APPLICATION OF VAPOUR PHASE CORROSION INHIBITORS FOR SILVER CORROSION CONTROL IN THE ELECTRONICS INDUSTRY

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ABSTRACT

The indoor corrosion of silver components used in the manufacture of electronic devices represents a hard challenge for the electronic industry in Mexico. In this work, a case of silver corrosion occurring in a TV manufacturing plant was documented, analysed and diagnosed. The main pollutant present in the indoor environment of the factory was hydrogen sulphide, which causes rapid silver tarnishing due to the formation of silver sulphide corrosion products. Silver corrosion rates were evaluated by gravimetric assays and surface SEM and EDX analyses were performed to characterize the corrosion film. In order to control the corrosion process VAPPRO vapour phase corrosion inhibitors were used.

Key words: silver, electronic devices, hydrogen sulphide, Vappro VCI, TROPICORR.

INTRODUCTION

Electronic equipment components, computers, integrated circuits (IC) and microchips in indoor atmospheres are exposed to a variety of environmental conditions and frequently corrosion failure of these devices occurs. Corrosion is becoming an even more significant factor in the reliability of electrical and electronic equipment /1/. Within the last decade, the electronic and electrical industries are increasingly applying more Vapour Phase Corrosion Inhibitors (VCI) for electronic components and devices. As electronics continue to shrink in size and grow in capacity, the importance of corrosion control increases /2,3/.

The interaction among electrical, metallurgical and environmental conditions, together with severe dimensional constraints, presents a unique set of corrosion problems, which lead to malfunction, failure and finally to operation interruption. These problems appear in several industries and technologies applying electronic components and devices, e.g., communications, information, control, avionics, medical, meteorological, military, robotics, space, missiles, satellites, domestic, etc.

Silver, copper and gold are important functional materials found in electrical/electronic devices. New technologies, tools, laboratory methods and instruments for failure analysis of electronic devices are being constantly introduced. The main objective of these activities is failure prevention /4-7/.

ENVIRONMENTAL CONDITIONS

The state of Baja California at the northwest of Mexico hosts more than 25% of the electronic devices manufacturing industry. Corrosion of silver components occurs at indoor conditions in several industrial plants located at Mexicali city, the state capital. Mexicali is a semi-desert zone irrigated by the Colorado River, which favoured the formation of the Mexicali Valley with extreme climatic conditions: hot in summer (48°C) and cold in winter (4°C). At 25 km to the south are located the Cerro Prieto volcano and the second largest geothermal field in the world, also named Cerro Priety. The geothermal vapour pollutes the atmosphere with hydrogen sulphide (H_2S) and other non-condensable gases /8/. The oxidation ponds for municipal waste-water treatment and the high quantity of automobiles circulating in the area are also considered as sources of sulphur compounds capable of polluting indoor installations and promoting corrosion of silver components.

Mexicali is a dusty city with strong winds that generate dust storms. Samples of Mexicali airborne dust, with a mean diameter of 10 μm (PM_{10}) are a mixture of clay minerals and quartz grains. Its chemical composition consists of 75% potassium aluminium silicate and 20% silica (SiO_2). These are hygroscopic mineral particles, facilitating the entry of humidity into the electronic devices affected by deposited dust particles.

The city of Mexicali, situated just on the border with the state of California, USA, applies the regulations of the National Institute of Ecology, pertaining to the Mexican "Secretaria de Medio Ambiente y Recursos Naturales" – SEMARNAT – for pollution control of the atmosphere. Several air-monitoring stations are installed and operated around Mexicali. On the other side of the international frontier, in Calexico and other nearby towns, the rules of EPA – the Environment Protection Agency – USA are enforced.

The corrosion of small and micro components of silver causes extensive losses to the electronics industry due to reject product, problems with soldering processes and production delays. The silver surface becomes tarnished by the effect of H_2S and, depending on exterior pollution, the problem can occur at controlled indoor conditions in clean rooms too. In this work, the causes of corrosion in silver electronic switches used in television manufacturing (Figure 1) and the employment of Vappro VCI to prevent these noxious events were studied.

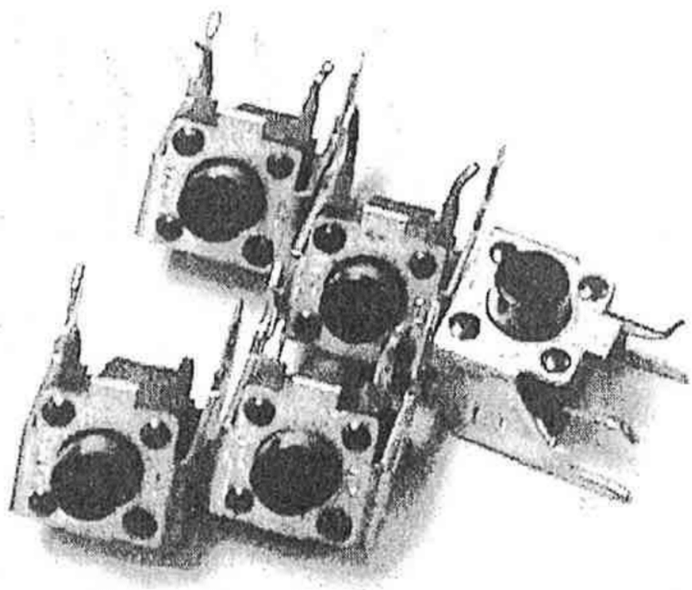

Fig. 1: Electronic TV switches showing corrosion on silver contacts.

EXPERIMENTAL PROCEDURES

The experimental sequence includes the characterization of pollutants present in the indoor atmosphere, gravimetric corrosion tests on silver coupons at indoor installations and surface analysis. The corrosivity of indoor conditions and the results of the corrosion tests were evaluated using ISO standards /9/, recommended for the electronics industry.

Based on our experience and due to the Mexicali air quality characteristics, there is strong evidence that the colored stains appearing on silver switches of the TV boards are due to corrosion by H_2S and formation of silver sulphide (Ag_2S). Several scientific papers have reported that a concentration of 100 ppb of H_2S in the indoor is enough to induce the build-up of sulphide films on the silver surfaces /10-13/.

Environment pollution and corrosivity

In order to identify the source of pollutants and the type of corrosion products, two approaches were followed:

- *Monitoring of air pollutants:* Two different sulphur compounds – H_2S and sulphur dioxide (SO_2) – in the range from 0 to 100 ppm, which are critical for silver corrosion, were monitored at different inside and outside locations of the plant, using portable gas analysers. The gas analyser apparatus consists of transducers and electronic circuitry and uses chemiluminescence and infrared absorption methods to detect pollutant gases in the environment.
- *Corrosion study on silver coupons:* The environment corrosivity was determined by the evaluation of several parameters:
  - ➢ Gravimetric corrosion tests on silver coupons by weight decrease or increase, in mg/m^2.year.
  - ➢ Indoor pollution by gases and variations of temperature and relative humidity (RH).

The silver coupons were made from metallic silver, 99.9% purity, in a rectangular form, 50mm length, 20mm wide and 1.1 mm thickness. Their surface was polished with SiC paper grade 120. The coupons were degreased with acetone vapour, weighed in an analytical balance and kept in a dry place before their installation at indoor plant locations.

Indoor pollutants such as SO_2 and H_2S were monitored in the range from 0 to 100 ppm with portable electronic devices. Readings were taken from several places of the production area a hourly intervals. A data logger type device was used to record the relative humidity and temperature.

Surface analysis

Several slightly corroded silver samples supplied by a TV manufacturing industry were initially analysed by scanning electron microscopy (SEM) and EDX without previous treatment in order to observe the corrosion products' morphology and their chemical composition. Also, some silver coupons exposed to corrosive environments were analysed using these techniques, to examine corrosion products and particulate matter deposited on their surface. The particulate matter deposited, such as dust, is critical because it adversely affects the soldering on the silver surface, generating failures in the electrical contact with other electronic components.

Indoor atmosphere corrosion categories

The corrosivity of indoor atmospheres was evaluated applying ISO/CD Standard 11844-A, which deals with metals, alloys and metallic coatings subjected to atmospheric corrosion influenced by air humidity, pollutant gases and solid substances. Corrosivity data are of fundamental importance for implementing suitable corrosion protection or for evaluatiing serviceability of metals in the electronics industry.

The evaluation of low corrosivity indoor atmosphere is accomplished by direct determination of corrosion attack of relevant metals or by measurement of environmental parameters, which may cause corrosion of metals and alloys applied in the electronics industry /7/.

Indoors atmospheres considered in this study are classified into five corrosivity, denoted IC1 to IC5, as given in Table 1. These categories are based on measurements of corrosion attack on standard metallic specimens after an exposure for one year. From the mass loss or mass increase the indoor corrosivity category for each metal is determined.

Table 1

Corrosivity categories of indoor atmospheres according to ISO/CD 11844

IC1	Very low indoor
IC2	Low indoor
IC3	Medium indoor
IC4	High indoor
IC5	Very high indoor

EVALUATION OF VAPOUR PHASE CORROSION INHIBITORS

In order to control the corrosion problems, the application of Vappro VCI was recommended to the TV manufacturer. Its efficiency was evaluated at the indoor conditions in the plant. The Vappro 870 Electro-Spray was provided by MAGNA Chemical Canada Inc. (15 Bowman Ave., Box 534, Matheson, Ontario P0K, 1N0, Canada). This company is devoted to the development of the most advanced and environmentally safe VCI technology, known as VAPPRO (Vapour-Phase-Protection). VAPPRO VCI technology comes in many forms, such as rust converters, VCI wax coatings and VCI grease, VCI emitters, VCI films, etc., and they are all effective for corrosion control. Magna Chemical Canada Inc. recommends using its VAPPRO 870 Electro-Spray product, a liquid solution composed of organic inhibitors in an isopropyl alcohol base. This specific VAPPRO VCI product is formulated for the galvanic corrosion protection of metals and alloys normally found in electronics applications such as copper, silver, aluminium, and other non-ferrous metals. For the purposes of this study, the VCI use must conform with several requirements, for instance: the VCI protective layer should not alter the thermal, electrical resistance or magnetic properties of the metal. The effectiveness of VAPPRO VCI has been demonstrated in numerous field and laboratory tests.

In order to evaluate the inhibitor efficiency, duplicate specimens of silver and copper were placed in the most aggressive indoor zone. One set of specimens was placed in a semi-closed container where VAPPRO 870 Electro-Spray was sprayed to saturate the space with VCI. Another separate set of specimens of similar metals were placed nearby without any application of VAPPRO VCI for comparative purposes. The specimens were tested for ten days and the surface conditions were evaluated by visual observation at the end of the test period. A soldering test using a rich tin lead free solder was performed on both silver specimens.

RESULTS

In order to carry out a diagnosis of the corrosion problems occurring, previous SEM and EDX assays on corroded silver samples were analysed. The results, shown in Figure 2, indicate that these samples are covered with corrosion products consisting of silver sulphide and chloride. The silver specimen exposed in the plant for one month appeared with a dark, dirty surface; silica was found, probably due to the contamination with fine dust particles. Tarnishing of these silver specimens occurs after 48 hours of exposure, due to the reaction with sulphur compounds present in the environment. The results of gravimetric corrosion tests performed in five different stations, four indoors and one outdoors, are shown in Fig. 3. Weight

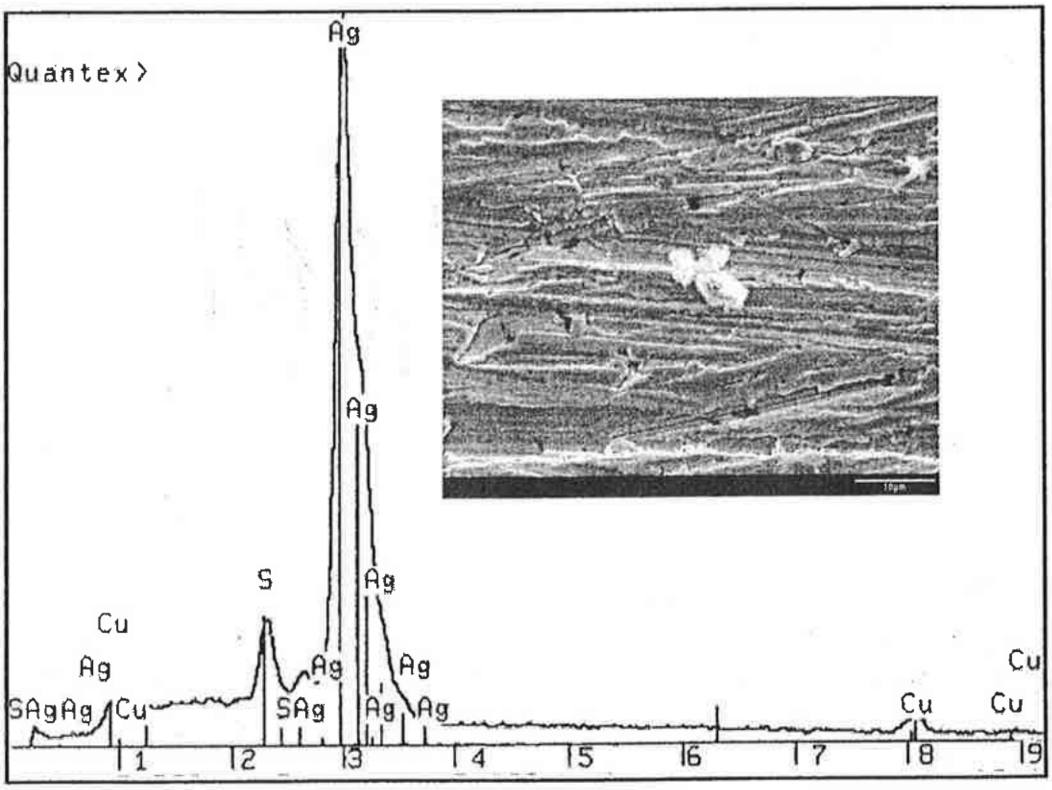

Fig. 2: EDX spectra for corroded silver contacts on electronic TV switches.

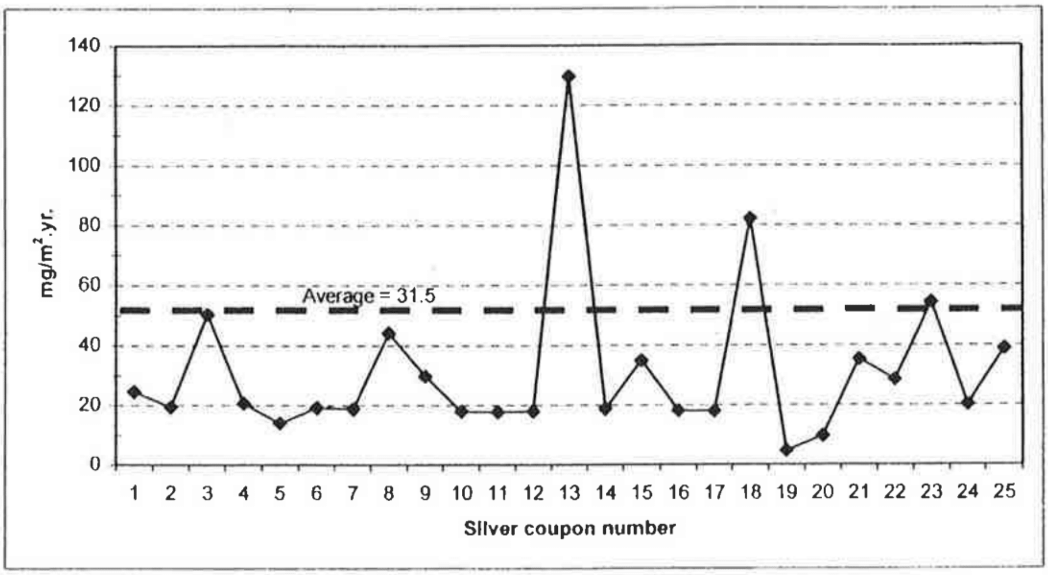

Fig. 3: Weight loss data for silver corrosion coupons at indoor conditions in a television manufacturing plant. Higher peaks correspond to the stations located at outdoor conditions.

loss for indoor conditions ranged between 20 to 40 mg/m^2.yr, with an average value of 31.5 mg/m^2.yr. These results are in good agreement with the corrosion phenomena occurring on silver surfaces, where the formation of corrosion product films diminishes the corrosion rate regarding time. The corrosivity categories for silver, following ISO/CD 11844, shown in Table 2, indicate that the most severe categories correspond to stations 4 (shipping area) and 5 (outdoor). In this case hydrogen sulphide was detected in concentrations of 1.5 ppm at indoor and 2.0 ppm at outdoor conditions, but

Table 2

Corrosion categories for silver coupons exposed for one month. The last two categories correspond to the materials arriving zone and the outdoor stations, respectively.

Coupons	Corrosivity category	Visual observations
1, 2	IC1 to IC2	Light gold – brown to metal blue
9, 10	IC1 to IC2	Light gold – brown to metal blue
17, 18	IC2 to IC3	Blue metal to dark brown
25, 26	IC3	Dark brown to gray
33, 34	IC3	Dark brown to gray

the H_2S concentration is not constant during the day. The presence of H_2S was detected during labour time, and it decreases after mid-evening to values undetectable by the sensor used (lower than 1 ppm). The average temperature in the plant was 22°C and the relative humidity controlled in the range from 25 to 38 percent. Records kept in the plant show that corrosion of silver increases during several periods when the temperature diminishes or the relative humidity increases. It is important to mention that the quality of the air supplied to the manufacturing process zone was not controlled. The indoor air supplied by several air conditioner handlers was insufficient to provide a positive pressure and to avoid the ingress of dust particles and other external environmental pollutants. The filters on the air system were for common use and incapable of retaining the chemical pollutants and also particulate matter in the range size from 2.5 to 10 micrometers.

The SEM and EDX results show a repetitive corrosion behaviour, silver sulphide compounds predominate as corrosion products, and typical dust particles from 2 to 15 micrometers were detected on silver coupon surfaces, observed in Figure 4. The morphology of a corroded silver surface and its chemical composition analysed by SEM and EDX are presented in Figure 5.

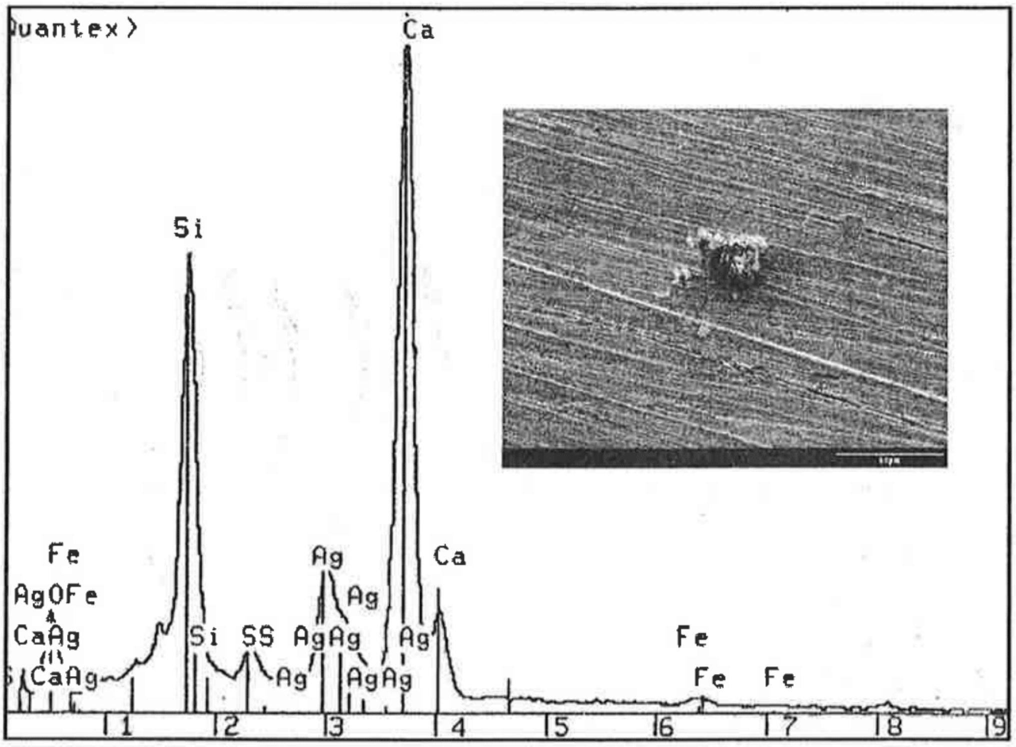

Fig. 4: SEM and EDX analysis performed on a dust particle deposited on the silver surface of a specimen exposed for one month at indoor conditions. The EDX analysis corresponds only to the dust particle.

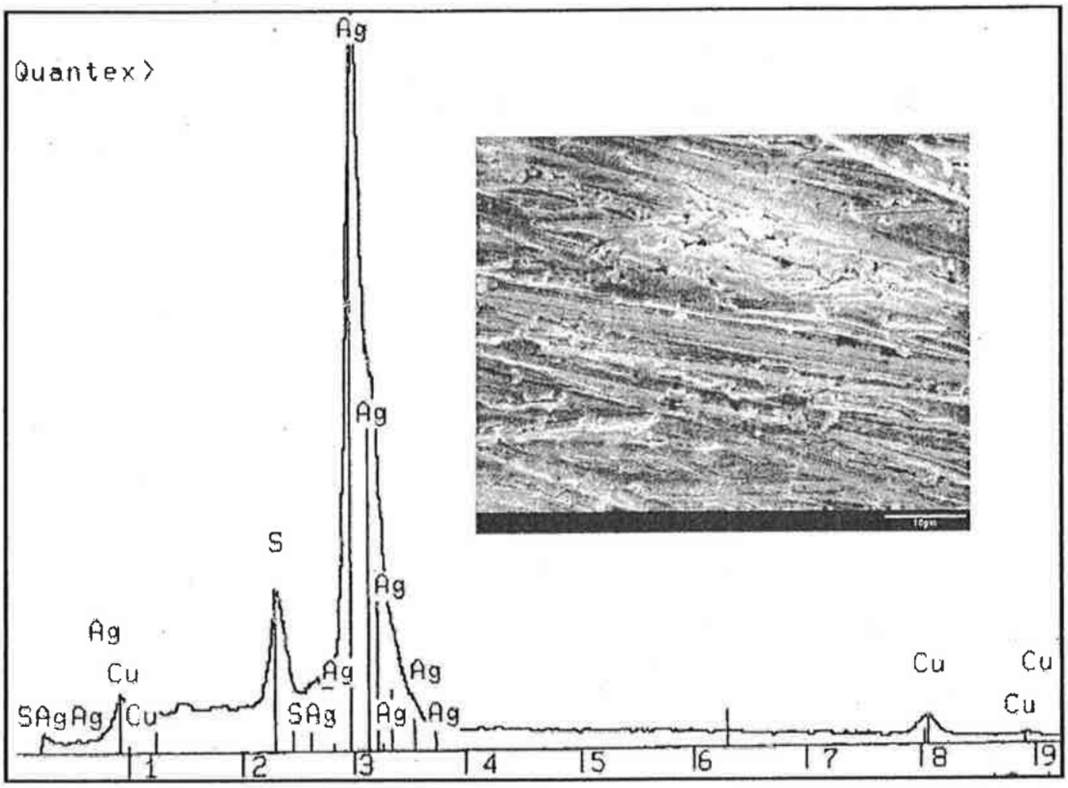

Fig. 5: SEM and EDX analysis performed on a corroded silver surface of a specimen exposed for one month at indoor conditions. EDX analysis corresponds to corrosion products.

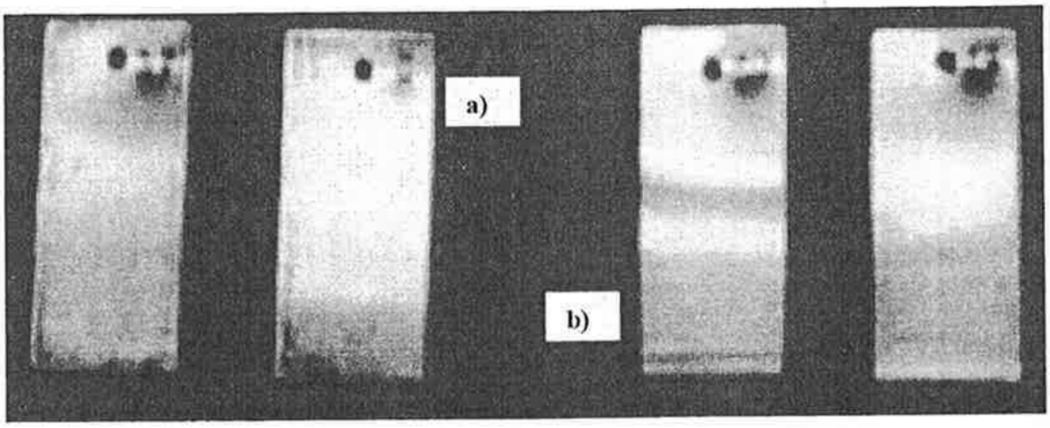

Fig. 6: Silver specimens exposed to a 10-day corrosion test at indoor plant conditions, a) without VpCI and b) with VpCI.

The results for the application of VAPPRO 870 VCI are shown in Figure 6. After ten days of testing, the silver specimens exposed without VCI under the indoor plant conditions exhibit tarnishing due to the formation of silver sulphide corrosion products, while the silver specimens protected with the

VCI remain unaffected without corrosion. It is clear that the concentration of H_2S in the indoor plant conditions was enough to attack the silver surface. It is interesting to note that after 20 days of exposure in the laboratory environment, the silver specimens already tested in the absence of VAPPRO 870 VCI suffered from further corrosion, with increase in size of the black stains and the appearance of additional black stains, spread out on the specimen's surface. In the stamped numbers of the specimens, containing residual, concentrated mechanical stresses, blue-green corrosion products become visible. This is a well-known phenomenon in specimens subjected to cold work, plastic deformation or strong mechanical effects. On the other hand, the silver specimens which were tested in the presence of VAPPRO 870 VCI exhibit a clear, shiny surface, without stains even in the stamped numbers. This is due to the continued protective action of the thin adsorbed film of the corrosion inhibitor. The copper specimens remained without any surface changes after the ten days assay, showing a very good corrosion resistance against the indoor environment, independently of the presence or absence of the VAPPRO 870 VCI.

A successful soldering test was performed using a rich tin lead free solder and flux, attaching a copper wire to the non-corroded silver surface. When the soldering was applied to the corroded silver surface, it failed immediately.

The VCI was also tested in storage racks containing electronic components and located at different points of the TV manufacturing plant, with excellent results in the corrosion inhibition of silver and other metals.

CONCLUSIONS

Silver sulphide (Ag_2S) was the main corrosion product detected on silver specimens exposed at indoor plant conditions. Less than 48 hours were required to tarnish the silver surface by the action of sulphur compounds.

Silver sulphide severely affects the performance of soldering operations avoiding a good electrical contact between silver pins and the frame board.

The sulphur compound responsible for the corrosion process was hydrogen sulphide (H_2S) produced by the exploitation of geothermal resources in the region.

The silver corrosion process was not influenced by the solutions and materials used during the fabrication of the TV boards. Also, no contamination caused by human activities was detected.

The absence of an air conditioning control system and adequate air filters were the main cause of contamination by particulate matter and gases in the indoor TV boards manufacturing zone.

The corrosion problem was resolved by the application of a Vapour Phase Corrosion Inhibitor (VCI) VAPPRO 870, supplied by Magna Chemical Canada Inc. The product prevented corrosion on silver components and retained their physical properties and the ability to solder these components.

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REFERENCES

1. J.D. Guttenplan. "Corrosion in the electronic industry", *Corrosion*, ASM, **13**, 1107 (1987).
2. "Corrosion costs and preventive strategies in the United States". Supplement to *Materials Performance*, July, 2002.
3. B. Miksic and A. Vignetti. "Vapor corrosion inhibitors successful field application in electronics", *NACE Corrosion Conference*, 2000; Paper 00707.
4. C. Boit. "The new millennium: challenges and opportunities", in: *Microelectronics Failure Analysis*, R.J. Ross, C. Boit and D. Staab (Eds.), EDFAS, ASM, March, 2001.
5. A.S. Brar and P.B. Narayan. "Materials and processing failures in the electronic and computer industries", ASM, March, 1998.
6. [[Author(s)?]]. "Metodologia para la simulacion acelerada del deterioro por corrosion atmosferica se presenta en equipo electronico", *Ingenieria, Investigacion y Tecnologia*, **III**(4), 145-156 (2002).
7. A. Ortiz-Prado, R. Schouwenaars and S.M. Cerrud-Sanchez. "Design, construction and tests of a system for accelerated simulation of damage by atmospheric corrosion on electronic equipment", *Corrosion Reviews* [this issue].
8. B. Valdez, N. Rosas, J. Sampedro, M. Quintero, J. Vivero, R. Velásquez and G. Hernandez. "Influence of elemental sulphur on corrosion of

carbon steel in geothermal environments", *Corrosion Reviews*, **17** (3-4), 167-179 (1999).

9. ISO/CD 11844-1. "Corrosion of metals and alloys – Classification of low corrosivity in indoor atmospheres – Part 1: Determination and estimation of indoor corrosivity", 2001.
10. H. Kim and J. Payer. "Tarnish process of silver in 100 ppb H_2S containing environments", *Journal of Corrosion Science and Engineering*, **1**, Paper 14 (1999).
11. R. Baboian. "Electronics corrosion", Chapter 70, in: *Electronics.* Electrochemical and Corrosion Laboratory, Texas Instruments Inc., 2001.
12. S. Zakipour, J. Tidblad and C. Leygraf. "Atmospheric corrosion effects of SO_2, NO_2 and O_3. A comparison of laboratory and field exposed nickel", *J. Electrochem. Soc.*, **144**, 10 (1997).
13. T. Burleigh, Y. Gu, M. Vida and D. Waldeck. "Tarnish protection of silver using a hexadecanethiol self-assembled monolayer and descriptions of accelerated tarnish tests". *Corrosion*, **57**, 12 (2001).

GENERAL REFERENCES

- R.P. Frankhental. "Electronic materials, components and devices", *Ulig's Corrosion Handbooks*, Second Edition, R. Winston Revie (Ed.), John Wiley and Soons, 2000.
- R.B. Comizzoli, R.P. Frankhental and J.D. Sinclair. "Corrosion engineering of electronic and photonic devices", in: *Corrosion and Environmental Degradation*, Vol. 19, Materials Science and Technology Series, Wiley-VCH, Weinheim, Germany [[year]].
- G.S. Frankel. "Corrosion of microelectronic and magnetic storage devices", in: *Corrosion Mechanisms in Theory and Practice*, P. Marcus and J. Oudar (Eds.), Marcel Dekker Inc., New York, 1995.