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Atmospheric Corrosion in Indoor of Seafood Industry in the Norwest of Mexico

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Abstract

The metallic cans used to packed seafood are made from rolls of steel sheet coated with appropriate films. The exposure of steel cans to aggressive environments generates internal and external damage of these containers, and for this reason are necessary use coatings. The main air pollutants that cause atmospheric corrosion (AC) in steel cans in the northwest of Mexico where are located the city of Ensenada, are the chloride ions (Cl-) and sulfur oxides (SOX) principally. The corrosion in food containers generates economic losses and damages to the health of the consumers. The food industry, spend large financings in the recovery of damaged cans. When in a steel roll are generated black spots on the internal and external of steel cans, even in a good cleaning process, can not be used for food packaging and this is material lost. A study using the Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES) techniques was carry out to determine the agents that react with the metallic surface of steel and know the thin layer of this films formed by the air pollutants. An evaluation of steel cans and sections of rolls of steel was made in three industrial plants, to know the reasons of the deterioration of materials, which caused economic losses. For the study was necessary analyze humidity and temperature parameters in indoor of the seafood industry of Ensenada and correlated with the corrosion rate (CR) of the internal and external areas of the steel cans using the ISO90001 standards, and also, determine the corrosivity levels (CL) in indoor of industrial plants. The information obtained was showed to specialized people and managers of the industries where was made the study to control the climatic factors and have the best clean environment with the minimum levels of Cl- and SOX. With these methods the CR decreased by 50%, and prevented economic losses and health problems with the consumers.

Key words: seafood industry, atmospheric corrosion, steel cans, SEM, AES.

Resumen
(Corrosión atmosférica en la industria de mariscos en el noroeste de México)

Los envases metálicos utilizados para la conservación de mariscos en la industria de alimentos, se fabrican de rollos de acero recubiertos con películas adecuadas. La exposición de las latas de acero a ambientes agresivos genera daños internos y externos en estos contenedores, y por esta razón son necesarios el uso de los recubrimientos. Los principales contaminantes atmosféricos que causan la corrosión atmosférica (CA) en las latas de acero en el noroeste de México, donde se encuentra la ciudad de Ensenada, son los iones cloruro (Cl-) y los óxidos de azufre (SOX) principalmente. La corrosión en los envases metálicos genera pérdidas económicas y daños a la salud de los consumidores. La industria de alimentos, gasta grandes financiamientos en la recuperación de latas dañadas. Cuando en un rollo de acero se generan puntos negros en la parte interna y externa de las latas, incluso en un proceso de limpieza bueno, no pueden utilizarse para el envasado de alimentos y es material perdido. Se realizó un estudio utilizando las técnicas del microscopio de barrido electrónico (MBE) y la de espectroscopia de electrones Auger (EEA) para determinar los agentes que reaccionan con la superficie metálica de acero y conocer las capas delgadas de estas películas formadas por los contaminantes del aire. Se llevó a cabo una evaluación de las latas de acero y secciones de rollos de acero, en tres plantas industriales de esta ciudad para evaluar la razón del deterioro de materiales que causaron pérdidas económicas. Para el estudio fue necesario analizar los parámetros de humedad y temperatura en el interior de la industria de mariscos de Ensenada y correlacionarlos con la velocidad de corrosión (VC) de las áreas internas y externas de las latas de acero, utilizando los estándares ISO90001 y determinar además, los niveles de corrosividad (CL) en el interior de plantas industriales. La información obtenida se mostró a las personas especializadas y gerentes de las industrias en las que se realizó el estudio para controlar los factores climáticos y tener el mejor ambiente limpio con los niveles mínimos de Cl-y SOX. Con estos métodos la VC disminuyó en un 50%, y se evitaron pérdidas económicas y un problema de salud con los consumidores.

Palabras clave: industria de mariscos, corrosión atmosférica, envases metálicos, técnica MBE, técnica EEA.

1. Introduction

The use of metal containers for food preservation comes from the early nineteenth century, and has been very important in the food industry [1]. This type of packaging was developed to improve the food conservation since the Napoleon age. Plastics materials have been used for several years, but the food was damaged in the food handling activities. For this reason, the metallic materials for fabricate steel cans (SC) have been utilized in the last years. This SC are exposed in the manufacturing process to aggressive air pollutants that penetrate through cracks and air conditioners systems to indoors of the seafood industry (SFI), and the corrosion process occurs [2]. On the Pacific Ocean in the northwest of Mexico, is located the Ensenada city, where are established some SFI, and have found recently AC in the steel rolls used to the metallic cans. This steel rolls are collocated in the warehouses and production areas, which are before than the manufacturing operations, and are damaged for the AC, that too deteriorate the SC fabricated. The steel cans are used to packed sardine and tuna in indoor of the seafood industry [3]. Currently, the cans are fabricated with the adequate treated methods using electrolytic processes for depositing tin. In addition, a variety of plastic coatings and lacquers are used to protect the steel rolls, to avoid the corrosion and produce the adequate brightness for printing legends on the outside of the metallic cans [4]. This analysis was made to characterize the chemical agents that generate the AC and damage the internal and external steel surface of metallic cans used in the SFI. With metal packaging, the food reaches 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 Mexican Official Standards (NOM). The AC in internal and external surfaces of cans appears frequently in the manufacturing processes of SFI in presence of humidity [5].

Sea food industry in Mexico

The main coastal cities in Mexico, with installed companies that fabricate metallic cans or handling the SC for conservation of sardines and tuna are Acapulco in Guerrero, Ciudad del Cabo in Baja California Sur, Ensenada in Baja California, Campeche city in Campeche, Mazatlan in Sinaloa and Veracruz port in Veracruz [6]. 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, is widely consumed in Mexico; containing vitamins B12, niacin and B1, used as energy nutrients (carbohydrates, fats and proteins) as a rich 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 eyes and also provides folic acid to pregnant women. Fat rich in omega-3, is ideal for people who suffer from cardiovascular disease [7].

Coatings

The food in steel can is protected by a metallic or plastic coating film, regulated by the FDA (Food Drugs Administration, USA) that does not generate any health problems in consumers [8]. The coating is adhered on the metal plate and its function is due to three main features:

- Thermal and chemical resistance, assuring the protection of the metal surface when a food produces a chemical attack by rancidity, changing the food taste.
- Adherence. The coating easily attaches to the inside can surface.
- Flexibility. Excellent resistance to mechanical operations in the manufacturing process, such as molding shapes.

The coatings used in the food industry are organosol type, with high solids content, creating dry films with thickness from 10 to 14 g/m^2, for manufacturing or recycling, allowing large deformation. To improve the steel strength, two layers of epoxy-phenolic are applied. If the food suffers decomposition, it generates an alert by a bulge [9]. Coatings are applied on the cans in the internal and external zones. Since the early twentieth century, coatings manufacturers have supported the food and beverage industries, using oleoresins resins, phenolic and later in 1935, a vinyl coating was applied in the beer cans. Later came the organosoles, acrylic and polyester to the SC[10].

Effect of weather on AC of steel cans

The steel cans used in the seafood industry suffer from corrosion, at high humidity levels principally. Air pollutants such as CO, NO_x and sulfides penetrate through the air conditioning systems [11, 12]. The AC is an electrochemical phenomenon that occurs in the wet film formed on metal surfaces by climatic factors. This film is the electrolyte which corrodes the metal, creating metal ions [13]. The main climate factors analyzed were humidity, temperature and wind in indoor of SFI. Their magnitude, measuring instruments and units are shown in table 1. In Ensenada, the winter mornings are cold around 5°C and in summer 30°C and the relative humidity in all time of the year are 75% and 90% in winter.

Table 1. Climatic factors and their measurement.

Factors	Measuring instrument	Unit
Humidity	Hygrometer	%
Temperature	Thermometer	ºC
Atmospheric pressure	Barometer	mmHg
Solar radiation	Pyranometer	W/m²
Pluvial precipitation	Rain gauge	Mm
Wind direction	Wind vane	º grade
Wind speed	Anemometer	m/s

Pollution and corrosion

Indoor atmospheric corrosion process involves deposition of particles as a major source of corrosive reactants. Fine atmospheric particles (0.2 mm or less in diameter) such as natural materials generated from rocks and soils, being usually not corrosive but can be abrasive in the SC [14]. They are prevalent because fine particles are difficult to remove by air conditioning filters. The most common ions found in these particles are NH_4^+, Cl- and SO_4^{2-}, typically present in roughly equal molar portions. Another important factor is the decreased levels of indoor atmosphere in oxidant agents as O_3, H_2O_2, NO_2 and HNO_3 [15, 16]. Also are included the different speeds of air flow in indoor air generated by the levels of RH and temperature in indoor of SFI, being an important factor in the moisture accumulation, in the generation of corrosion process. RH values above 75%, temperatures lower than 15°C in special in winter, and levels of chlorides, that overpass the air quality standards (AQS) in Ensenada, promotes and increases the corrosion [1]. The composition of the steel surface was obtained by the Auger spectra, showing localized corrosion from the first to six months of exposure, and appearing the uniform corrosion from six months. The particles and gases contaminants deposited on the metal surfaces of food containers, are generated in industrial areas with manufacturing operations which use chemical agents and is a factor that originates the deterioration. Metallic containers fabricated in industrial plants are exposed to aggressive atmospheres in the indoor environments of the SFI where are formed the thin films of water very easy and generating uniform corrosion, with efficiency of O_2 [4]. In contrast, in the outdoor environments of the SFI, the wet film on the metal surface where are collocated by some periods of time the steel rolls, are formed more slowly the thin wet films and appear the pitting corrosion. Sometimes the indoor temperature and RH are controlled and, consequently, the amount of adsorbed water surfaces is minimal and therefore the film is not formed [7].

2. Materials and methods

Steel is used in the food industry due to its mechanical properties and is very susceptible to the AC at the indoor polluted conditions [11].

Climatic factors measurements

Climate is composed of several parameters, where the RH and temperature are the most important in the damage of SC. These climatic factors are measured with specialized equipments, which consist of a hygrometer and thermometer that send the information of values to a PC to be evaluated. The information is organized in hourly, daily, weekly, monthly, seasonally and yearly periods, to be correlated to other parameters. Scientists that analyze the AC, consider that the grade of deterioration of metallic cans is due to the CL, originated by drastic changes in the humidity and temperature in certain times of the year, as is expressed in the ISO 9223 standard [16]. Managers and technicians of companies and people of health institutions in Mexico are concerned in some periods of the year, by the quality of the seafood contained in SC, for the generation of black spots in its containers [17].

Environmental parameters

The concentration levels of SOX and Cl- were evaluated with the sulfate technique plate (SPT) and wet candle method (WCM), [18, 19]. This analysis was organized in similar periods as the RH and temperature obtained and mentioned above. The evaluation was made to correlated with the CR and to obtain the CL [2].

Corrosion testing

Ten pieces of steel rolls were prepared weekly for corrosion testing simulating the complete SC, to evaluate the corrosion rate with the gravimetric method, which were exposed at indoor conditions of the SFI for periods of one, three, six and twelve months in Ensenada, following the ASTM standards G1, G4, G31 [20, 21, 22]. The results were correlated with RH, TOW and temperature parameters. 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 SC with dimensions of 3 cm. x 2 cm. and 0.5 cm of width, were cleaned by immersion in an isopropyl alcohol ultrasound in a bath for 15 minutes [23]. Immediately after the cleaning process, the steel probes were placed in sealed plastic bags, ready to be installed in the test indoor and outdoor sites. After each period of exposure the steel specimens were removed, cleaned and weighed to obtain the weight loss and to calculate the CR.

Examination techniques

The corrosion products morphology was examined by the SEM and the AES techniques [24].

- SEM. This 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. As the SEM technique determines the chemical composition of the corrosion products, that are formed by the chemical reactions in the SC and steel rolls. The difference with the SEM technique is that, the AES equipment evaluate at nanoscale [25]. AES analysis was performed in Bruker Quantax and ESCA / SAM 560 models, which was and bombarding the 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 Ar + 5keV and current density of 0.3 uA / cm3 to remove CO2 from the atmosphere. The sputtering process indicates the type and wide of the films formed on the metallic surface of steel, and showed the deterioration of the SC and steel rolls.

Statistical methods of analysis

Statistical data was evaluated by Excel and organized in tables and graphs to the corrosion process in the SC. The variations of RH and temperature, and the concentration levels of air pollutants were correlated by a regression and correlation methods to quantify the association between the variables evaluated.

3. Results

The corrosion in SC was promoted by the formation of the wet thin film in their surface and the exposition of chlorides and sulfurs. It is very common in the buildings located in this coastal city. This causes bad appearance of metallic containers which with insalubrities conditions and after a large period of be manufactured, are necessary to throw.

Deterioration of SC

Ranges of RH and temperature were higher than 75% and lower than 15ºC during the winter period, with a minimum of 35% of RH and maximum of 35ºC in the summer season with a bit heat winds. Levels of RH and temperature were higher than 75% and 35 °C, accelerating the CR. In summer the CR was lower after one year, but in winter was very fast. For temperatures in the range from 25 ºC to 35 ºC, and RH levels of 55% to 85%, the CR was very high. Furthermore, in winter, at temperatures around 10 ºC to 20 ºC and RH levels from 25% to 85%, water condensates on the metal surface and the CR increases rapidly. Variations of RH in the range from 25% to 75% and temperatures from 5 ºC to 30 ºC, and the concentration levels of air pollutants such as sulfides and chlorides, which exceeds the permitted levels of (AQS), that increase the corrosion process. In the autumn and winter, the corrosion was uniform and in and in spring and summer was pitting corrosion [26, 27]. Exposition of SC to SO2 indicates mores damage, compared with the effect of the chlorides in the metallic surface of steel probes. The maximum CR represents the damage, derived by the exposition of SO2, being 208.7 mg/m^2 year in winter, and influenced by the high concentration levels of 0.53 ppm and levels of RH and temperature of 87.9 % and 22.9 °C. The minimum level of CR was 56.7 mg/m^2.year in spring, and the minor with concentration levels of 0.17 ppm and, levels of RH and temperature of 29.1 % and 23.8 °C. The correlation process was at weekly of 0.89, monthly 0.94, seasonally of 0.91 and at the year 0.91 showing the good association between climatic and air pollutants, and the fast presence of the corrosion. 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 2).

SEM analysis

The metallic samples was exposed at 1, 3, 6 and 12 months to the steel analyzed showed localized corrosion with small spots, from the three to six months, and at one year were observed larger, being more concentrated the corroded areas and generating uniform corrosion. Air pollutants added to steel surface forms thin layers, with more chloride ions (light color) and other with less concentration of sulfur (dark color), as showed in the AES analysis. Some micro corrosion products in the interior were deteriorated, emerging from the SC and added to the sardine as showed in figure 1. Figure 1a show the SEM images at 500µm and 1b at 5µm in the internal area and Figure 2a shows the SEM images at 500µm and 2b at 5µm in the external zone, where are observed the film broken, emerging of a corroded steel can exposed at one year, in indoor of the SFI. These were the principal corrosion products, rich in chlorides and sulfides in the SC covered by tin.

AES examination

AES analyses were carried out to determine with major precision the chemical agents that reacted with the SC. The Auger spectra of SC were generated using a 5keV electron beam (Figure 1c). The AES spectra show the surface analysis of two points evaluated in different zones of the steel probes.

Table 2. Effect of RH, temperature and AP in the CR of steel in Ensenada (2010).

Climate factors	Sulphur oxide (SO_2) RH[a]	T[b]	C[c]	CR[d]
Spring				
Max	77.5	21.7	0.25	144.3
Min	27.6	13.8	0.21	126.2
Summer				
Max	83.2	34.1	0.30	88.9
Min	29.1	23.8	0.17	56.7
Winter				
Max	87.9	24.5	0.53	208.7
Min	22.9	16.1	0.37	146.3

Climate factors	Chloride (Cl^-) RH[a]	T[b]	C[c]	CR[d]
Spring				
Max	74.2	24.3	288	151.2
Min	25.2	14.5	144	101.3
Summer				
Max	79.4	32.1	156	99.5
Min	32.2	19.9	99	65.7
Winter				
Max	82.1	24.5	301	192.1
Min	23.2	11.2	202	143.4

[a] RH. Relative Humidity (%), [b] T. Temperature (ºC), [c] C. Concentration Level of Air Pollutant (ppm), [d] CR- Corrosion rate (mg/m^2.year).; Source. TPS and WCM.

The peaks of steel appear between 700 and 705 eV, finding the chlorides and sulfides. In figure 2c, the spectra reveal the same process as figure 1c in the external steel surface. The chemical composition in the both analysis was reveled, with different concentrations of chloride, sulfur, carbon, nitrogen, oxygen, which damage the steel surface.

4. Conclusions

Corrosion is the general cause of the destruction of most of natural materials. The majorly of seafood industries in Mexico are in the coast, as the case of this study occurred in Ensenada, where chloride ions and sulfates were the most aggressive agents that generated the corrosion process in the SC. Other air pollutant that was contributed to the increasing of the CR was the nitrogen oxides. Both air pollutants mentioned are from traffic vehicles and from the thermoelectric industry as produced H_2S, located between around 50 km from Ensenada. The major corrosion occurred

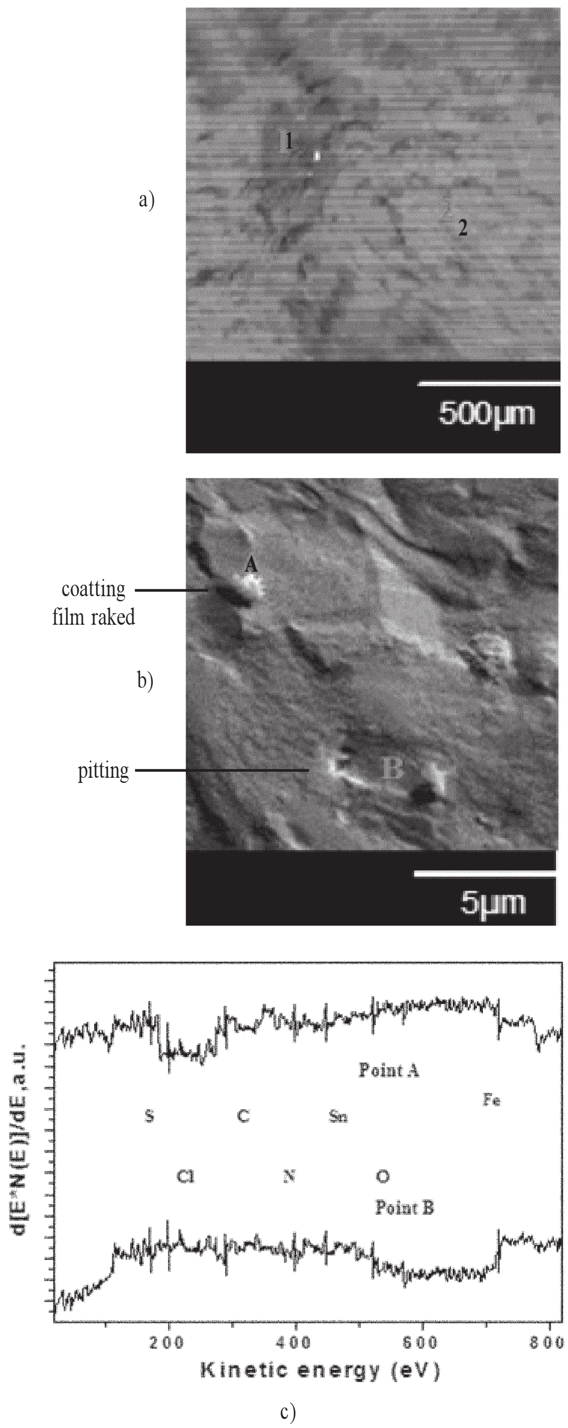

Fig. 1. Internal evaluation of atmospheric corrosion in tin plate steel cans: (a) SEM 500X, (b) SEM 5X at point 1 and (c) AES analysis of SEM 5X exposed at six months.

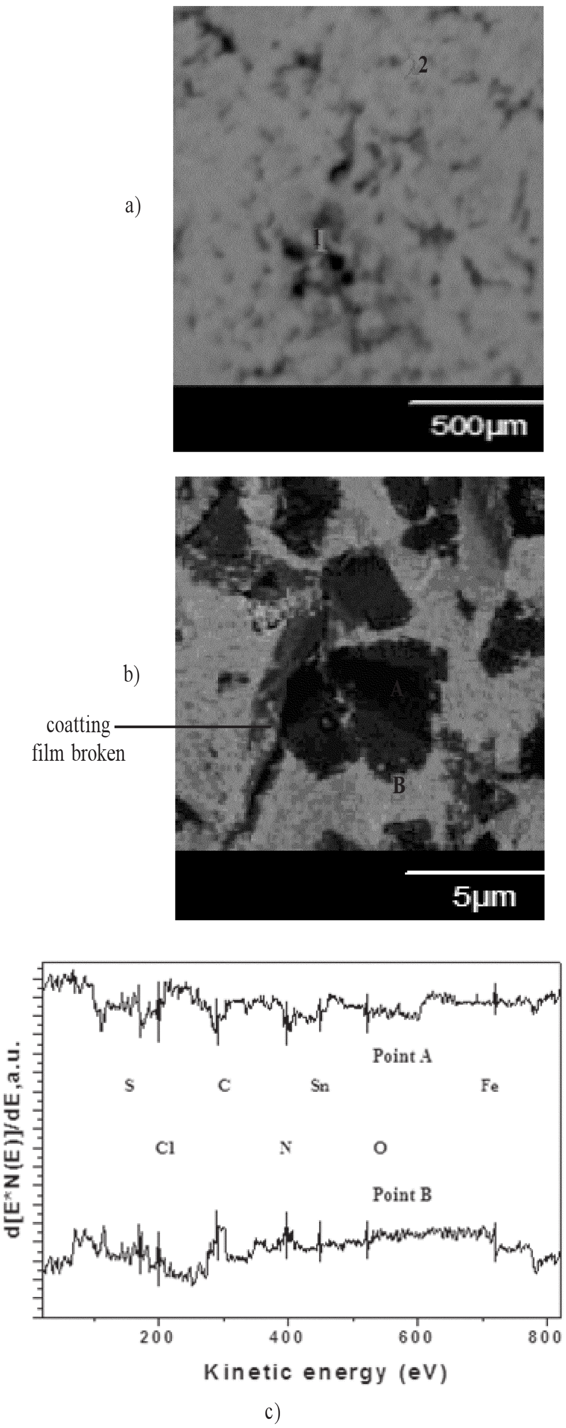

Fig. 2. External evaluation of atmospheric corrosion in tin plate steel cans: (a) SEM 500X, (b) SEM 5X at point 1 and (c) AES analysis of SEM 5X exposed at six months.

in cans with tin plate steel cans and the minor in steel cans with plastic coatings, indicating that the material without the tinned process is better to conserve sardine and tuna in good conditions. The correlation values indicates, that at low interaction of ions in the metallic surface of SC, was generated the protective film in almost the surface, excepting the isolated zones where was braked the films. Microphotographs of SEM show the corrosion products with some light stains of chlorides and the dark tarnishing of sulfates. The gravimetric method presented the maximum loss mass with 208.7 mg/m2.year and the minimum of 56.7 mg/m2.year on the experimental steel rolls probes and SC, used to evaluate the internal and external surfaces. The AES analyses show the chemical composition with major precision and the images of deterioration of SC and steel rolls, after the sputtering process.

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