# SOLDERABLE PLATED ELECTRODEPOSITS

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## Introduction

The joining of metal surfaces by soft soldering is used today in many industrial applications. One very important such application is the production of electrical and electronic equipment where many thousands of satisfactory soldered joints are made daily at high rates of production and reliability. Components are often mounted on printed circuit boards or molded into plastic blocks, and the soldering of such so mounted components is accomplished by automated methods. The assembled circuit boards or block is brought into contact with a surface of a soldered bath, or it is passed through a standing solder wave. Many joints are thus made in one operation with the time and temperature often restricted to one to two seconds so as to maintain proper production rates and to avoid possible heat damage to either the board block or its components. Under these conditions, the ease of solderability is of prime importance and the solderability of the surfaces being brought together at the solder pot, must be of the highest quality to produce consistently satisfactory joints. The surfaces involved are often coated with pure tin or a tin alloy deposit.

## Requirements of a Solder Joint

Five distinct factors are involved to properly construct the soldered joint:

1. The basis metal and its surface condition;
2. The selection and application of a coating which is itself solder able and will protect the basis metal surface;
3. The storage conditions and additional manufacturing procedures to which the parts are subjected between the coating application and the soldering step;
4. The choice of solder and the conditions of the soldering procedure;
5. Post soldering treatment and exposure conditions.

## Definition of Solder ability

Solderability may be defined as the property of a surface which permits molten solder to readily wet that surface under the fluxing, time of exposure, and soldered temperature conditions that are compatible with the particular application involved. Once all surfaces

involved are fully wetted penetration and filling of the space between the parts being joined occurs easily by capillary action thus completing the joint.

## Definition of Wetting

Wetting occurs when a metallurgical bond is established between the tin in the solder and the basis metal surface producing layer of an intermetallic compound such as Cu, Sn, and Cu, Sn. When copper is the basis metal. The first requirement for wetting is that the basis metal surface must be completely free of grease, dirt and heavy oxide films. Time, temperature and solder composition all influence the alloy reaction and therefore the rate of wetting. Fluxes do assist the wetting action but those required in the electronics industry are only capable of removing the last traces of basis metal oxide or tarnish and in keeping the molten solder free of oxide. They are not capable of coping with the other contaminants mentioned. Cleaning must therefore be thorough because a satisfactory solder joint is just not possible unless the metallurgical bond required for wetting is established. In all soldering, it is the basis metal which must be clean and free of all contaminants in order to provide the metallurgical bond, which is the basis of the soldered joint. If a solid piece of copper is immersed into a solder pot and soldered, or whether that piece of copper is coated with an electrodeposit the soldering bond is the bond between the base copper and the solder. The electrodeposit is only an intermediate to assist in the formation of the metallurgical bond between the tin and the solder and the basis metal copper.

## Basis Metals

The required metallurgical bond may be established in either of two ways. The clean metal surface may be immersed in liquid tin or solder in which case wetting occurs instantaneously. If the basis metal surface is not sufficiently clean, dewetting or nonwetting will be immediately evident. The metallurgical bond may also be established by bringing the basis metal surface to the required degree of cleanliness by a typical pre-electroplating cleaning cycles and then electroplating a protective coating which is itself solderable. With a fusible, coating, alloying will occur at the time of soldering and the effects of an unclean basis metal will become evident. The substrate must be fully and rapidly wetted by the tin in the protective coating with the solder being applied. Wetting is accompanied by a metallurgical reaction that produces intermetallic compounds (alloys) of specific composition.

## Intermetallic Compounds

It is required that intermetallic compounds are produced before a joint can be completed. Because tin and typical substrate materials also interfuse in the solid state, intermetallic compound layers of significant thickness can develop during the time between the coating application and the soldering operation without the coating having been melted. The wetting of a solder joint is accomplished by the formation of a metallurgical bond between the tin and the solder and the basis metal. These intermetallic compounds are alloys of specific composition. They are in the case of copper basis metals Cu, Sn and Cu, Sn. This is an important factor because of the growth rates involved and the effects

of the compound layers on component solderability and the joint properties. Intermetallic layers grow at the interface of the substrate and the protective solder able tin or tin lead coating during long-term storage even at ambient temperatures. This can result in loss of solderability under mass soldering conditions specifically because the intermetallic layers reduces the thickness of the remaining unreactive coating. Additionally, if the electrodeposited coating is thin enough and the growth of the intermetallic layer is large enough the basis metal may in effect, migrate to the surface of the coating and oxidize thus preventing the formation of satisfactory solder joint.

## Protective Coatings

Once the basis metal is brought to a solderable condition by cleaning, it is virtually impossible to maintain that condition through storage and the various assembly steps until soldering is attempted without the application of some type of protection. The obvious answer is to apply a solderable coating to the clean surface which will protect it until soldering. Available coatings may be classified as: fusible, soluble and nonsoluble. A fusible coating is one which itself becomes molten at the soldering temperature and in effect fuses with the solder to assist in completion of the soldering operation in the shortest possible tome. Tin and tin lead (preferable 60-40) coating s constitute this category and are considered to be excellent for protecting, and to maintain the solderability of electronic components.

Soluble coatings are ones that do not become molten at the soldering temperature but are rapidly with the soldering which can also be helpful in promoting and the completion of the soldered joints. Soluble coatings include gold, silver, tin (if soldering temperature is below its melting point) and copper.

When soluble coatings are used the possibility always exist that solution of the coating into solder may result in joints that exhibit less then desirable characteristics. The joint may not become homogeneous a condition which seems to lead to the development of cracked joints under conditions of undue stress. Solution of the coating into the solder may also result in metallurgical problems such as brittleness. Nonsoluble coatings include nickel, iron, and tin/nickel. These coatings are least troublesome with respect to the pints just mentioned because they alloy less rapidly with the solder. This means that they are also more difficult to solder which is an important factor in the electronic industry. Nickel or iron coating are most valuable when they are used as a barrier layer over troublesome basis materials in which case a fusible or solderable coating could well be applied as the final finish to provide the required solderability. The protective coating may be applied by hot-dip coatings 5-7.5 micrometers thick on printed wiring boards by the use of centrifugal tinning equipment, provide the board material is capable to withstanding temperatures of at least 250°C. The application of tin by hot dipping method usually requires a tinning temperature in the range of 250-300°C while the temperature as low as 220°C may be used when 60 tin 40 lead is being applied. It is difficult to specify the exact temperature, time of immersion and centrifuging conditions since each individual item presents different requirements and therefore requires different

tinning procedures. One of the major draw backs of hot dipping techniques is the thinning of the deposit on the edges on non-round components.

Electroplated coatings may be applied to any desirable thickness although 7.5 micrometers (0.3 mil) is a reasonable coating thickness. One difficulty with electroplated coatings has been that excessive thicknesses may occur at high current density areas if required thicknesses are obtained at points of low current density. Processes are now available which minimizes this problem. Numerous types of electrodeposits are available for protective coatings on basis materials to be soldered. Alkaline stannate baths, fluroboric baths and acid tin baths all fall into this category. The most commonly seen in production today are the acid tin baths and will be discussed more fully here.

## Acid Tin Electrolytes

Acid tin electrolytes consist primarily of stannous sulfate in a sulfuric acid media of typically 10%. It is extremely important when choosing an acid electrolyte that they be free of organic brightening agents. Organic brightening agents codeposit with the tin and at the time of soldering are released from the molten tin solution and form oxidation products on the surface of a soldered joint. This minimizes the action of the flux and generally led to unsatisfactory soldered joints. These are typified by voids, pinholes etc. Only a solderable acid tin electrolyte should be chosen for high solderability reliability. These are baths that contain only grain refiners such as beta napthanaI peptone and Janis Green B Dye. Solderable tin deposits are characterized by good throwing power, matt finishes, low codeposited carbon any may be used on components which are manufactured with glass. Typical commercial baths of this type are the Lea Ronal Sat-Tin Process and the Enthone Process.

## Pre-Assembly Conditions

Once the basis metals involved have been rendered solderable, and a protective coating has been applied, the composite should not be subjected to conditions which will adversely affect its properties. Exposure to a humid atmosphere, or to one laden with dust or industrial pollutants, may alter the surface in such a way that it will not be possible to remove the resulting contamination under the soldering conditions permissible in the industry, and poor solderablity will result. It is necessary, therefore, that the storage of such parts and components be sufficient to avoid this type of contamination, and that assembly and soldering operation be carried out under reasonably controlled conditions. These may range form covered storage, with the assembly and soldering operations being located in a clean area of the plant for normal production, to the use of sealed storage conditions and white room assembly and soldering areas for very high reliability production.

Another condition which will serve to destroy solderability during the time between plating and assembly is exposure to high temperature environments. When a tin or tin-lead coating on a copper based alloy is exposed to high temperature, the rate at which copper-tin compound forms is greatly accelerated. This compound layer is required for

wetting, and thus soldering, but as so often where a little bit of something is necessary, a large amount may be detrimental. The development of an excessive compound layer affects solderability by consuming tin from the coating, so that it is no longer available to merge with the solder and assist joining. If, by chance, all of the tin applied is consumed in this way, the resulting compound surface is not solderable with rosin fluxes, and dewetting will occur. In instances where it is known that components having a tin, or tin lead, protective coating over a copper basis material may be exposed to high temperature processing, testing or storage before assembly, the coating should have a minimum thickness of 7.5 micro inches to ensure that free tin will still be available to assist soldering when this is undertaken. A second adverse effect is that the intermetallic compound is brittle, and an excessive compound layer tends to be subject to fracture when stressed.

This means that great care must be exercised in the manufacture and storage of solderable electronic components. If high reliability is expected ate the time of assembly and soldering, the previous conditions to which the components have been subjected must be of an equally high quality.

The quality of components obtained from outside sources is important in this respect also, and the solderability of a representative sample from each incoming lot should be tested upon receipt. Components which are not found to be satisfactory must either be rejected, or rendered solderable in-plant before their use. It should never be assumed that such materials are automatically solderable, since the introduction of unsatisfactory components into the assembly line can be disastrous. The condition of the leads of components which require the application of heat during their manufacture is an example of this type of difficulty. Such leads are usually copper or high copper materials, and would be badly oxidized and damaged during the component manufacturing cycle. The lead wire could be protected from this effect by a solderable tin or tin lead coating, but at the temperatures involved an excessive amount of copper tin compound would develop, and this too is undesirable. Instead, a coating high in lead is applied, and this protects the copper surface from oxidation during manufacture without the development of an appreciable copper tin layer. This high lead coating will not meet the solderability requirements in this industry, however, and such leads will be found to be unsolderable unless the coating is altered after component manufacture. The solution is to replace the high lead coating with one of near eutectic composition. This may be done by the component manufacturer, or by the customer, so long as it is done before assembly and soldering is attempted.

## Solder and Soldering

When the choice of solder is considered, we recommend the use of the eutectic alloy, 63 tin 37 lead. Being eutectic, this alloy provides a desirable instantaneous solidification point. Figure 9 shows that the solidification curves for solders lower in tin pass through a pasty range between the liquids and solidus points. Although these alloys are good solders, any movement of the components during that period will result in damage joints, which can lead to subsequent failure. It is also true that alloys lower in tin are slightly

less expensive, but their wetting action is noticeably slower since only tin is involved in the wetting, and longer times in contact with the solder are required to complete the joints. An increase in soldering temperature, and this increases the possibility of component or board damage. We recommend, therefore, that the use of alloys containing less that 60% tin should not be considered.

Solder purity is also important, since the presence of even small amounts of readily oxidized elements such as zinc and aluminum forms tenacious oxide films on the molten solder which can prevent intimate contact with component surfaces. Although the presence of up to 0.5% antimony does not seem to significantly affect the wetting time involved, it does seem sufficiently well codumented that best results are obtained in the electronic industry and high purity solder.

Some amounts of such impurities as copper, iron, nickel, silver, gold and perhaps palladium may be dissolve in the solder pot from the materials being soldered. When present in significant amounts, these will result in the presence of particles of finely dispersed intermetallic compound within the solder joint. The presence of these particles may modify the metallurgical structure of the solder sufficiently to produce a dull appearance, and an excess can result in the loss of mechanical strength in the solder joint. Under normal operation conditions, it is not expected that the levels of these impurities, except for copper, should be sufficient to cause difficulty.

Zinc Contamination of the solder pot can result from the soldering of brass components, while use of equipment made of aluminum will produce aluminum contamination. Some amounts of these metals can be removed by bubbling air or steam through the molten solder metal, and removing the dross which forms on the pot surface. Gross contamination by either may require replacing the solder metal.

There is a tin copper eutectic of .07% of the tin content in the solder, and, as the dissolved copper exceeds this amount, the temperature at which the solder is fully fluid is affected. If it is suddenly noted that the usual temperature is not sufficient to maintain fluidity and proper flow of solder into the joints, the solution is not to increase the temperature until proper fluidity is achieved. Such action merely postpones the difficulty for a short while, because the copper solution rate increases with increasing temperature. The proper remedy is to remove the copper from the pot. This is a simple matter of reducing the pot temperature during downtime to the point that the solder is just still molten. The copper tin compound present will then be precipitated as crystals in the solder and can be easily removed with a perforated ladle or other convenient means. The copper content can be reduced to 0.7% of the tin content in this manner. The presence of other impurities which produce particles of compound may also be reduced in this way. When impurities are so removed, it must be remembered that part of the material taken from the pot will be tin. This may result in the tin content being lower than, desire, and an analytical check should be made to determine whether pure tin needs to be added to the solder pot to return to the proper composition.

Gold, when present as a coating, will also be rapidly dissolve into the solder pot. A recent report, however, indicates that up to 1% may be tolerated in the pot without producing a serious effect on the soldered joint. As mentioned above, it is not believed that gold dissolved in the solder would exceed this amount under today's technology. If sufficient component surfaces in a system are gold plated so that this amount is exceeded, it may be necessary to either replace the gold coating with solder just before assembly to reduce gold pick-up in the pot, or to replace the solder in the pot at more frequent intervals, as the gold content reaches undesirable levels.

The solution of these metals by liquid solder is a fact which provides the metallurgical bond required for good solderability, and also produces the contamination by these metals can be avoided only through the use of coating which will not alter the solder composition, i.e., coatings of tin or tin lead, or by the use of barrier coating which are less soluble and will therefore reduce solderability.

Ideal conditions at the solder pot, or wave machine, permit soldering to be cone in the minimum time at the lowest possible temperature. Considering that we have been discussing the production of highly solderable components, it should be possible to complete all joints in an assembly with a solder pot temperature of 230-260°C and a contact time not in excess of 2-3 sec, except in unusual cases. If conditions outside these guidelines are required, there is every possibility that reliability will be affected.

## Zinc Migration

A problem of continuing concern when soldering onto brass components is the migration of zinc from the brass basis materials into the tin coatings. It has been known for sometime that tin coated brass basis metals are more prone to the loss of solderability then other basis metals similarly coated. It has been documented that detectible amounts of zinc were always present on or near the surface soon after coating is done. When hot-dipped coatings are applied it is understandable the sufficient zinc could be dissolve during the wetting and coating action and therefore be present throughout the coating layer. Somewhat less readily obvious, however, is the fact that races of zinc may also be immediately detected in an electrodeposited coating on brass. This appears to be related to the high atomic mobility of zinc at the surface during electrode position. Molecules of zinc are very small in comparison to spatially large tin molecules. Molecules of zinc readily migrate outward form the basis metal as plating proceeds remaining in the vicinity of the surface at all times. This phenomena is independent of plating thickness as the presence of zinc has been detected at the surface of coatings as thick as 20 micrometers (0.8 mils) at the termination of plating. Zinc disperses throughout the coating and diffusion continued from the substrate after plating is completed.

The presence of zinc in the coating s and on its surface does not seriously effect solderability unless storage conditions are such that corrosion of zinc occurs in which case poor solderability inevitable will result. Zinc is a very active metal and its corrosion occurs very readily. Therefore, the best solution of this problem of zinc oxidation is to minimize the amount of zinc which can be found on the surface of the electrodeposit.

The diffusion of zinc may be avoided by the use of copper or nickel undercoat as a barrier layer. Because of the possible difficulty which can be encountered it is recommended that an undercoat should always be used when tin is plated on brass basis materials.

## Electrical Break In

Many electrical components today upon completion of manufacture undergo an electrical breaking period wherein these components are operated at approximately 150°C for 168 operation hours under an electrical bias. When the components are operated under these conditions, the solderable components which are either made of copper or are preplated with copper prior to the tin electroplate, incur significant oxidation and migration of the copper undercoating. Since it is the copper basis metal upon which subsequent soldering will take place, this mode of operation can cause excessive solderability problems. It is therefore recommended that any electronic components which will see this type of initial break in service have an intermediate layer of nickel plated between the tin and the copper basis metal or copper electrodeposited layer. Care must be exercised with the surface conditions of the nickel layer to insure coating adhesion and wetting. Use of the type of a nickel under layer will significantly reduce poor solderability and dewetting conditions.

# RECOMMENDED SOLDERABLE TIN SPECIFICATION

A. **Electrolyte Type-** only highly solderable tin electrodeposits are to be applied for solderability considerations. These are deposits which are free of codeposited organic bath additions. Analysis of the plate for carbon deposits should show less than 0.5-1.0% carbon. An acid tin electrolyte with only grain refiners meets the requirements producing a highly solderable deposit.

B. **Diffusion Barrier**- a copper diffusion barrier is recommended on all brass substrates of 0.0001”-0.0002” to minimize zinc diffusion. This layer is also recommended on copper, iron and aluminum substrates to insure a chemically clean surface on which to conduct future soldering. If the electrical components are to be subjected to a high temperature break in period, a nickel diffusion layer of 0.0001”-0.00015” is recommended over a copper plate or basis material. This will minimize copper diffusion into the tin electrodeposit under high temperature and minimize intermetallic deposit growth.

C. **Electrodeposit Thickness**- A solderable tin thickness of 0.0002”-0.0003” average is recommended on any component to be soldered at the point of interest for the formation of the solder joint. This thickness of tin would allow for adequate residual tin after the formation of intermetallic tin compounds induced by storage or accelerated aging. The thickness should be measured by any acceptable technique. The most common types of measurement found in industry today utilizes beta backscatter or X-ray fluorescence methodology. The location of the measurement of the electrodeposit thickness should be specified.