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Integrated Environmentally Compatible Soldering Technologies Final Report

F. M. Hosking, D. R. Frear, R. L. Iman, D. M. Keicher, E. P. Lopez,
H. C. Peebles, N. R. Sorensen, and P. T. Vianco
Sandia National Laboratories
Albuquerque, New Mexico 87185

Abstract

Chemical fluxes are typically used during conventional electronic soldering to enhance solder wettability. Most fluxes contain very reactive, hazardous constituents that require special storage and handling. Corrosive flux residues that remain on soldered parts can severely degrade product reliability. The residues are removed with chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), or other hazardous solvents that contribute to ozone depletion, release volatile organic compounds into the atmosphere, or add to the solvent waste stream. Alternative materials and processes that offer the potential for the reduction or elimination of cleaning are being developed to address these environmental issues. Timing of the effort is critical, since the targeted chemicals will soon be heavily taxed or banned. DOE's Office of Environmental Restoration and Waste Management (DOE/EM) has supported Sandia National Laboratories' Environmentally Conscious Manufacturing Integrated Demonstration (ECMID). Part of the ECM program involves the integration of several environmentally compatible soldering technologies for assembling electronics devices. Fluxless or "low-residue/no clean" soldering technologies (conventional and ablative laser processing, controlled atmospheres, ultrasonic tinning, protective coatings, and environmentally compatible fluxes) have been demonstrated at Sandia (SNL/NM), the University of California at Berkeley, and Allied Signal Aerospace-Kansas City Division (AS-KCD). The university demonstrations were directed under the guidance of Sandia staff. Results of the FY93 Soldering ID are presented in this report.

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Contents

Background.....	4
FY93 Task Progress.....	8
(1) Inert Atmosphere Wave Soldering with Low Solids Flux.....	10
(2) Activated Acid Vapor Soldering of PWB Surfaces.....	10
(3) Fluxless Ultrasonic Pretinning.....	11
(4) Laser Ablative Cleaning, Pretinning, and Solderability Restoration of Leaded Components.....	13
(5) Multiplexing of Fluxless Laser Soldering.....	15
(6) Aging Effects on Copper Coated with an Organic Inhibitor.....	16
(7) Cleanliness of Surfaces Soldered with Low Solids Fluxes.....	16
(8) Fluxless Soldering of Gold Metallizations.....	17
(9) Reliability Issues Related to Low-Residue Soldering.....	18
(10) ECMID Technology Integration and Transfer.....	19
Summary and Conclusions.....	20
References.....	20

Figures:

1	Fluxless Soldering Technology Diagram.....	22
2	Environmentally Compatible Soldering Technology Diagram.....	22
3	Strategy matrix for integrating ECM Soldering Technologies.....	23

Background

Rosin-based fluxes are typically used when soldering electronic circuits. Flux residues which remain on a soldered surface must be removed with chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), or halogenated solvents to guarantee the long term reliability of soldered devices. While these chemicals have been routinely used by the DOE nuclear weapons design and production facilities and throughout the commercial and military electronics industry, the phaseout of ozone depleting chemicals (ODCs) and restrictions on other halogenated solvents have changed the way in which electronic devices are being made. SNL/NM has participated actively in this international effort to develop alternative soldering and cleaning technologies that are "environmentally conscious" [Refs. 1-15]. The work was funded by DOE's Office of Environmental Restoration and Waste Management (DOE/EM). Laboratory experiments at SNL/NM during the last three years have demonstrated the feasibility of controlled atmospheres, protective coatings (metallic or organic), lasers, and ultrasonic pretinning as fluxless or "no clean" soldering alternatives with dual-use potential. Technology qualification and integration are final elements of the task.

The primary objectives of the ECM soldering task were to reduce or eliminate solvent use during electronics assembly and minimize the subsequent solvent waste stream by developing and integrating alternative soldering materials and processes. The short range goals were to (a) demonstrate the selected technologies on prototype hardware, (b) characterize solder joint properties, and (c) evaluate surface cleanliness and the effects of aging on reliability. Intermediate goals included (a) qualifying the various technologies and then (b) incorporating them into assembly specifications. The final goal was to extend these technologies for solving other environmental problems common to DOE and industry.

Environmentally compatible soldering processes will reduce the number of cleaning steps normally required during electronics assembly, especially if step (or multiple) soldering is involved. A typical spray cleaning operation can consume approximately 0.5 lb. of solvent per circuit board after wave or drag soldering. Technologies that require less cleaning, therefore, will have a significant environmental impact on the solvent waste stream and complement the efforts to develop solvent substitutes or aqueous cleaning methods. SNL/NM's Integrated

Environmentally Compatible Soldering task includes several technologies (materials and processes) that reduce or eliminate cleaning at the soldering level. The complexity of most high reliability electronic devices makes it nearly impossible to develop a single technology that can be universally applied. Integrating several of these soldering technologies offers the greatest potential to minimize waste stream hazards. The ECM task has focused on five critical areas: fluxless and "no clean" soldering technologies, protective coatings, laser ablative cleaning/soldering, alternative fluxes, and materials/process reliability. These subtasks directly supported the "umbrella" ECMID program.

Fluxless and "no clean" soldering covers a variety of technologies (Fig. 1) that utilize various "clean" or reducing atmospheres to either maintain or produce a solderable base surface. Vacuum, inert or reducing gas, reactive plasma, and activated acid vapor atmospheres have been applied to fluxless soldering. These atmospheres reduce metal oxides and/or restrict the supply of oxygen to the workpiece during the heating and soldering operations. The "no clean" (or low-residue) soldering concept typically couples controlled atmospheres with the use of a low solids flux. Flux residues are generally negligible. Work conducted at Sandia has shown that the gas species (molecular, atomic, or ionic) have a significant effect on the rate of oxide reduction and subsequent solder wettability. Although thermodynamic data suggests that the reduction of metallic oxides in hydrogen or vacuum is feasible at typical soldering temperatures, 200-300°C, the rate of reaction is very low. Reactive gases have a greater potential for effectively reducing surface oxides. Engineers at Sandia have characterized the effect of reactive gases (e.g., atomic hydrogen) on directly wetting metallic surfaces.

A dilute acid vapor in an inert gas atmosphere has worked especially well to facilitate solder wettability. Although there are commercial systems available that use variations of this soldering process, the wetting fundamentals are not well understood. Dilute additions of formic or acetic acid vapor are typically added to argon or nitrogen to promote fluxless wetting by reducing metal oxides and protecting the cleaned surfaces. In industrial practice, adipic acid is also added to promote wetting. Adipic acid is a major constituent of low solids or "no clean" fluxes. As with most low solids fluxes, adipic acid residues on a soldered component must be removed with a solvent rinse to satisfy long term reliability requirements found in most weapons complex soldering specifications. Sandia has characterized

the effect of these acid vapors on reducing oxides without applying additional flux. The acid-gas mixture, gas flow rate, soldering temperature, and time are important parameters that influence the ability to make good solder joints.

Fluxless laser and ultrasonic soldering techniques have also been characterized. These methods typically utilize directed mechanical or thermal energy to break up surface oxides and promote wetting of the underlying exposed metal by the molten solder. SNL/NM has recently developed a fluxless laser soldering process to fabricate closure joints and attach leaded devices to printed circuit boards. The technique uses the combined features of controlled atmospheres, nonoxidizing metallizations, and conventional laser heating. To promote fluxless wetting, a slightly reducing atmosphere was introduced over the fixtured parts to protect the base and solder alloy surfaces during heating. The localized, higher temperatures of laser soldering significantly enhance the reduction of most metallic oxides (e.g. Cu, Ni, Fe, Sn, and Pb), especially in conjunction with a protective atmosphere. Sandia has also developed ultrasonic soldering for pretinning applications. The process uses an ultrasonic probe or horn immersed in a solder bath to generate acoustic energy that mechanically ablates thin oxide layers through surface cavitation. Once surface oxides are removed, erosion of the underlying metal becomes the dominant process mechanism. Ultrasonic pretinning has been demonstrated on typical circuit board and component surface finishes at SNL/NM with a commercial ultrasonic soldering system.

The use of protective coatings (metallizations and organic preservatives/inhibitors) can also reduce the need for a flux. Nonoxidizing surfaces, such as Au or other noble alloys, have been used for many years to promote solder wetting without fluxing. A thick metallization layer is generally required to guarantee a nonporous surface barrier that adequately insures the wettability of the underlying base metal. However, the thickness of Au must be carefully controlled when using Sn-based solder alloys. Au reacts with Sn to form a brittle intermetallic that could consequently embrittle a solder joint if excess Au is applied. Conversely, a thin, porous layer of Au might expose the underlying metal that would be then susceptible to oxidation or corrosion in a poorly controlled storage environment. These porous metallizations can be protected during storage by applying organic inhibitors. Sandia has collaborated with the University of California at Berkeley (UC-Berkeley) to characterize the effects of deposition method, surface roughness,

and microstructure of Au-Ni surfaces on fluxless wetting. The State University of New York at Stony Brook (SUNY-Stony Brook) has studied the bonding behavior of organic inhibitors on metallic surfaces. Results from the two university programs have been used by SNL to design metallization and inhibitor systems that facilitate fluxless soldering or allow the use of more environmentally compatible fluxes.

Laser ablative cleaning involves the use of very short pulses of high peak power laser radiation to rapidly heat and vaporize microscopically thin layers of oxidized metal surfaces in an inert gas environment. The vaporized material quickly condenses on contact with the cooler ambient gases forming submicron particles that are easily transported from the "cleaned" surface by a flowing gas stream. These waste particles can be collected with a submicron filter canister. When performed under an inert gas atmosphere and coupled with a secondary heating source, laser ablative cleaning can be used to induce the wetting of liquid metal solders on a variety of metal substrates without the use of a chemical flux. The inert cover gas prevents recontamination of the laser cleaned surfaces before the solder is applied. SNL has recently developed a laser ablative fluxless soldering (LAFS) process that yields high quality metallurgical bonds without the use of reactive chemicals. The combination of high spatial resolution and low thermal impact makes LAFS an attractive process for application on microcircuits and high density printed circuit boards. Wetting evaluations, conducted with LAFS on Al, Cu, Ni, and Kovar surfaces have been highly successful. In particular, Al and Kovar surfaces are extremely difficult to wet directly with solder using the flux systems now commonly available for electronics assembly. The use of LAFS on these surfaces could potentially eliminate the need for surface preparations such as Sn or Au plating which are currently used to make these surfaces solderable. A Robotics-controlled LAFS system was recently installed at Sandia for pretinning typical leaded integrated circuit (IC) devices. The system is ideal for restoring solderability of aged components.

The final technical element of SNL/NM's Integrated Environmentally Compatible Soldering effort is the use of organic acid, water soluble and low solids, "no clean" fluxes. Although these fluxes sometimes require cleaning after soldering, electronic assemblies can be cleaned by more environmentally compatible methods (e.g. alcohol or aqueous based cleaners). Since most soldering lines have been set up for rosin-based fluxes, some modification of the existing process is usually necessary

before using these alternative fluxes. Sandia has been working with AS-KCD to integrate water soluble and low solids fluxes into ECM practice. A nontoxic, nonflammable, citric acid based flux has also shown potential. Solderability and ionic/visual cleanliness issues associated with these fluxes are being examined.

The cornerstone of the Integrated Environmentally Compatible Soldering Technologies task was direct support of the ECMID. The goal of the ECMID was to implement a total systems approach to Environmentally Conscious Manufacturing through a balanced integration of alternative solvent, aqueous cleaning, fluxing, and soldering technologies (Fig. 2) that would lead to cost-effective elimination of waste in the manufacture of electronic and electromechanical components. The soldering technology task supported the immediate and long term goals of the ECMID with the final task objective of full integration into WR manufacturing. The effort emphasized teaming with other government and industrial partners to assure program success.

FY93 Task Progress

Significant progress was achieved in the areas of activated acid vapor soldering, laser soldering, and ultrasonic soldering. Work was also conducted to characterize protective metal and organic coatings at UC-Berkeley and SUNY-Stony Brook under the guidance of Sandia staff. Metallized surface roughness and thickness were important factors affecting solder wettability. SUNY used surface analyses to benchmark the bonding behavior between commercial inhibitors and typical electronics metal surfaces. Other activities included the evaluation of water soluble and low solids fluxes, laser soldering of discrete components, and participating on a low-residue soldering task force. Laser ablative cleaning was also demonstrated for solderability restoration of aged Ni surfaces and fluxless soldering directly onto bare Kovar surfaces. Technology transfer was facilitated through technical presentations and publications.

The final Soldering Integrated Demonstration (ID) focused on the integration of controlled atmosphere soldering in inert and activated acid vapor environments, fluxless ultrasonic pretinning of PWB surfaces and leaded components, laser ablation cleaning and pretinning of aged IC pins, laser soldering of surface mount

devices, solderability preservation with organic coatings, fluxless soldering with Au metallizations, and cleanliness evaluations of low solids ("no clean") fluxes. The work was conducted primarily at SNL and AS-KCD on prototype hardware. "No clean" processing of electronic components for neutron generators, firing sets, programmers, radar modules, and advanced microwave assemblies is an integral part of AS-KCD's ECM and Production Capability Assurance Programs. SNL/NM's Center for Solder Science and Technology continued to work closely with several major manufacturers (AT&T, TI, DEC, Hamilton Standard, Ford, General Motors, and Cray Research) on solving their environmental problems. These industrial contacts were valuable resources for implementing the dual-use concept. Reliability issues were also considered.

Specific Soldering ID activities were as follows:

- (1) demonstrate wave soldering in an inert atmosphere with a low solids ("no clean") flux on a common PWB test vehicle.
- (2) demonstrate solder wettability of a PWB test vehicle in a mixed atmosphere of inert gas and dilute formic acid vapor.
- (3) demonstrate fluxless ultrasonic pretinning of leaded devices and transfer the technology to AS-KCD.
- (4) demonstrate laser ablative solderability restoration of dual-in-line electronics packages with aged Ni plated connector pins, and laser ablative cleaning and fluxless pretinning of bare Kovar pins containing no preparatory surface metallizations.
- (5) demonstrate multiplexing of fluxless laser soldering on surface mount devices in coordination with AS-KCD counterparts.
- (6) demonstrate the effects of aging in a typical indoor industrial environment on the solder wettability of copper surfaces pretreated with an organic solderability preservative.
- (7) demonstrate the cleanliness of surfaces coated with low solids ("no clean") fluxes.
- (8) demonstrate the effectiveness of Au metallizations for fluxless soldering.
- (9) investigate technology costs, producibility, and reliability issues related to the "no clean" soldering process.
- (10) couple the above demonstrations to the ECMID or other industrial test vehicle equivalent, where applicable.

Individual subtask summaries comprise the remainder of this report.

(1) Inert Atmosphere Wave Soldering with Low Solids Flux:

An Electrovert Econopak Wave Soldering machine at SNL's PWB Electronic Processing laboratory was retrofitted with nitrogen inerting capabilities. The field retrofit substantially reduces solder dross and the environmental problems associated with handling dross waste. With the coupling of low solids flux and the inert atmosphere, post-solder cleaning can be significantly reduced. Solder consumption is also reduced. Installation of the retrofitted hood and nitrogen gas handling system has been completed. Electrovert field engineers instructed Sandia staff on how to operate and maintain the equipment. Prototype boards were soldered to evaluate the modified system. An AT&T low solids fluxer was also added to the machine. The fluxer reduces flux consumption and the frequency of cleaning after soldering.

(2) Activated Acid Vapor Soldering of PWB Surfaces:

Activated acid vapor fluxless soldering is a process that replaces liquid flux with a dilute solution of vaporized acid in an inert carrier gas. By a strict definition, the acid vapor is a flux, in that its function is to reduce surface metal oxides to enhance solderability. However, the acid vapor leaves little, or no, residue that requires cleaning if the acid concentration is relatively low.

The process of acid vapor soldering involves passing the carrier gas and acid vapor over the metallized surface to be joined. The acid chemically attacks the surface oxide as the metal is heated, removing the oxide from the surface. In this manner, the surface is "activated" for wetting by the solder. The protective atmosphere prevents reoxidation of the metallized surface during solder wetting. The process normally involves the use of solder preforms but it can be applied to wave soldering.

This effort examined the solderability of metal surfaces in a variety of acid vapor atmospheres. The objective of the work was to determine optimum conditions for the acid vapor (e.g., temperature and acid concentration) to remove surface contaminants and allow the formation of a good solder joint. The experimental

tests were performed on printed wiring board test vehicles (to simulate actual production environments).

Experiments were performed using a Sandia-designed acid vapor fluxless soldering system with a variety of gases including: baseline ambient air with rosin mildly activated (RMA) flux, argon cover gas, forming gas (3.5 vol. % hydrogen in argon), and formic or acetic acid vapors (1% to 7% in nitrogen). Initial tests were conducted with simple flat coupons. Their surface finishes were Cu and Au-plated over Ni. Experiments showed that inert gas (argon) and forming gas without acid vapor additions do not promote wetting on either metallization. Experiments using formic and acetic acids in dilute solutions of inert gases showed potential. Dilute solutions of formic acid (~5%) in Ar on both Cu and Au-plated on Ni surfaces produced wetted surfaces similar to that obtained with RMA flux. Similarly, acetic acid concentrations of ~3% resulted in good wetting. However, acetic acid concentrations in excess of 3% showed a delay in wetting, perhaps due to the formation of an inhibiting acetate layer on the metallization surface.

Experiments were also run on printed wiring board test vehicles to examine the effectiveness of the acid vapor in a more realistic electronics application. In these experiments, the printed wiring board consisted of copper lines connected to pads. The solderability was evaluated as a function of the distance the solder flowed from the pad down the length of the line. The experiments were performed in formic acid and acetic acid. The results were promising and indicated that the acid vapor fluxless soldering technique could be used for reflow applications on actual printed wiring board assemblies. Further testing is needed to confirm the cleanliness of boards processed in acid vapor atmospheres.

(3) Fluxless Ultrasonic Pretinning:

Previous experiments examined the solder coating of simple geometric shapes. The objective was to identify the fundamental properties of solder wetting under ultrasonic activation. An important observation of these fundamental experiments was that the removal of the oxide film from the metal surface was not through a direct erosion mechanism; rather, the surface oxides were removed by cavitation in the solder generated by the sonic energy which had coupled with the substrate material. The data suggests that the ultrasonic energy could selectively remove

oxide layers from metal surfaces on printed circuit boards, allowing such features to be solder coated without the use of fluxes and their associated cleaning processes. A series of experiments was performed with a commercial ultrasonic soldering system, using 63Sn-37Pb solder at 250°C to evaluate ultrasonic pretinning of printed circuit boards.

Preliminary experiments were performed on a small circuit board with two pads and a conductive back plane. The board was made of 0.159 cm thick polyimide-quartz laminate with 1 oz. bare copper features; no solder mask was applied to the laminate or Cu surfaces. Wetting of the pads and back plane was assessed under various test conditions with particular interest in the microstructure of the solder film and the copper pads. The pads and back plane were readily solder coated without a significant reduction in copper thickness; copper dissolution did increase, however, as the power level and power-on time was increased. No damage to the copper pad-laminate interface or to the laminate structure was observed. The tests demonstrated the feasibility of fluxless pretinning and identified the operating parameters suitable for solder coating the copper features on a printed circuit board.

More detailed experiments were conducted on a single-sided, surface mount printed circuit board (FR-4 laminate with 1 oz. copper features and solder mask). As was the case with the first experimental circuit boards, no damage to the laminate or to the copper pads was noted for all of the testing conditions. An increase in sonic energy "available" to the circuit board (i.e., through more power, higher solder temperature, increased immersion time, and shorter distance between the board and the horn) reduced the variability of wetting. The results clearly illustrate the viability of using ultrasonic activation to hot coat PWB conductor features (pads and traces) without the use of a flux.

Hot solder coating is also required on component leads constructed of one of the low-expansion alloys that is electroplated with nickel followed by a gold finish. The nickel film becomes the "solderable" finish; that is, the nickel is the surface to which the solder is intended to wet. The gold layer forms the "protective" finish; it prevents contamination and oxidation of the underlying nickel film. In the hot dipping process, the gold layer is dissolved into the bath as the solder wets the nickel finish.

A set of experiments was conducted to determine the effectiveness of ultrasonic activation to remove the gold electroplated coatings from leads typically used on ceramic quad flat-packs. Two leads were exposed to one of the following conditions: (1) 5 s. with 25% ultrasonic power; (2) 5 s. with 50% ultrasonic power; (3) 5 s. immersion using a rosin-based, mildly activated flux (no ultrasonics); and (4) 5 s. immersion with no flux (no ultrasonics). Gold concentration as a function of distance along the coated lead surfaces were determined. First, the Au concentration of the RMA flux coated samples exceeded the 4 wt. % limit usually regarded as causing embrittlement of a solder joint. Secondly, the gold concentration of the lead exposed to ultrasonic energy was lower than that observed for the fluxed specimen. The same trend was observed on the sample exposed to the lower ultrasonic power level. In summary, the ultrasonic hot dipping process provides a viable means of solder coating electronic component leads for assembly onto printed circuit boards. A commercial ultrasonic soldering pot has been set-up at AS-KCD and will eliminate the need for fluxing and post-cleaning during the pretinning of resistor leads.

(4) Laser Ablative Cleaning, Pretinning, and Solderability Restoration of Leaded Components:

Almost all soldering processes used in electronics assembly require some type of chemical reagent to remove metal oxides and other contaminants from joining surfaces. Even when the amount of residues left behind is low, these residues represent a potential source of metal corrosion that can not be completely ignored. Consequently, in electronic devices where high reliability is of paramount importance, a final solvent cleaning step will always be necessary whenever chemical reagents are employed in the soldering process. Laser ablative processing allows the solder coating of electronic components without the use of a chemical flux, thereby eliminating the need for any type of post-cleaning step to remove flux residues. A Q-switched Nd:YAG laser is used to ablate metal oxides and other contaminants from joining surfaces under an inert gas environment. The very short nanosecond pulses of laser radiation rapidly heat and vaporize the contaminants from the metal surface. However, due to a much slower rate of thermal conduction on a relative scale, very little thermal energy is deposited into the substrate. Laser cleaned surfaces can be wet directly with solder without the need for any type of chemical activating agent. Solder joints can then be formed in the

same inert gas environment using standard reflow techniques. Very little material is removed from the metal surface during the laser cleaning step. Waste generation in the form of gas phase metal particles is on the order of 50 milligrams of material per square meter of surface cleaned. The particles are swept from the surface in a flowing gas stream and captured in a canister filter.

Laser ablative solderability restoration was demonstrated on 48 pin dual-in-line electronic packages (DIP). The DIP leads were composed of Kovar (an Fe-Ni alloy) with a pure Ni overplate. The DIPs were baked in air at 600°C to degrade pin solderability. Attempts to coat the pins on control parts with 63Sn-37Pb eutectic solder using commercial RMA and organic acid fluxes resulted in very poor wetting. A six axis robotic arm was used for manipulation of the IC packages in a helium inert gas glove box. Using a standard vacuum chuck, the robot picked up the DIPs from a feed chute, passed the pins on the IC packages thorough the laser beam and then coated the pins with 63Sn-37Pb eutectic solder by hot dipping in a solder bath at 220°C. The robot provides the precision motion required for accurate laser cleaning and solder coating of the DIP pins with tight tolerances close to the package surface and also facilitates the rapid throughput of packages thought the system. Results showed excellent solder wetting on the pins cleaned with the laser ablation process demonstrating total solderability restoration of these pins after air bake aging. This result is significant from the standpoint that excessive surface contamination from the industrial environment represents a common problem in electronics manufacturing. Whenever such contamination occurs, joining surfaces cannot be wet with solder using the standard weak RMA type fluxes and stronger, and much more potentially corrosive chemical reagents must be employed to achieve acceptable joining results. The 600°C air bake used in this demonstration represents an extreme aging condition. The resulting thickness of the metal oxide formed on the Ni surface is much greater than any surface contamination expected to be encountered in normal manufacturing operations. Nevertheless, laser ablative cleaning was able to restore the air baked Ni surface to a solderable condition without the use of potentially corrosive chemical reagents and without the generation of large amounts of hazardous waste products.

Laser ablative pretinning was also demonstrated on bare Kovar DIP leads without any type of preparatory surface metalization using 63Sn-37Pb eutectic solder. In this case the DIPs were used as-received from the manufacturer without any type of

surface aging. Attempts to coat the pins on control parts with solder using commercial RMA and organic acid fluxes resulted in virtually no surface wetting. However, after laser ablative cleaning and hot dipping in the inert gas glove box, excellent solder wetting on the bare Kovar surfaces was observed. The significance of this result stems from the fact that metal overlayers on Fe-Ni alloy IC package leads are necessary to enhance lead solderability whenever chemical fluxes are employed in the soldering process. These overlayers are normally deposited by electrochemical techniques generating large amounts of hazardous waste. In addition, when certain overcoating materials, such as Au, become incorporated into the solder joint in excessive amounts, significant degradation of solder joint properties can result. Laser ablative pretinning of solder joining surfaces can potentially eliminate the need for metalization overlayers in most soldering operations, eliminating in turn both the hazardous waste and manufacturing costs associated with the formation of these metal overlayers. In addition, because subsequent joint formation can immediately be accomplished without the use of a chemical flux, many of the solvent cleaning steps currently required in electronics assembly can be eliminated as well.

(5) Multiplexing of Fluxless Laser Soldering:

With the growing complexity of printed wiring assembly designs, laser soldering is gaining more acceptance as an alternative attachment technology. Despite the many advances in optical manipulation of laser beams, the process still depends on producing only one solder joint at a time and has been consequently limited to specialized applications. The ability to perform fluxless or low-residue soldering with a laser has increased interest in expanding the technology by multiplexing the beam. The multiple beams can be directed through fiber optics. The split beams would provide a means to significantly increase process throughput and satisfy environmental constraints.

Tests were conducted to determine the typical operating parameters required to solder a leaded surface mount device to an FR-4 PWB. Line spacing was 0.050". The leads were solder coated by the supplier. Laser soldering was done with a U.S. Laser CW Nd:YAG system. Good joints were obtained at 15 watts laser power for 0.6 second or 6 watts laser power for 1.0 second in air with a low solids flux. Representative solder joints were shear tested with breaking loads of 4-6 pounds.

Hardware was purchased to demonstrate the multiplexing concept. The laser system is being modified to accommodate the beam splitting element and fiber optic delivery stage. Test conditions selected from the above experiments will be used as the baseline for the final technology demonstration.

(6) Aging Effects on Copper Coated with an Organic Inhibitor:

Solder wetting on baseline and aged Cu substrates coated with benzotriazole (BTA) was evaluated. The primary goal of the demonstration was to maintain solder wettability over an extended period under typical indoor industrial storage conditions. The BTA coating was applied to copper test coupons immediately after degreasing. The baseline (control) wetting experiments were conducted approximately 30 minutes after applying the inhibitor. Aged coupons were solder tested immediately following their removal from the environmental test cell. Accelerated aging was done in a mixed flowing gas chamber and simulated corrosion and oxidation of typical electronic contact and connector materials.

Organic inhibitors (or solderability preservatives) offer the potential for retaining solder wettability on metallic surfaces that are stored for limited periods in typical indoor environments. Baseline experiments (no aging) showed that the organic films did not significantly degrade wettability, although initial wetting was slower. Lower wetting rates and slightly longer wetting times were also observed. The simulated aging tests were more discriminating. Preliminary results suggest that storage for one year in a typical storage environment would significantly degrade the ability to solder coat a bare copper surface. The application of a BTA layer to Cu protects the metal surface during storage and subsequent handling before soldering. This inhibitor technology couples very well with the use of organic acid and low solids fluxes.

(7) Cleanliness of Surfaces Soldered with Low Solids Fluxes:

One of the major issues associated with the use of low solids (low-residue or "no clean") fluxes is whether the residues remaining after soldering, although only a trace, should be removed. Current soldering specifications make cleaning mandatory. Sandia is working closely with others in government and industry to address this problem. Preliminary work was performed to determine the ionic

cleanliness of mixed technology printed wiring assemblies that were soldered with a low-residue flux.

Military soldering specifications limit the amount of ionic contamination that can be left on a circuit board to 20 μg NaCl equivalents per square inch. Sandia specifications are even more stringent with the upper contamination limit set at 10 μg NaCl equivalents per square inch. Ionic cleanliness measurements on boards processed with the low-residue flux in a nitrogen atmosphere revealed that the ionic contamination was nominally 5 μg NaCl equivalents per square inch or less. The demonstration boards are being analyzed for solder defects and nonionic surface debris that could bridge fine line spacings. Surface insulation resistance (SIR) testing can also be used to monitor board cleanliness, but was not part of this study.

(8) Fluxless Soldering of Gold Metallizations:

Solder does not readily wet most metals used in the electronics industry. This is the result of surface oxides which form prior to soldering and prevent contact between the solder and the metal substrate. The oxide barrier may be overcome by the application of a reducing flux or a protective coating. Because gold does not oxidize under ambient conditions, surface coatings of gold have been used as a functional substitute for fluxes. For wetting to succeed, the oxide of the base substrate must be reduced prior to gold deposition.

The effectiveness of gold as a barrier to oxidation depends upon the deposit thickness, the method of deposition and the choice of substrate. As with any diffusion barrier, protection is enhanced by increasing the thickness, or path length. However, this eventually becomes an unattractive option; aside from cost considerations, gold forms intermetallic compounds with tin which embrittle solder joints. Thus, to limit the formation of Au-Sn intermetallics, and to minimize plating costs, it is desirable to determine the minimum gold thickness which will protect the base metal.

Fluxless wetting of gold-plated nickel by Pb-Sn eutectic solder was assessed as a function of plate thickness and deposition technique. Wetting force measurements were used to determine specimen wettability. Surface characterization and chemical analyses were also performed.

Au-sputter coated specimens failed to wet. The gold layer was typically 0.15 μm thick. The shape of the wetting force curve suggested possible dewetting as a result of oxygen at the Au-Ni interface (confirmed by Auger analysis). The oxygen was attributed to nickel oxide formed prior to gold deposition. Sputter deposition does not chemically reduce oxides, and will not physically remove an oxide at low sputtering energies.

Gold thickness directly affected the wettability of the electroplated specimens. A thickness of 0.14 μm produced a positive wetting force and was the minimum gold thickness necessary to produce wetting. Further increases in gold thickness did not improve wetting. Auger chemical analysis of the electroplated specimens revealed defects, or pinholes, where nickel oxide had formed. Away from these small pinholes, however, a Au-Ni interface was found that was free of oxides. Special effort was made to examine the Au-Ni interface in areas adjacent to the pinholes. These regions were also found to be oxide-free.

For fluxless soldering to succeed, the surface oxide of nickel must be reduced and then protected from oxidation during storage and soldering. The wettability of electroplated specimens indicated that nickel oxide is reduced during electrodeposition of gold, creating a Au-Ni interface which is initially oxide-free. A sufficiently thick Au coat protects the Ni from subsequent oxidation so that dissolution of Au causes contact between the solder and a wettable nickel substrate. The results clearly demonstrate the effectiveness of gold plating for fluxless soldering applications. Sputter deposition, however, does not provide the same advantage, regardless of gold thickness.

(9) Reliability Issues Related to Low-Residue Soldering:

A joint industry, military, and government task force was formed to evaluate and qualify low-residue ("no clean") soldering technologies for military and high reliability applications. Sandia is one of the principal task organizers. Low-residue soldering was selected since the technology is widely used in commercial and military applications and provides a cost-effective means of eliminating hazardous chemicals while still yielding reliable electronic solder joints. The task force is utilizing the expertise and analytical resources from industry, the DOE nuclear

weapons complex, DoD, and EPA to insure that the effort will demonstrate the viability of the low-residue process and facilitate its use on a broader range of applications compared to the present contract-by-contract basis.

A list of requirements for the test program were determined in April 1993. The list covered circuit characteristics, materials, circuit technology, solder processes, flux application, reliability test methods, and analysis. A follow-up meeting in July, 1993 reviewed the drafted test plan. Details of the PWB test vehicle design were discussed at subsequent meetings. The test vehicle is a functional board with circuitry divided into four major sections: high voltage and low current, low voltage and high current, high speed digital, and high frequency.

Each major board section contains a mixed technology of plated through hole (PTH) and surface mount technology (SMT) components. Half of the boards will be manufactured from polyimide while the other half will use FR-4 epoxy. The functional test vehicles will be fabricated using different assembly processes including wave, reflow, and hand soldering. Soldered assemblies will be subjected to ionic cleanliness, surface chemistry, electrical, and conformal coating adhesion analyses. A second test vehicle is based on the IPC-B24 surface insulation resistance (SIR) test board and will be used to evaluate the degradation of electrical insulating properties in the presence of flux residues in an elevated humidity and temperature environment.

(10) ECMID Technology Integration and Transfer:

Information was supplied to a variety of electronic manufacturers through trade journal articles, society-sponsored technical conferences, workshops, site meetings, and phone conversations. Task progress was presented at an ECMID review at Salt Lake City, Utah in July. Direct support to AS-KCD was also given in the form of consultation on integrating laser soldering, ultrasonic soldering, controlled atmosphere soldering, organic inhibitors, and water soluble/low solids fluxes into production use. Every electronics assembly has a unique solution to solving the many environmental problems. The solution is a technology integration strategy that can be optimally applied at the different assembly levels (e.g., lead tinning, mass component attachment, discrete component attachment, cable/connector manual attachment, and rework). This strategy was illustrated with the above fluxless and

low-residue soldering technology demonstrations. A typical strategy flowchart is shown in Fig. 3.

Summary and Conclusions

Integrated environmentally compatible soldering technologies were demonstrated on a variety of prototype test vehicles and surface finishes. The ECM Soldering demonstrations focused on the integration of controlled atmosphere soldering in inert and activated acid vapor environments, fluxless ultrasonic pretinning of PWB surfaces and leaded components, laser ablation cleaning and pretinning of aged IC pins, laser soldering of surface mount devices, solderability preservation with organic coatings, fluxless soldering with Au metallizations, and cleanliness evaluations of low solids ("no clean") fluxes. Reliability issues of low-residue soldering are also being considered. Technology integration is the key to success since each assembly level presents a different challenge that must be met.

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Figure 1. Fluxless Soldering Technology Diagram.

Figure 2. Environmentally Compatible Soldering Technology Diagram.

Figure 3. Strategy matrix for integrating ECM Soldering Technologies.

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