TIN WHISKER GROWTH IN THE COMMUNICATION INDUSTRY

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ABSTRACT

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The growth of filiform crystals (whiskers) on tin coated surfaces can cause short-circuit failures in electrical systems particularly in miniaturized equipment. Tin whiskers grow sometimes in a matter of days and other times only after years to lengths up to 9 mm. (3/8in.) and 0.05 - 5.8 μm (2-240 microinches) in diameter. The mechanism of spontaneous growth is beleived to be a strain releif phenomenon and is affected by the temperature, atmospheric conditions, plating thicknesses and substrate, plating composition and operating bath conditions.

The co-deposition of 20-40 percent lead in the tin deposit reduces to a minimum the hazards associated with tin whisker growth and ensures a reliable corrosion protection and a good solder joint. Annealing in an inert atmosphere at a temperature of 191°C (375°F) - 218°C (425°F) for 4 hr after plating retards whisker formation.

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ABSTRACT

The growth of filiform crystals (whiskers) on tin coated surfaces can cause short-circuit failures in electrical systems particularly in miniaturized equipment. Tin whiskers grow sometimes in a matter of days and other times only after years to lengths up to 9 mm. (3/8in.) and 0.05 - 5.8 μm (2-240 microinches) in diameter. The mechanism of spontaneous growth is beleived to be a strain releif phenomenon and is affected by the temperature, atmospheric conditions, plating thicknesses and substrate, plating composition and operating bath conditions.

The co-deposition of 20-40 percent lead in the tin deposit reduces to a minimum the hazards associated with tin whisker growth and ensures a reliable corrosion protection and a good solder joint. Annealing in an inert atmosphere at a temperature of 191°C (375°F) - 218°C (425°F) for 4 hr after plating retards whisker formation.

CHAPTER I

INTRODUCTION

Electrical components in the communication industry are protected by metallic finishes to increase their corrosion resistance and solderability. The spontaneous growth of filiform metallic crystals (or whiskers) from a variety of metals (tin, silver, copper, zinc cadmium and aluminum) and their alloys have been reported under various conditions[1-3]. These electrically conductive filaments have been found to bridge gaps between components and thus can cause unexplained short-circuits in the equipment.

Whisker growth was observed on electroplated tin, zinc and cadmium in both high and low relative humidity within periods of days to years after plating. Figs. 1 and 2 show a relay contact spring electroplated with tin that grew whiskers and was responsible for a grounded circuit. Also some electro-deposited alloys such as tin-zinc, tin-cadmium, tin-nickel and tin-lead have developed whiskers. Whisker growth of copper and silver occurred only in the presence of sulfur or sulfur bearing materials.

At room temperature, hot-dipped, sprayed and evaporated metals developed whiskers on metallic and non-metallic

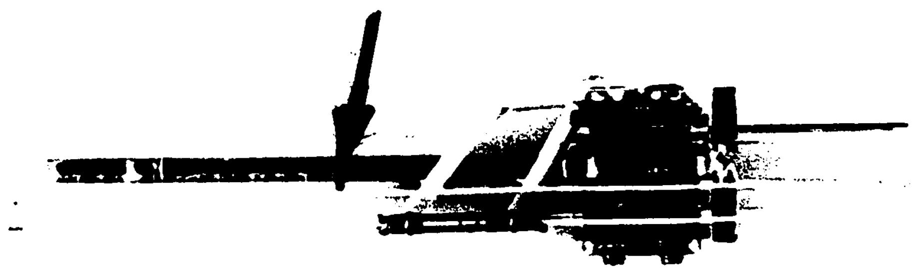

Fig. 1 - Relay contact spring.
Magnification 1.25X.

Fig. 2 - Tin whiskers on relay contact spring.
Magnification 13X.

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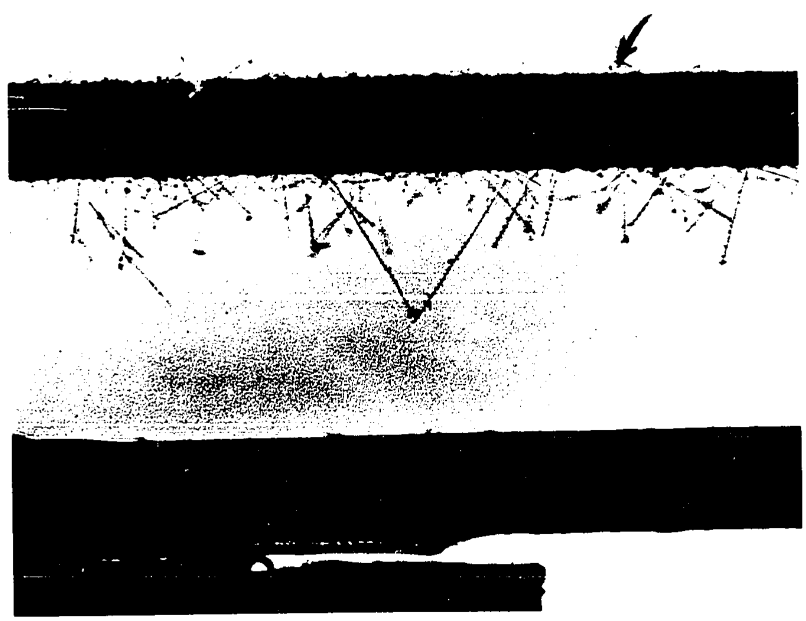

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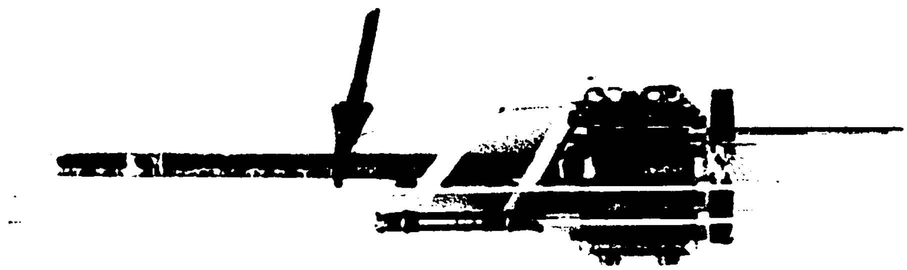

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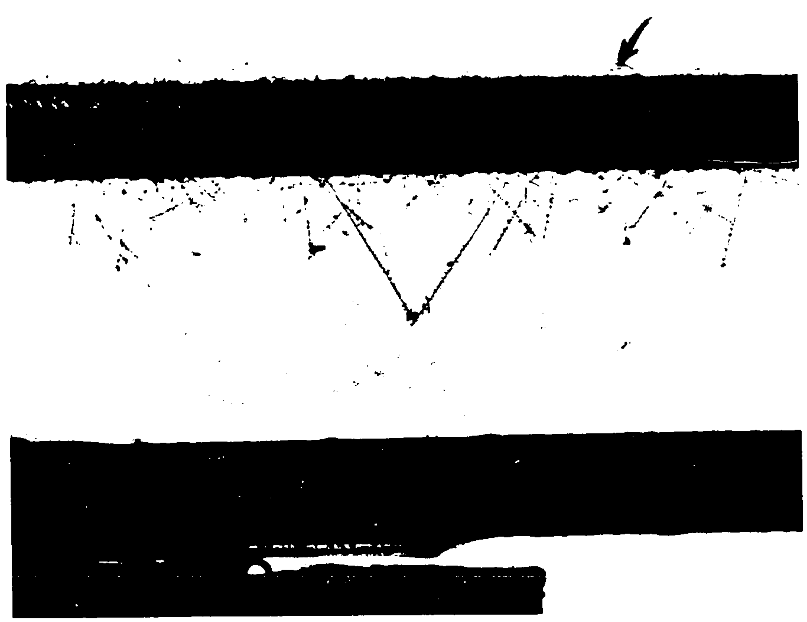

Fig. 2 - Tin whiskers on relay contact spring.
Magnification 13X.

substrates. Tin whiskers have grown on tin films evaporated onto paper and freshly cleaned mica but the growth process is usually longer and the whiskers smaller. Whiskers have also grown on bulk materials such as tin, cadmium and zinc. Solder alloys containing 30 percent lead, tin-lead-silver alloy containing 34 percent lead and 6 percent silver, and tin-aluminum alloys developed whiskers. No whiskers have been reported on lead.

At elevated temperatures, brass (65 copper - 35 zinc), columbium, copper, gold, iron, lead, magnesium, molybdenum, nickel, palladium, platinum, silver, tantalum, titatium, tungsten and zinc developed whiskers[4,5]. In Fig. 3 the growth occurred at a temperature of 400°C (752°F) during a period of 60-140 hr of heating except for lead where whiskers appeared at 200°C (392°F)[5].

Whiskers have not been observed on high purity metal, such as zone refined tin, or on single tin crystals of nominal purity, but whiskers were observed at grain boundaries of polycrystalline materials and on the surface of the individual grains. Crystals in whisker forms have been grown from non-metallic materials such as silicon dioxide, silicon carbide, aluminum oxide, sapphire and graphite (Figs. 4-6).

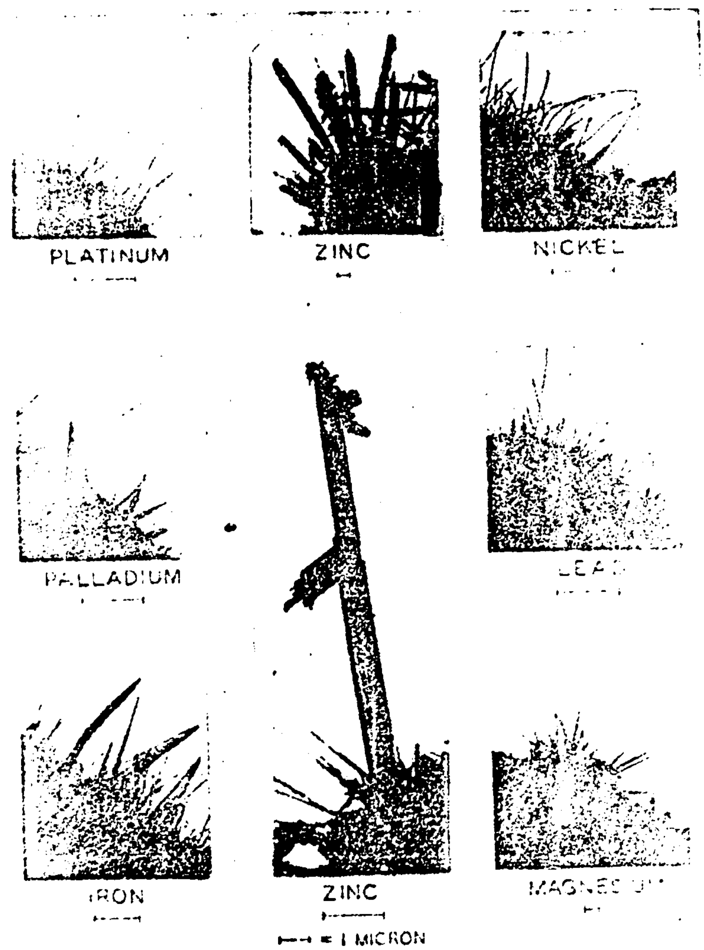

Fig. 3 - Whisker growth at elevated temperatures[5].

Fig. 4 - Aluminum nitride-oxide whiskers.

Fig. 4 - Aluminum nitride-oxide whiskers.

ABSTRACT

The growth of filiform crystals (whiskers) on tin coated surfaces can cause short-circuit failures in electrical systems particularly in miniaturized equipment. Tin whiskers grow sometimes in a matter of days and other times only after years to lengths up to 9 mm. (3/8in.) and 0.05 - 5.8 μm (2-240 micro-inches) in diameter. The mechanism of spontaneous growth is beleived to be a strain releif phenomenon and is affected by the temperature, atmospheric conditions, plating thicknesses and substrate, plating composition and operating bath conditions.

The co-deposition of 20-40 percent lead in the tin deposit reduces to a minimum the hazards associated with tin whisker growth and ensures a reliable corrosion protection and a good solder joint. Annealing in an inert atmosphere at a temperature of 191°C (375°F) - 218°C (425°F) for 4 hr after plating retards whisker formation.

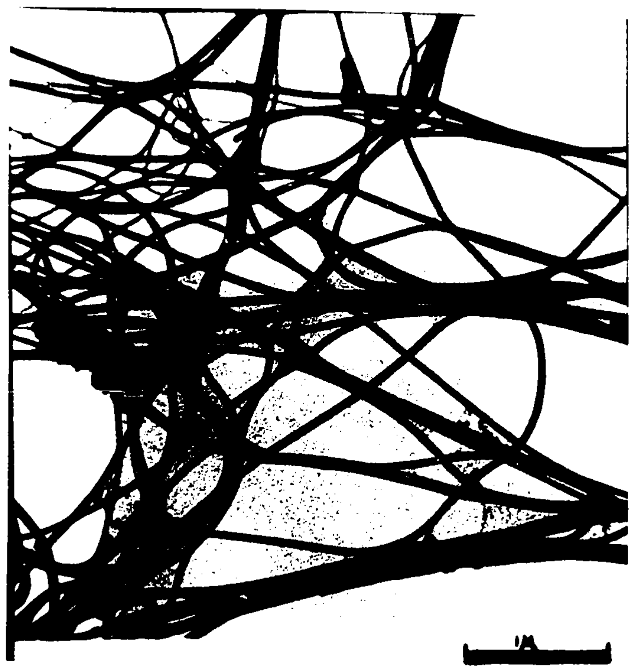

Fig. 5 - Cobweb sapphire wool
Average whisker thickness: 0.035 μm
(1.4 microinches)

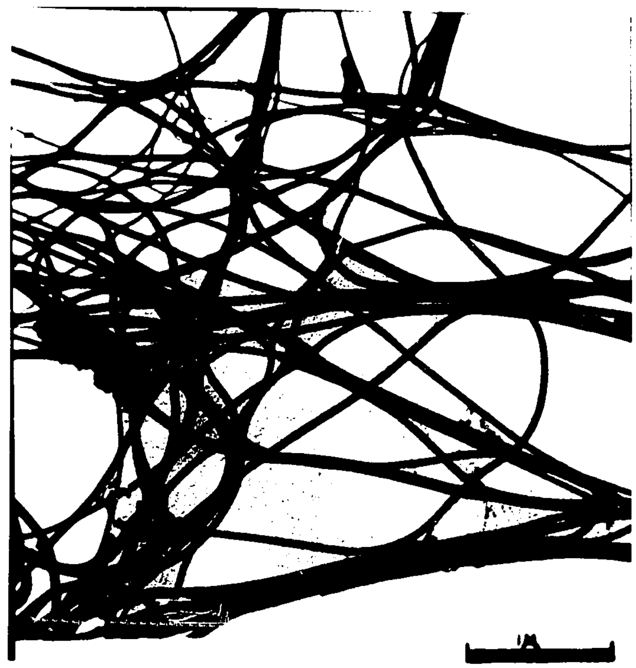

Fig. 5 - Cobweb sapphire wool
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Fig. 6 - Sapphire whiskers at grain boundaries of cast aluminum - copper alloy. Whisker thickness: 10-30 μm (400-1200 microinches)

Fig. 6 - Sapphire whiskers at grain boundaries of cast aluminum - copper alloy. Whisker thickness: 10-30 μm (400-1200 microinches)

Although in the communication industry the whisker growth phenomenon can cause serious problems in miniaturized electrical systems where spacings between components are small, the high strength filaments of the whiskers have been exploited to make high strength composite materials[6-9]. Composite materials of high strength and relatively low density such as the combination of silica whiskers and aluminum have been fabricated successfully; also other combinations such as sapphire whiskers in silver and various whiskers in nickel, epoxy and phenolic plastics have found practical use. The tensile strengths of whiskers tend to decrease with the increase in diameter, for example silicon carbide whiskers of 0.5 μm (20 microinches) in diameter exhibit a tensile strength of 10 million psi, but with increase in the whiskers' diameter to 1.5 μm (60 microinches) the tensile strength is reduced to 1.5 psi.

CHAPTER II

TIN PLATE

Tin plating is used on miscellaneous components to provide both solderability for reliable connection and corrosion protection against atmospheric conditions.

Tin also has a good shelf life, which is the time elapsed between the tinning and soldering processes. In general, a 6-month shelf life is considered satisfactory; after this period the corrosion products on the tin surface cause problems in soldering. Tin is easily soldered with other metals without the use of corrosive fluxes and readily alloys with most metals: when molten tin wets another metal it dissolves some of the solid surface. In some cases an interfacial layer of an intermetallic compound is formed. Tinning by electroplating or hot tin dipping will improve the surface conditions for a good joint in soldering.

Electroplating of tin can be performed by a variety of plating solutions depending on the application[10-12]. The most popular plating bath is the sodium or potassium stannate bath where the main chemicals are alkali metal stannates and alkali metal hydroxides. The operating temperature is 77^{o}C (170^{o}F). The deposit is dull white in colour and has a relatively good shelf life.

The stannous sulfate bath was not fully exploited until the recent introduction of the bright acid tin plating process[13]. The bath is composed of stannous sulfate and sulfuric acid with brightener agents and operates at room temperature. The deposit is bright and white in colour and has a longer shelf life and superior solderability than the stannate bath.

The fluoborate bath has been mainly used when high tin plating rates are required as in wire plating. The bath consists of stannous fluoborate with beta-naphtol and gelatin as addition agents and operates at room temperature. The deposit is usually white in colour and smooth, it has a good shelf life and can be easily soldered.

CHAPTER III

PROPERTIES OF TIN WHISKERS

Tin whiskers are single crystals commonly 1-2 µm (40-80 microinches) in diameter, but can vary from 0.05 to 5.8 µm (2-240 microinches). Lengths up to 9 mm (3/8 in.) have been reported[5,14] (Fig. 7). Whiskers are usually straight, but a change in the direction of growth can occur and the growth can be in the form of kinks and spirals (Figs. 8-10).

Tin whiskers may be solid, perforated or hollow[15]. They are tetragonal in section and it was found that the $\langle 001 \rangle$ and $\langle 101 \rangle$ crystallographic axes are whisker growth directions[5]. The external surfaces of the whiskers often have striations extending longitudinally along the length. These do not appear to have crystallographic origin and it was shown that some of the deeper striations were boundaries between two whiskers growing together[14].

Tin whiskers can grow in a relatively short period. Whiskers have been observed to grow in periods varying from days to years. It has been reported that individual whiskers grew 750 µm (1/32 in) in a month[5]. The rate of growth was not always constant. After a whisker has reached a certain length, its growth usually becomes slower and then ceases completely.

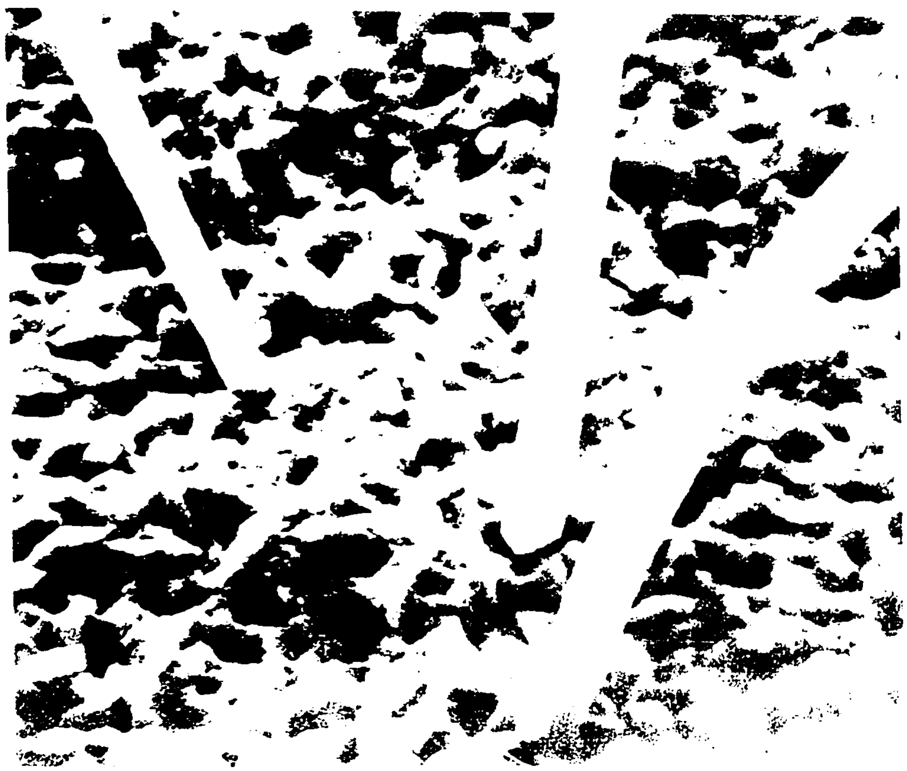

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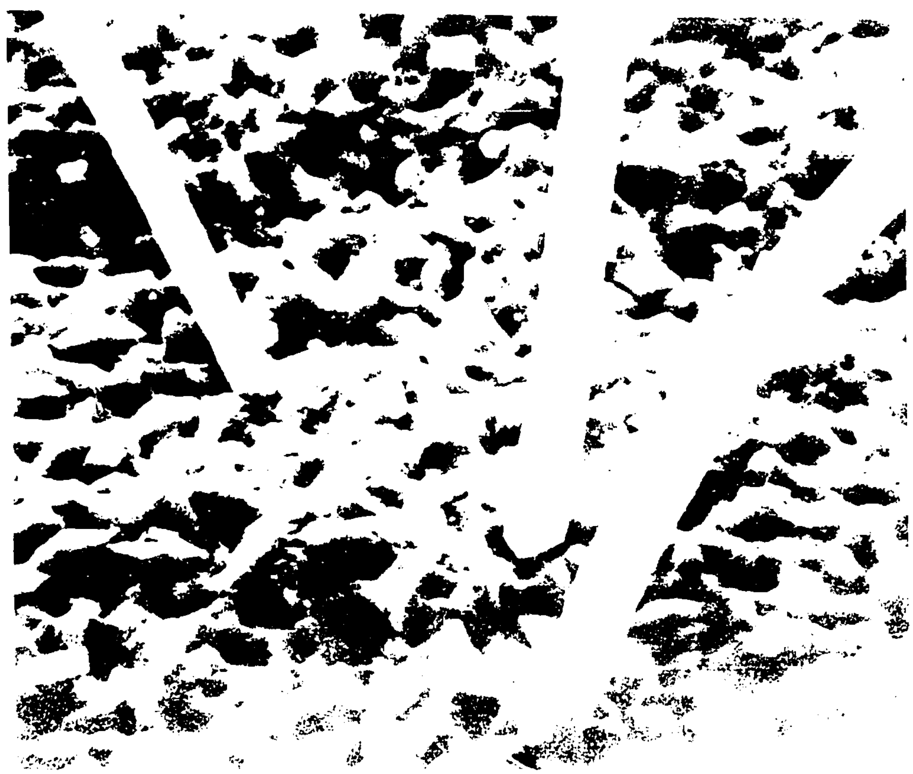
Fig. 7 - Tin whiskers .
Diameter: 5 μm (200 microinches).



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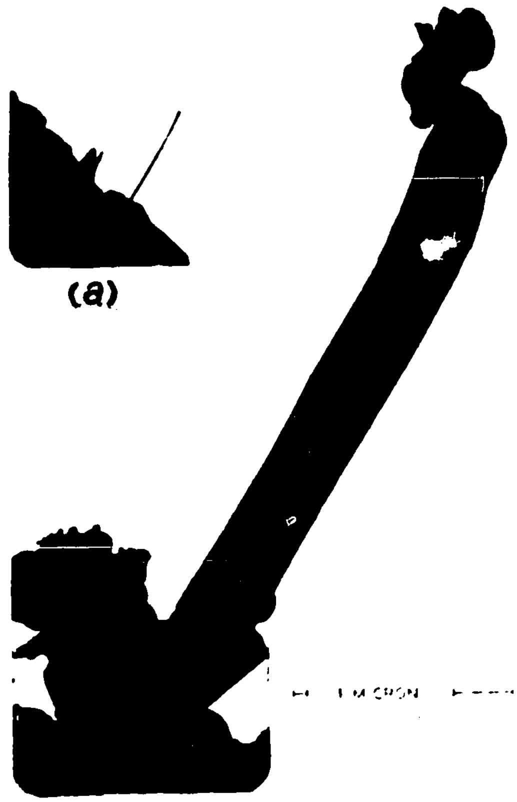


(a)

(b)

Fig. 8 – Tin whiskers growing straight[5].
Diameter: a) 0.05 µm (2 microinches)
b) 5.8 µm (240 microinches)

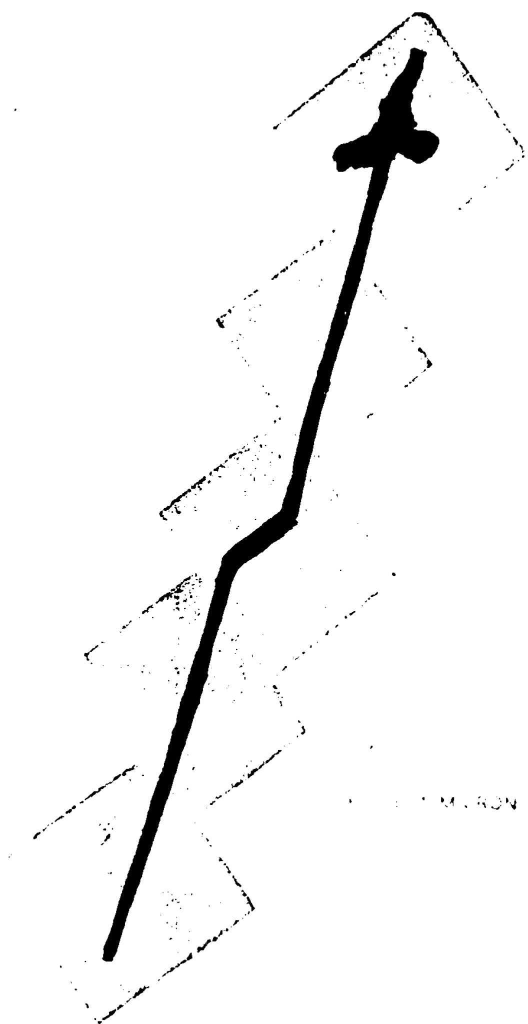


Fig. 9 - Change in direction during tin whisker growth[5].

Fig. 10 - Tin whiskers growing in spirals[5].

The electrical resistance of a tin whisker 3mm (1/8 in.) long is about 50 ohms and it has been reported that such a whisker has carried a current of 10 ma before burning out[5].

Tin whiskers have extremely high yield strengths and elastic strains of 1-3 percent were obtained which are as much as 100 times the maximum observed for the bulk material[16]. While possessing high intrinsic strength, tin whiskers can be easily broken by mechanical shocks and easily moved by a current of air.

CHAPTER IV

MECHANISM OF GROWTH

Although the exact cause and mechanism of tin whisker growth are not fully understood, several theories have been proposed to explain such behaviour.

It has been suggested that the whiskers develop at the site of a dislocation[17]. The driving force to produce the whiskers was thought to be an oxidation reaction on the tin plate surface which develops a stress which would cause a screw dislocation in the main mass to travel around the root of the whisker[18]. If the combination of the dislocation and oxidation theories were responsible for whisker growth, no whiskers could have developed in the absence of oxygen, but it was shown that tin whiskers could grow in vacuum[5,19], thus discrediting the dislocation-oxidation theory.

A second theory explained that the reason for whisker growth is the releif of stresses caused by hydrogen produced during the electroplating process and absorbed or occluded in the deposit[20]. Pockets of hydrogen accumulated under high pressure thus creating extremely high internal stresses in the metal much like the phenomenon of hydrogen embrittlement in steel[21]. The plated metal contained impurity particles which acted as weak points in the deposits through which the whiskers were extruded under the force of the entrapped hydrogen. However it was observed that tin deposited from a vapour phase on paper or freshly cleavaged mica grew whiskers under conditions that no hydrogen could have been present[2,5,15,19]. Furthermore, tin whiskers have grown on bulk metal[5,19] indicating that hydrogen evolved during electroplating is not a necessary cause.

The stresses in the deposit and the substrate play an important role in whisker growth. It has been determined that when compressive stresses are applied to bulk or electroplated metal, whiskers grow rapidly in proportion to the applied stresses[22]. Highly stressed bright tin deposits and bright copper undercoatings applied prior to tinning showed a marked increase in whisker density[23-25]. It was found that annealing prior and after plating tends to retard whisker formation[23], thus leading to the conclusion that the mechanism of whisker growth is a strain relief phenomenon.

It has been observed that the whisker tip remains unchanged during the period of growth, thus indicating that the accretion of material at the base is responsible for the whisker growth[19,26] (Fig.11). The energy required for growth arises from microstrains present in the metal. The absence of thinning of the tin plate around the base of the whisker[14] indicates that material is supplied to the base of the

Fig. 11 - Stages in growth of tin whiskers[19].

whisker by diffusion from the bulk material[15]. It seems that the atoms diffuse along screw dislocations in the material and that the whisker is extruded outwards by the applied external stresses or the internal stresses in the deposit.

CHAPTER V

FACTORS INFLUENCING WHISKER GROWTH

The results of many experiments into the factors affecting crystal growth are summarized as a background to selecting methods of controlling whisker growth in industrial applications. The most important factors which were found to affect the growth of tin whiskers serve as titles for the following subsections.

One difficulty encountered in setting out the summary was the conflicting findings from similar studies by different authors. For example, some specimens developed whiskers of various lengths, growth densities and incubation periods while others prepared identically by other researchers did not produce any whiskers. The non-uniformity of results is probably due to minor variations in specimen preparation which were not considered to be important and hence not noted, for example, slight differences in substrate conditions, or in operation of cleaning or plating baths.

5.1 Temperature

The ambient temperature shows marked effect on the rate of whisker growth. The optimum temperature for tin has been determined to be 52°C (125°F). Whisker growth decreases noticably above 121°C (250°F) and is completely eliminated above 150°C (300°F)[19]. At low temperature, whisker formation is not prevented but is only temporarily retarded. Whiskers were grown at temperatures as low as -40°C (-40°F)[5,19]. At such low temperatures, there appears another phenomenon, commonly called tin disease, tin pest or grey tin transformation which is characterized by eruption of the electroplated tin deposit and the formation of a powdery substance[27]. This happens as a result of the transformation of metallic tetragonal white β tin to non-metallic diamond-cubic α tin below 13°C (56°F). The accompanying increase in volume (27 percent) causes cracks and powdering of the deposit.

5.2 Atmosphere, Irradiation and Stress

The growth of tin whiskers is not directly related to the surrounding medium. It was shown that whiskers developed under a variety of conditions ranging from high vacuum to high relative humidity[5,19]. In support of this, whisker growth was noted at room temperature in an atmosphere of oxygen at 98 percent relative humidity and in a vacuum of 10^{-3} mm Hg[24]. Whiskers were reported in perfectly sealed components, in evacuated containers, or when exposed to dry nitrogen[2,5,19]. An increase in the relative humidity tends to increase the whisker density[2,5].

When tin plated specimens were exposed to neutron bombardment for approximately 30 days at a flux density of 10^{12} cm^{-2} sec^{-1}, a dense growth of whisker density was observed after one year. In comparison, specimens not irradiated showed very little growth[5].

High frequency vibration of tinned or soldered joints on piezoelectric devices produced stresses in the joints and initiated whisker growth[2].

High compressive stresses from screws, bolts and pressure clamps developed whiskers regardless of the coating composition[2,28]. It has been reported that a pressure of 3,000-4,000 psi will cause whiskers to develop in a matter of seconds to lengths normally requiring 6 or 8 months when exposed under atmospheric pressure[19].

5.3 Thickness of Tin Deposits

Thinner tin electrodeposits were found to be more susceptible to whisker growth than thicker coatings[1,5,23,24]. Observations on three different tin plating thicknesses: 1.25 μm (50 microinches), 5 μm (200 microinches) and 12.5 μm (500 microinches) revealed that all specimens grew whiskers, but the ones with the thinner coatings developed the highest whisker density[1]. On the other hand it was observed that no whiskers formed on 0.5 μm (20 microinches) tin deposits[24] which is probably due to the fact that the plating thickness was less than the average whisker diameter.

In general the highest internal stresses have been found in thin electroplated deposits, and upon further plating stresses decrease as deposits thicken. This fact emphasizes the idea that internal stresses in the deposits play an important role in tin whisker growth.

5.4 Substrate of Tin Deposits

The base metal or the undercoating prior to tin electroplating plays an important role in whisker formation.

Several investigations have shown that no whiskers developed on tin plated steel[23,25]. However, other investigations revealed the presence of whiskers on tin plated steel[1,5,14,19,24], but their growth seems to be slower than with other base metals.

It has been reported that whiskers did not grow on tin coatings on brass[5], but other works[1,14,19,23,25] showed a high whisker density and a short incubation period (which is the period elapsed between tinning and the appearance of the first whisker) when tin was plated directly on brass.

Whiskers were found on tin plated onto copper substrates[5,14,19,24] but their growth density was small. Other tin plated substrates developed whiskers such as beryllium-copper, phosphor bronze[14], zinc, nickel and tin[24].

The minimum incubation period and the maximum rate of whisker growth was found on tin coated brass and zinc. The rate of whisker growth on tin coatings plated on brass is more than that on tin coated to steel[24].

Whiskers developed on tin coatings applied to a copper under-coating plated on a brass substrate prior to tinning[5,19,23,25]. Slight whisker formation was observed on tin plated onto a gold undercoating on brass[5]. No whiskers were observed on tin coatings applied to tin-nickel undercoatings on brass[25]. Tin plated onto an iron undercoating on brass produced heavy whiskers[15,19].

It was observed that tin applied to a copper undercoating on a steel substrate developed whiskers[1,23,25]. No whiskers were found on tin coatings applied to either a silver or a gold undercoating on steel[23,24]. It was determined that no whiskers were formed in the case of a nickel undercoating on steel[23], but other experiments with the same undercoating revealed the presence of tin whiskers[24]. An iron under-coating on steel did not give rise to whiskers on the tin surface[24]. A tin plated duraluminum substrate with a zinc or copper undercoating developed whiskers, but did not with a nickel undercoating[24].

The susceptibility of tin coatings to whisker growth has some parallel with the extent to which they diffuse with the substrate[24,25]. Analysis of tin whiskers from a brass substrate revealed that they contain tin and zinc, thus leading to the assumption that the zinc atoms diffused from the brass substrate to the tin coating[24].

5.5 Tin Plating Bath Compositions

Although it has been reported that bright tin deposits did not grow whiskers[13], there is substantial evidence that bright tin deposits are more prone to grow whiskers that matt coatings[23,25]. In a series of experiments, deposits from both the dull stannate and bright sulfate plating baths were analyzed under various conditions and results show that all the specimens from the bright tin bath developed heavier whiskers than the stannate bath except in the case of a nickel undercoating where no whiskers were observed in either cases[23]. The reason for more pronounced whisker growth on bright tin plating might be due to the high internal stresses in the deposits and the greater rate of diffusion from the substrate to the bright tin coatings than with the matt ones[25]. Others experiments showed that tin deposits on a brass substrate from a stannate bath have a longer incubation period than deposits from a sulfate bath; but in the case of a steel substrate the incubation period is longer for tin deposits from a sulfate bath than from a stannate bath[24].

5.6 Tin Plating Operating Conditions

An unusually high current density of 9 amp/dm^2 (90 amp/ft^2) in an acid bright tin bath was shown to give a short incubation period and whiskers developed within days on a copper wire[25]. On the other hand it was shown that the current density in the range of 0.3 - 1.2 amp/dm^2 (3-12 amp/ft^2) in an acid sulfate bath without brightening agents does not affect the rate of tin whisker growth; but when the current density was raised to 2-3 amp/dm^2 (20-30 amp/ft^2) the rate of whisker growth decreased by 50 percent and the incubation period was increased by 3-4 months[24]. An increase of 11 ^oC (20 ^oF) in the potassium stannate bath temperature resulted in a marked decrease in whisker density[23]. It was found that tin coatings deposited from an acid sulfate bath at low temperatures are more susceptible to whisker growth than the ones deposited at room temperature[24].

The use of periodic reverse current in the plating bath was claimed to eliminate whisker formation by dissipating the hydrogen produced in the plating process and thus reducing the stresses in the deposit[20]. However it was shown that this does not eliminate the whisker formation, but rather has a tendency to reduce its density[23]. Another investigation found that the periodic reverse current in the plating bath does not affect tin whisker growth[24].

The use of ultrasonic agitation in the plating bath to dissipate any entrapped hydrogen in the deposit was claimed to eliminate the formation of tin whiskers[20]. Even though tin deposits were whisker free after a 6-year period[23], the theory linking the growth to hydrogen occluded in the deposit during the electroplating operation has been discredited as mentioned in Chapter IV.

5.7 Alloying Tin Deposits

In order to obtain a coating that has approximately the same characteristics as tin with respect to solderability and corrosion resistance and that is a safe finish regarding whisker growth, studies were carried out on tin-alloys to determine their tendency to whisker formation.

Tin-arsenic, tin-zinc, tin-cadmium deposits were investigated but all of them grew whiskers. Tin-nickel coatings were found free of whiskers for over 9 years, but the introduction of nickel made the deposit more difficult to solder[24,28]. Tin-copper deposits showed a marked improvement in the reduction of whisker growth density and an increase in the incubation period[24,28]. Tin-bismuth, tin-tellerium, tin-sodium and tin-antimony showed some slight improvement in the whisker reduction[24]. Bismuth and antimony in the deposit are also effective in preventing tin conversion from white to grey tin[27].

It was found that the plating solutions used to produce tin-alloy deposits were not practical to operate in production and tight controls were required to maintain the proper concentrations of the poisoning metals.

It has been shown that tin-lead deposits containing 40 percent lead have a higher incubation time than tin deposits[24]. Even though some whiskers were reported on tin-lead coatings containing 30 percent lead at room temperature[5], their maximum length of approximately 50 µm (2,000 microinches) means that they are of much less consequence than those on pure tin[28]. Another investigation carried out on various tin-lead alloy compositions[14] determined the absence of whiskers after 4.5 years on 20 and 40 percent lead alloy deposits. Some nodule-like structures or rounded protruberances were observed on 0.5 and 5 percent lead alloy deposits, the maximum length obtained on the 5 percent lead specimen was about 10 µm (400 microinches). The same nodule-like structures were found on one percent lead alloy deposit and their maximum length was about 7.5-10 µm (300-400 microinches)[28].

Whisker formation on tin-lead alloys of various concentrations is limited to an extended nodular growth from the surface of the deposit and are rather curved than straight. Moreover the tin-lead plating process is easily carried out and can be adjusted to the desired alloy composition[10-12]. The most popular bath is the fluoborate bath with peptone, bone glue or proprietary brighteners as addition agents to provide grain refinement. Lead-tin deposits have a good shelf life and are easily soldered without the use of corrosive fluxes[29].

5.8 Annealing

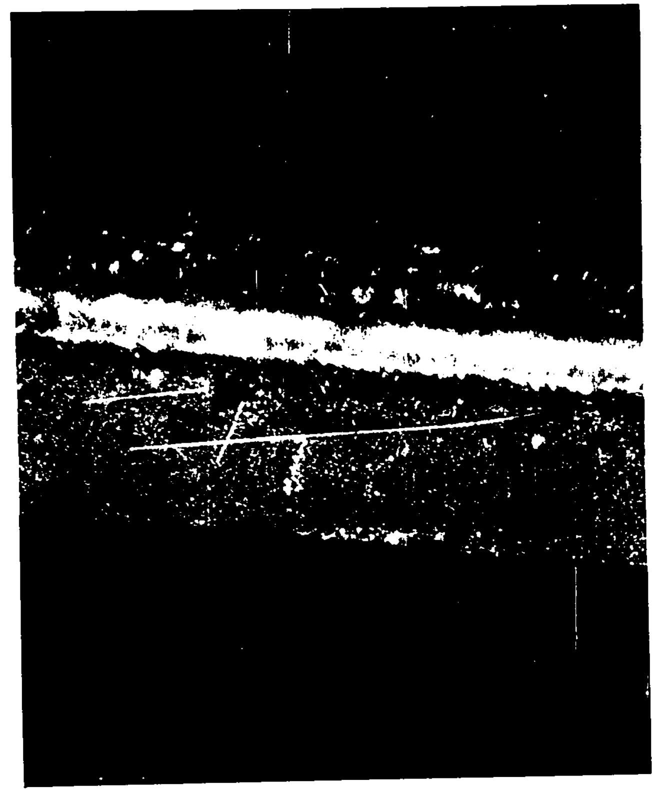
Annealing of tin deposits after plating was found to have a retarding effect on the whisker growth[23,24]. The process consists of heating the tin plated parts in an inert atmosphere for 4 hr at a temperature between 191°C (375°F) and 218°C (425°F) in order to relieve stresses in the plating[30]. Nitrogen is usually used in order to prevent the tin from oxidizing during annealing. The highest annealing temperature and the longest heating period result in a slower whisker growth rate and an increase in the incubation period. After a period of 3.5 years no whiskers were observed on tin which was plated on a copper undercoating from either the sulfate or stannate baths and which had been annealed at temperatures between 100°C (212°F) for 6 to 9 hr and 180°C (350°F) for 1 hr[24].

No whiskers were observed after a 4 and 6 year periods on brass specimens which had been plated from a potassium stannate bath when they were annealed at 191°C (375°F) for 3 hr[23]. Annealing the parts prior to tin plating at 191°C (375°F) for 3 hr also seems to result in a decrease in whisker density as compared to unbaked parts[23,30].

There have been reports which do not agree with the above results. Whiskers were reported when tin plated specimens on steel substrates were annealed at 165°C (329°F)[1]. Also whiskers were found after a period of 4 years on tin coatings applied to a copper undercoating plated on steel from the potassium stannate bath, which were annealed at 194°C (380°F) for 4 hr in a nitrogen atmosphere[31]. Figs. 12 and 13 show tin whiskers that grew after annealing to a length of 2.25 mm (3/32 in.).

Bright tin deposits from a sulfate bath developed few whiskers in a 4 year period when annealed in nitrogen at 191°C (375°F) for 4 hr after plating[23]. Unfortunately at such temperature, the bright tin coatings blister and form brittle deposits due to the occlusion of organic brighteners in the coating (Figs. 14-16). One report[32] stated that this blistering and cracking effect occurred only in bright tin deposits plated in barrels and baked in a nitrogen atmosphere at temperatures between 160°C (320°F) and 218°C (425°F) but not on parts plated on racks in a bright sulfate bath and subsequently baked. However, in actual production runs parts either rack or barrel-plated in a proprietary bright sulfate bath did develop blisters and cracks when baked in a nitrogen atmosphere between 160°C (320°F) and 218°C (425°F). One must then

Fig. 12



31 Fig. 13

Tin whiskers after annealing .
Length: 2.25 mm (3/32 in.) after 4 years.
Magnification 34X

Fig. 12

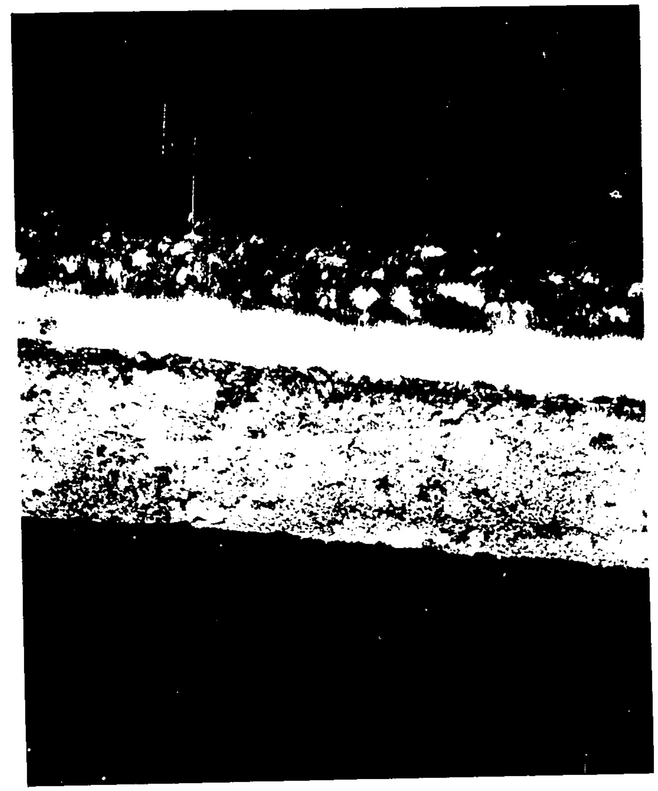


Fig. 13

Tin whiskers after annealing .
Length: 2.25 mm (3/32 in.) after 4 years.
Magnification 34X

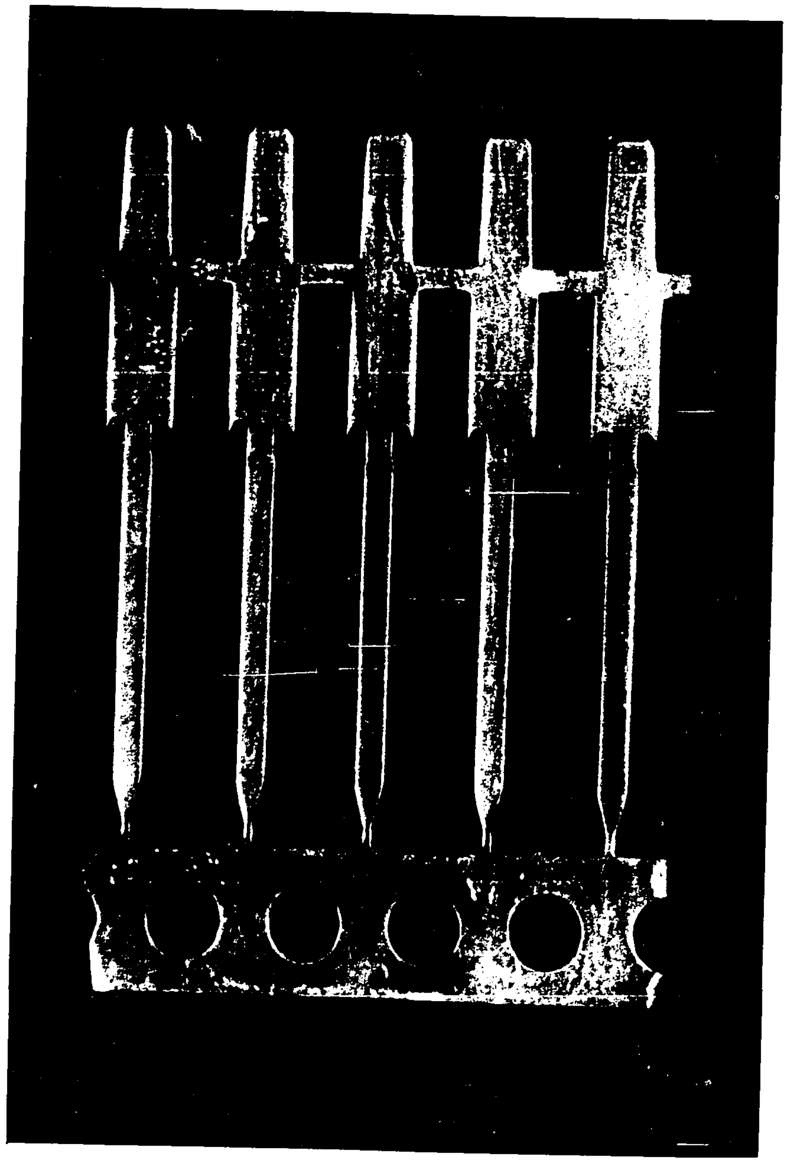


Fig. 14 - Bright tin deposit.
Magnification 3.3X

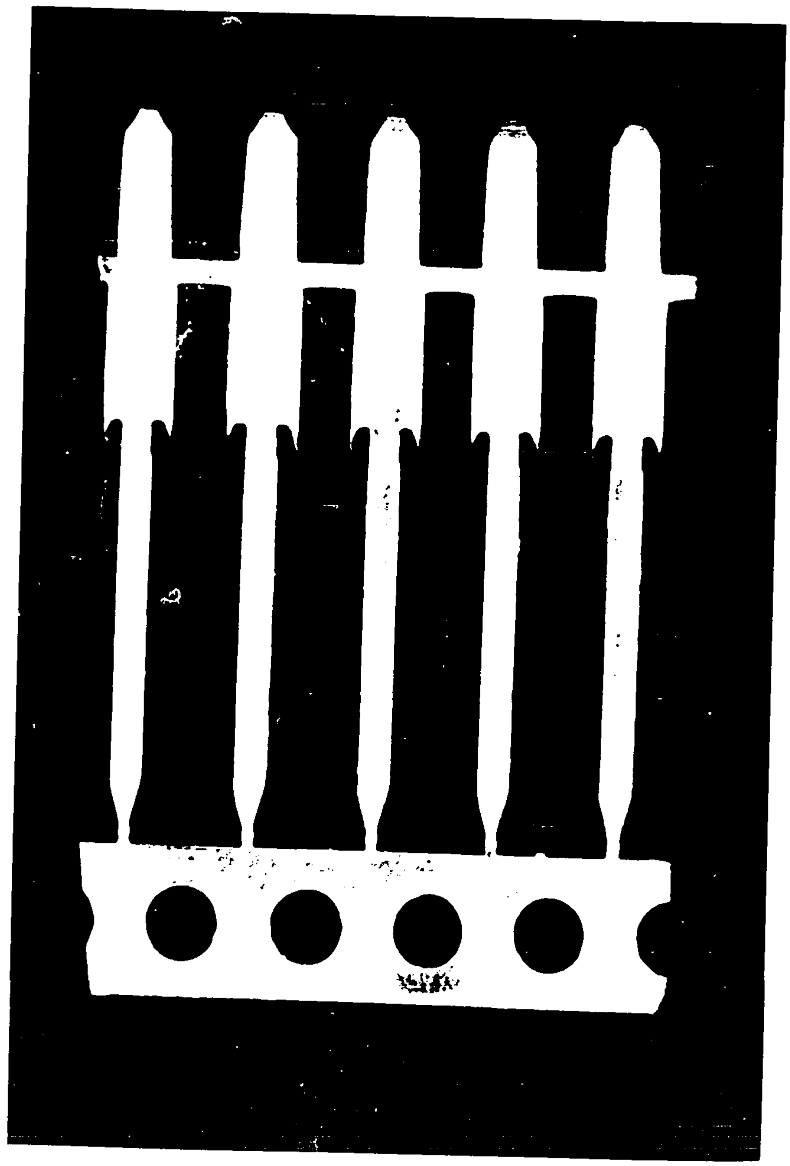


Fig. 14 - Bright tin deposit.
Magnification 3.3

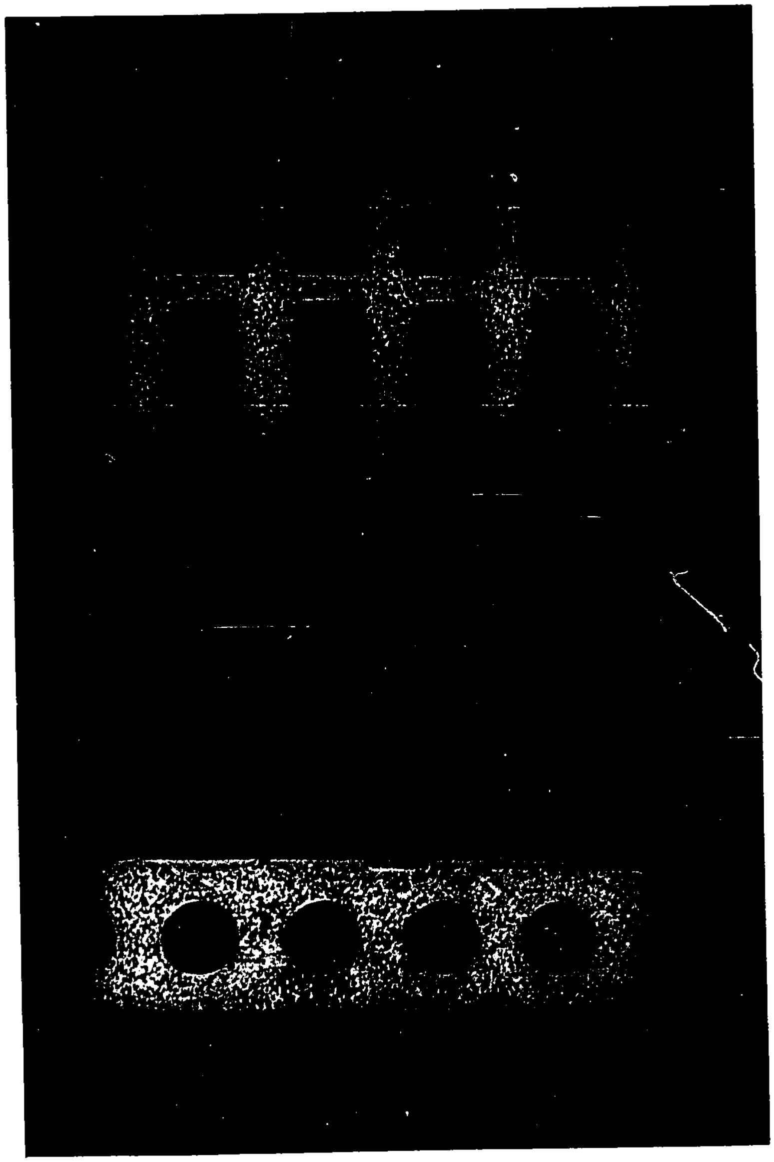


Fig 15 - Blisters on bright tin deposit after annealing at 191°C (375°F) for 4 hr in nitrogen. Magnification 3.3X

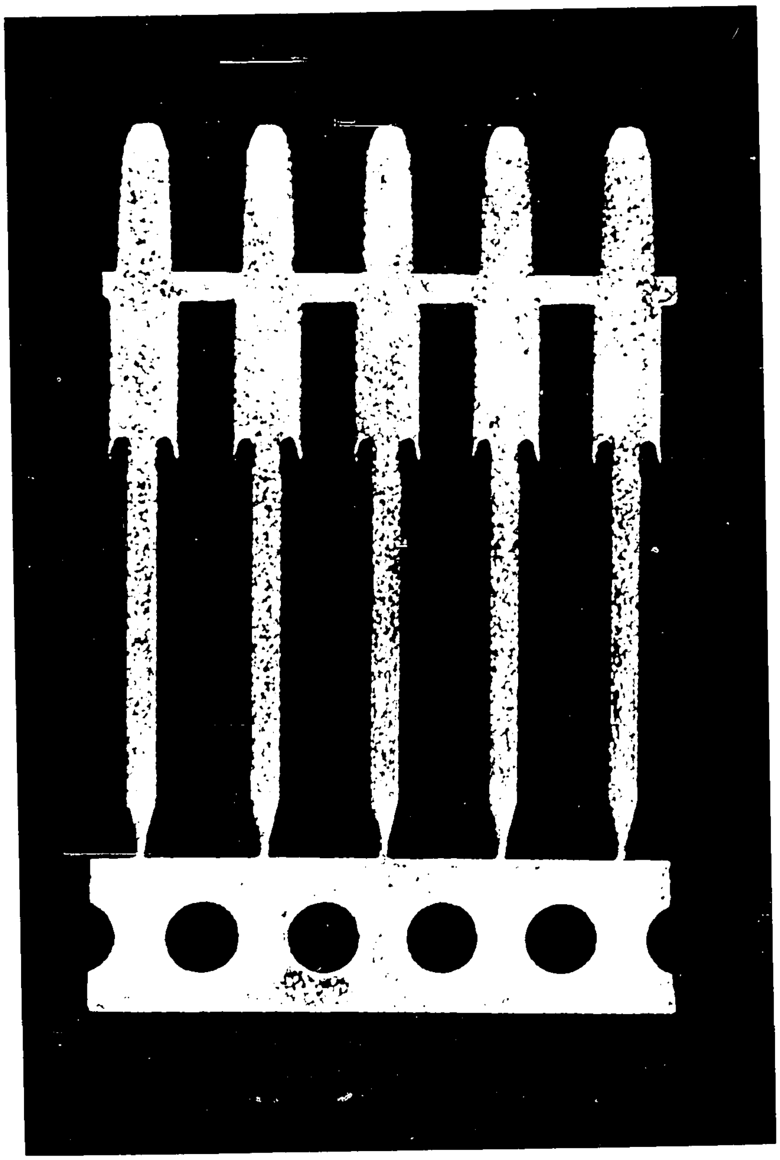


Fig [illegible] – [illegible]
after [illegible]
for 4 hr [illegible]
Magnification [illegible]

Fig. 16 - Brittle bright tin deposit bent after annealing at 191°C (375°F) for 4 hr in nitrogen. Magnification 3.3X

Fig. 16 - Brittle bright tin deposit bent after annealing at 191°C (375°F) for 4 hr in nitrogen. Magnification 3.3X

conclude that the baking operation as a means to control whisker growth is not suitable for bright tin deposits plated from proprietary sulfate baths.

The effectiveness of the heat treatment of tin plated parts with a copper undercoating for retarding whisker growth[23,24] is partly due to the formation of an interdiffusion layer of copper and tin after annealing at a temperature of 191°C (375°F). It was also determined that substantial thickness of the diffusion layer did not form in a reasonable time at temperature below 150°C (300°F)[31].

As shown in Figs. 17 and 18, there are three distinct layers: brass, copper and tin prior to annealing. In Fig. 19, after annealing, a copper-tin diffusion layer is formed. In Fig. 20, after annealing, no copper zone was left since the copper and tin had interdiffused and zinc had diffused from the brass into the copper-tin layer. The interesting fact in this figure is that a copper-tin alloy of various concentrations is formed after annealing.

Annealing of tin plated parts is thus a method of retarding the formation of whiskers but has by no means eliminated their growth. The retardation effect of annealing supports the theory that internal stresses in the deposits have a major function in the mechanism of whisker growth.

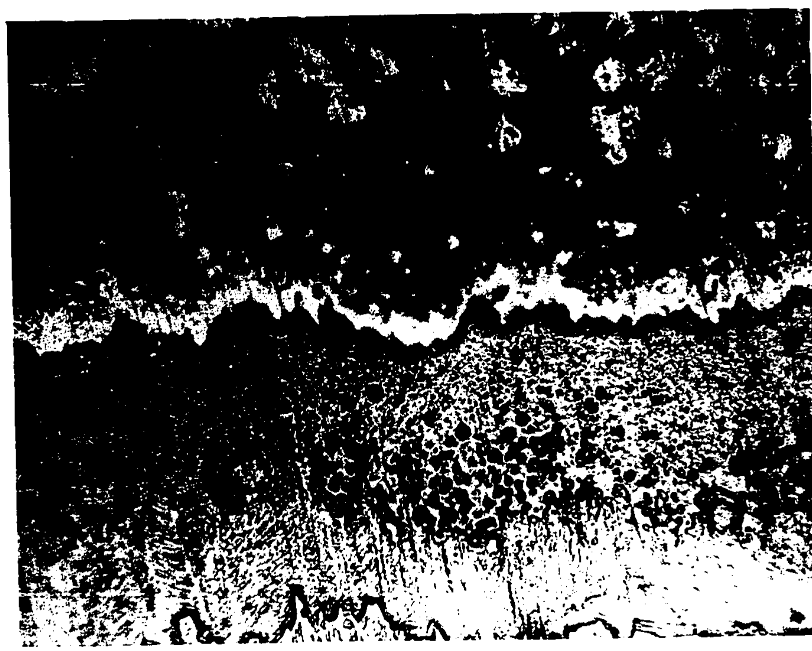


Fig. 17 - Cross-section of tin plated onto a copper undercoating on brass.[31]

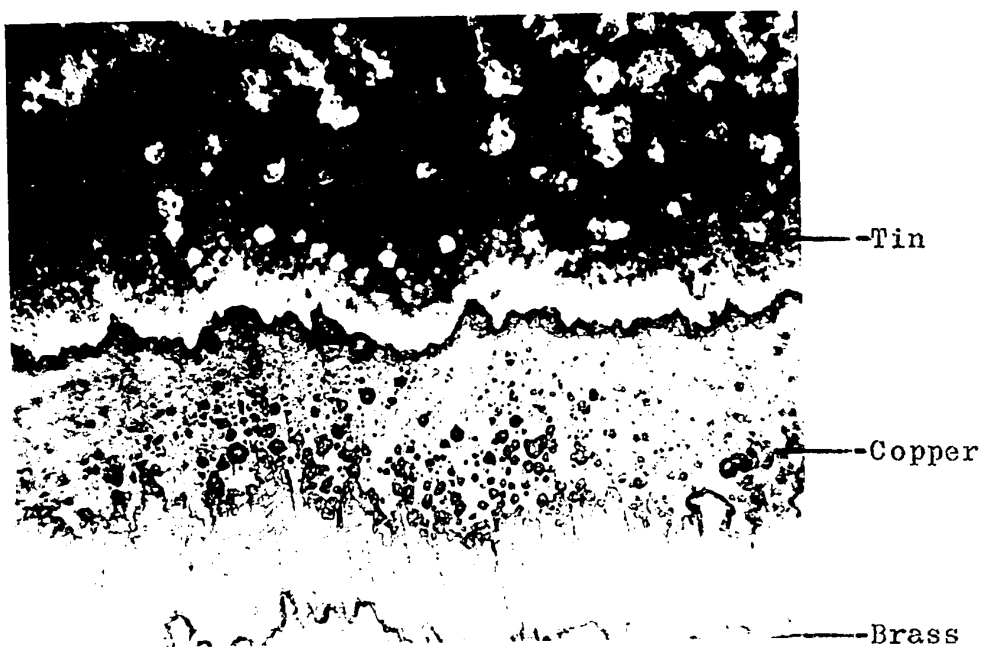


Fig. 17 - Cross-section of tin plated onto a copper undercoating on brass.[31]

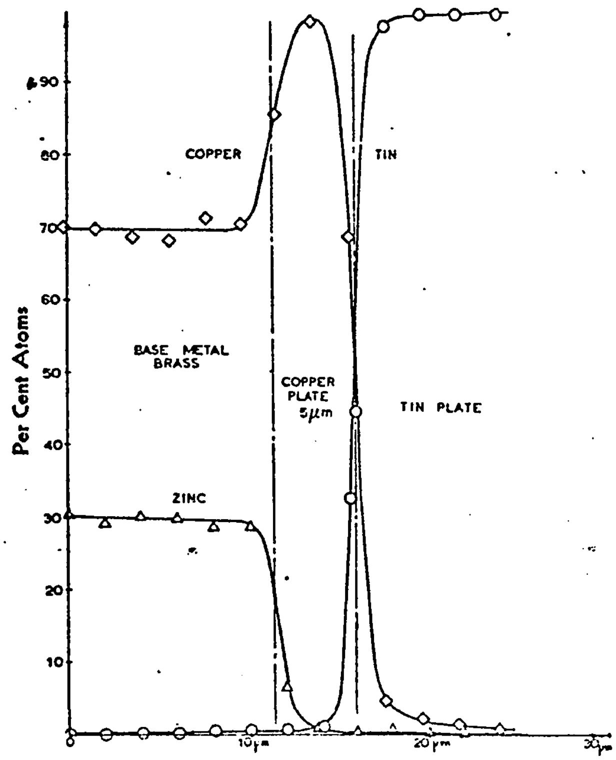


Fig. 18 - Concentrations of copper, zinc and tin of tin plated onto a copper undercoating on brass.[32]

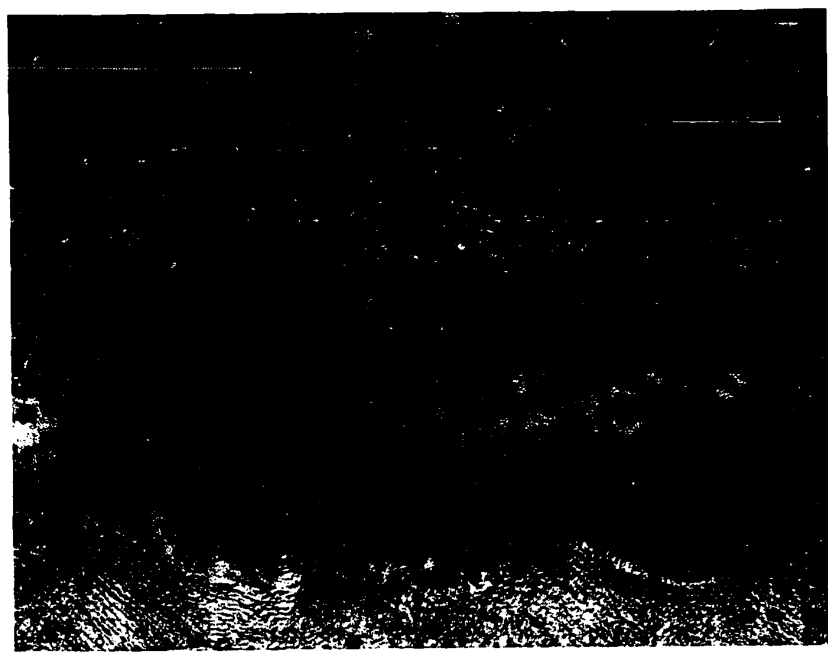


Fig. 19 - Cross-section of tin plated onto a copper undercoating on brass after annealing at 191°C (375°F) for 4 hr in nitrogen[31].

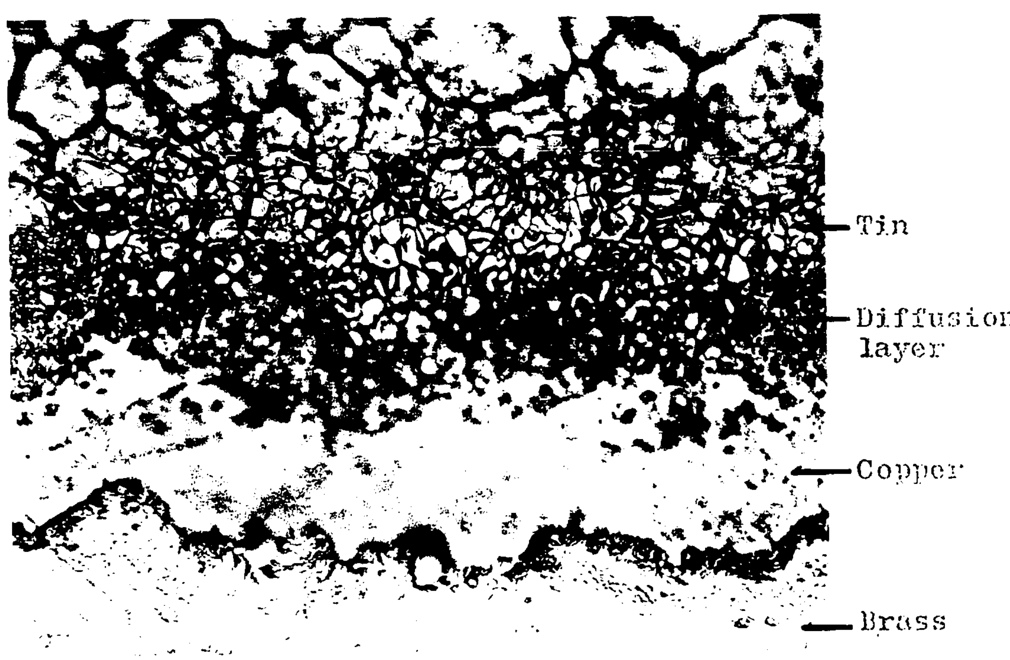


Fig. 19 – Cross-section of tin plated onto a copper undercoating on brass after annealing at 191°C (375°F) for 4 hr in nitrogen[31].

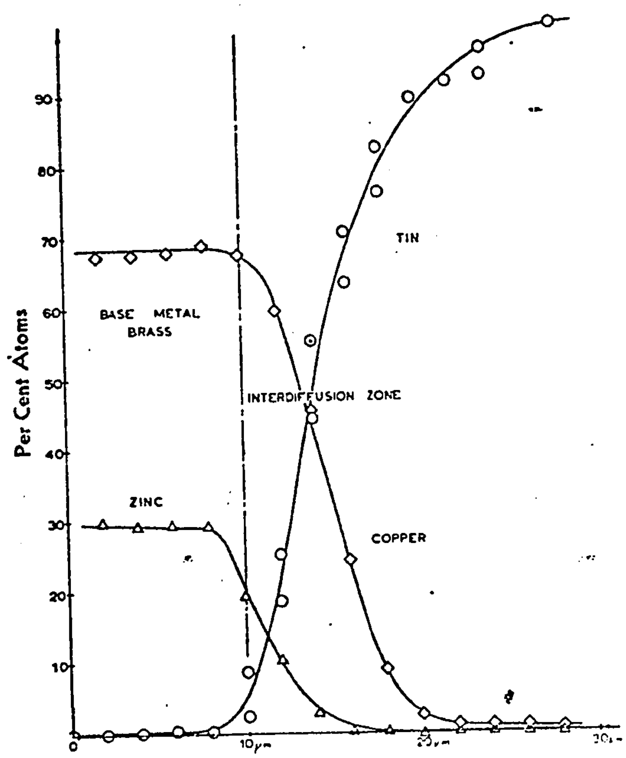


Fig. 20 - Concentrations of copper, zinc and tin of tin plated onto a copper undercoating on brass after annealing at 191°C (375°F) for 4 hr in nitrogen[32].

CHAPTER VI

EXPERIMENT ON COMBINED FACTORS

6.1 Experimental Techniques

In order to understand the behaviour of tin whiskers and select methods to repress or minimize their growth, an investigation was carried out on tin electroplated deposits by applying stresses to the specimens and varying the operating plating and annealing conditions[23].

Square U-shaped channels, made from steel and brass, were plated in baths of different compositions to a uniform thickness of 1.25 μm (50 microinches) and subjected to a variety of treatments. The channels were then fixed on jigs (Fig. 21) and were twisted in order to induce sufficient stresses to accelerate the rate of whisker growth.

The specimens were stored undisturbed in a dark steel cabinet at room temperature and normal atmospheric conditions for periods of 2,4 and 6 years. The specimens were withdrawn and examined under a low power microscope (30X) and in doubtful cases under higher magnification (60X).

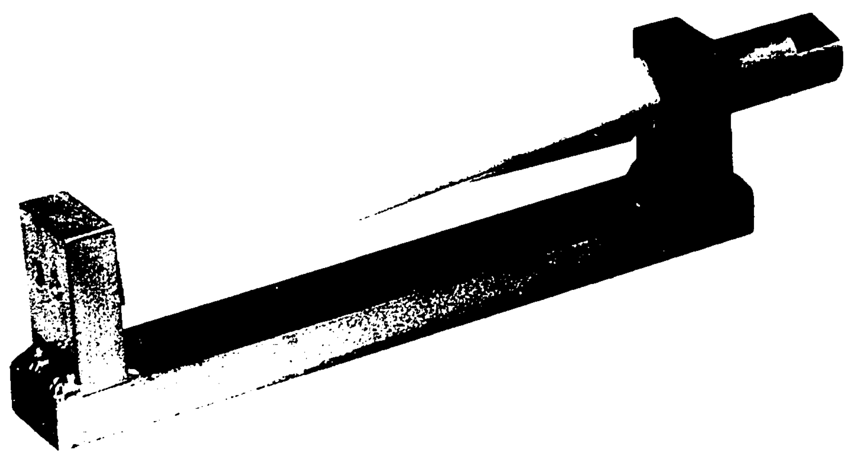


Fig. 21 - Square U-shaped channels under stresses[23].

6.2 Experimental Results

The results for channels made of brass and plated from a potassium stannate bath are given in Table 6.1. The deposit was matt in appearance after plating. Variations such as bath temperature, and cleaning solutions altered the growth behaviour slightly. Pre-annealing or reverse polarity plating reduced whisker growth markedly (Fig. 22). Ultrasonic agitation or post annealing resulted in preventing whisker growth entirely.

The results for channels made of carbon spring steel and plated from a potassium stannate bath are given in Table 6.2. The deposit was matt in appearance after plating. Pre-annealing reduced whisker growth. Copper undercoating plated on the channels increased whiskers formation. Gold, silver, or nickel undercoatings on the channels resulted in preventing whisker growth.

The results for channels made of brass and plated from a bright sulfate bath using proprietary brighteners are given in Table 6.3. The deposit was bright in appearance after plating. Post treatment reduced whisker growth. Copper undercoating plated on the channels increased whisker growth. Nickel undercoating plated on the channels resulted in prevention of whisker formation.

TABLE 6.1

Effect of Plating Operating Conditions and Annealing

on Whisker Growth

from a Potassium Stannate Bath

Sample #	No of Samples	Base Metal	Pre-treament	Bath Temp.	Current Density Power Supply	Post Treatment	Results of Examination after 4 yrs	Results of Examination after 6 yrs
1.	(3)	brass	$HNO_3+H_2SO_4$	77°C(170°F)	3amp/dm²(30amp/ft²) D.C.	Nil	heavy whiskers	same result as after 4 yrs
2.	(3)	"	"	88°C(190°F)	"	"	light whiskers	"
3	(3)	"	Annealed at (191°C) 375°F for 3 hr then cleaned as in #1	77°C(170°F)	"	"	very light whiskers	"
4	(2)	"	5% Na cyanide	88°C(190°F)	"	"	light whiskers	"
5	(2)	"	Same as #1	77°C(170°F)	"	Annealed at 191°C (375°F)for 3 hr	no whiskers	"
6	(2)	"	Same as #1	"	3amp/dm²(30amp/ft²) Reverse polarity 7:1 2 1/2 min.	Nil	very few single whiskers	"
7	(3)	"	Same as #1	"	3amp/dm²(30amp/ft²) Ultrasonic Agitation 2 min.	"	no whiskers	"
8	(3)	"	Same as #3	"	"	Annealed at 191°C (375°F) for 3 hr	"	"

TABLE 6.2

Effect of Undercoatings on Whisker Growth

from a Potassium Stannate Bath

Sample #	No of Samples	Base Metal	Pre-treatment	Bath Temp.	Current Density Power Supply	Post Treatment	Results of Examination after 2 yrs	Results of Examination after 6 yrs
9	(2)	carbon spring steel	heat treated to RC 35-40	77°C(170°F)	3amp/dm^2(30amp/ft^2) D.C.	Nil	no whiskers	same result as after 2 yrs.
10	(2)	"	same as #1 plus Cu 1.25 µm (50 microinches) annealed at 205°C (400°F) 4 hr	"	"	"	short whiskers	"
11	(2)	"	same as #1 plus Cu 1.25 µm (50 microinches)	"	"	"	heavy whiskers	"
12	(3)	"	same as #1 plus Au 1.25 µm (50 microinches)	"	"	"	no whiskers	"
13	(3)	"	same as #1 plus Ag 1.25 µm (50 microinches)	"	"	"	"	"
14	(2)	"	same as #1 plus Ni 1.25 µm (50 microinches)	"	"	"	"	"

TABLE 6.3

Effect of Undercoatings and Annealing on Whisker Growth from a Bright Sulfate Bath

Sample #	No of Samples	Base Metal	Pre-treatment	Bath Temp.	Current Density Power Supply	Post Treatment	Results of Examination after 4 yrs
16	(3)	Brass	$HNO_3+H_2SO_4$	20°C(68°F)	1 amp/dm^2(10 amp/ft^2) D.C.	Annealed at 191°C (375°F)for 4 hr	few whiskers
17	(3)	"	"	"	"	Nil	heavy whiskers
18	(3)	"	$HNO_3+H_2SO_4$ Cu 1.25 μm (50 microinches)	"	"	Annealed at 191°C (375°F) for 4 hr	very few single whiskers
19	(3)	"	"	"	"	Nil	whiskers up to 750 μm (1/32 in)
20	(3)	"	$HNO_3+H_2SO_4$ Ni 1.25 μm (50 microinches)	"	"	"	no whiskers

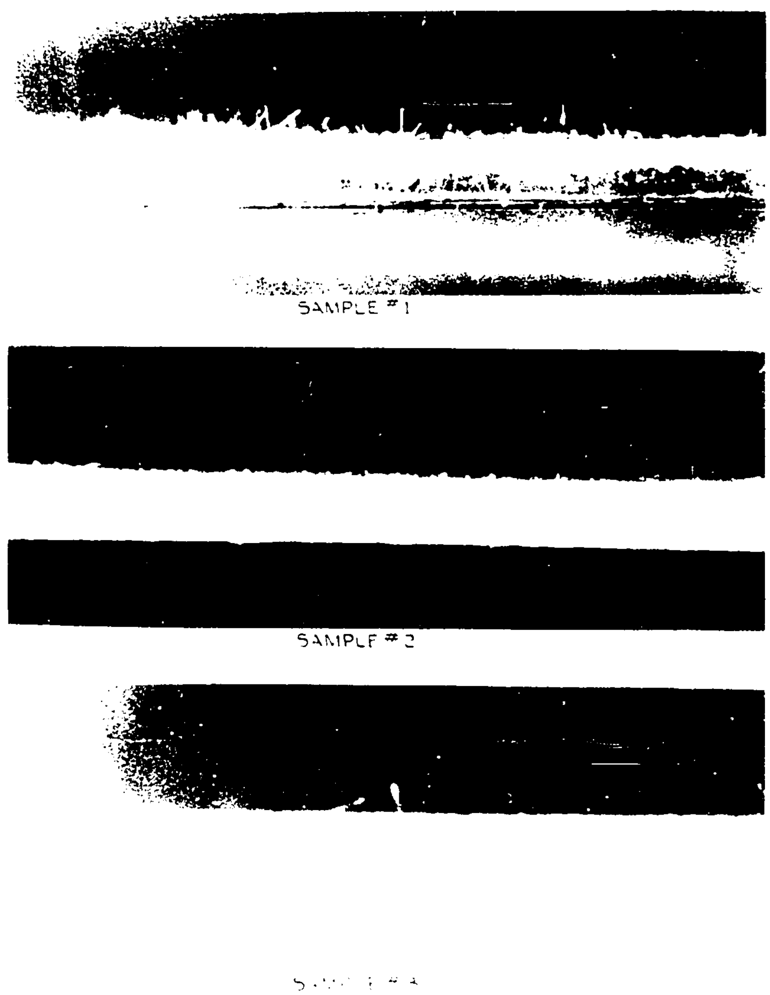


Fig. 22 - Whiskers on tin coatings as plated on brass from a potassium stannate bath[23].
Sample # 1 - Bath temperature: $77^{\circ}C$ ($170^{\circ}F$).
Sample # 2 - Bath temperature: $88^{\circ}C$ ($190^{\circ}F$).
Sample # 3 - Annealed at $191^{\circ}C$ ($375^{\circ}F$) for 3 hr prior to plating.

6.3 Summary of Results

i) Bright tin deposits are more susceptible to whisker growth than matt deposits.

ii) A steel substrate is less prone to whisker growth than brass.

iii) A copper undercoating on tin plated steel increases whisker growth, but gold, silver or nickel undercoatings seem to repress their growth.

iv) A copper undercoating on tin plated brass increases whisker growth.

v) The use of reverse polarity during plating results in a decrease in whisker density.

vi) The use of ultrasonic agitation in the plating bath seems to reduce whisker growth.

vii) Annealing tin plated parts from the acid sulfate or stannate bath retards whisker formation.

CHAPTER VII

CONTROLLING TIN WHISKERS

The recommendations on the measures to be taken to reduce or minimize the hazards associated with tin whisker growth are presented below:

i) The maintenance of a low temperature and a low relative humidity will reduce, although not entirely prevent, the growth of whiskers.[2,5,19].

ii) A minimum thickness of 5 μm (200 microinches) for electroplated tin coatings will give reduced internal stresses[30] which cause thin coatings to be prone to whisker formation[1,5,23,24].

iii) Bare steel substrates are preferable to brass and copper substrates or undercoatings, on which tin deposits are more susceptible to grow whiskers[23,25].

iv) Co-deposition of lead in the tin deposit at various alloy concentrations will prevent the formation of tin whiskers or reduce their growth to a degree that would eliminate any hazards of short-circuiting.[14,28].

v) Stress-relief of tin deposits by annealing at a temperature between 191°C (375°F) and 218°C (425°F) for 4 hr in an inert atmosphere will result in a definite retardation in whisker formation and a decrease in their growth density[23,30].

vi) Fusion of tin deposits after electroplating will result in a reduction in whisker growth due to stress relieving[2,29].

vii) Hot-tinning could be used as an alternative since hot-dipped tin shows less tendency to whisker formation than electroplated tin due to substrate interdiffusion and stress relieving[2]. However, hot-tinning is not a suitable method of application for small electrical components, but has found practical use in tinning sheets, wires and large items.

viii) Sprayed or vacuum evaporated tin which have found limited application in tinning electrical components are not recommended on various substrates since it has developed whiskers[2,5,15,19].

ix) Immersion of tin-plated surfaces in oil or coating them with grease, was, silicone, lacquer or paint did not stop whiskers from growing either through them or through cracks in the protective coatings[5,19,24].

CHAPTER VIII

RESTORING DEFECTIVE EQUIPMENT

When failures in electrical equipment in service have been traced to the presence of metallic whiskers. The following methods have been used to restore it to operation. These procedures extend the life of the devices but do not permanently prevent the whiskers from growing again.

8.1 The Electric Shock Treatment

This treatment consists in passing enough current through the circuit to burn off the whiskers[19]. This method will eliminate the whiskers responsible for shorting the circuit but not those that did not grow long enough to bridge the system. This is not suitable for equipment in which high voltage and current can cause damage to the elements.

8.2 The Pressure-Vacuum Technique

This method has been used to remove whiskers from short circuited-electrical equipment[30] and consists of applying a high-pressure air blast on the suspected surface and collecting the dust and whiskers by vacuum (Fig. 23). Fig. 24 shows a collection of dislodged whiskers after the cleaning operation. It has been shown that by using this method, whiskers bent or broken off by the air blast but were not completely removed[14].

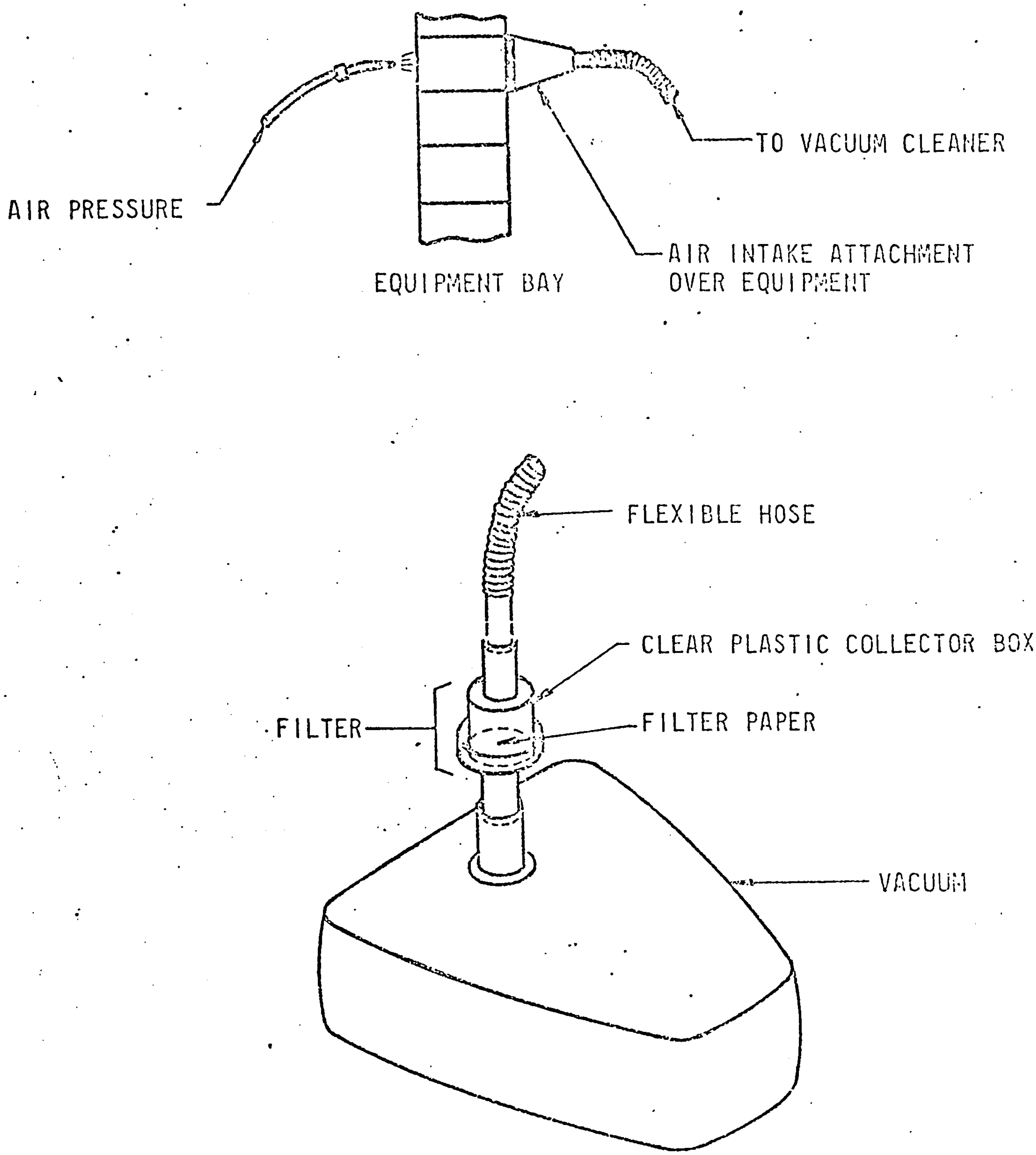


Fig. 23 - Pressure - vacuum equipment used to remove whiskers.

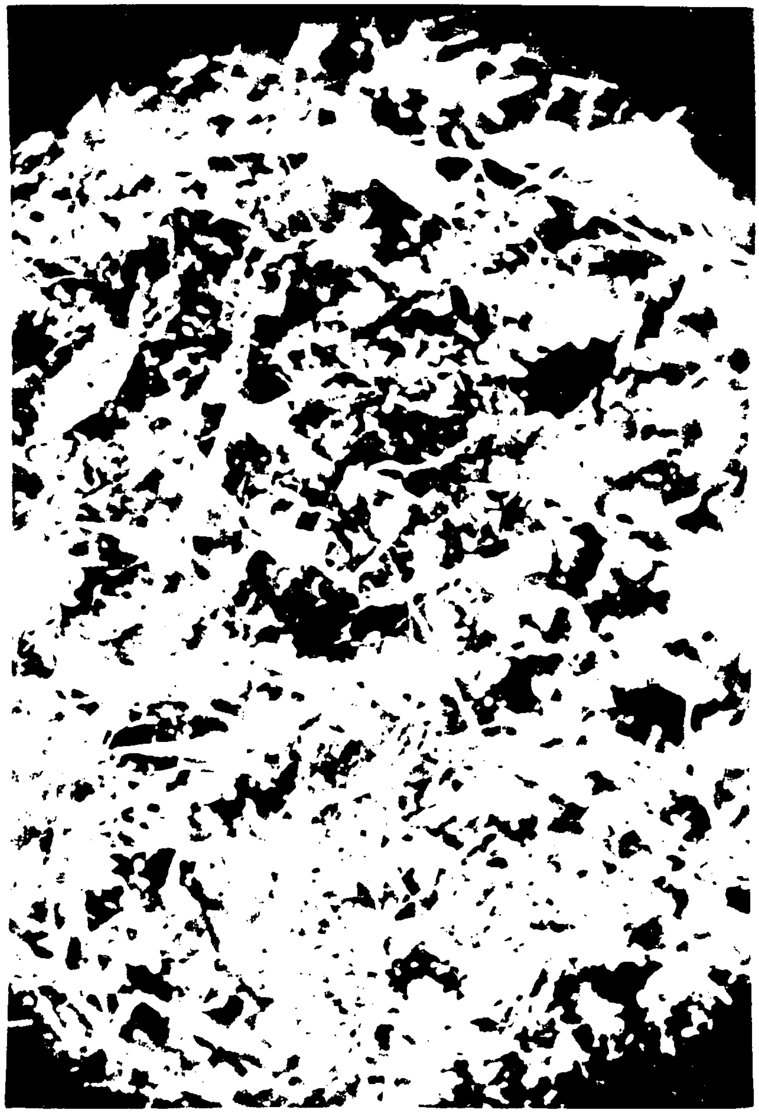


Fig. 24 - Tin whiskers collected by the pressure-vacuum technique.

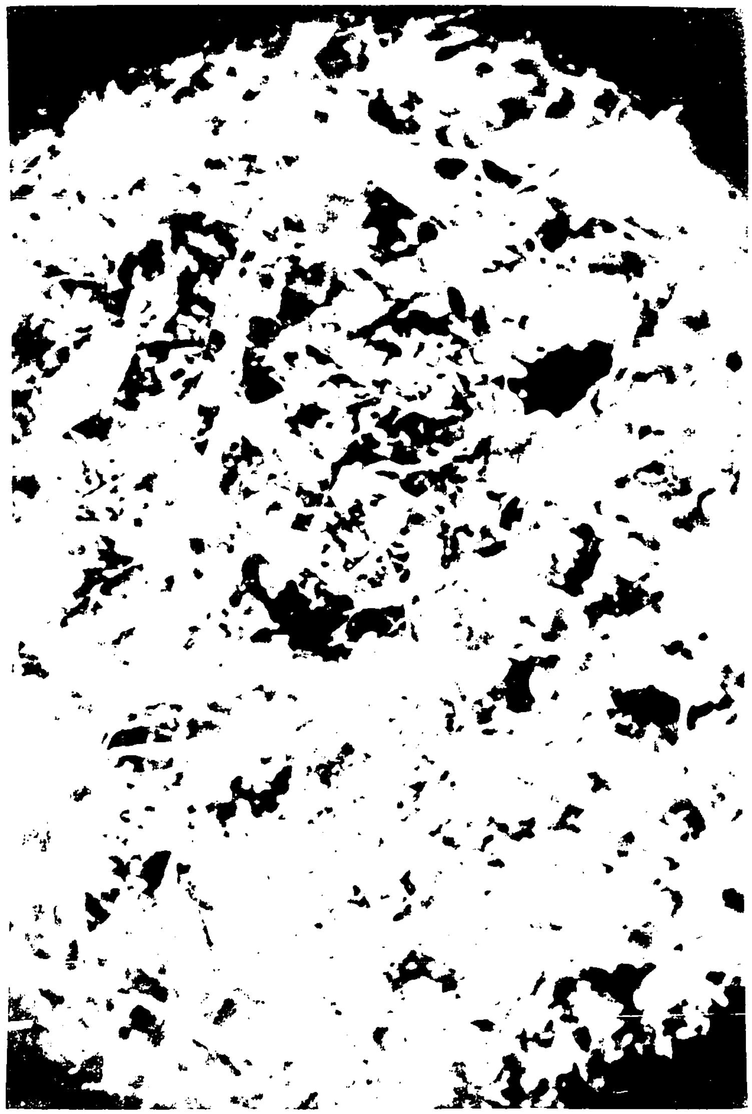


Fig. 24 - Tin whiskers collected by the pressure-vacuum technique.

8.3 Chemical Etching

Removal of tin whiskers by etching in a solution of one percent hydrochloric acid in ethyl alcohol proved to be partially successful because not all the whiskers were removed[14].

CONCLUSIONS

1. The mechanism of tin whisker growth is believed to be a strain releif phenomenon.

2. The substrate plays an important role in whisker growth.

3. The co-deposition of lead in tin deposits at various alloy compositions reduces to minimum the hazards associated with tin whiskers. High lead-tin alloys are so effective in suppressing whiskers that they are considered safe with regard to whisker growth.

4. Annealing tin coatings after plating in a controlled nitrogen atmosphere for 4 hr between 191°C (375°F) and 218°C (425°F) results in an increase in the incubation period and a decrease in the rate whisker growth.

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