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THE INFLUENCE OF THE EXTERNAL SALINITY IN THE OSMOTIC BLISTERING ON MARINE COATINGS IN TOTAL IMMERSION

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Abstract

The use of anticorrosive paints to protect the hulls of ships is essential. These coatings are deteriorating because they are completely submerged. One phenomenon that appears in the degradation of the coating is blistering. This type of blistering has two origins, the cathode and osmotic. The cathodic blistering occurs as a result of the cathodic reaction of corrosion process, that takes place on the metallic substrate. The osmotic blistering is caused by the difference of concentration of the solutions (pollution solution interface and external). Applying these coatings on nonmetallic substrates would result in blistering, therefore, of osmotic origin. This article presents a study in plastic surfaces painted with chlorinated rubber pigmented with iron oxide. These were contaminated with NaCl at the interface substrate / paint and immersed in water with different (salt concentrations) salinities in order to recreate the various salinities of sea water which can be exposed the ship's hull.

The objective of this work is to analyze the influence of external salinity on the emergence of such blistering.

Key words: Osmotic blistering, interface contamination, chlorinated rubber coating.

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INTRODUCTION

One of the phenomena of degradation in the marine paintings in conditions of total immersion is the blistering. The blistering, however, doesn't have an only origin. Funke said that the formation of blisters may be due to four causes (Funke, 1981):

1. The inclusion or formation of gases (Van Laar,1961).
2. The volume's expansion of the coating film (Brunt,1964; James,1960).
3. The osmotic processes originated by the presence of soluble pollutants in the interface coating / substrate (Bullet, Rudram,1961).
4. Electroendosmotic effect (Berendsen, 1989).

It would be necessary to add to that exposed two causes:

5. Vapours or liquids in the interface.
6. The permeability of the coating films.

Osmosis can be defined as the unidirectional diffusion of water and other solvents through a semipermeable membrane. In the beginning, could only cross the membrane solvent, although some authors suggest that most of the paint films may allow the diffusion of inorganic salts such as chlorides and sulfates.

In this process, the solvent passes from low concentration solution to the most concentrated, through the paint film which lies between the two solutions. The osmotic flow will continue until the concentrations of the two solutions are equal, or until it reaches the maximum pressure that the membrane can withstand. . The osmotic blistering occurs as a result of increased osmotic pressure in the area that initially had higher concentration of solute, the membrane bending to increase the volume of this area, thus reducing the pressure.

The factors necessary to bring the phenomenon of osmosis are:

1. A solution containing salts.
2. A semipermeable membrane (painting film).
3. A source of solvent (the water).
4. An impermeable substrate (steel hull of the ship or methacrylate).

The combination of these four factors often occurs in the hulls of ships, because the painting operations are performed in the vicinity of the sea. This causes the salt particles are attached to the hull surface In making the painting, this substrate contaminated with salts be covered with a layer of paint that will act as a semipermeable membrane. When the ship is in the sea, the underwater hull is submerged in water with some degree of salinity. By having different salt concentrations of seawater and the interface is produced by the process described above, resulting in blistering of the paint.

The aim of this article is the analysis of the osmotic blistering and the influence that the contamination interface has in its appearance. In this study we have used acrylic surfaces, which ensures that everything is osmotic blistering.

This work is part of a wider project that is carrying out for the authors about the mechanisms of osmotic and cathodic blistering of marine paintings in continuous immersion that is carried out in the University of the Basque Country.

EXPERIMENTAL

The testing procedure carried out in this study consisted of the measure of the degree of blistering generated by osmosis in plastic specimens. In order to generate the osmotic process, the interface substrate / paint was contaminated with 500 mg/m^2 Cl^-. We considered the following parameters to observe its influence:

1. External NaCl concentration: the specimens were immersed in 8 NaCl solutions: 0 – 5 – 10 – 20 – 25 – 30 – 35 and 40 g/l (NaCl), simulating different concentrations of seawater.
2. Coating thickness: thickness of 50, 100 and 150 μm.
3. Time of exposure in these conditions twelve months and periodic inspections during this time.

The total number of specimens used for this research was 48, that is, since two specimens were tested for each of the 24 possible combinations. As both sides were used for each specimen, the total number of test surfaces was 96.

The specimens consisted of 12 x 8 cm pieces of plastic. The specimens were cleaned and the substrate/coating interface was contaminated with 500 mg/m^2 Cl^-.

After these operations, the specimens were painted by means of a special tool, able to provide the uniform thickness required in each case: 50, 100 and 150 μm.

Once the specimens were prepared, they were placed into 8 plastic boxes, containing the above mentioned external solutions. They were exposed in these conditions at 25°C and continuous air flux during 12 months.

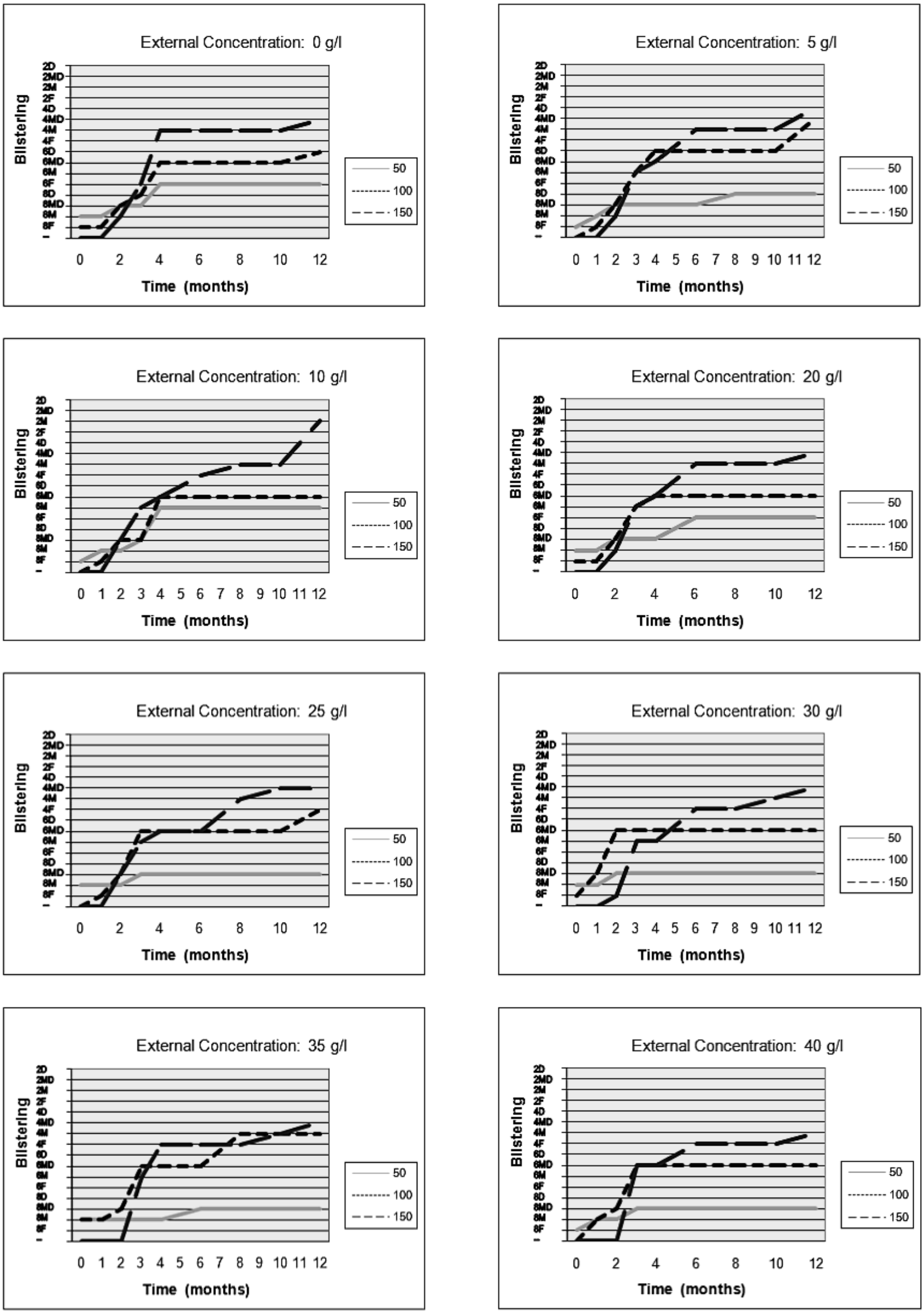
During this time, periodic visual inspections were conducted to assess the degree of osmotic blistering presenting the specimens. The ASTM D-714 Standard was used to classify the size and density of blisters (ASTM, 1987). Different levels of blistering are established in this Standard, as follows:

1. Size: 8 (very small blisters), 6 (small blisters), 4 (big blisters) and 2 (very big blisters)
2. Density of blistering: F (very few density), M (medium density), MD (medium dense) and D (much density)

After sorting the size and density of blisters, the photographs were taken of the most representative examples.

RESULTS

Figure 1 shows the evolution with time of blistering during 12 months exposure, in total immersion conditions, with 8 NaCl concentrations. As above mentioned, in



External Concentration: 0 g/l

External Concentration: 5 g/l

External Concentration: 10 g/l

External Concentration: 20 g/l

External Concentration: 25 g/l

External Concentration: 30 g/l

External Concentration: 35 g/l

External Concentration: 40 g/l

Figure 1: Variation of blistering, according to ASTM D-714, throughout time / *Interface contamination:* 500 mg/m^2 Cl$^-$.

all the cases, the substrate/coating contamination was 500 mg/m^2 Cl$^-$. The lines showed in each graph represent the coating thickness (50, 100 and 150 μm).

Besides, the sequence of photographs showed in figures 2 and 3 represent the evolution of blister formation throughout 12 months in specimens with different levels of the external salinity and coating thickness of 100 and 150 μm.

As a first result of this study, the blistering appear in all the tested specimens. This blistering process begins at very early ages.

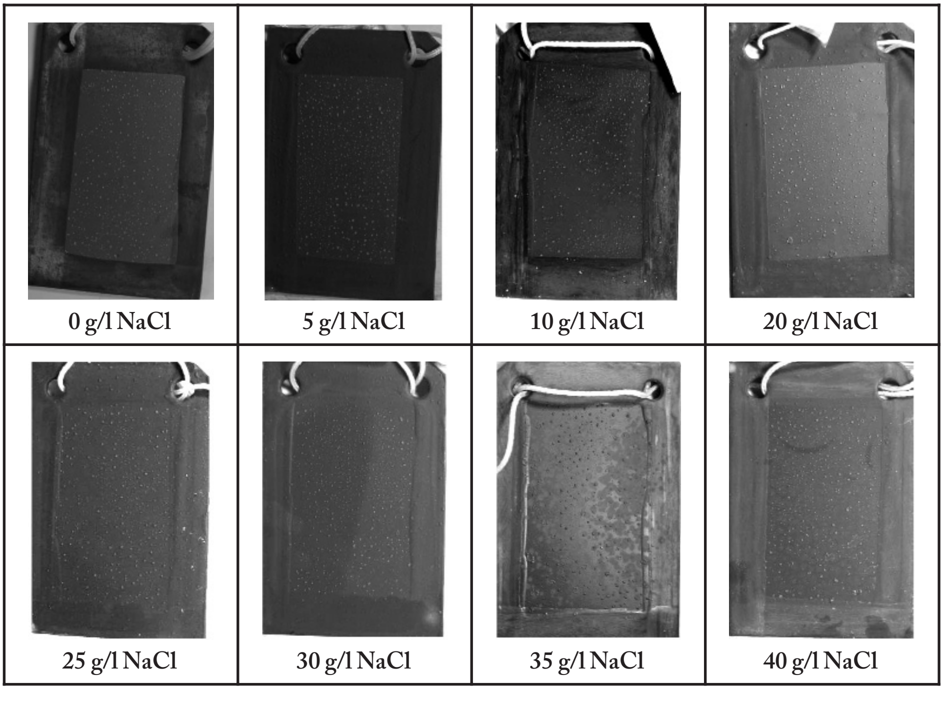
The blistering starts before specimens containing paint thinner.

The blisters size increases with the time.

The influence of the external salinity is not significant in the blistering (with high level of substrate/coating contamination).

The blistering process begins first in the specimens of 50μm of coating thickness, later in those of 100 μm and lastly in those of 150μm.

The size of the bladders taken place in the specimens of 50 μm is smaller than those of 100 and 150 μm.



0 g/l NaCl

5 g/l NaCl

10 g/l NaCl

20 g/l NaCl

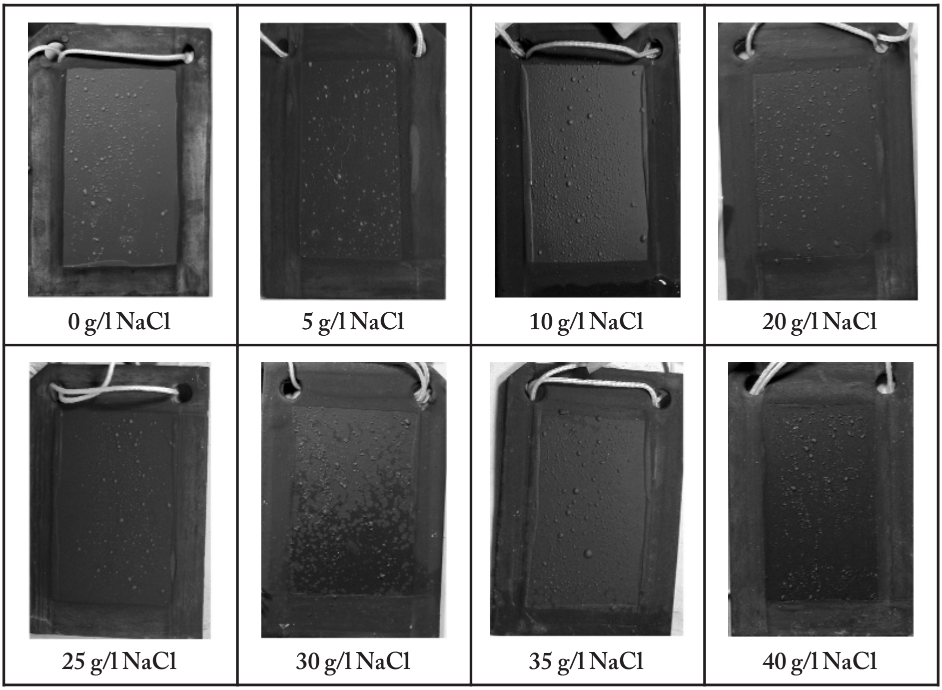
25 g/l NaCl

30 g/l NaCl

35 g/l NaCl

40 g/l NaCl

Figure 2: *Coating thickness:* 100μm / *Time:* 12 months / *Interface contamination:* 500 mg/m^2 Cl$^-$.



0 g/l NaCl | 5 g/l NaCl | 10 g/l NaCl | 20 g/l NaCl | 25 g/l NaCl | 30 g/l NaCl | 35 g/l NaCl | 40 g/l NaCl

Figure 3: *Coating thickness:* 150μm / *Time:* 12 months / *Interface contamination:* 500 mg/m^2 Cl^-.

DISCUSSION

The blistering process appear in all the specimens with 500 mg/m^2 Cl^-. The specimens are made of plastic, therefore this blistering is due to osmotic processes. The water from external solutions (more diluted than interface) comes into the interface through the coating film, trying to make equal both concentrations.

The blistering process begins before in the specimens of 50 μm of thickness because it is more permeable. The increment of the coating thickness slows the beginning of the blistering process.

In the osmotic blistering process, the solvent, diffuses from the most concentrated solution to the most diluted, passing through the coating film placed between both solutions. The osmotic flow continues until both solutions have reached the same concentration. The blisters will grow while this process continues or the coating film is able to support the osmotic pressure.

In the osmotic blistering process (with high level of substrate/coating contamination) the influence of the external salinity is not significant.

The effect of the coating thickness is not very significant, although in this experiment, the blisters specimens of 50 μm are smaller than in those of 100 and 150 μm.

The results of adhesion test according to ASTM D 4541-85, demonstrated that the adhesive force is greater in the test specimens of 50 μm of thickness that in those of 100 μm and 150 μm.

CONCLUSIONS

1. The osmotic blistering process, in chlorinated rubber paints pigmented with iron oxide with high level of contamination on interface, is not highly influenced by the salinity of the external solution.
2. The coating thickness increased, only delays slightly the onset of the blistering process.
3. The blisters increase in size over time.
4. The osmotic blistering process (with high level of substrate/coating contamination) begins at very early ages.
5. The effect of coating thickness on the osmotic blistering process seems not to be very significant. (In this experiment, the blisters specimens of 50 μm are smaller than in those of 100 and 150 μm because the adhesive force is greater).

REFERENCES

ASTM D 714 (1987): Standard Test Method for Evaluating Degree of Blistering of Paints. Philadelphia.

Berendsen A.M. (1989): Marine Painting Manual. Great Britain: Graham & Trondman 253-254.

Brunt, N.A. (1964): J. Oil. Colour Chem. Assoc. 47, 31.

Bullet, T.R. and Rudram, A.T.S. (1961): J. Oil. Colour Chem. Assoc. 44, 787.

Funke, W. (1981): Progress in Organic Coatings. 9 , 29-46.

James, D.M. (1960): J. Oil. Colour Chem. Assoc. 43, 391-658.

Van Laar, J.A. (1961): Paint Varn. Prot. 51 (8), 30-35.

INFLUENCIA DE LA SALINIDAD EXTERIOR EN EL AMPOLLAMIENTO DE PINTURAS MARINAS EN INMERSIÓN TOTAL

Resumen

El uso de las pinturas anticorrosivas para proteger los cascos de los buques es imprescindible. Estas pinturas se deterioran debido a que se encuentran totalmente sumergidas. Uno de los fenómenos que aparece en el deterioro de las pinturas es el ampollamiento. Este tipo de ampollamiento tiene dos orígenes, el catódico y el osmótico. El ampollamiento catódico se produce como consecuencia de la reacción catódica del proceso de corrosión que tiene lugar sobre el substrato metálico. El ampollamiento osmótico tiene su origen en la diferencia de concentración de las disoluciones (contaminación interfase y disolución exterior). Si aplicamos estas pinturas sobre substratos no metálicos el ampollamiento resultante será, por tanto, de origen osmótico.

En este artículo se presenta un estudio realizado en probetas de metacrilato pintado con clorocaucho pigmentado con óxido de hierro. Estas se contaminaron con ClNa en la interfase substrato/pintura y se sumergieron en agua con diferentes (concentraciones de sal) salinidades con el fin de recrear las variadas salinidades del agua de mar a las que puede estar expuesto el casco del buque.

El objeto del estudio fue analizar la influencia que tiene la salinidad exterior en la aparición de este tipo de ampollamiento.

METODOLOGÍA

La ósmosis puede definirse como la difusión unidireccional de agua y otros disolventes a través de una membrana semipermeable. En el principio, sólo el disolvente podría atravesar la membrana, aunque algunos autores sugieren que la mayoría de las películas de pintura pueden permitir la difusión de sales inorgánicas, como los cloruros y sulfatos.

En este proceso, el disolvente pasa de la solución con menor concentración a la más concentrada, atravesando la película de pintura que se halla entre las dos disoluciones. El flujo osmótico continuará hasta que las concentraciones de las dos disoluciones se igualen, o hasta que se alcanza la presión máxima que la membrana puede soportar. El ampollamiento osmótico se produce como consecuencia del aumento de presión osmótica en la zona que inicialmente tenía mayor concentración de soluto, curvando la membrana para aumentar el volumen de esta zona, disminuyendo así la presión.

Los factores necesarios para que aparezca el fenómeno de la ósmosis son los siguientes:

1. Una disolución que contenga sales.
2. Una membrana semipermeable (la capa de pintura).

3. Una fuente de disolvente (el agua).
4. Un substrato impermeable (el acero del casco del buque o la placa de metacrilato).

Para este estudio se han usado probetas de metacrilato de 120 x 80 mm. y de 1,5 mm. de espesor. Estas fueron lijadas con el fin de mejorar la adherencia del metacrilato y limpiadas escrupulosamente. Se contaminó la intercara substrato/pintura con 500 mg/m^2 de Cl$^-$.

Los parámetros de este estudio son los siguientes:

1. Concentración exterior NaCl: las probetas se sumergieron en 8 concentraciones de NaCl de: 0 – 5 – 10 – 20 – 25 – 30 – 35 y 40 g/l NaCl simulando las diferentes concentraciones del agua de mar.
2. Espesor del recubrimiento: 50, 100 y 150 μm de espesor.
3. Tiempo de la exposición en estas condiciones, doce meses de exposición, e inspecciones periódicas durante este tiempo.

El número total de probetas usadas en este estudio fue de 48, ya que se ensayaron dos probetas para cada una de las 24 posibles combinaciones. Como se usaron las dos caras de cada probeta el número total de superficies de ensayo fue de 96.

Una vez listas las probetas, éstas fueron introducidas en 8 cubetas de plástico que contenían las disoluciones exteriores anteriormente citadas. Manteniéndose estas soluciones durante todo este estudio (12 meses) en condiciones de 25°C y con aireación constante.

Durante este tiempo se realizaron inspecciones visuales periódicas para evaluar el grado de ampollamiento osmótico que presentaban las probetas, usando la Norma A.S.T.M. D-714.

CONCLUSIONES

1. La salinidad de la disolución exterior no influye en gran medida en el ampollamiento de las pinturas de clorocaucho pigmentado con óxido de hierro con alto nivel de contaminación en la intercara substrato/pintura.
2. El aumento del espesor de la pintura sólo retarda el comienzo del ampollamiento.
3. El tamaño de las ampollas aumenta con el tiempo.
4. El ampollamiento (con alto nivel de contaminación en la intercara substrato/pintura) comienza a edades tempranas.
5. La influencia del espesor de pintura no es muy significante. (En este experimento las ampollas aparecidas en las probetas de 50 μm son más pequeñas que las de 100 y 150 μm., debiéndose esto a la menor fuerza de adhesión al substrato de las capas de pintura de 100 y 150 μm espesor).