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Corrosion of electronic devices of the electronics industry of Mexicali, B.C. México influenced by H_2S pollution
La corrosión de los dispositivos electrónicos de la industria electrónica de Mexicali, B. C. México influenciado por la contaminación del H_2S

Gustavo López Badilla[1], Rosa Angélica Arreola Álvarez[2], Lluvia S. Martínez Valdez[2], Yuliana Mendieta Rodríguez[2], Mariela García Rodríguez[2], María del Carmen Pérez Marmolejo[2] y José L. Rocha Crespo[2]

[1]Dirección de Manufactura, Universidad Politécnica de Baja California, Mexicali
[2] Estudiantes de Ingeniería en Tecnologías de la Manufactura, Universidad Politécnica de Baja California, Mexicali

México

Gustavo López. E-mail: glopezbadilla@yahoo.com

Abstract

Hydrogen sulphide (H_2S) is a weak and diprotic acid, which is dispersed into the air, by winds when is emitted from natural and anthropogenic sources, principally from industrial plants. It is a pollutant with a high level of toxicity, impairing the environment quality. It air pollutant attacks to metals used in the electronics industry as carbon steel, cooper and silver alloys, and forming thin films as corrosion products or dendrite whiskers as sulfides in the metallic surfaces, enhancing the metallic corrosion. This gas enter to indoor of industrial plants, by inlets of air conditioning systems, holes, roofs, in any time of periods of year. In the autumn, winter and spring seasons, people in companies leave open some doors with knowledge of the negative effect of H_2S in metallic components of electronic components, and this corrosive acid enter easily. For this reason, a study was conducted in indoors of two electronics plants in Mexicali exposed at low concentrations of H_2S, to determine the damage caused to this electronic devices. The Scanning Electron Microscopy (SEM) technique was applied to determine the type of corrosion types formed: uniform, crevice and pitting, and the chemical agents that reacted with the metallic surfaces of electronic components. The SEM technique shows the microphotographies and the information of the corrosion products presented in this study, correlated with the relative humidity (RH) and temperature levels.

Keywords: H_2S, corrosion, air pollutants, electronics industry, microscopy analysis

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Resumen

El sulfuro de hidrógeno (H_2S) es un ácido débil que se dispersa en el aire, por el viento cuando se emite a partir de fuentes naturales y antropogénicas, principalmente de las plantas industriales. Es un contaminante con un alto nivel de toxicidad que afecta a la calidad del medio ambiente. Es un contaminante atmosférico agresivo que ataca los metales utilizados en la industria electrónica como acero al carbono, cobre y aleaciones de plata, y formación de películas delgadas como productos de corrosión y dendritas, siendo los sulfuros los más comunes que dañan las superficies metálicas, promoviendo la corrosión metálica. Este gas ingresa a los interiores de las plantas industriales, por los sistemas de aire acondicionado, agujeros, techos, en cualquier período del año. En las temporadas de otoño, invierno y primavera, el personal en las empresas deja algunas puertas abiertas en ciertas áreas de las empresas, por no tener sistemas de aire acondicionado, con el conocimiento del efecto negativo del H_2S en los componentes metálicos de componentes electrónicos, y este ácido corrosivo penetra fácilmente. Por esta razón, se realizó un estudio en el interior de dos plantas de la industria electrónica en Mexicali expuestos a bajas concentraciones de H_2S, para determinar el daño causado a estos dispositivos electrónicos. Se aplicó la técnica de Microscopía Electrónica de Barrido (MBE) para determinar los tipo de tipos de corrosión formados: uniforme o picaduras principalmente, y conocer con mayor exactitud los agentes químicos que reaccionan con las superficies metálicas de los componentes electrónicos. La técnica MBE muestra las microfotografías y la información de los productos de corrosión presentados en este estudio, en correlación con la humedad relativa (HR) y los niveles de temperatura.

Palabras clave: corrosión, contaminantes del aire, industria electrónica, microscopía de análisis

Introduction

The geothermic industry, which generates electricity to urban and rural locations are activities that control the emission of air pollutants as H_2S, but in some times it air pollutant are emitted at levels higher than the air quality standards. It originates the deterioration of the outdoor atmospheres, affecting the microclimate of indoor in the industrial plants. H_2S is aggressive agent with characteristics as foul odor of expired eggs perceptible at concentrations as low as 0.00047 parts per million (ppm), originating atmospheric corrosion, and impairing the indoor air quality of companies (Rocak et al, 2005). The principal air pollutants in the northwest of Mexico where are located the Mexicali city, are the H_2S. Other air pollutants that originate corrosion in electronic devices are the SO_X, which are a compound derived derivates of H_2S, generated by the geothermic plant installed at 25 km of this city, and also of industrial processes, oxidation lakes and deterioration of organic matter. The presence of H_2S at low concentrations generates drastic problems in electronic devices used in the electronics industry. The emission of H_2S by bacterial deterioration of organic matter in the absence of oxygen, and its acid is generated principally in clean rooms of the electronic industry, where are fabricated the microcircuits (G. Lopez et al, 2011). This dangerous pollutant is disintegrated in hydrogen ion and sulfur compounds, causing corrosion:

$$H_2S <-> H^+ + HS^- <-> S^{2+} \quad (1)$$

The H_2S is slightly heavier than air, and with air compounds as oxygen could be an explosive mix, generating a blue flame which forms the sulfur dioxide (SO_2) and with the water of the atmosphere, act as a reducing agent. A solution of H_2S at levels higher of the air quality standards mixed with water, change their color and forms a dangerous cloudy which are corrosive to the electronic components (Kawanobe et al, 2006). This is due to the slow reaction of the hydrogen sulfide with the oxygen dissolved in water, producing sulfurs, which are precipitated. The H_2S reacts with metal ions forming metal sulfides, which are the corrosive agents, and then the metals have a dark color (Lopez G., 2008).

Atmospheric corrosion

The atmospheric corrosion (AC) influenced by H_2S is a destructive attack of a material by the reaction with the environment to which exposed. Serious consequences of corrosion are a problem of great significance worldwide (L. Veleva et al, 2008). The sulfurs compounds generated by the H_2S in the atmosphere of Mexicali penetrate to indoor of industrial plants originating aggressive environments and deteriorate the materials used in the electronics industry. An important aspect is know the type and form of the materials which are deteriorated and the different types of corrosion that occurs in different environments, causing a production downtime in the industrial plants. Also is necessary consider the depreciation of resources or materials considered as waste products, products contaminated, reduction of the production yielding, maintenance costs, and large time expired on the design operations (Moncmanova, 2007). The multidisciplinary aspects of corrosion problems, combined with the associated complexity of the electronic devices, increase the cost of products by the corrosion phenomenon (Lopez et al., 2007).

Electronics industry

The electronic equipments suffer from corrosion, at low and high levels of humidity that is an important factor in the generation of this electrochemical process. The other air pollutants that have an adverse effect with less intensity in the operation of electronic devices are the Carbon Monoxide (CO) and the Nitrogen oxides (NO_X), which enter to indoor of industrial plants as the sulfides. The corrosion phenomenon affects the connections of electronic components which have a protection of plastic or metallic materials as a coating (Lopez G., et al, 2010). The AC is an electrochemical phenomenon that occurs in the wet film formed on metal surfaces originated by climatic factors as humidity and temperature. The corrosion products form dendrites or whiskers in the metallic joints and connectors. The rate of reaction of aggressive compounds from H_2S on copper (Cu) surface that generate corrosion, determines the oxidation and reduction processes, that depend of wide or thin of the film, and remains as a continuous factor of corrosion or in any time as a protective film. The wet film grows and causes the corrosion and in some times occur cracks and pores and it's are non-protective films, reducing and avoiding the electrical conductivity. Both process take place for film formed in the surface in all or some areas of the copper surface (Lopez B. G. et al, 2010).

Electronics industry in Mexico

The electronics industry was born in our country during the sixties with the manufacture of electronic products as radios, phonographs and televisions. In the seventies the development decreases for the diminution of the external competition. In 1986, Mexico was added to the General Agreement on Tariffs and Trade (GATT) to restructure the electronics industry in our country (Lopez B. Gustavo, 2011). In 1994 Mexico signed the North American Free Trade Agreement (NAFTA) with Canada and the United States and with this the electronics industry was a very important source of the Mexican economy. In the nineties, some transformations are made in the electronics industry with the NAFTA. With this occurs the installation in Mexico of global and national companies. This industry acquired great importance in the electronics plants to export electronic products and generate employments (Lopez B. G., et al, 2007).

Functionality of electronic equipment

The efficiency of an industrial operation is based on productivity in the industrial plants, and the main features that show the efficiency of a manufactured product are their good appearance, low cost, ease of operation and safe (Samuels, 2003). The electronic devices and equipments used in warehouses, production and shipping areas are exposed to environmental factors in indoor of industrial plants, influenced by the outdoor atmospheres (Lopez G., 2008). The climatic factors such as relative humidity (RH) and temperature in combination with sulfates, affects the operation of the electronic systems.

Factors that cause corrosion

The levels of RH and temperature higher of 70% and 35 º C, are the principal factor of the corrosion and increases the corrosion rate (CR), and this climatic parameters, generates a higher valence change in the state of the active metals, damaging the metals very fast (Lopez G. et al, 2010). This occurs when the oxide films formed on the surface of Cu, are not covered uniformly, and are covered only in some zones of the Cu surface, causing the pitting corrosion. The levels of SO_X generated by H_2S in some periods of the year in Mexicali overpass the air quality standards.

Experimental Procedure

The deterioration of electrical connectors and connections of Cu used as a metallic probes, was evaluated by the gravimetric method; and was correlated with the minimum, average and maximum RH and temperature levels of outdoor atmospheres, in different seasonal periods (ASTM G1, 2003, ASTM G4, 2008). The electrical properties of a material are at least partially a function of the amount of humidity and pollutants present in the indoor environment, because the corrosive effect increases after the moisture and ionic compounds mixed (Anderson T., 2003). The corroded metals were analyzed by the SEM technique coupled to an electron disperse X-ray analyzer (SEM EDX, Philips XL ESEM). With this technique was obtained important information of the corrosion products morphology, being better the gravimetric analysis. The corrosion products were observed in an optical microscope and the SEM before being cleaned and reweighed to obtain the mass loss on an analytical balance to the nearest 0.0001 g of reliability. After the cleaning was evaluated the electrical connectors and connections to determine the type of corrosion occurred. To determine the concentration of sulfate in indoor of industrial plants the sulfate plate technique was used inside industrial plants.

SEM analysis

This is an important technique used in the electronics industry, even knowing that the equipments of analysis are very expensive, but is necessary in their manufacturing processes. The functions of SEM are complex and can be learned by specialized personal. Once it determines the chemical composition of elements and compounds in the samples, and we can observe the spatial distribution of these, in order to know the major and minor pollutants that were reacted with the metal. It promotes the generation of the corrosion process. It makes a distinction between the different compounds to find out the possible state of oxidation of the metal ions involved in the corrosion products (Lopez, 2008).

Results

A comparative analysis of the four periods mentioned, represents principally a higher intensity of uniform corrosion in both industrial plants in winter, where are showed localized corrosion and crevice and pitting corrosion in summer, with different corrosivity levels (CL) showed in table 1.

Table 1 CL in indoor of the two electronics industries in Mexicali

Time, months	Corrosivity levels	
	Industrial Plant 1	Industrial Plant 2
1	1	1
3	2	2
62	2	3
12	2	3
24	2	3

Influence of climatic factors and the air pollutants in the CR

The values of RH and temperature were above 70% and 45 º C in summer and a minimum of 20% and 5 º C in winter, with warm desert winds in summer increases very fast the CR. With the levels of RH and temperature mentioned above, accelerate the CR. In summer in both companies, in the first six months of exposure, the CR increase lowly, but from this period, was observed significant increases. The ranges of temperature from 25 to 35 º C with a RH level of 30% to 70%, the CR were the highest. Moreover, in winter, temperatures around 15 º C to 25 º C and RH was 35% to 75%, water was condensed on the surface of Cu, was formed the protective films and the CR was low. However when temperatures were above 35 º C, were generated some wetted zones of Cu surface and later observed originated isolated stains and pits, crevices and cracks. Other factor was the levels of sulfurs, which exceeded the permitted levels of air quality standards, and the levels of RH and temperature described in the range of 30% to 80% 0 ° C and 35 º C, originated the corrosion. At temperatures above 35 º C with RH levels from 50% to 85%, protective films were formed in the Cu surface (Lopez G. et al, 2010). In Tables 2 and 3 show the effect of copper exposure to air pollutants: H_2S and SO_2, RH and temperature levels, concentration of air pollutants and the CR. In summer, the highest CR was 382 mg/m2 at year in the industrial plant 1, with values of RH and temperature of 87.5% and 25.6 º C, and levels of H_2S of 0.42 mg/m2.año over passing the air quality standards, which is 0.03 for one hour. In winter, the highest CR was 338 mg/m2 at year at 88.8% RH and temperature of 22.3º C, concentration levels of 0.67 ppm of H_2S, over passing the air quality standards too.

Table 2 Correlation of CR with climatic factors and air pollutants in the industrial plant 1 (2010)

Climatic factors	Hydrogen sulfide (H^2S) RH[a]	T[b]	C[c]	CR[d]	Sulfur Dioxide (SO_2) RH[a]	T[b]	C[c]	CR[d]
Spring								
Max	88.8	33.4	0.15	255	85.6	23.2	0.34	176
Min	34.5	17.6	0.09	130	46.7	15.1	0.23	112
Summer								
Max	89.9	42.1	0.14	265	88.2	39.9	0.45	245
Min	38.5	24.3	0.11	181	42.3	28.2	0.18	114
Winter								
Max	87.5	25.6	0.42	382	88.8	22.3	0.67	338
Min	43.2	17.8	0.26	245	38.9	12.3	0.25	136

[a] RH. Relative humidity, %, [b] T. Temperature, ºC, [c] C. Air pollution concentration (C), ppm
[d] CR. Corrosion rate, mg/m^2.year

Table 3 Correlation of CR with climatic factors and air pollutants in in the industrial plant 2 (2010)

Climatic factors	Hydrogen sulfide (H^2S) RH[a]	T[b]	C[c]	CR[d]	Sulfur Dioxide (SO_2) RH[a]	T[b]	C[c]	CR[d]
Spring								
Max	86.5	32.4	0.21	210	88.8	28.9	0.51	212
Min	33.4	19.6	0.13	140	46.8	19.1	0.33	124
Summer								
Max	87.7	41.4	0.19	288	83.2	42.3	0.62	228
Min	42.3	27.8	0.14	160	44.1	29.3	0.24	145
Winter								
Max	89.5	31.6	0.45	330	85.5	26.7	0.89	299
Min	38.7	26.6	0.33	178	43.2	17.7	0.36	181

[a] RH. Relative humidity, %, [b] T. Temperature, ºC, [c] C. Air pollution concentration (C), ppm,
[d] CR. Corrosion rate, mg/m^2.year

A SEM analysis showed the corrosion products formed in the cooper surfaces represented in the figures 1 and 2 was made. Figure 1 show the corrosion process in the industrial plant 1 located in the northeast of Mexicali near of the geothermic plant. In the first three months as showed in the figure 1, the Cu surface shows tarnishing presented low electrical conductivity in the industrial equipment, and was covered by the sulfurs oxide and in this period of deterioration, the electrical conductivity was low. Then, at six months appeared the corrosion products as copper sulfides, the CR was increased, and was decreasing the electrical current, and at one year the corrosion products enhanced, causing the total electrical failures, and avoiding the electrical conductivity. At two years the copper surface was deteriorate around 80% and was necessary changed the electrical connector. In the industrial plant 2 located in the southeast, the corrosion process showed more deterioration compared with the industrial plant 1. At three months showed in the figure 2, was appeared corrosion products and n the six months were increased, generating low electrical conductivity. At one year in the copper surfaces were formed copper sulfides products and in the two years the electrical conductor of the equipment was changed, occurring the same process as in the industrial plant 1.

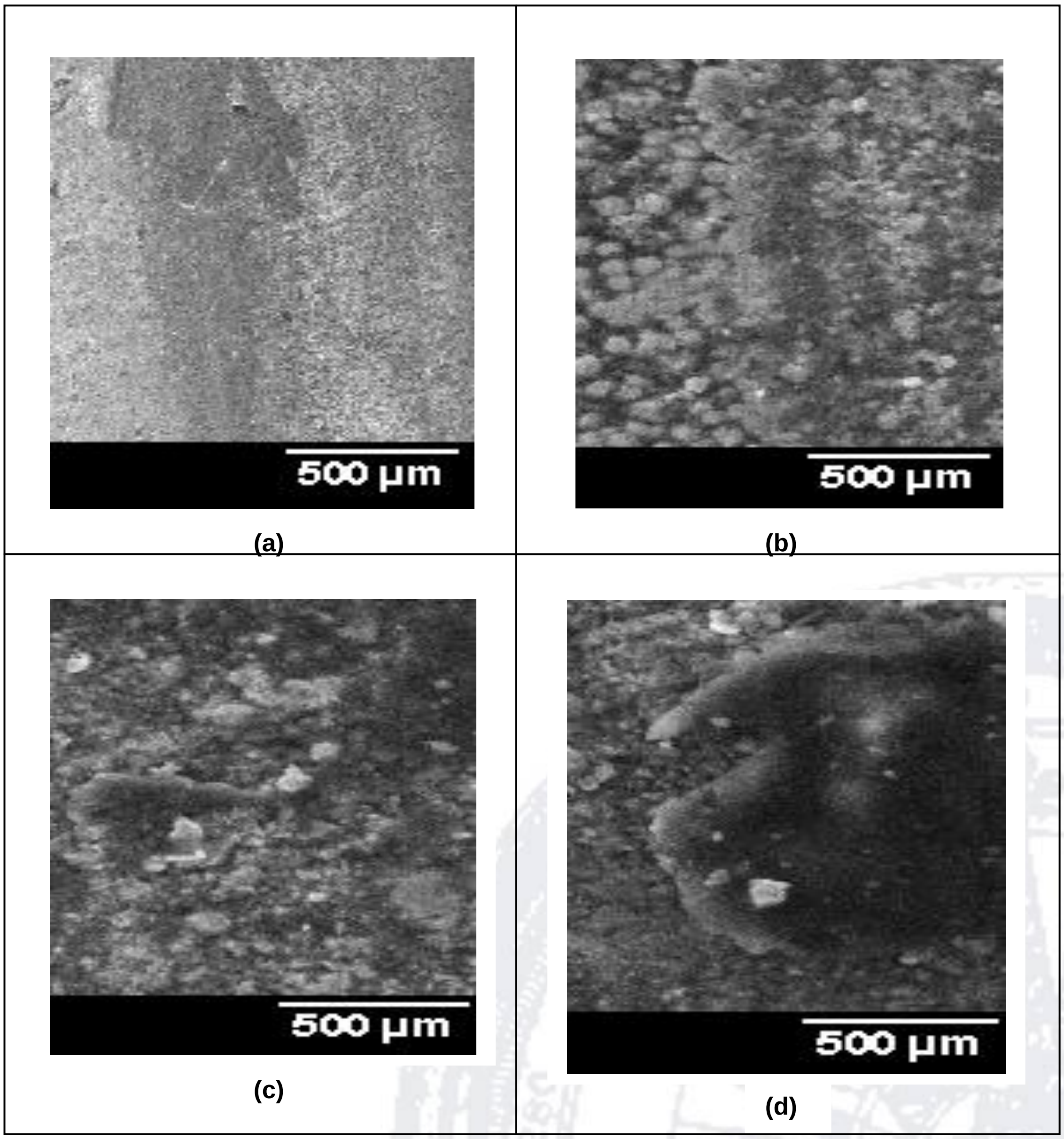

Figure 1 SEM analysis of copper surfaces at: (a) three, (b) six, (c) twelve and (d) twenty four months in the electronics industry 1.

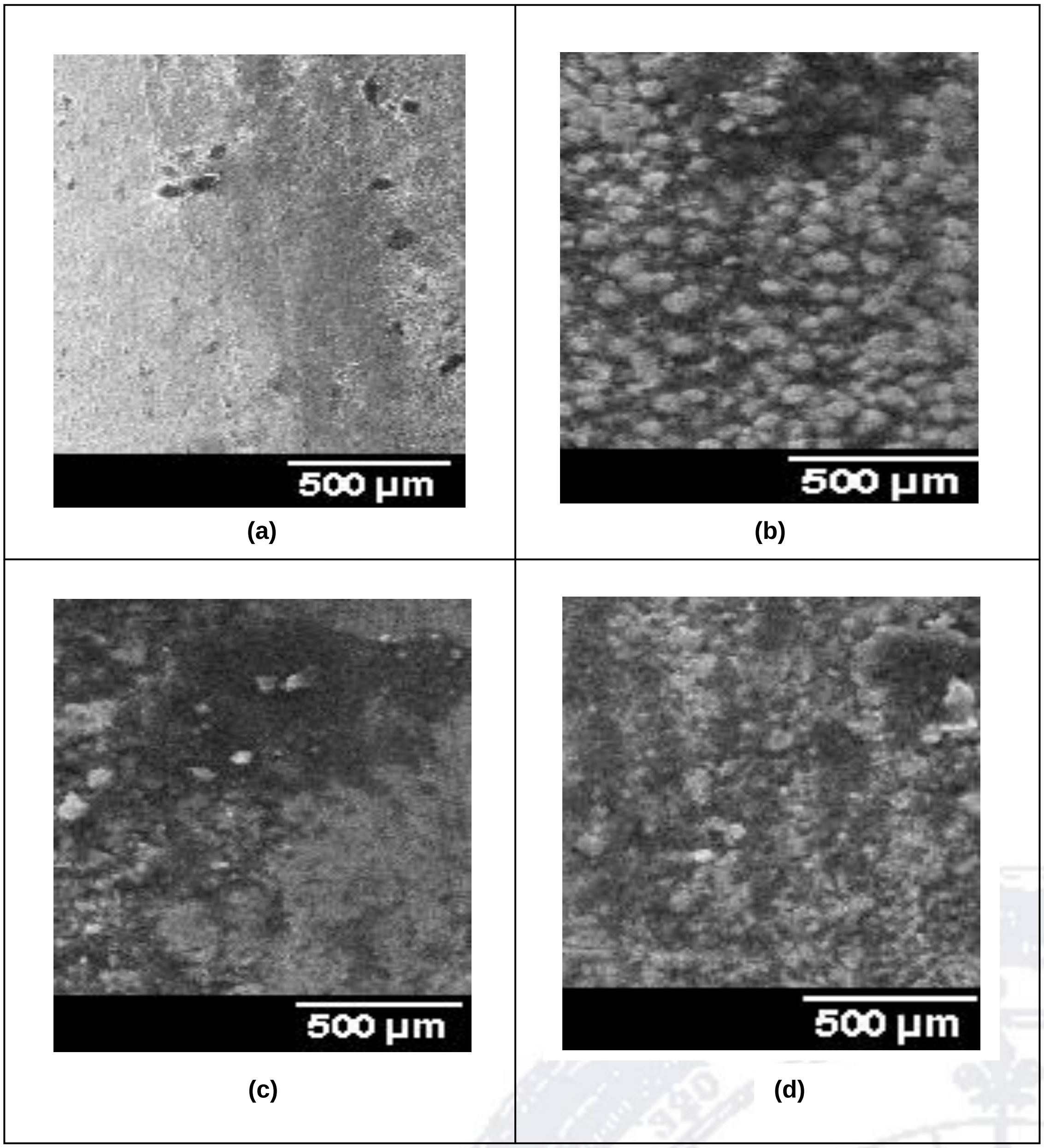

Figure 2 SEM analysis of copper surfaces at: (a) three, (b) six, (c) twelve and (d) twenty four months in the electronics industry 2.

Conclusions

The main sources of corrosive emissions in Mexicali was the geothermic plant, followed of the traffic vehicle (around 250,000 new and old models of cars in this city), and as the last factor as the manufacturing process which emit sulfurs. Sulfates penetrate to the indoor of industrial plants by air currents, cracks, access doors and air conditioning systems that not have special filters, causing damage in the electronic devices. The information obtained from the sulfurs was used to classify the level of corrosivity of a specific area, such as conditions in the electronics industry. After one year, the CR increased rapidly at approximately twice the value of to the previous period. When the metallic probes were exposed for two years, the CR was very fast. Results of this technique, represents the chemical reaction of atmospheric agents that forms thin films on the Cu surface. According to the objective of this research we can conclude that without an indoor climate control in the industrial electronics, and with of RH and temperatures values higher than 70% and 35 ° C, was promoted the CR very fast, presenting pitting and crevice corrosion in this arid zone as in Mexicali. At RH values and temperatures lower than 50% and 25 ° C, was formed a protective oxide on the surfaces of Cu of electrical connectors and connections of the electronic devices. This study is of great importance to consider these factors and avoid economic losses or accidents.

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