONSIDERATIONS IN THE SELECTION, SPECIFICATION, AND DEVELOPMENT OF THICK-FILM CONDUCTOR INKS

One ink will not perform all functions in hybrid circuits. For example, Pt-Au inks are used for soldered connections, and thermocompression (T.C.) bonding is done to gold inks. Inks based on other noble metals and alloys can be substituted for these with some cost savings, but problems have been found. Even within the narrower class of frit-bonded gold inks, a single ink will probably never suffice for all applications. Yet the various vendors are reluctant to stop production of outdated ink materials and/or to add new inks to their product lines. Still, as basic knowledge improves, the requirements for better inks can be stipulated; then vendors will comply and produce such inks.

As discussed in Section II.B., internal and interfacial stresses are of little concern in gold and silver films since the metals are very ductile. In harder alloy metallizations such as Au-Pt, Au-Pd, and Ag-Pd, these stresses are much more likely to cause adhesion problems. On the other hand, Au-Pt, Au-Pd, and Ag-Pd are some of the more chemically active of the noble metal thick-film conductors and have good adhesion when properly fired.

In recent years, it has become evident that Ag, Au-Pd, and Ag-Pd metal-lizers are subject to drastic reduction of the structural adhesion strength when high-tin tin-lead solders are applied to these metallizations and the structures are aged at temperatures of $\sim 150^{\circ}\text{C}$ for many hours[8,9].

A partially proved explanation of the phenomenon is that the diffusion of Sn through the thick-film metallization to the flux-metal interface results in the formation of Sn_xM -type intermetallic compounds. These destroy the chemical adhesion at the interface. If mechanical interlocking with the glass phase was present, structural integrity could be maintained. If it was absent, the structures would easily delaminate. Lead-based solders containing a low percentage of tin for use on Ag-Pd metallizations, or Au-Pt metallizations which possess reduced diffusion rates for Sn, and the protection of structures from thermal aging are all logical solutions to the

8. A. A. Milgram, "Influence of Metallic Diffusion on the Adhesion of Screen Printed Silver Films," *Metallurg. Trans.* 1, 695 (1970).
9. W. A. Crossland and L. Hailes, "Thick Film Conductor Adhesion Reliability," *Proc. Intl. Soc. for Hybrid Microelectronics Symposium*, p. 3.3.1 (1970).

problem. On the other hand, a 95 Pb-5 Sn solder used on Au-Pt metallization has been found in one case to cause drastic leaching. Apparently, zealous attempts to circumvent thermal aging problems ran afoul of an unexpected dissolution phenomenon. At this time, only a hypothesis exists to explain the leaching.

Such anomalies are the rule rather than the exception in thick-film technology. Most systems are used because they work - not because they are understood.

Thick-film ink compositions and firing conditions usually must be selected to provide good bondability as well as good adhesion strength. Unfortunately, however, some trade-offs must be made. In particular, increase in the glass content of thick films increases adhesion strength but decreases bondability, as shown in Fig. 1. The range of peak firing temperatures

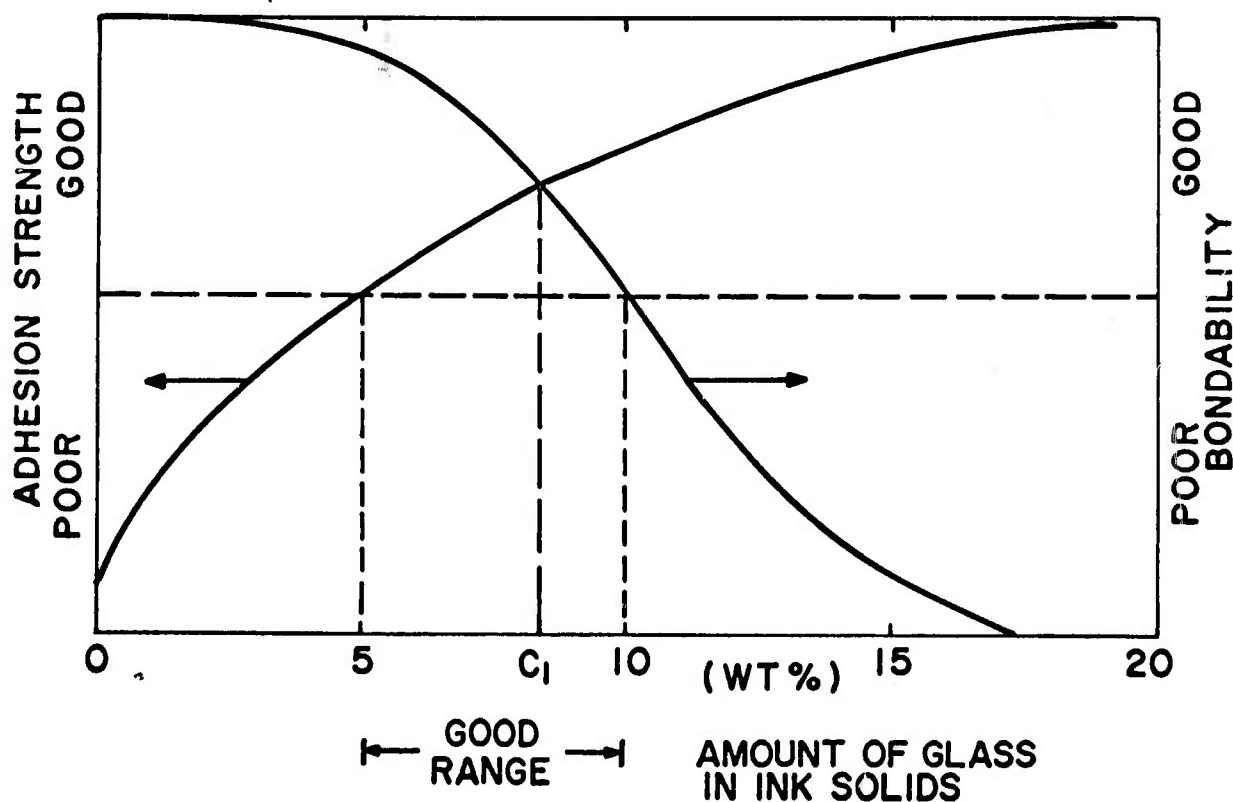
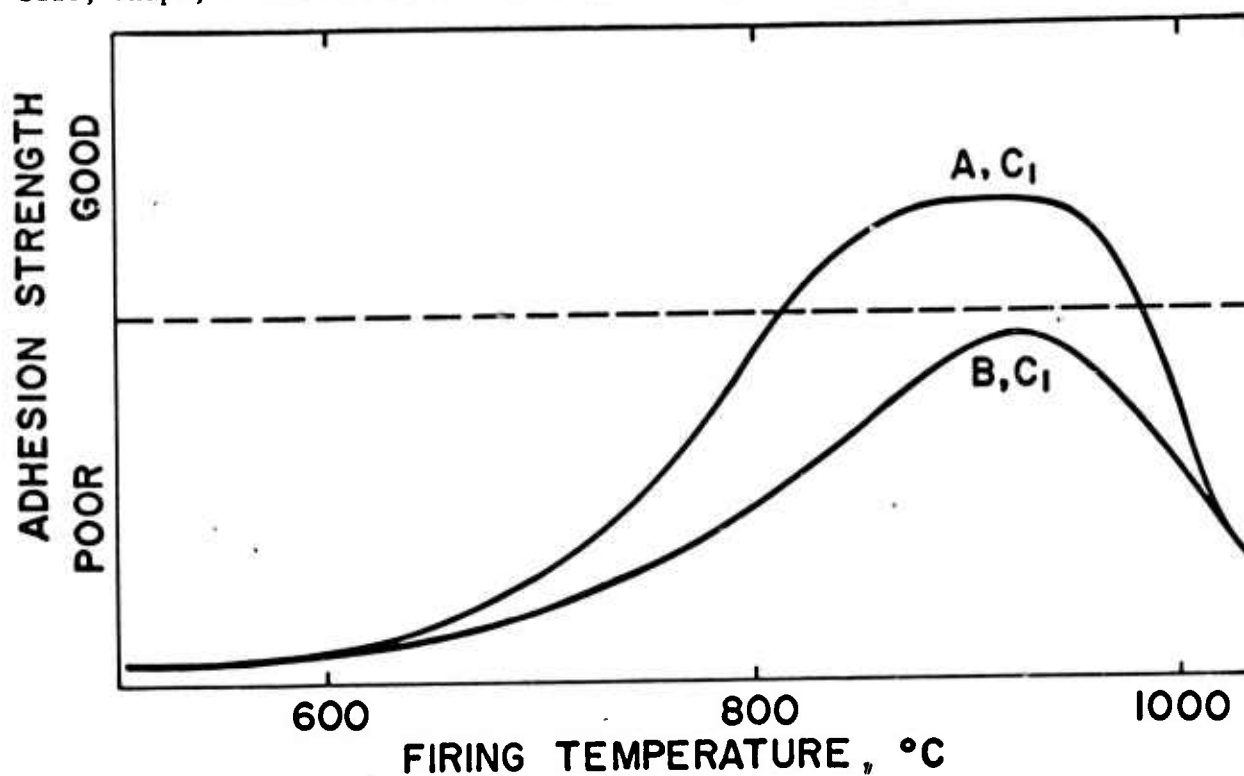


Figure 1. Adhesion strength and bondability as a function of glass content in ink solids.

over which adhesion is acceptable may vary with the glass and metal particle size, shape, and size distribution, as indicated in Fig. 2. Both adhesion



POSSIBLE REASONS FOR A → B BEHAVIOR SHIFT: GLASS PARTICLE SHAPE, SIZE DISTRIBUTION; METAL PARTICLE SHAPE, SIZE DISTRIBUTION.

NOTE: A AND B HAVE SAME GLASS TYPE AND GOLD CONTENT.

Figure 2. Adhesion strength as a function of firing temperature.

strength and bondability tend to increase with firing temperature, but not necessarily at the same rate. Figure 3 illustrates a system in which adhesion strength peaks at a firing temperature of ~850°C but bondability does not become acceptable unless firing is performed at a temperature above 950°C. With some systems, bondability might continue to increase with increasing firing temperature, rather than reaching a peak. Understanding the interrelationships of such systems and using that understanding to optimize processing and to define requirements for improved materials are the objectives of this contract study.

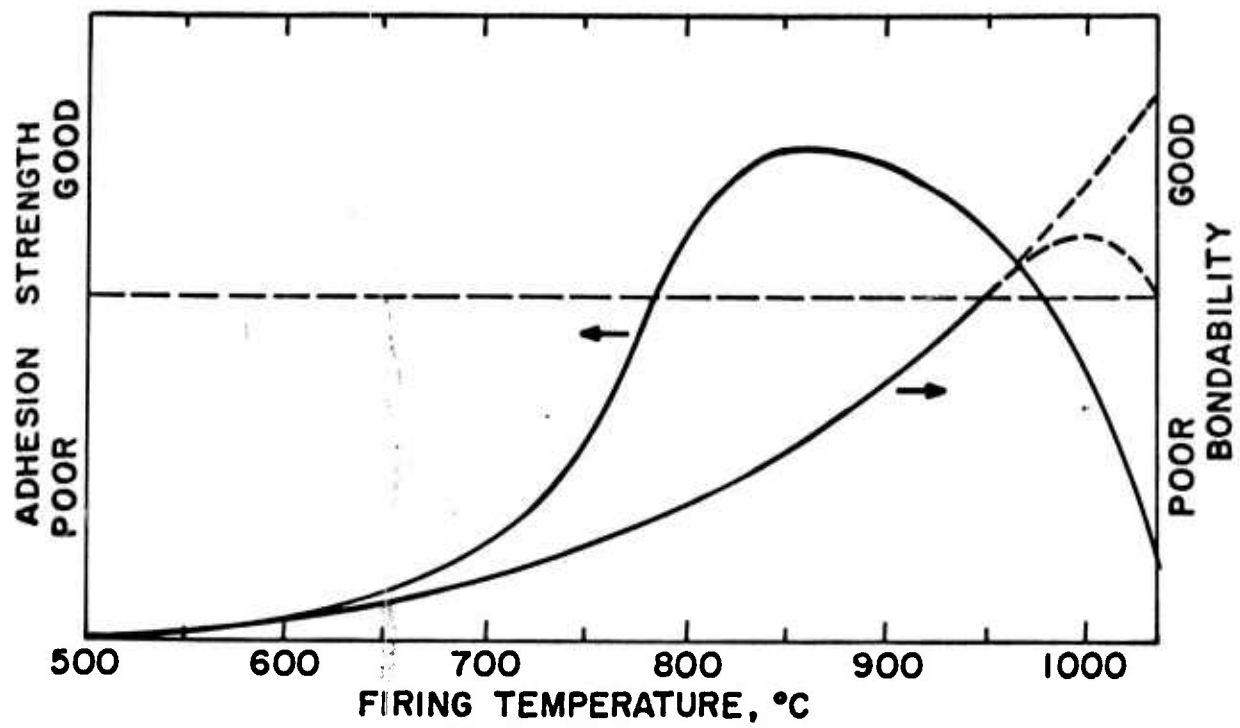


Figure 3. Comparison of adhesion strength and bondability as a function of firing temperature.

III. SCOPE OF THIS STUDY

Attempting to understand the entire thick-film process of manufacturing resistors, capacitor and crossover dielectrics, various conductors on several substrate types, in all their ramifications, within one study, is truly an enormous task. On the other hand, the several unique capabilities of the thick-film process (including power dissipation, design turnaround time, packing density, circuit ruggedness, component trimmability, and others) require a much more fundamental understanding of the behavior of these materials than has been realized to date. In this study, as in others being pursued concurrently[10-12], particular phases of thick-film materials and processes are being studied with a view to fundamental understanding.

This study has been limited to understanding adhesion in gold-based conductor inks. In Sections I and II we have described the importance of both gold films and the property of adhesion strength. An additional delineation of emphasis has been drawn between RCA and the Naval Research Laboratories (NRL), who are performing a coordinated study. NRL is concentrating its study on the ceramic-adhesive agent interface while RCA has made the adhesive agent-metal phase interface its area of principal interest. Each group maintains and constructively criticizes the work of the other. Communication and cooperation are developing between the two laboratories, and the effects appear synergistic to both efforts.

A wide variety of experiments are under way at RCA that will attempt to simplify and to explain the events which occur in gold conductor films during conventional thick-film processing. Experiments with hybrid thin films will be among the techniques used to model parts of the behavior of thick-film conductors.

10. R. W. Vest, "Conduction Mechanisms in Thick Film Microcircuits," Contract Grant Nos. DAHC15-73-G7 and DAHC15-73-G8 at Purdue University, under the sponsorship of the U. S. Air Force.
11. Y. Taketa and M. Haradome, "The Basic Reactions, Compositions, and Electrical Properties of Pd-Ag Thick Film Resistors," IEEE Trans. on Parts, Hybrids, and Packaging PHP-9, No. 2, 104 (1973).
12. Y. Taketa and M. Haradome, "Mechanism of Aging in Pd-Ag Thick Film Resistors," IEEE Trans. on Parts, Hybrids, and Packaging PHP-9, No. 2, 115 (1973).

IV. PROGRESS OF THE CONTRACT STUDY

In the first quarter of this new study, three efforts have received the bulk of the RCA effort. These are:

1. Procurement and arrangement to procure the materials to perform the remainder of the contract studies.
2. Analysis of a large group of thick-film gold conductor inks, purchased from vendors, with a view to selecting a few of the better, representative inks for further study.
3. Design of test fixtures and sample configurations, and selection of test materials for a number of adhesion tests.

The first two of the above tasks have progressed sufficiently to be reported here in some detail. The third has also advanced and will be reported in the next quarterly report.

A. PROCUREMENT OF MATERIALS

1. Commercial Gold Conductor Inks

One or more ounces of 20 different thick-film gold conductor inks have been purchased from eight major thick-film ink vendors. Table 2 is a condensation of these manufacturers' descriptions of the inks on hand. It is our intention to complete a preliminary screening of these inks to select a much smaller number, perhaps five, on which to perform the most detailed study. The 20 inks purchased include frit-bonded and reactively bonded types of inks, as well as a new glass-fluxed, reactively bonding gold ink. One frit-bonded ink is included which can be fired either in hydrogen or in air.

Only two generic types of gold-thick-film inks have been omitted from this study. These are the "overlay"-type materials and the photo-processible inks. The first of these are gold inks which contain no intentional addition of bonding agent. Overlay materials have no value without the preparation of the ceramic by the deposition of another metallization. The photo-processible materials represent an interesting concept of some value for special purposes, but they require special handling, which most thick-film vendors will tend to avoid. Therefore, neither of these two ink types was judged sufficiently pertinent to the present study to warrant its inclusion.

Table 2. Summary of Manufacturers' Data on Inks

| <u>Ink</u> | <u>Type</u> | <u>Comments</u> | <u>Firing Conditions</u> | <u>Sheet Resistance</u> |
|------------|--|---|--|-------------------------------------|
| A-1 | Au; die and wire bonding. Micro-wave strip lines | 99% + 0.5% Au in fired film. No burnishing. Glassless. | Range: 875°-980°C 5-6 min. | .001-.002 ohm/sq., .75 mil thick |
| A-2 | Au; wire and die bonding | 96% Au in fired film, Sn-Pb and Sn-Pb-Ag solders, no burnishing required, 800 psi adhesion. | Optimum: 800°-950°C, 5-6 min. | .003-.0035 ohm/sq., .5 mil thick |
| B-1 | Au; die and wire bonding, high conductivity | 5 mil lines with 7 mil spaces. Some leach resistance to Sn-Pb solder. | Range: 600-925°C 5-15 min. Optimum: 850°C. | .003 ohm/sq., .5 mil thick |
| B-2 | Au; die and wire bonding, micro-wave | Fine line. 99% Au when fired. 5 mil lines. Glassless, high adhesion. | Range: 950°-1020°C 10 min. Optimum: 1000°C. | .003 ohm/sq., .5 mil thick |
| C-1 | Au; die and wire bonding, micro-wave | High conductivity, almost all gold. High adhesion. | Range: 650°-1000°C. | .0018-.0022 ohm/sq., 1 mil thick |
| C-2 | Au; die and wire bonding | 5 mil lines, 5 mil spaces. Firable in air or in a reducing atmosphere. | Range: 900-950°C 10 min. 1050-1100°C (if Au melting is not a problem). Optimum: 850°C > 10 min. | .003-.005 ohm/sq., 1 mil thick |
| C-3 | Au; die and wire bonding | 4 mil lines, 4 mil spaces. Fine line, high conductivity. | Range: 875°-1000°C 10 min. Optimum: 900°-950°C. | .002-.006 ohm/sq., 1 mil thick |
| D-1 | Au; die and wire bonding, high adhesion | 92% Au when fired. Soldering not recommended with Sn-Pb solders. | Range: 815°-1010°C 5-15 min. | <.005 ohm/sq., 1 mil thick |
| D-2 | Au; die and wire bonding, micro-wave | 97-98% Au when fired | Range: 850-1000°C Optimum: 985°C 7-9 min. | .002 ohm/sq., 1 mil thick |

Table 2. (Continued)

| <u>Ink</u> | <u>Type</u> | <u>Comments</u> | <u>Firing Conditions</u> | <u>Sheet Resistance</u> |
|------------|---|---|---|-------------------------------------|
| E-1 | Au; die and wire bonding, beam-lead bonding | Fine line. 2 mil lines on 4 mil centers with metal mask. Slight leach resistance to Sn-Pb solders | Range: 850°-950°C Optimum: 900°C 5-10 min. | .003 ohm/sq., 1 mil thick |
| E-2 | Au; die, wire, and beam-lead bonding | 5 mil lines, 5 mil spaces. Fine line, high conductivity. | Range: 760°-950°C. Optimum: 850°C, 6-10 min. | .003 ohm/sq., .6 mil thick |
| F-1 | Au; die and wire bonding | Dense fine-line prints. | Range: 730°-1000°C Optimum: 840°-950°C, 8-10 min. | .0032-.0036 ohm/sq., 1 mil thick |
| F-2 | Au; die and wire bonding | Dense, fine-line prints, high conductivity. | Range: 730°-1000°C. Optimum: 840°-950°C, 8-10 min. | .0028-.0032 ohm/sq., 1 mil thick |
| F-3 | Au; die and wire bonding, high conductivity | Dense, fine-line prints. Glassless, ~100% Au in fired film. Modest Sn-Pb solder leach resistance. | Range: 950°-1030°C. 1030°C. | .0013-.0017 ohm/sq., 1 mil thick |
| G-1 | Au; die and wire bonding | 3 mil lines, 3 mil spaces. Fine-line prints, high conductivity. | Range: 600°-1000°C Optimum: 950°C, 15 min. | .003 ohm/sq., .7 mil thick |
| G-2 | Au; die and wire bonding | 5 mil lines, 5 mil spaces Fine line. | Range: 850-1000°C. Optimum: 950°± 1°C, 15 min. | .003 ohm/sq., .6 mil thick |
| H-1 | Au; wire, die, and beam-lead bonding | Fine line, glass-free, high conductivity. Peel strength 2 to 3 times greater than fluxed gold. Thermal conductivity high. High compatibility with most resistor and multilayer dielectrics. | Optimum: 980°-1020°C, 5-15 min. at peak. | .003 ohm/sq., .5 mil thick |

2. Alumina Substrates

Alumina substrates have been purchased in 96 and 99.5 wt pct purities with (standard) as-fired surfaces; each type was purchased from two of the larger vendors of ceramic substrates. A standard substrate size of 1 in. x 1 in. x 0.025 in. was chosen. A number of special substrates also have been ordered for use in some fundamental studies of the effects of material character.

3. Ink Vehicle Systems

A number of widely available commercial vehicle systems which have been tested at RCA in the past were rejected for use in this study. Two vendors of thick-film inks consented to sell limited quantities of their proprietary vehicles and thinners for the contract study. Both of the vehicles demonstrate desirable thixotropic-pseudoplastic (shear thinning) rheological properties. One of the materials, vehicle VF-1, is a gel-type material at rest, and thus permits wide latitude in solids loading. Vehicles of a nongelling nature, such as the second proprietary vehicle, VA-1, require a high volume fraction of solids loading to obtain good printing properties. The high loading fraction is usually desirable, however.

4. Gold Metal Powders

Several gold metal powders have been purchased; a few are commercially available. A series of spherical powders was made available for sale by a commercial ink vendor particularly for this study. In our first study of thick-film adhesion[4], an ink made from one of these powders demonstrated unusually high adhesion strength. This series of powders is designated MG-1 through MG-4. Two additional spherical gold powders, MI-1 and MJ-1, have also been purchased.

Other gold powder particle shapes are also under study, including a widely used mixture of hexagonal and triangular platelets and smaller spheres, which has been designated MB-1. These materials are being considered for use in the model ink investigation.

B. ANALYSIS OF COMMERCIAL THICK-FILM GOLD INKS

1. Approach

Our prior experience in the analysis of vendor inks has guided our efforts in this phase of the study during the first quarter[4,5]. Detailed study is being made of both the identities and the amounts of the constituents of the inorganic solids portion of the inks. Since those are the materials which will be present in the fired conductor films, we consider them to be more important than the organic phases. The methods of sample preparation we are using provide information only about the amount of organic material in the ink.

This concentration of effort should not be taken to imply that a low importance is ascribed to the ink vehicle system. The potential complexities of vehicle materials have been reported for other ink systems[13] and the necessity has been noted for surface-active agent additions and other precautions to prevent the agglomeration of gold particles during 3-roll milling of the inks. The priorities of this study, however, force the consideration of ink vehicles to be subordinate to several other areas. The purchase of the two proprietary vehicles has made our position much easier to accept.

2. Analytical Procedure

In preparation for analysis of the inks, about 3/4 g of as-received ink is spread, after stirring, onto a preweighed platinum foil, weighed, and dried for one hour at 125°C to 150°C (depending on the manufacturer-suggested drying temperature of the ink), and weighed again. The loss of weight from the ink is ascribed to volatile organic constituents. The dried ink and foil are then baked in flowing oxygen at 350°C for four hours before reweighing. The weight loss in oxygen baking is attributed to the burn-off of organic binders.

In our earlier work[3,4], a 350°C burn-off usually proved satisfactory, but in certain inks, notably IB-2, a high residual carbon content, revealed by solids ~~mass~~ spectrometry, forced the use of a more rigorous burnout treatment.* Final analyses of all materials will be conducted on material which

13. L. F. Miller, *Thick Film Technology and Chip Joining*, (Gordon and Breach, New York, 1972), p. 83.

* This problem was judged to be due to the inclusion in this ink of organo-metallic resinate compounds. These materials require higher temperatures for burn-off than common organic vehicles do.

has also been fired 8 hours at 450°C in flowing oxygen. Chemical analysis of the ink solids is proceeding, using four principal analytical tools which are described briefly in Table 3. The data obtained to this point are shown in Table 4. The data are the arithmetic means of optical emission spectrometry (E.S.) and solid mass spectrometry (M.S.) results. Where only M.S. detects particular elements (W, Ta, S, P, Cl, F, etc.), the raw M.S. data are shown. Study of ink solids particles, with regard to particle size and shape, for the 20 commercial inks will be performed on powders prepared by oxygen baking or other methods of organic removal. Scanning electron microscopy is a principal method which will be employed for study of the particles.

Table 3. Methods of Chemical Analysis

| <u>Analytical Methods</u> | <u>Used to Detect</u> | <u>Error Factor[14]</u> |
|--------------------------------------|--|-------------------------|
| Optical emission spectrometry (E.S.) | 70 elements: all cations except W and Ta. Sensitive to concentrations of a few ppm by wt. | 3.0 |
| Solids mass spectrometry (M.S.) | All elements - most detectable at concentrations of a few ppm atomic. | 3.0 |
| Atomic absorption spectrometry | Will be used to assay for more important glass formers, bonding agents, fluxes identified by E.S. or M.S. Sensitive to 70 elements: all cations except W, Ta. | 1.02 |
| Wet chemistry | Will be used for gold. | 1.001 |

14. R. E. Honig, "Materials Characterization at RCA Laboratories," Solid State Technology 13, 59 (March 1970).

Table 4. Analysis of Inks - Preliminary Results*

| NOBLE METALS | A-2 | B-1 | B-2 | C-2 | F-1 | F-2 | F-3 | G-1 | G-2 | H-1 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ag | .03 | .05 | .05 | .03 | .06 | .03 | .03 | .06 | .05 | .02 |
| Au | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 | 80+20 |
| Pd | .002 | .01 | .007 | | .03 | | .002 | .007 | .002 | .02? |
| Pt | .002 | | | | | | | | .002 | |
| <u>Glass-Active Cation and Function[15] Code</u> | | | | | | | | | | |
| Al - I, F | .06 | .05? | .003 | .08? | .02 | .04 | .002 | .003 | .2 | |
| As - F | .001 | | | | | | | | | |
| B - F | .06 | .1 | | .4 | .3 | .3 | | .2 | .3 | |
| Ba - M | .01? | | | 20? | .004 | .006? | | .03 | .4? | |
| Ca - M | .001 | .003 | .05? | .02 | .002 | .002 | | | .004 | |
| Cd - M, I | | | .5 | | .002 | | | .02 | .01? | .4 |
| Cs - M | | | | | | | | | .001 | |
| K - M | .007 | | | .01 | | | | | .08 | |
| Mg - M | | .002 | .001 | | | | | | .002 | |
| Na - M | .006 | .003 | .005 | .02? | .002 | .005 | .02? | .01 | .05? | .003 |
| Pb - M, I | 10. | 4.? | .003 | .05 | 3.? | 3.? | .005 | 4.? | 2. | .002 |
| Rb - M, I | | | | | | | | | .003 | |
| Si - F | .2 | .06 | .03 | .6 | .4 | .4 | .02 | .2 | .4 | .03 |
| Sn - M | | | | | | | | | | .003 |
| Sr - M | .002 | | | .3 | | .003 | .002 | .002 | .007 | .002 |
| Ti - I | .05 | .006 | .003 | .03 | | | .003 | .06 | .02 | .002 |
| Y - M | | | | | .001 | .001 | | | | |
| Zn - M, I | .008 | .002 | .002 | .02 | .002 | .002 | .003 | .02 | .004 | |
| Zr - I, F | | .001 | | .06? | .3? | .4? | .001 | .04 | .002 | |
| <u>Other Cations</u> | | | | | | | | | | |
| Bi | | .002 | 3.? | .009 | 20.? | 20.? | .003 | .003 | .003 | |
| Co | | | | | .02? | | | | .03 | |
| Cr | .001 | | | | .003 | .002 | .001 | | .002 | .001 |
| Cu | .004 | .004 | .4 | .002 | .004 | .002 | 1.? | | .002 | .64* |
| Fe | .004 | | .003 | | .02? | .002 | | .08 | .02 | .001 |
| Ni | .01? | | | .003 | .004 | | .001 | | | |
| W | | | | | 3. | 3. | | | | |
| <u>Anions</u> | | | | | | | | | | |
| Cl | .01 | | .001 | .007 | .004 | .02 | .002 | .025 | .02 | .002 |
| F | | | | | | | | | .001 | |
| I | .2 | | | | | | | | | |
| S | .002 | .002 | | | .002 | .002 | .001 | .003 | .001 | |

Legend: "?" - Results of optical emission spectrometry and solids mass spectrometry differed strongly.

"F" - Glass former; "I" - Glass intermediste; "M" - Glass modifier.

"*" - Determined in earlier study [5] by atomic absorption spectrometry.

* All the data shown are expressed as wt pcts of the inorganic solids, which remained after oxygen baking the inks.
 15. W. D. Kingery, *Introduction to Ceramics*, (John Wiley & Sons, Inc., New York, 1960), pg. 148.

3. Selection of Inks for Further Study

The selection procedure is itself a fairly detailed study of the inks and their adhesion properties. When the analytical studies are completed, three principal items in the initial study will remain to be done before selection can be made of those inks which will receive more extensive study. These are the adhesion testing of parts made using each of the inks with two lots of substrates: a 99.5 wt pct alumina and a 96 wt pct alumina and the application of the two techniques developed at RCA Laboratories[3,4]: mercury vapor leaching and scrutiny of the microstructures thus rendered visible and cross-polarized light metallography.

For the adhesion tests, each of the inks will be printed on a minimum sample size of five substrates of 96 wt pct alumina and five of 99.5 wt pct alumina; these will be fired according to two schedules:

- (1) The optimum single firing recommended for the conductor by its manufacturer.
- (2) The firing above, followed by imposition of two firings such as would be required for crossover dielectric and three firings appropriate to compatible resistor pastes, i.e., a total of six firings.

Adhesion tests will be performed on these samples and their adhesion properties will be ranked. Crossed-polarized light metallography and mercury-vapor leach investigation of structures will be used to correlate the adhesion properties with the sample firing histories.

Selection of the inks for further study will be made on the basis of the adhesion strength after the vendor's recommended firing, the insensitivity of the adhesion strength to refiring, and a value judgment of the compatibility of the ink with thick-film circuit processing.

4. Description of Gold Metal Powders

The most obvious requirement for a metal powder which will be used in thick-film conductor inks is that it have a sufficiently small particle size to pass through the finest mesh screen to be used for depositing conductor circuit elements. The finest mesh used in general practice is 325-mesh

(wires/inch) with a 0.0011-in. wire size. The maximum size particle which can pass through this screen is 50 μm in diameter. (A 325-mesh sieve with 0.0014-in. wire - the National Bureau of Standards, Tyler, and U.S. standard used for separating size fractions of powders - has a 44- μm opening.) Some 400-mesh screens are beginning to be used for fine-line work. With 0.0010-in. diameter wire, a 400-mesh screen has an opening size of 37 μm ; therefore, only particles that can pass through a 400-mesh screen (this sieve fraction is commonly referred to as minus 400 mesh) have any value for use in thick-film synthesis, if general utility for the ink is desired.

Some sieve fractionating was done on an atomized gold powder. The size and shape of the minus 400-mesh gold sphere obtained is illustrated in Fig. 4.

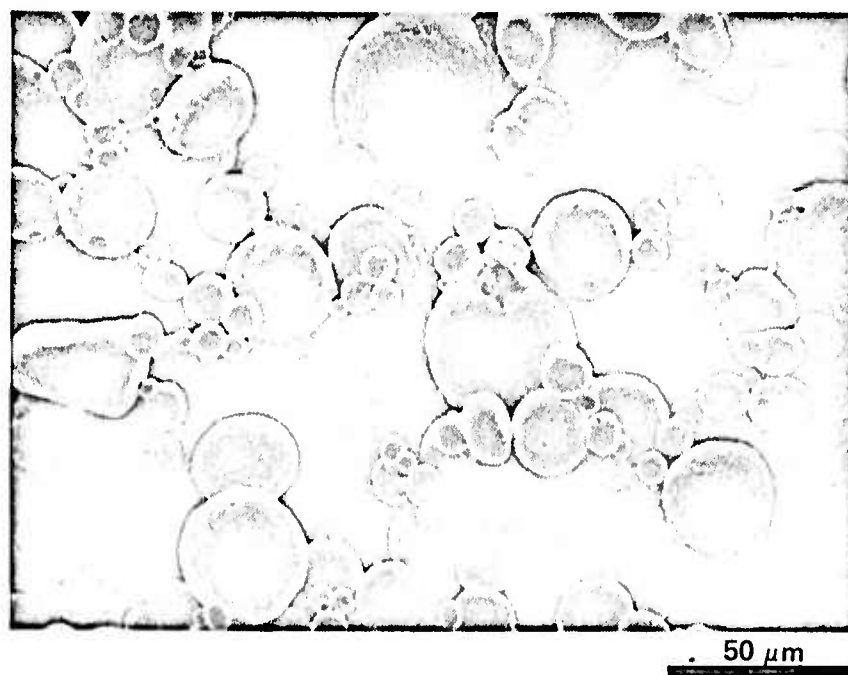


Figure 4. Atomized gold powder MI-1. Scanning Electron Micrograph (SEMograph) of -400 sieve fraction. Note low magnification.

A more important condition than mere passage through the screen, however, is the surface energy of the sphere. Surface energy is, of course, the driving force for sintering of the metal particulates into a highly conductive film.

On the first order assumption of a uniform surface energy, which is invariant with particle size, the surface energy per unit mass of metal spheres varies inversely with the particle diameter.

Packing density of the unfired metal powder is also important. Chemically precipitated powders of very fine particle size and irregular particle shape often suffer so much shrinkage on sintering that fine lines screened with inks made from such powders become discontinuous on firing.

The gold metal powders used in commercial thick-film pastes have been examined. SEMographs of these powders, shown in Figs. 5 through 10, reveal a much smaller particle size than those of Fig. 4, and two distinctive shapes - spheres and platelets.

Our initial model ink studies will contrast the behavior of a spherical powder such as MG-2 with the mixed sphere and platelet powder MB-1.

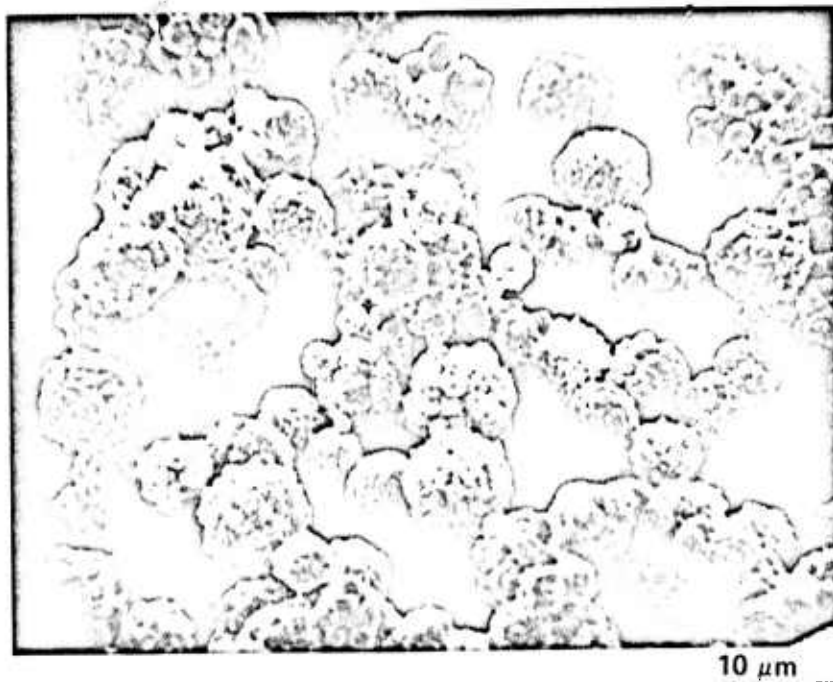


Figure 5. SEMograph of proprietary gold powder MG-1. Note apparent lack of density of agglomerates.

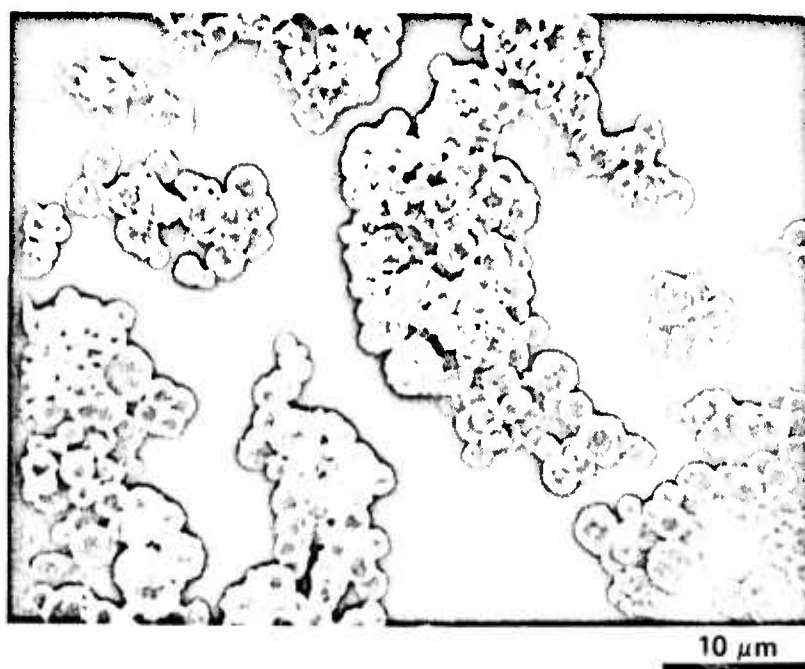


Figure 6. SEMograph of proprietary gold powder MG-2. This is the smallest sphere size among the MG series powders. The powder appears to be the one vendor G uses to manufacture ink G-1.

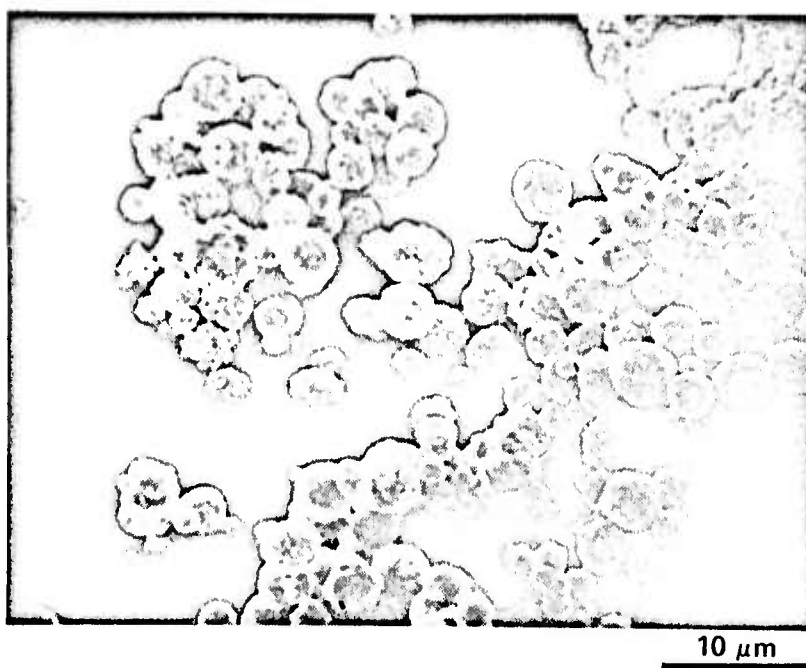


Figure 7. SEMograph of proprietary gold powder MG-3. Average sphere size is between those of MG-1 and MG-2.

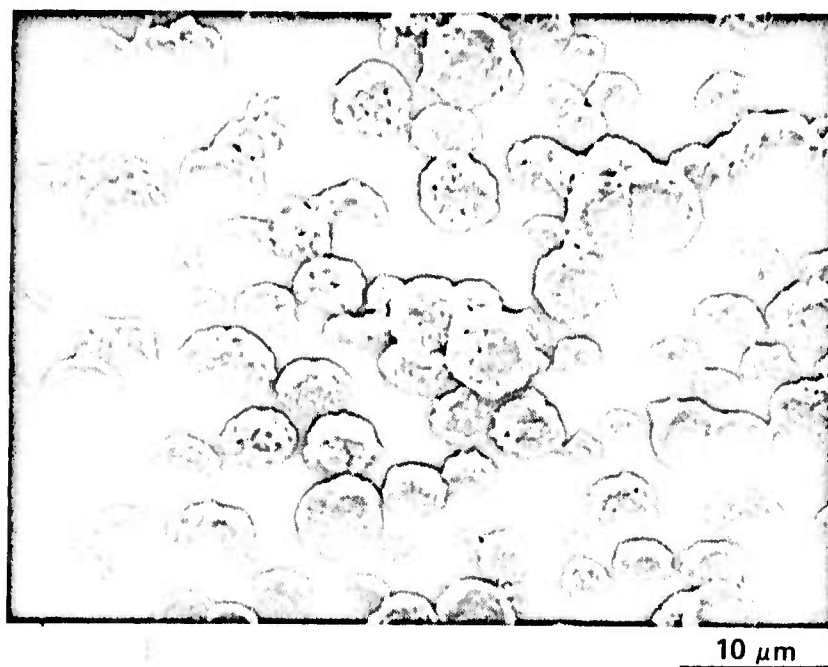


Figure 8. SEMograph of proprietary gold powder MG-4. Average sphere appears dense; its size is larger than MG-3 and perhaps smaller than MG-1.

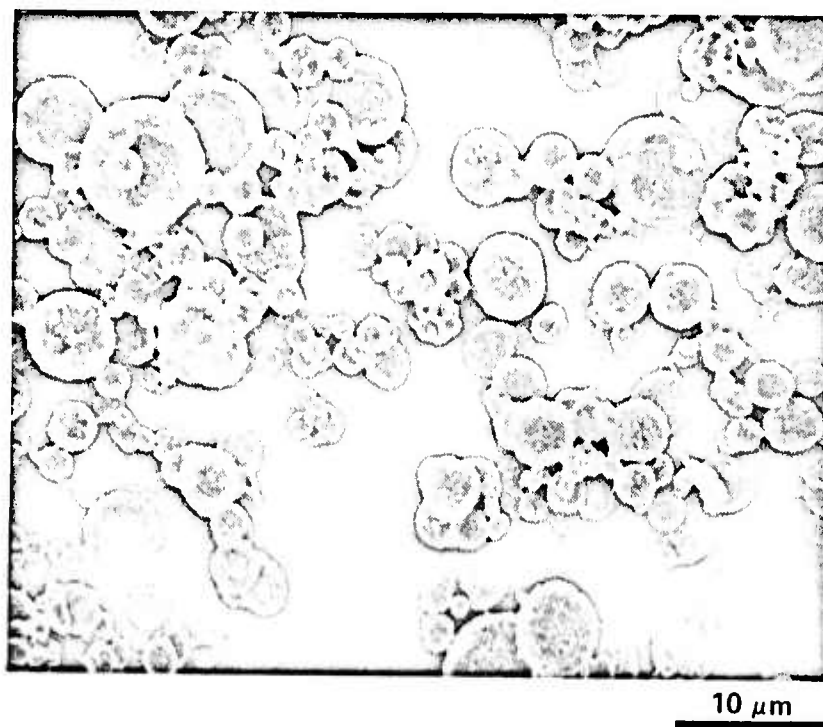


Figure 9. SEMograph of gold powder MJ-1. Spheres appear dense. A large range of sphere sizes is evident.

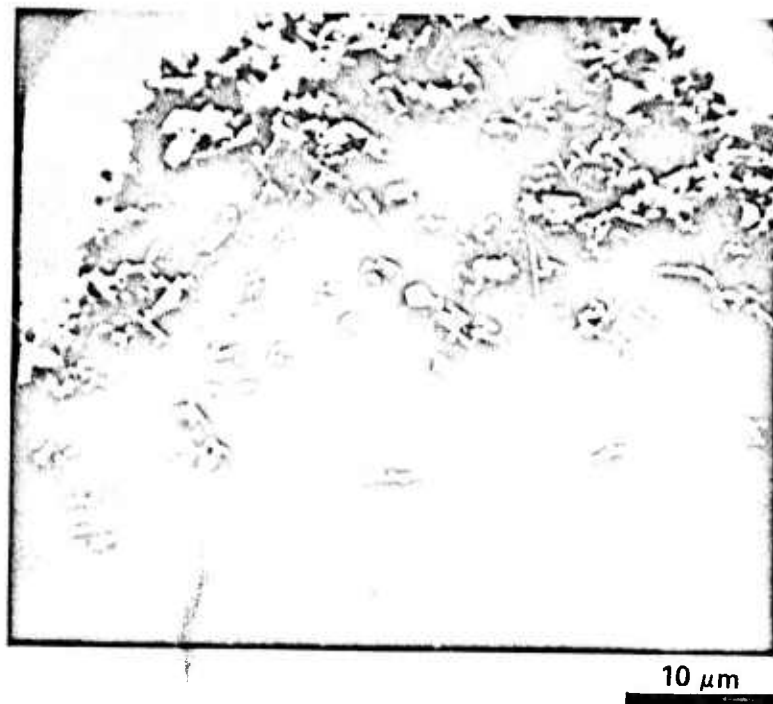


Figure 10. SEMograph of mixed sphere and hexagonal and triangular platelet gold powder MB-1. An apparent feature of this material is good packing density.

V. WORK DURING THE NEXT PERIOD

As noted in the Background (Section II), a major problem in doing basic research on thick-film adhesion is that poor standards exist for the tests by which most of the literature data have been taken. Literature adhesion data and test methods for gold thick-film conductors are particularly limited. For these reasons much of the first two quarters of this study is being devoted to comparison of the adhesion of a wide variety of gold thick-film conductors formed by firing commercial materials. This work is being done to provide a base of data that is broader than that of existent data[4,5,7].

In addition to the comparison of commercial inks and substrates, an important part of the overall study that will be emphasized in the next quarter is the physical and theoretical comparison of adhesion test methods. A comparison is under way of several test methods mentioned in the literature[16] with each other and with some innovative adhesion test techniques. Where they appeared useful in reducing experimental data scatter or the influence of preparation technique, fixtures and specifications for sample preparation and testing are being developed. Some of these will be useful to the adhesion testing of other thick-film conductors besides those which are gold-based.

Although there are many fundamental aspects to the two investigations discussed above - the physical and analytical comparison of commercial thick-film materials and the comparison of adhesion test methods - several other substudies which are planned are intrinsically more fundamental in nature. These include the following:

Glasses of carefully characterized composition and properties will be used to study wetting and spreading rates as a function of temperature on gold surfaces as well as on ceramic surfaces of various natures.

The effects of gold solubility (if any) in the glasses on the rate of sintering will be investigated since it has been shown that liquid-phase sintering is an important mechanism in the sintering of silver-palladium inks[17] (as well as a host of other powder metallurgical systems).

16. L. Jacobson, "Testing for Adhesion of Hybrid Films," Proc. IEEE and EIA Electronic Components Conf., p. 474 (1971).
17. S. S. Cole, "The Sintering Mechanism in a Silver-Palladium Film," Proc Intl. Soc. for Hybrid Microelectronics Symposium, p. 2.A.1.1 (1972).

Studies are planned of the effects of gravity during firing and of the effects of the sizes and shapes of gold and glass powders on the development of adhesive structures. Such structures have been shown to cause the optimum adhesion of gold films in frit-bonded systems, through the mechanism of physically interlocking the glass and gold phases[4].

The above list of studies should not be considered complete. Several other substudies are planned. Still other experiments, which may strongly contribute to our understanding, will doubtless be suggested by the results of experiments now under way.

VI. ADMINISTRATIVE DATA

A. FINANCIAL DATA

During the report period \$25,984 of the funds allocated to the contract were expended. The remaining amount is \$74,011.

B. EXPENDITURES OF MAN-HOURS AND FUNDS

Both the planned expenditure of funds and the actual expenditure during the report period are shown in Fig. 11. Similarly, planned and actual man-hour efforts are plotted in Fig. 12(a) and (b).

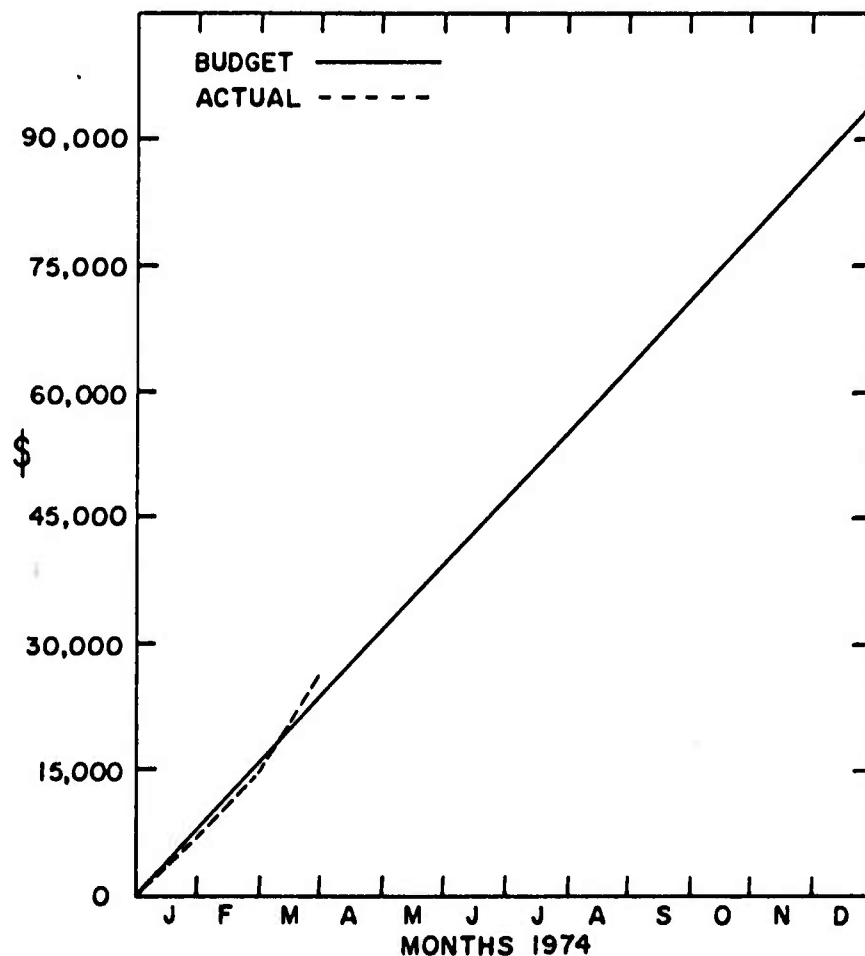
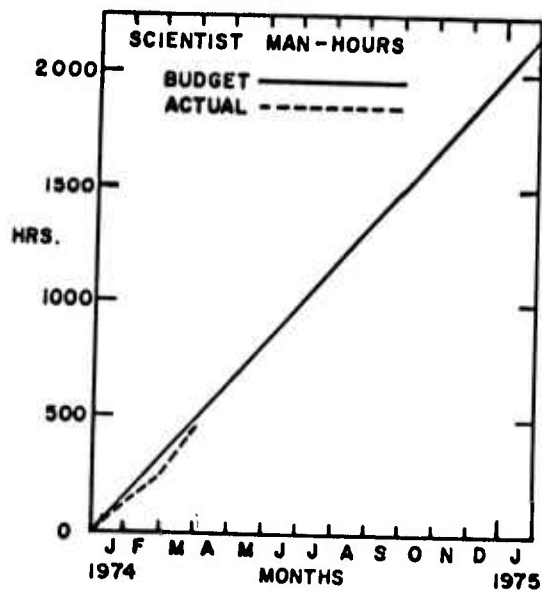
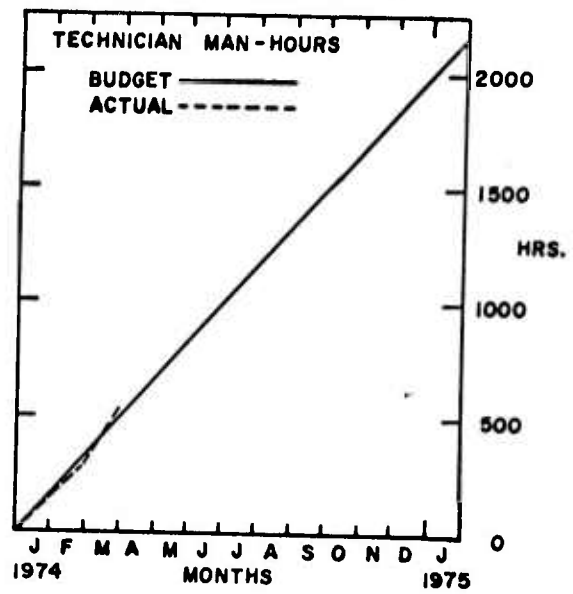


Figure 11. Funds expenditure chart.



(a)



(b)

Figure 12. Man-hour expenditure charts: (a) scientist effort and (b) technician effort.

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