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Reduction of Solvent Use Through Fluxless Soldering*

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Abstract:
Conventional soldering typically requires fluxing to promote wetting. Halogenated solvents must then be used to remove the flux residues. While such practice has been routinely accepted throughout the DOE weapons complex, new environmental laws and agreements will eventually phaseout the use of these solvents. Solvent substitution or alternative technologies must be developed to meet these restrictions. SNL, Albuquerque is characterizing and developing alternative fluxless soldering technologies that will reduce solvent use and be compatible with prototypic packaging materials. The program is focusing on controlled atmosphere (vacuum, inert/reducing gas, reactive plasma, and activated acid vapor) soldering, metallization and inhibitor technology, and thermomechanical surface activation (laser, infrared, solid state diffusion, and ultrasonic) soldering. Since there is no universal method that can be applied to every electronic application, the study is defining technological options and limitations. Fluxless soldering would reduce the number of cleaning steps and the subsequent volume of mixed solvent waste. This paper will present an overview of the effects of atmosphere, materials, and processing conditions on attaining a fluxless operation. Examples of applying these technologies to electronic packaging will be given.

Keywords: Chlorofluorocarbons (CFCs); Solvents; Fluxes; Fluxless Soldering; Controlled Atmosphere Soldering; Thermomechanical Surface Activation Soldering; Metallizations; Organic Inhibitors.

Introduction

There has been increasing concern about the environmental effects of chlorofluorocarbons (CFCs) by the scientific and political community over the past decade. CFCs have been identified as a source of the depletion of stratospheric ozone. Continued ozone depletion would seriously affect both the environment and human health. The evidence for this scenario is well documented (1-3). The most celebrated example of ozone depletion is the ozone hole discovered over the Antarctic. It is being extensively studied and monitored. The hole has been associated with the emissions of fully halogenated CFCs and halons. The Montreal Protocol, which is an international agreement that was originally drafted and submitted for signature in 1987 and has gone through several revisions, attempts to reverse this depletion problem. The current Protocol schedule requires a complete phaseout of controlled CFCs by 2000. Other fully halogenated CFCs, carbon tetrachloride, and methyl chloroform will be also affected by the Protocol controls (4).

The international restrictions on CFCs will significantly impact the electronics industry. Cleaning is a major element in electronic manufacturing, especially as a part of solder processing. An electronic package is typically populated with many devices (surface mount devices, capacitors, resistors, chips carriers, leaded devices, etc.) that are attached to the host board by one of several soldering methods. Whether the operation is manually performed with a soldering iron or batch processed with a wave soldering machine, each method has the

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common feature of using a flux to help the molten solder alloy wet the base material (5). The flux has three functions. The first is to chemically remove surface oxides and provide a protective layer over the cleaned surface while solder wetting occurs. The second is to assist heat transfer to the joining surfaces. The third is to assist the removal of the reaction products. The reaction products and flux residue must be removed after soldering. Although the residues are generally nonconductive, they are corrosive and could create a reliability problem, especially for applications where extended storage in uncontrolled environments is expected. These conditions make mandatory their complete removal from the assembly.

Most military electronic applications use rosin fluxes when soldering. The flux residues are typically removed with halogenated solvents. This practice is changing because of the impact of the Montreal Protocol. New solvents, fluxes, and cleaning methods are being consequently developed to satisfy the CFC phaseout. Terpene solvents, aqueous based cleaning, water soluble fluxes, and low solids ("no clean") fluxes are showing promise. Alternative technologies, such as fluxless soldering, must also be developed to supplement these other activities.

Fluxless soldering is not intended to eliminate all cleaning during electronic manufacturing, but it will reduce the total number of cleaning steps and the subsequent quantities of mixed solvent waste that must be handled. An example of this is step soldering where two or more solder alloys with different melting temperatures are used to attach more than one components in multiple processing sequences. If fluxing could be reduced or eliminated during these multiple steps, the need for cleaning could also be reduced and a significant quantity of solvent saved. This quantity is dependent on the number and size of parts processed, but for a typical hybrid microcircuit, up to 250 ml of mixed solvent waste can be generated from one cleaning cycle.

The purpose of this paper is to present an overview of the Fluxless Soldering activities that Sandia National Laboratories, Albuquerque (SNL) has in progress. SNL is characterizing and developing several alternative technologies that will be applied to waste minimization in the DOE weapons complex. The work is being funded by the DOE Office of Technology Development (DOE/OTD) which is committed to developing faster, better, cheaper, and safer processes and materials which can achieve and sustain environmental restoration and waste management compliance. The project objective is to safely integrate these alternative technologies onto the production floor.

Fluxless Soldering Technology Overview

SNL's Fluxless Soldering effort covers a broad range of technologies (6) that either reduce surface oxides or prevent surface oxidation prior to and during soldering. Most of the technology currently exists but has not been fully applied to soldering. Fluxless soldering is consequently not well understood and must be better characterized and developed if it is to succeed in reducing solvent use at the manufacturing level. There are four key elements to the SNL task. They involve the characterization and development of Controlled Atmosphere Soldering, Thermomechanical Surface Activation Soldering, Metallization Technology, and Inhibitor Technology, Figure 1. These activities are being supported by thermodynamic and kinetic analyses and wetting experiments. Figure 2 lists the principal contacts in SNL's Metallurgy Department 1830 who are involved in the investigation.

Controlled atmosphere soldering utilizes various "clean" or reducing atmospheres to maintain or produce a solderable base surface. These atmospheres typically depend on a vacuum, inert or reducing gas, reactive plasma, or dilute acid vapor-inert gas mixture (eg. formic acid and nitrogen). More will be said on the use of these controlled atmospheres for fluxless soldering in the next section.

Thermomechanical surface activation soldering depends on kinetic or directed thermomechanical energy to spall or ablate the surface oxide and facilitate wetting of the underlying, pristine metal. Laser, solid state diffusion, and ultrasonic soldering are typical ways in which this can be accomplished. These processes can be done in air or in a controlled atmosphere. An example of fluxless laser soldering coupled with metallization and controlled atmosphere technology will be given in the next section on controlled atmospheres.

Ultrasonic soldering uses an ultrasonic probe which is immersed in a solder bath and generates ultrasonic vibrations that reduce thin oxide layers through cavitation. It is difficult, however, to accurately direct these ultrasonic waves. There is also a lack of fundamentally understanding the interaction effects between the process parameters and materials. SNL is conducting experiments to characterize these fundamental properties. Cu and Al substrates are being fluxlessly and ultrasonically tinned with elemental Sn. The effects of tinning temperature, probe separation, probe power, probe angle/position in reference to the base surface, and vibration time on wetting are being studied. Preliminary results on flat Cu substrates have shown that excellent wetting can be achieved on both sides of the immersed substrate, but cavitation is very sensitive to sample thickness.

Protective coating technology also shows promise as a compliment to fluxless soldering. Nonoxidizing surfaces, such as Au, have a long history of being readily wettable without fluxing. Their deposition, however, must be closely controlled. A thick layer of Au is generally required to guarantee complete coverage and wettability of the underlying metal. However, the metallization must not be too thick or the extra Au will produce a brittle solder joint. Au metallizations should generally not exceed 3-5 wt. % in a 63Sn-37Pb solder joint. The resulting compromise in thickness typically results in a thinner, porous layer of Au that exposes the underling metallic surface, usually Ni, and degrades subsequent wettability under oxidizing conditions, Figure 3. These porous metallizations can be protected by applying organic inhibitors, especially if stored in an uncontrolled environment before soldering. SNL is working with the University of California at Berkeley to characterize the microstructures and the fluxless wettability of Ni-Au platings and the State University of New York at Stony Brook to study the bonding behavior of organic inhibitors on metallic surfaces and their effect on subsequent solder wetting. Work is underway to examine the effects of Au thickness and porosity on the degradation of wetting under fluxless soldering conditions. These protective coatings generally work in both air or a controlled atmosphere, although a dry, nonoxidizing cover gas is more effective.

The above fluxless soldering technologies must be compatible with not only the base and filler metals, but also with any neighboring materials that might be exposed to the same process during soldering. Sensitivity to lasers, infrared heating, or reactive plasmas is of special concern since they could effect the functional performance of an electronic component. Materials such as alumina, glass frits, epoxy, polyester, phenolic, polyimide, plastics, and conformal coatings could be degraded by exposure to these processes.

Controlled Atmosphere Soldering Technologies

Controlled atmosphere soldering (7) utilizes vacuum, inert or reducing gas, reactive plasma, or acid vapor-inert gas mixtures that function as either a protective or reducing cover during processing. Vacuum and inert/reducing atmospheres restrict the supply of oxygen to the workpiece with oxygen levels as low as 5 ppm. Although thermodynamic data suggests that the reduction of metallic oxides in hydrogen or vacuum is feasible, the kinetics for it to occur at typical soldering temperatures, 200-300°C, is negligible and the oxide remains relatively stable requiring the use of a flux. If fluxless vacuum or inert gas soldering is to succeed, therefore, the base metal must be oxide-free throughout the heating and wetting cycle. Gas flow rates are important because volatile contaminants must be removed from the work area with a dynamic flow of "clean" process gas. Metallizations, whether they are plated or tinned, provide an added margin for fluxless soldering in vacuum or inert atmospheres. Controlling the time at which the solder alloy is molten is also critical since extended soldering times could cause excessive solder alloy and base metal reaction and produce a new surface (eg. intermetallic) that could dewet. Infrared heating helps to minimizes thermal gradients and heating times and is consequently being applied to various controlled atmosphere soldering systems.

A Controlled Atmosphere Solder Wettability System is being constructed at SNL to study the effects of vacuum, inert gas, and dilute hydrogen reducing gas atmospheres on fluxless wetting. A schematic of the system is shown in Figure 4. The system uses an electrobalance to measure wetting force as a function of time. An auxiliary video system can record the wetting event and analyze the wetting images to determine the effects of processing conditions (pretreatment, atmosphere type, soldering temperature, immersion time, flow rates, etc.) and materials (base metal, metallization, solder alloy, inhibitor, etc.) on achieving fluxless wetting. A second system is available to perform area-of-spread (sessile drop) experiments in activated acid vapor-inert gas atmospheres.

SNL has developed fluxless laser soldering to fabricate the closure joints on an electronic radar package. The process utilizes the combined features of controlled atmosphere , metallization, and thermomechanical surface activation soldering. The application joins Ni-Au plated Kovar pieces with Sn-Pb, In-Pb-Ag, or In-Pb solder alloys and a 100 watt CW Nd:YAG laser, Figure 5. The laser beam is directed on the solder preform because of high the reflection properties of the Au plating that would inhibit the absorption of the laser energy. Satisfactory hermetic joints were achieved with a 90 watt, 0.4 mm spot size, and 5 mm/s travel speed laser setting in a forming gas cover of 5 vol. % hydrogen in argon. Figure 6 shows a cross-section of a typical laser soldered joint from the parametric study. Although the process is being developed for closure joints, it can be readily applied to attaching discrete leaded devices.

Reactive gases or plasmas are also being investigated. Reducing plasmas can be used in a two step process that cleans the base metal and solder alloy during the first step and uses an auxiliary heat source, such as a heated platen, laser, or infrared heater, to make the solder joint in the second step, Figure 7. Compatibility between the plasma and the packaging materials is an important consideration. Reactive gases have the potential for effectively reducing surface oxides. For example, thermodynamic data suggests that atomic and ionic hydrogen have a higher copper oxide reduction potential than molecular hydrogen at 250°C, Figure 8. Ionic hydrogen appears especially effective. Preliminary cathodic plasma cleaning experiments on heavily oxidized Cu have resulted in oxide-free solderable surfaces, Figure 9. Experiments are underway to comprehensively characterize the effect of ionic hydrogen on Cu and Ni oxide reduction and fluxless wetting.

The final element of SNL's controlled atmosphere soldering effort is focused on acid vapor-inert gas mixtures. Although there are commercial systems available that use variations of this process, the fundamentals of their operation are not well characterized. The process is readily applicable to wave or batch furnace soldering, Figure 10. Dilute additions of formic or acetic acid vapor are added to argon or nitrogen to promote fluxless wetting through the reduction of metallic oxides:

$$MO + 2HCOOH \longrightarrow M + 2CO_2 + H_2 + H_2O$$

In actual practice, it is difficult to reduce most surface oxides and an adipic acid additive is generally required to achieve wetting. Adipic acid is a major constituent of low solids or "no clean" fluxes. As with the low solids fluxes, the adipic acid residues left on a soldered component must be completely removed to satisfy the long term reliability requirements imposed on most military electronic applications. SNL is characterizing the effect of these acid vapor additions on oxide reduction and fluxless soldering. The acid-gas mixture, gas flow rate, activating additives, soldering temperature, time, and materials are important parameters that influence wetting and their interaction effects are being determined. The objective is to develop a scientific understanding of how the process works and what must be done to attain true fluxless wetting.

Summary

Fluxless soldering is a viable and supplemental technology to solvent substitution for the electronics industry. It has a high potential for reducing the storage and handling of hazardous fluxes, environmentally harmful solvents, and the subsequent mixed solvent waste generated by flux residue removal. Since there is no universal method that can be applied to every soldering application, technologies must be identified, characterized, and developed to satisfy the increasing number of environmental, safety, and health regulations. The objective is to quickly integrate these fluxless processes into full scale manufacturing.

SNL, Albuquerque has an active program that is evaluating various fluxless soldering technologies. It includes controlled atmosphere soldering, thermomechanical surface activation soldering, metallization technology, and inhibitor technology. These processes offer a wide range of fluxless soldering options which can be combined to enhance the reliability of the final product. Laser and atmosphere soldering are excellent examples of this dual technology concept. The key to fluxless soldering is to maintain a "clean" surface that the molten solder will directly wet or to reduce surface oxides that the solder will not wet. Materials compatibility must also be considered. Otherwise, the functional performance of the final product could suffer if the selected process degrades sensitive components near the solder joint.

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SNL, ALBUQUERQUE IS DEVELOPING SEVERAL FLUXLESS SOLDERING TECHNOLOGIES

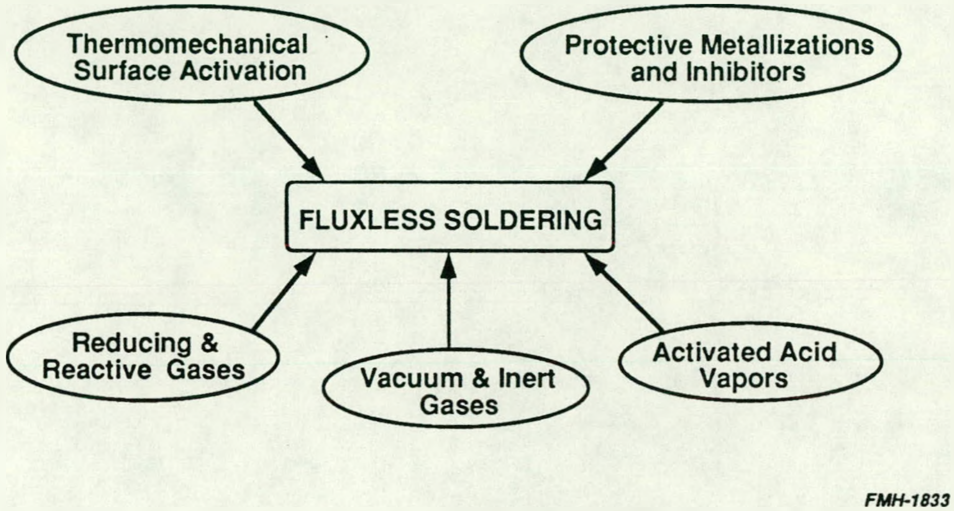

Figure 1. Flow chart for the SNL DOE/OTD Fluxless Soldering Task.

SNL METALLURGY DEPARTMENT 1830 FLUXLESS SOLDERING INVESTIGATORS

- *Thermodynamic/Kinetic Analyses - Charlie Robino, 1831*
- *Controlled Atmosphere Soldering - Darrel Frear, 1832*
  Mike Hosking, 1833
  Jim Jellison, 1833
  Dave Keicher, 1833
  Mark Smith, 1833
  Janda Panitz, 1834
- *Thermomechanical Surface Activation (Ultrasonic & Laser) Soldering - Paul Vianco, 1831*
  Dave Keicher, 1833
  Mike Hosking, 1833
- *Metallization Technology - Darrel Frear, 1832*
  Mike Hosking, 1833
  (UC-Berkeley)
- *Inhibitor Technology - Rob Sorensen, 1834*
  Mike Hosking, 1833
  (SUNY-Stony Brook)

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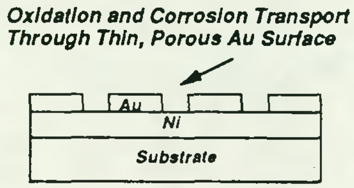
Figure 2. Fluxless Soldering group responsibilities in SNL's Metallurgy Department 1830.

Oxide Free Surfaces Are Necessary If Vacuum or Inert Gas Soldering Is to Succeed



- Au metallizations can provide an oxide free, solderable (fluxless) surface.
- Control of the Au thickness is critical; too thick and Au inter-metallics will embrittle the joint; too thin and porous Au will allow oxidation of the underlying metal.
- Recommended Au thickness is 50-75 μin. (1.3-1.9 μm).
- Fraction of Au in a 63Sn-37Pb solder joint should not exceed 3-5 wt. %.

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Figure 3. Fluxless soldering can be achieved in a controlled atmosphere by overlaying the base metal with Au.

Solder Wettability In Controlled Atmospheres Can Be Determined With A Wetting Balance

Controlled Atmosphere Solder Wettability System

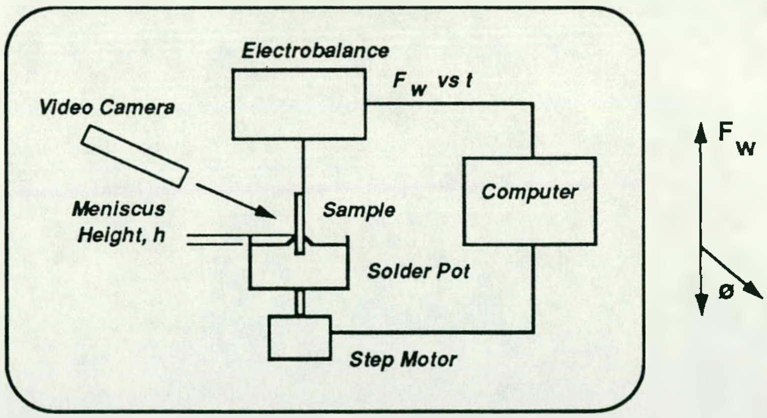

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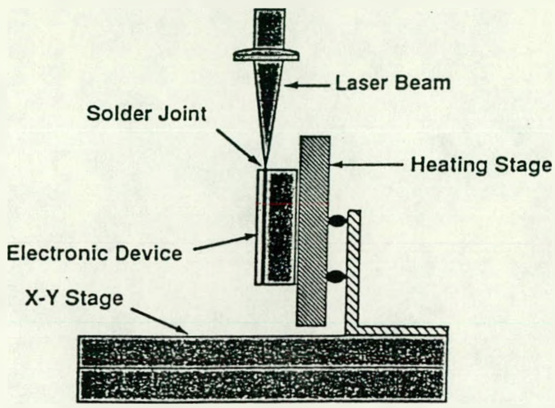
Figure 4. Diagram of the Controlled Atmosphere Solder Wettability System which is under construction and will characterize the effect of controlled atmospheres on fluxless wetting.

Laser Inert/Forming Atmosphere Soldering of Discrete Electronic Devices

100W CW Nd:YAG Laser



Objective: Attach discrete electronic components in a protective inert or forming cover gas with laser heating and no fluxing.

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Figure 5. Laser and controlled atmosphere soldering can be combined to produce a fluxless soldering operation.

Optical Micrographs of SnPb Laser Solder Joints

Ni-Au Plated Kovar Base Plates
(100W, 0.035", 30 ipm test parameter)

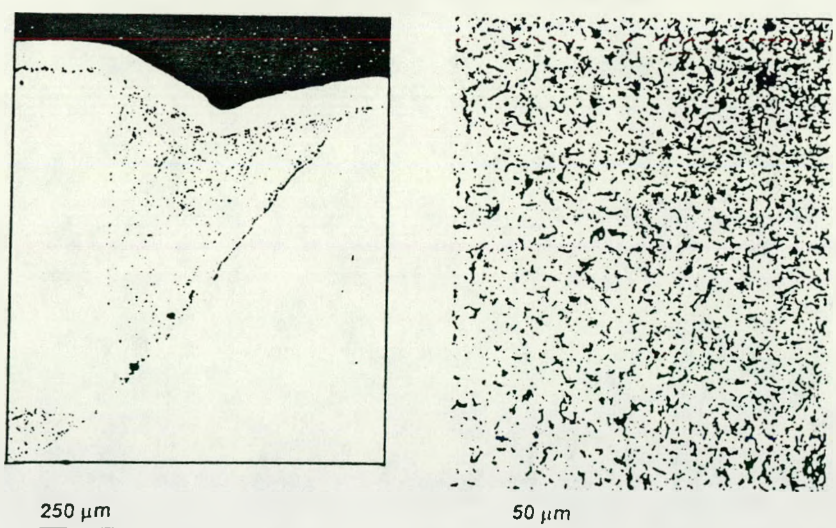

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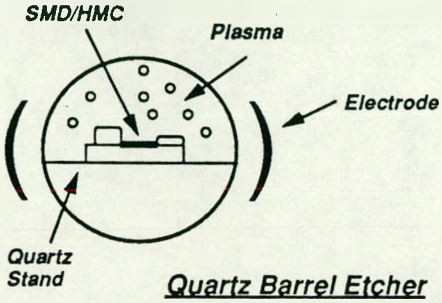
Figure 6. Optical micrographs of a typical, fluxlessly laser soldered joint showing excellent solder wetting and flow.

Two Step Plasma Cleaning and Soldering Is Best Suited for Batch Processing

EXAMPLE



Quartz Barrel Etcher

- ***Reducing plasma produced by an RF electric field.***

- ***Cleaning Variables -***
  - *a) power*
  - *b) chamber pressure*
  - *c) time*
- ***Soldering (fluxless) assisted with auxiliary heating (hot stage, laser, infrared)***

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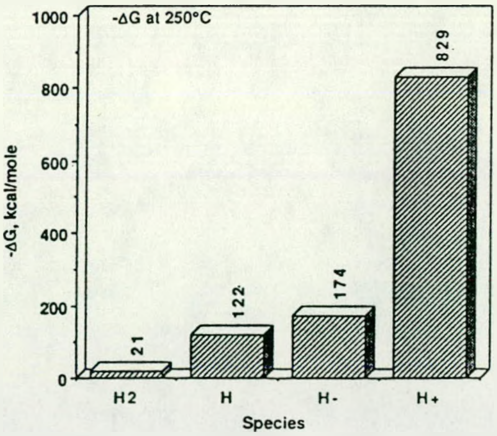
Figure 7. Fluxless soldering can be accomplished in a two step operation: plasma cleaning immediately followed by soldering with an auxiliary heat source.

Thermodynamics of the Reduction of Cu_2O at 250°C Suggests That Ionic Hydrogen Has the Best Potential



Gas Species	Reduction Factor
H_2	1
H	6
H-	8
H+	39

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Figure 8. Thermodynamic data demonstrating the oxide reduction potential of ionic hydrogen.

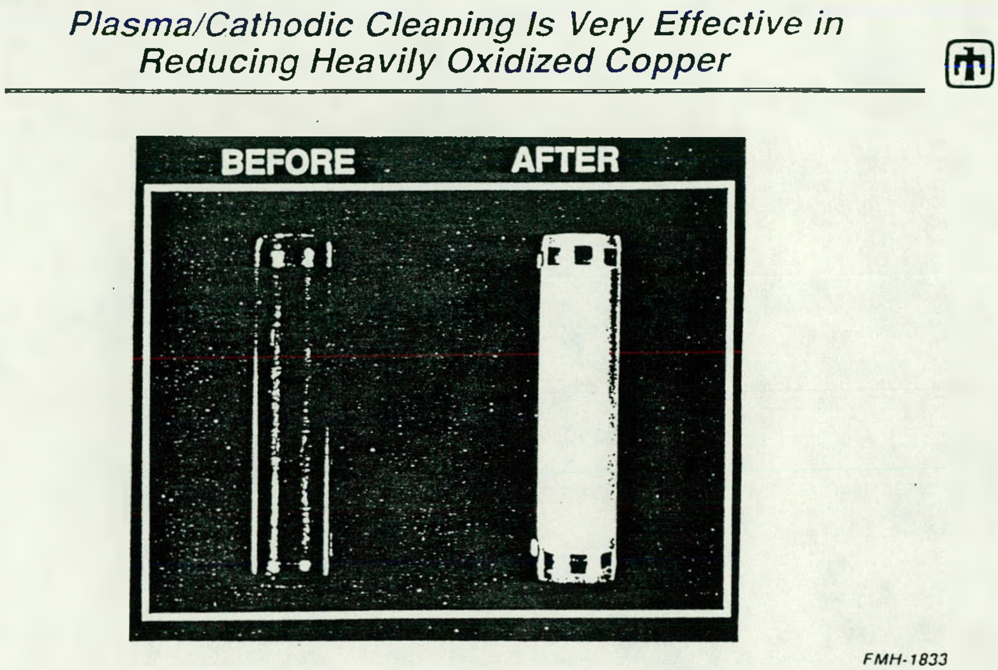

Figure 9. Heavily oxidized copper tube cleaned with a reducing plasma.

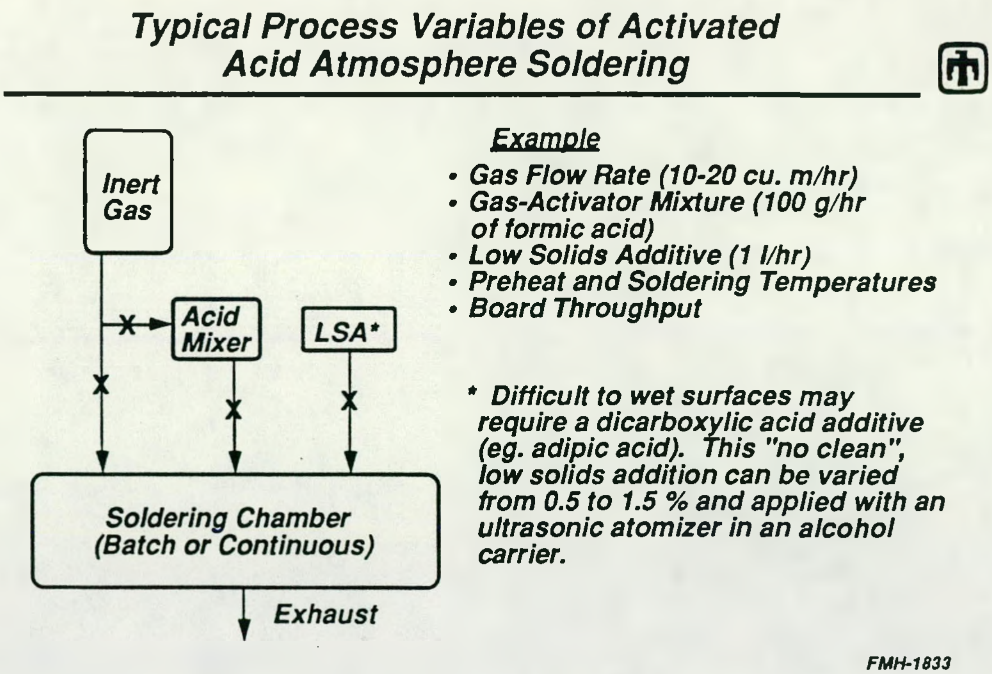

Figure 10. Dilute additions of formic or acetic acid vapor to an argon or nitrogen atmosphere have the potential for fluxless soldering.