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Micro and Nano Corrosion in Steel Cans Used in the Seafood Industry

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1. Introduction

The use of metal containers for food preservation comes from the early nineteenth century, has been important in the food industry. This type of packaging was developed to improve food preservation, which were stored in glass jars, manufactured for the French army at the time of Napoleon Bonaparte (XVIII century), but were very fragile and difficult to handle in battlefields, so it was decided the produce metal containers (Brody et al, 2008). Peter Durand invented the metallic cans in 1810 to improve the packaging of food. In 1903 the English company Cob Preserving, made studies to develop coatings and prevent internal and external corrosion of the cans and maintain the nutritional properties of food (Brody, 2001). Currently, the cans are made from steel sheets treated with electrolytic processes for depositing tin. In addition, a variety of plastic coatings used to protect steel from corrosion and produce the adequate brightness for printing legends on the outside of the metallic cans (Doyle, 2006). This type of metal containers does not affect the taste and smell of the product; the insulator between the food and the steel, is non-toxic and avoid the deterioration of the food. The differences between metal and glass containers, as well as the negative effects that cause damage to the environment and human health are presented in Table 1.

The wide use of steel packaging in the food industry, from their initial experimental process, has been very supportive to keep food in good conditions, with advantages over other materials such as glass, ceramics, iron and tin. The mechanical and physicochemical properties of steel help in its use for quick and easy manufacturing process (Brown, 2003). At present, exist a wide variety of foods conserved in steel cans, but in harsh environments, they corrode. Aluminum is used due to its better resistance to corrosion, but is more expensive. With metal packaging, the food reaches to the most remote places of the planet, and its stays for longer times without losing its nutritional properties, established and regulated for health standards by the Mexican Official Standards (NOM). The difference between using metal cans to glass (Table 1) indicate greater advantages for steel cans (Finkenzeller, 2003). In coastal areas, where some food companies operate, using steel cans, three types of deterioration are detected: atmospheric corrosion, filiform corrosion and microbiological corrosion. Even with the implementation of techniques and methods of

protection and use of metal and plastic coatings, corrosion is still generated, being lower with the use of plastics (Lange et al, 2003). Variations of humidity and temperature deteriorate steel cans (Table2).

1.1 Steel

Steel is the most used metal in industrial plants, for its mechanical and thermal properties, and manufacturing facility. It is an alloy of iron and carbon. Steel manufacturing is a key part of the Mexican economy. Altos Hornos is the largest company in Mexico, with a production of more than 3,000,000 tons per year, located in Monclova, Coahuila, near the U.S. border (AHMSA, 2010). Steel is used in the food industry, especially in the packaging of sardines and tuna (Lord, 2008).

PROPERTIES AND UNPROPERTIES		NEGATIVE EFFECTS	
METAL	GLASS	METÁL	GLASS
Resist the irregular handling and transport	Fragile and easily broken	Generation of filiform and microbiological corrosion	Cause spots of black color
Hermetically sealed	Not sealed; air enters	Bad sealed, creates rancidity by microbiological corrosion	High percentage of microorganisms by poor seal
Good shelf life without refrigeration at room temperature	Necessity of refrigeration of marine food	At warm and cold temperatures, foods lose their nutritional properties	At warm and cold temperatures, foods lose their nutritional properties
Accessibility manufacture	Manufacturing process complex by its fragility	By bad handling and the internal deterioration of the coating, generates filiform corrosion	Cover deformation generates gas food deterioration
No frequent supervision	Frequent supervision	Susceptible to atmospheric corrosion in indoor and outdoor environments	Broken pieces of glass are mixed with food, generating health damage
Easy recycling	Difficult to recycle	Sterilization time is 20 minutes	In sterilizing process, glass cans remains in hot water for 10 to 15 minutes and can generate bacteria

Table 1. Differences between metallic cans and glass containers in the food industry and their effect on health and environment

1.2 Metallic cans

The steel cans consist of two parts: body and ring or three parts: body, joint and ring (Figures 1a and 1b). When a steel can is not properly sealed, it is damaged by drastic variations of humidity and temperature creating microorganisms, which cause an injury on the health of consumers (Cooksey, 2005). Every day millions of cans are produced, the companies express their interest in research studies to improve their designs. There are two main types of steel cans: tin plated and plastic coated. Plastic coatings have good resistance to compression, and the resistance to corrosion is better than the tin plate. Since the oxide layer that forms on the container surface is not completely inert, the container should be covered internally with a health compatible coating (Nachay, 2007).

Corrosion	Climatic factors	Coatings	
		Metallic	Plastic
Atmospheric External	High levels of humidity and temperature	In aggressive environments, is generated external and internal damage of steel cans	Originates stains and bad appearance without damage
Filiform Internal	Low levels of humidity	In harsh environments, are generated cracks under the coatings and, is formed the filiform corrosion	No formation of cracks in coatings as in the steel cans
Microbiological Internal	High levels of humidity	Dense black spots are formed by OH- and rancidity	Isolated black spots

Table 2. Corrosion types in coated metallic cans used in the food industry

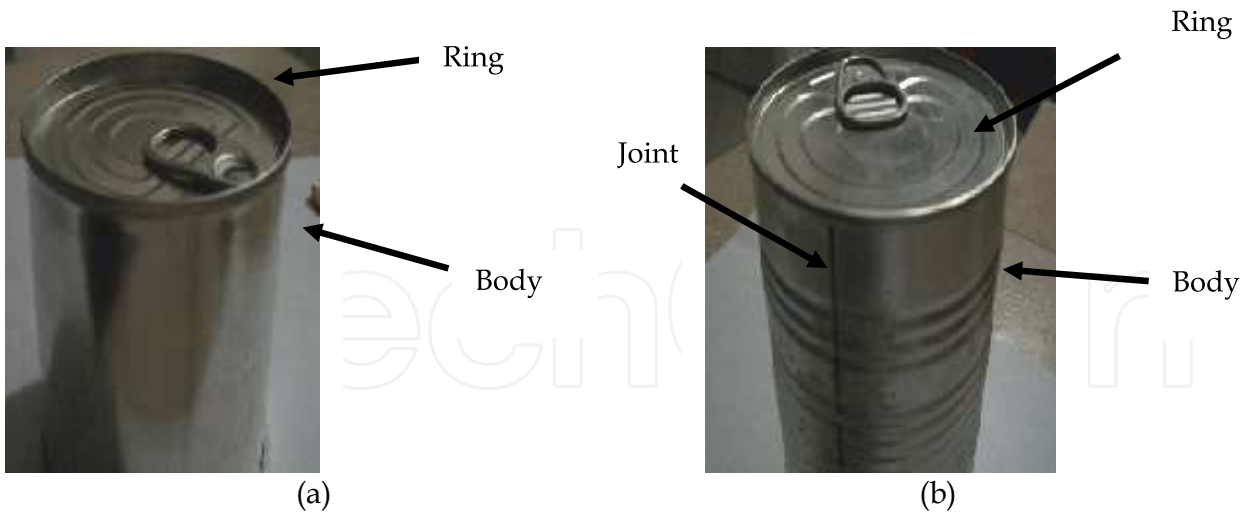


Fig. 1. (a) Aluminum cans without seams, in two parts: ring and body (b) Steel cans with seams: body, joint and rings

1.3 Production stages

The manufacture stages in a food industry are shown in Figure 2 (Avella, 2005): Washing: Cans are cleaned thoroughly to remove the bacteria that could alter the food nutritional value.

Blanching: The product is subjected to hot water immersion to remove the enzymes that produce food darkening and the microorganisms that cause rancidity.

Preparation: Before placing food in the can the non-consumable parts of the sardine and tuna are removed, then the ingredients to prepare the food in accordance with the consumption requirements are added.

Packaging: The food is placed in the can, adding preservatives such as vinegar, syrup, salt and others to obtain the desired flavor.

Air removal: The can pass through a steam tunnel at 70 ° C, to avoid bad taste and odor.

Sealing: by soldering or with seams.

Sterilization: It is of great importance for the full elimination of microorganisms that might be left over from the previous stages, when the can is treated at temperatures of 120 ° C.

Cooling. Once sterilized the cans are cooled under running cold water or cold water immersion, from the outside without affecting the food quality.

Labeling. On the can label are placed legends with product ingredients, expiration dates and lot numbers of production.

Packaging, is made to organize the food steel cans in boxes.

Food technology specialists considers, that an adequate manufacturing process of canned foods, helps to keep certain products up to several months and years, as the case of milk powder to nine months, some vegetables and meat foods two and up to five years. A diagram summarizing all these stages is displayed in Figure 2.

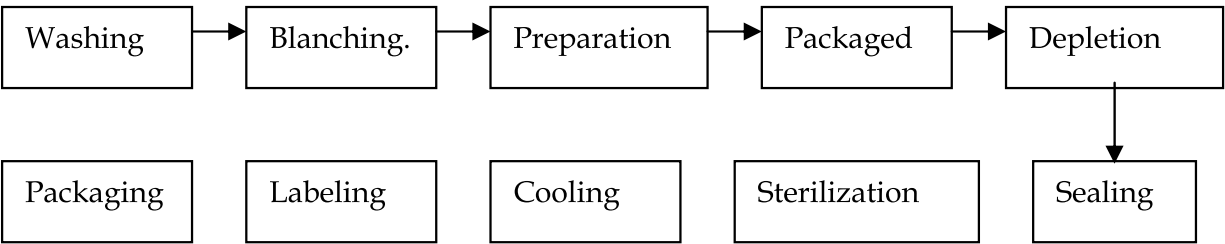


Fig. 2. Manufacturing steps in a food industry.

1.4 Sea food industry in Mexico

The main coastal cities in Mexico, with installed companies that fabricate metallic cans for sardines and tuna conservation are Acapulco, Guerrero, Ciudad del Cabo in the State of Baja California Sur; Ensenada, Baja California, Campeche, Campeche, Mazatlan, Sinaloa, Veracruz, Veracruz (Bancomext, 2010). The sardine is a blue fish with good source of omega-3, helping to lower cholesterol and triglycerides, and increase blood flow, decreasing the risk of atherosclerosis and thrombosis. Due to these nutrition properties, its widely consumed in Mexico; it contains vitamins B12, niacin and B1, using its energy nutrients (carbohydrates, fats and proteins) as a good diet. This food is important in the biological processes for formation of red blood cells, synthesis of genetic material and production of sex hormones. Tuna is an excellent food with high biological value protein, vitamins and minerals. It has minerals such as phosphorus, potassium, iron, magnesium and sodium and vitamins A, D, B, B3 and B12, which are beneficial for the care of the eyes and also provides folic acid to pregnant women. Fat rich in omega-3, is ideal for people who suffer from cardiovascular disease (FAO, 2010).

1.5 Atmospheric corrosion

Atmospheric corrosion is an electrochemical phenomenon that occurs in the wet film formed on metal surfaces by climatic factors (Lopez et al, 2011, AHRAE, 1999). One factor that determines the intensity of damage in metals exposed to atmosphere is the corrosive chemical composition in the environments. The sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon oxide (CO) and sodium chloride (NaCl) that generates chloride ions (Cl^-), are the most common corrosive agents. The NaCl enters to the atmosphere from the sea; SO_x , NO_x and CO, is emitted by traffic vehicle. The joint action of the causes of pollution and weather determine the intensity and nature of corrosion processes, acting simultaneously, and increasing their effects. It is also important to mention other factors such as exposure conditions, the metal composition and properties of oxide formed, which combined, have an influence on the corrosion phenomena (Lopez, 2008). The most important atmospheric feature that is directly related to the corrosion process is moisture, which is the source of electrolyte required in the electrochemical process. In spite of existing corrosion prevention and protection systems as well as application of coatings in steel cans the corrosion control, is not easy in specific climatic regions, especially in marine regions. Ensenada which is a marine region of Mexico on the Pacific Ocean has a marine climate with cold winter mornings around 5 °C and in summer 35° C. Relative humidity (RH) is around 20% to 80%. The main climate factors analyzed were humidity, temperature and wind to determine the time of wetness (TOW) and the periods of formation of thin films of SO_x and Cl^- which were analyzed to determine the corrosivity levels (CL) in outdoors and indoors of seafood industry plants (Lopez et al, 2010).

1.6 Corrosion of steel cans

Corrosion of tinplate for food packaging is an electrochemical process that deteriorates the metallic surfaces (Ibars et al, 1992). The layer of tin provides a discontinuous structure, due to their porosity and mechanical damage or defects resulting from handling the can. The lack of continuity of the tin layer allows the food, product to be in contact with the various constituents of the steel, with the consequent formation of galvanic cells, inside of the cans. The presence of solder alloy used in the conventional container side seam is a further element in the formation of galvanic cells. Corrosion of tin plate for acidic food produces the dissolution of tin and hydrogen gas formation resulting from the cathodic reaction that accumulate in the cans. At present, the problems arising from the simultaneous presence of an aggressive environment, mechanical stress and localized corrosion (pitting) are too frequent (CGB, 2007).

1.7 Coatings

The food in steel can is protected by a metallic or plastic coating regulated by the FDA (Food Drugs Administration, USA) that does not generate any health problems in consumers (Weiss et al, 2006). The coating is adhered on the metal plate and its function is due to three main features:

- Thermal and chemical resistance assures the protection of the steel surface when a food produces a chemical attack by rancidity, changing the food taste.
- Adherence. The coating is easily attached to the inside can surface.
- Flexibility. Resistance to mechanical operations that modify the structure of the can, in the manufacturing process, such as molding shapes and bad handling.

Currently, new materials and coatings are analyzed to fit them to food variety, beverages and other canned products (Table 3). The coatings used in the food industry are organosol type, with high solids content, creating dry films with thickness 10 to 14 g/m², for manufacturing or recycling, allowing large deformation (Soroka, 2002). To improve the strength of steel, two layers of epoxy-phenolic are applied, in the organosol film. If the food suffers decomposition, it generates deformation in the can (Yam et al, 2005). Coatings are applied on the cans on the inside and outside. Since the early twentieth century, coatings manufacturers have supported the food and beverage industries, using oleoresins resins, phenolic and later in 1935, was applied vinyl coating in the beer cans. Later comes the epoxy-phenolic coatings, organosoles, acrylic and polyester (Ray, 2006).

CLASIFICACION	
COATINGS	DEFINITION
Protection in indoors of cans	They are in contact with the packaged product and are called "health coatings"
Exterior coatings pigmented	Are used to underlie the decorative printing of packaging, called "white enamel" or "white lacquer. "
Exterior coatings transparent	Are used to underlie print, called "coatings of hitch. " Protects the printing inks of defectives manipulations, known as "clear coatings".
FUNCTIONS	
Protects the metal of the food	
Protects the product from contamination when steel parts from the can, are detached	
Facilitates the production	
Provides a basis for decoration	
Acts as a barrier against external corrosion and abrasion	
CHARACTERISTICS	
Must be compatible with the packaged product and to resist their aggressiveness	
Have a high adhesion to the tin or other metal	
Are free of toxic substances	
Not affect the organoleptic characteristics of the packaged product	
Not contain any items prohibited by the health legislation	
Is resistant of the sterilization and / or treatment, that is subject to packaging the product	
Adequately support to the welding of the body in two and three pieces of containers	
TYPES	
METALLIC	PLASTICS
Tin compound	Oleoresins, phenolic, epoxy, vinyl, acrylic, polyester
COMPOSITION	
COATING MATERIAL	COMPOSITION
Acrylic Polyester Copolymer	The polyester is inserted in the acrylic
Polyester resin	The resin is unsaturated
Crosslinker	The polyester contains acrylic acid, or maleic anhydride with styrene.

Table 3. Coatings used in the food industry

2. Materials and methods

2.1 Climate factors

The climate is composed of several parameters; RH and temperature are the most important factors in the damage of steel cans. Scientists that analyze the atmospheric corrosion, consider that the grade of deterioration of steel cans is due to the drastic changes in the humidity and temperature in certain times of the year, as expressed in ISO 9223 (ISO 9223, 1992). Managers and technicians of companies and members of health institutions in Mexico are concerned in some periods of the year, by the quality of seafood contained in steel cans (Moncmanova; 2007).

2.2 Corrosion testing

Pieces of steel rolls were prepared for corrosion testing simulating steel cans, which were exposed at indoor conditions of seafood plants for periods of one, three, six and twelve months in Ensenada, following the ASTM standards G 1, G 4, G 31 (ASTM, 2000). The results were correlated with RH, TOW and temperature parameters. The concentration levels of SO_x and Cl^- were evaluated with the sulfatation technique plate (SPT) and wet candle method (WCM), (ASTM G 91-97, 2010; ASTM G140-02, 2008). The industrial plants of seafood in this city are located at distances at 1 km to 10 from the sea shore. Steel plates used to fabricate steel cans with dimensions of 3 cm. X 2 cm. and 0.5 cm of width, were cleaned by immersion in an isopropyl alcohol ultrasound bath for 15 minutes (ISO 11844-1, ISO 11844-2, Lopez et al, 2008). Immediately after cleaning the steel probes were placed in sealed plastic bags, ready to be installed in the test indoor and outdoor sites. After each exposure period the steel specimens were removed, cleaned and weighed to obtain the weight loss and to calculate the corrosion rate (CR).

2.3 Examination techniques

The corrosion products morphology was examined by the scanning electron microscope (SEM) and the Auger Electron Spectroscopy (AES) techniques.

- SEM. Used to determine the morphology of the corrosion products formed by chemical agents that react with the steel internal and external surface. The SEM technique produces very high-resolution images of a sample surface. A wide range of magnifications is possible, from about 10 times to more than 500,000 times. The SEM model SSX-550 was used; revealing details less than 3.5 nm, in size from 20 to 300,000 magnifications and 0.5 V to 30kV by step.
- AES. It determines the chemical composition of elements and compounds in the steel cans and rolls, and analyzes the air pollutants deposited on the steel. With this technique we knew in detail, quickly and with a good precision, the structural form and location of corrosion at surface level which determined the type of corrosion (Clark, et al, 2006). AES analysis was performed in Bruker Quantax and ESCA / SAM 560 models, and the bombarding were obtained when samples with a beam of electrons with energy of 5keV. We made a clean surface of steel specimens analyzed with an ion beam with energy $\text{Ar}^+ 5\text{keV}$ and current density of $0.3 \text{ uA} / \text{cm}^3$ to remove CO_2 from the atmosphere (Asami et al, 1997). The sputtering process indicates the type of film formed on the metallic surface of steel and the corrosion on separated points such as pitting corrosion.

2.4 Numerical analysis

A mathematical correlation was made applying MatLab software to determine the CL in indoors of seafood industry in Ensenada in summer and winter (Duncan et al, 2005). With this simulation we find out the deterioration grade of steel probes, correlating the climate factors (humidity and temperature) and air pollutants (CO, NO_x and SO_x), with the corrosion rate (CR).

3. Results

The generation of corrosion in steel cans is promoted by the formation of the thin film of corrosion products in their surface and the exposition of chlorides and sulfides. The seafood industry is concerned with the economic losses caused by bad appearance of the containers and the loss of nutritional properties of sardine and tuna.

3.1 Deterioration of steel cans

Levels of humidity and temperature bigger than 75% and 35 °C accelerated the CR. In summer the CR was higher after one year. For temperatures in the range from 25 °C to 35 °C, and RH level of 35% to 75%, the CR was very high. Furthermore, in winter, at temperatures around 10 °C to 20 °C and RH levels from 25% to 85%, water condensates on the metal surface and the CR increases very fast. Variations of RH in the range from 25% to 75% and temperatures from 5 °C to 30 °C, and the concentration levels of air pollutants such as sulfides and chlorides, which exceeds the permitted levels of the air quality standard (AQS), increase the corrosion process. In the autumn and winter, corrosion is generated by a film formed uniformly on the steels (Lopez et al, 2010). Exposition to SO₂ indicates more damage, compared with the effect of the chlorides on the steel surface. The maximum CR representing the deterioration with steel exposed to SO₂ was in winter for the high concentration levels of RH and the minimum was in spring. The major effect of Cl⁻ on the deterioration of metallic surface occurred in winter and the minimum was in spring, same with the exposition of SO₂ (Table 4).

Climate factors	Sulphur oxide (SO ₂)				Chloride (Cl ⁻)			
	RH ^a	T ^b	C ^c	CR ^d	RH ^a	T ^b	C ^c	CR ^d
Spring								
Max	76.3	21.4	0.24	68.8	73.5	25.6	234	59.3
Min	24.3	13.5	0.20	35.7	24.3	13.3	122	24.8
Autumn								
Max	82.7	29.8	0.31	145.7	78.9	30.6	267	136.7
Min	28.4	20.7	0.18	109.8	16.7	15.8	187	99.8
Winter								
Max	88.9	23.4	0.51	205.6	84.3	31.2	299	178.9
Min	23.2	15.6	0.36	144.6	22.1	13.7	197	122.3

[a] RH. Relative Humidity (%), [b] T. Temperature (°C), [c] C. Concentration Level of Air Pollutant (ppm), [d] CR- Corrosion rate (mg/ m2.year).; Source. TPS and WCM.

Table 4. Effect of RH, temperature and air pollutants on the CR of steel (2010)

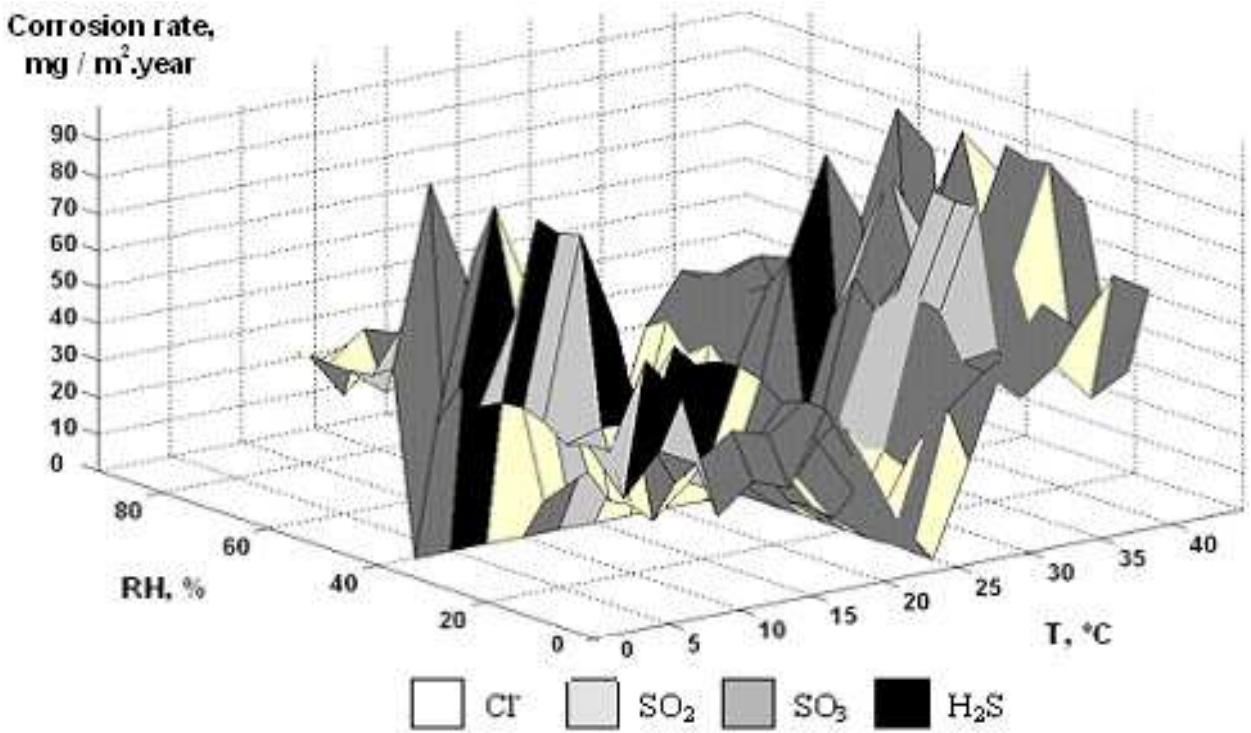


Fig. 3. CL of steel during summer exposition in Ensenada.

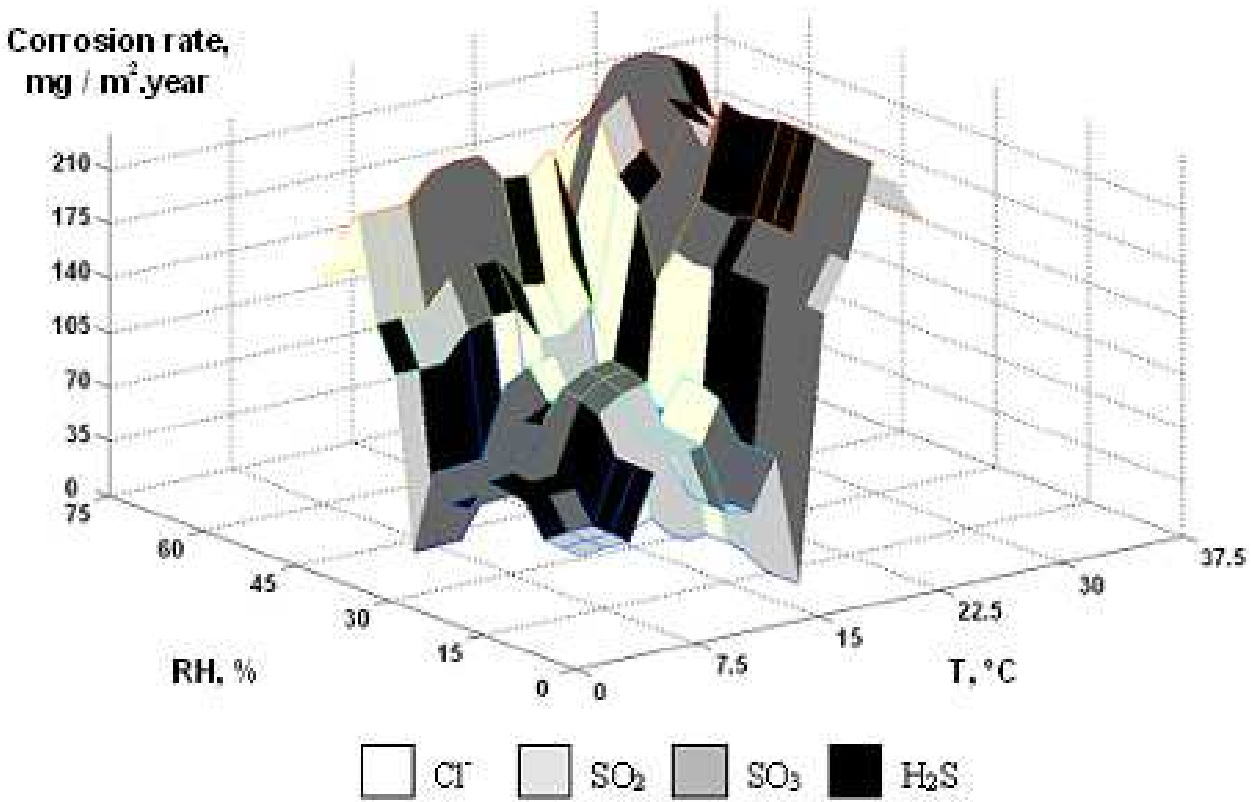


Fig. 4. CL of steel during winter exposition in Ensenada.

3.2 Corrosivity analysis

A computer model of atmospheric corrosion has been used to simulate the steel exposed to air pollutants: Cl^- , SO_2 , NO_2 , O_3 and H_2S from a thermoelectric station located between Tijuana and Ensenada. RH was correlated with the major CR was 35% to 55% with temperatures of 20°C to 30°C . In summer CR was different than in winter, and in both environments (Figures 3 and 4). Air pollutants such as Cl^- , NO_2 and sulfide penetrate through defects of the air conditioning systems. Figure 3 shows the CL analysis of indoors in summer, indicating the level 1, as the major aggressive environment and levels 4 the low aggressiveness grade which generate high deterioration grade of this type of materials. Some sections of the Figure 4, represents the different grades of aggressiveness, with high areas of level 1 and 2 but levels 3 and 4 exists in less percentage. RH and temperature ranges were from 25% to 80% and 20°C to 30°C with CR from $30\text{ mg} / \text{m}^2\cdot\text{year}$ to $100\text{ mg} / \text{m}^2\cdot\text{year}$ with RH and temperatures from 40% a 75% and 20°C to 35°C , with CR from 10 to $160\text{ mg} / \text{m}^2\cdot\text{year}$.

3.3 SEM analysis

The steel samples of 1, 3, 6 and 12 months show localized corrosion with small spots during the summer period and more corroded areas with uniform corrosion in the winter. Air pollutants that react with steel surface form corrosion products, in some zones of steel cans and rolls with chloride ions (light color) and other with sulfides (dark color), as shown in the AES analysis. Some corrosion products in the internal of steel cans appeared on the surface contaminating the sardine (Figures 5 and 6). Various microorganisms and microbial metabolites are human pathogens in sardine and tuna conserved in steel cans were detected (Figures 7 and 8). According to the most common source of these organisms, they can be grouped as follows:

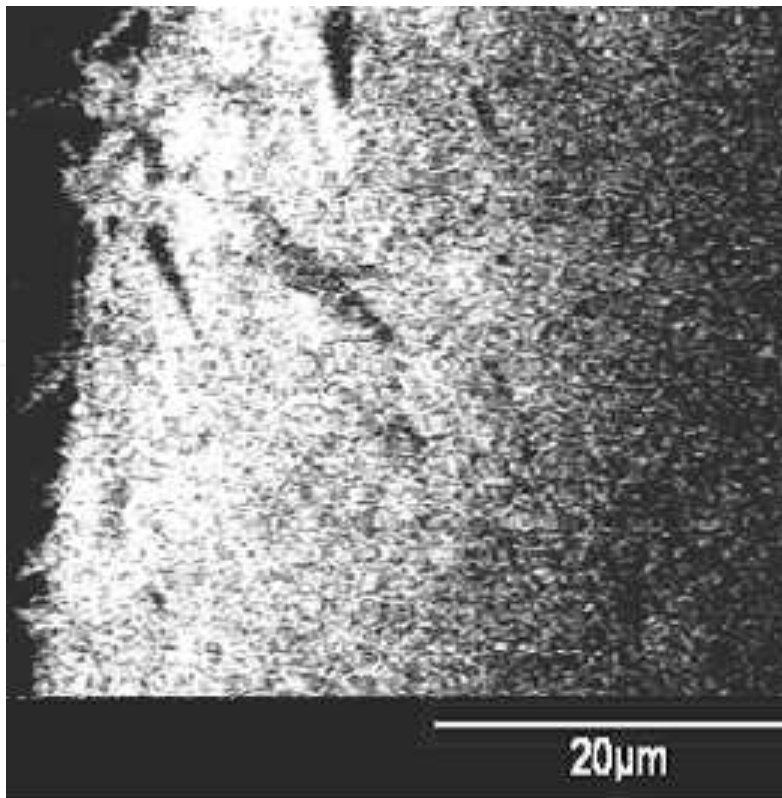


Fig. 5. Sardine contaminate with tin plate steel corrosion products.

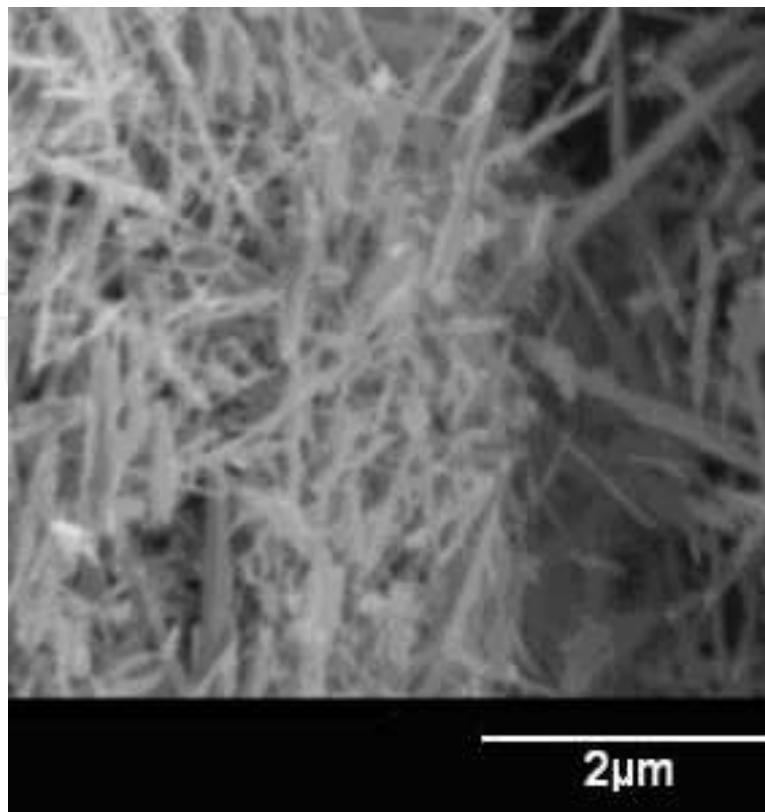


Fig. 6. Filiform corrosion formed in internal of tin plate steel cans

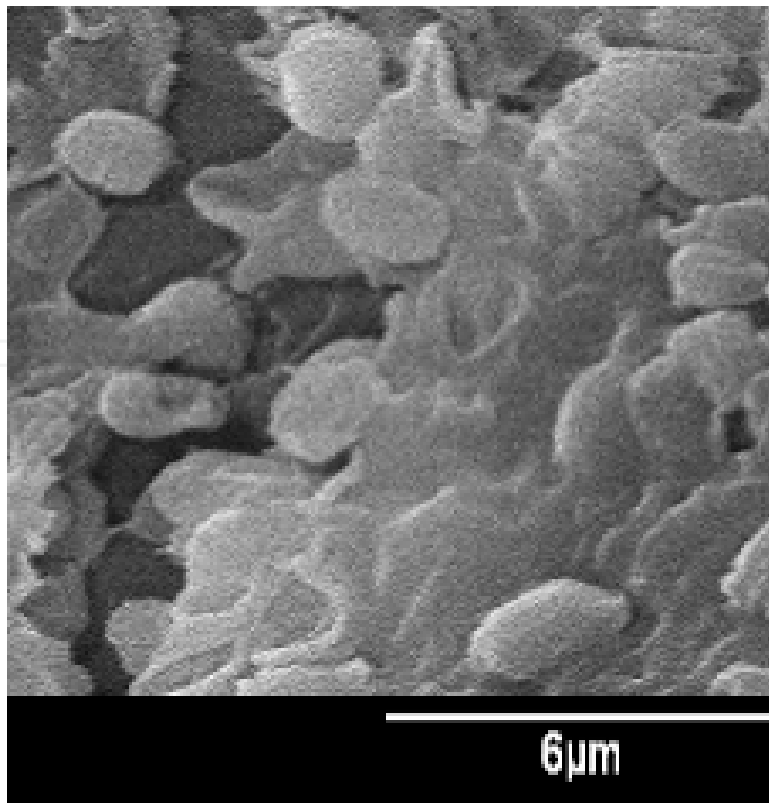


Fig. 7. Microbiological corrosion in internal of steel cans with plastic coatings.

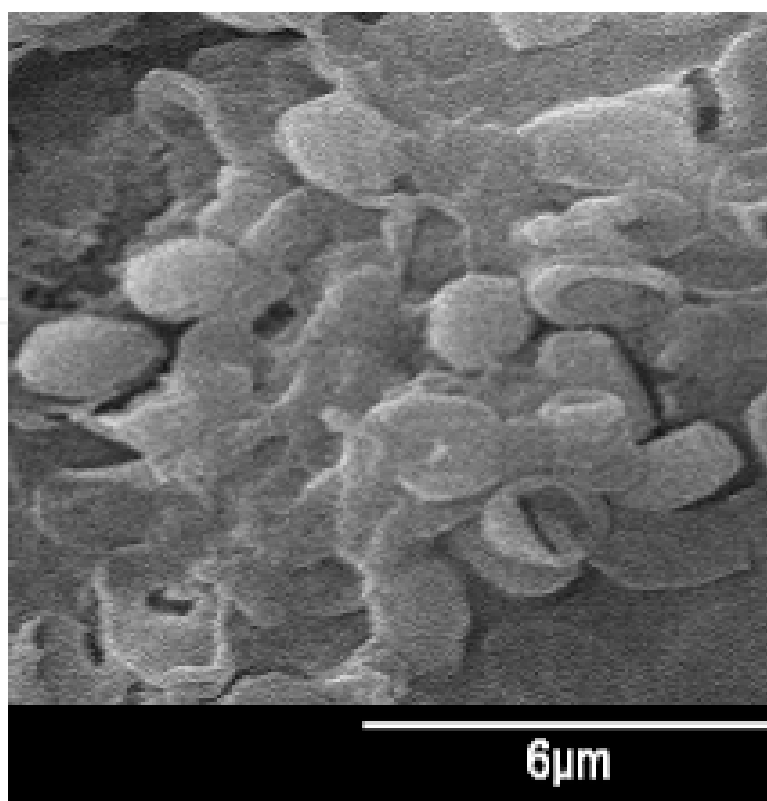


Fig. 8. Microbiological corrosion in internal of steel cans with tin coatings.

1. Endogenous. Originally present in the food before collection, including food animal, which produces the zoonoses diseases, transmitted from animals to humans in various ways, including through the digestive tract through food.
2. Exogenous. Do not exist in the food at the time of collection, at least in their internal structures, but came from the environment during production, transportation, storage, industrialization. Fungi are uni-or multicellular eukaryotic type, their most characteristic form is a mycelium or thallus and hyphae that are like branches.

3.4 AES examination

AES analyses were carried out to determine the corrosion products formed in indoor and outdoor of the steel cans. Figure 9a show scanning electron micrograph (SEM) images of areas selected for AES analysis covered by the principal corrosion products which are rich in chlorides and sulfides in tin plate steel cans evaluated. The Auger map process was performed to analyze punctual zones, indicating the presence of Cl^- and S^{2-} as the main corrosive ions present in the steel corrosion products. The Auger spectra of steel cans was generated using a 5keV electron beam (Clark et al, 2006), which shows an analysis of the chemical composition of thin films formed in the steel surface (Figure 9b). The AES spectra of steel cans in the seafood plants show the surface analysis of two points evaluated in different zones of the steel probes. The peaks of steel appear between 700 and 705 eV, finding the chlorides and sulfides. In figure 10, the spectra reveals the same process as in figure 9 with plastic coatings, with variable concentration in the chemical composition. In the two regions analyzed, where the principal pollutant was Cl^- ion. In the region of steel surface were observed different concentrations of sulfide, carbon and oxygen, with low levels concentrations of H_2S , which damage the steel surface.

The standard thickness of 300 nm of tin plate and plastic coatings of internal and external of steel cans was determined by the AES technique with the sputtering process.

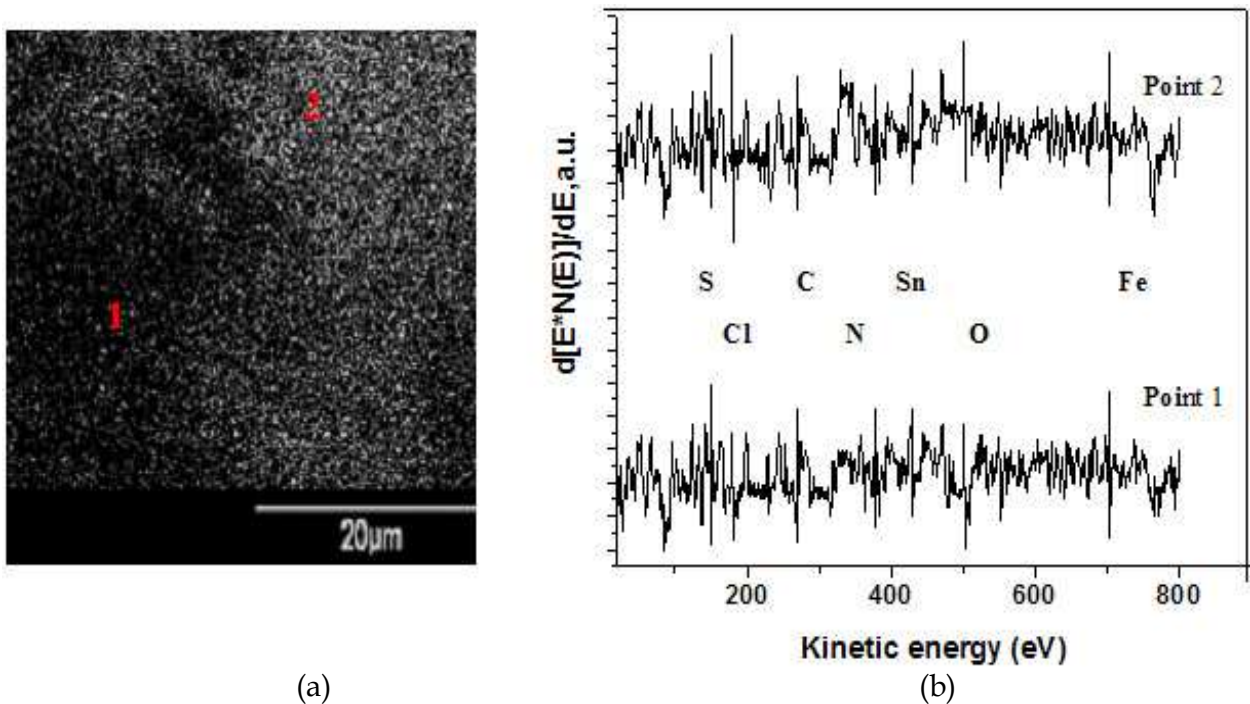


Fig. 9. Corrosion products of tin plated steel: (a) SEM microphotograph and (b) AES analysis, three months exposure.

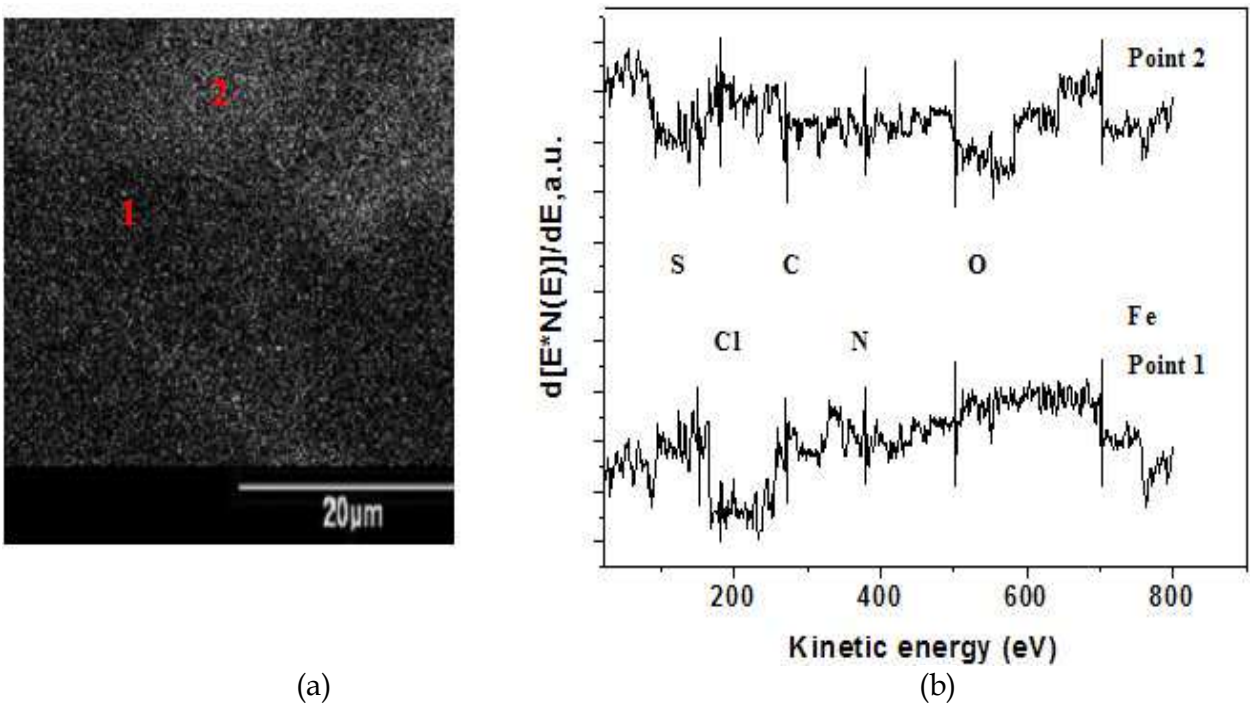


Fig. 10. Corrosion products of plastic coatings: (a) SEM microphotograph and (b) AES analysis, three months exposure.

4. Conclusions

Corrosion is the general cause of the destruction of most of engineering materials; this destructive force has always existed. The development of thermoelectric industries, which generates electricity and the increased vehicular traffic, has changed the composition of the atmosphere of industrial centers and large urban centers, making it more corrosive. Steel production and improved mechanical properties have made it a very useful material, along with these improvements, but still, it is with great economic losses, because 25% of annual world steel production is destroyed by corrosion. The corrosion of metals is one of the greatest economic losses of modern civilization. Steel used in the cannery industry for seafood suffer from corrosion. The majority of seafood industries in Mexico are on the coast, such as Ensenada, where chloride and sulfide ions are the most aggressive agents that promote the corrosion process in the steel cans. The air pollutants mentioned come from traffic vehicles and from the thermoelectric industry, located around 50kms from Ensenada. Plastic coatings are better than tin coating because, on the plastic coatings do not develop microorganisms and do not damage on the internal surface.

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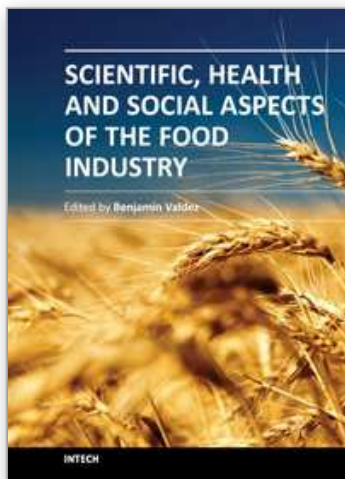
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This book presents the wisdom, knowledge and expertise of the food industry that ensures the supply of food to maintain the health, comfort, and wellbeing of humankind. The global food industry has the largest market: the world population of seven billion people. The book pioneers life-saving innovations and assists in the fight against world hunger and food shortages that threaten human essentials such as water and energy supply. Floods, droughts, fires, storms, climate change, global warming and greenhouse gas emissions can be devastating, altering the environment and, ultimately, the production of foods. Experts from industry and academia, as well as food producers, designers of food processing equipment, and corrosion practitioners have written special chapters for this rich compendium based on their encyclopedic knowledge and practical experience. This is a multi-authored book. The writers, who come from diverse areas of food science and technology, enrich this volume by presenting different approaches and orientations.

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