

Chemical, Petroleum and Environmental Engineering

Evaluation the Effect of Vibration on the Corrosion Rate of Automotive Paints

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ABSTRACT

This paper studies the influence of temperature on the corrosion rate of coated AA6111 aluminum alloy used in vehicle bodies under static and vibration states. The vibration test system was collected laboratory and used for testing of five different types of paints (EASI, Numix, Lesonal, DENSO and Polaron paints) in the 5 % NaCl solution using immersion test method. Lesonal paint provided the best corrosion protection, while DENSO paints show large values of corrosion rate, other coatings exhibit moderate values. Model of paints corrosion was developed to characterize the corrosion processes occur at the surfaces. It is found that corrosion rate obtained at vibration cases is larger than static cases and vibration effect on the coating protection rate.

Key Words: vibration, vehicle paint, AA6111 aluminum alloy, immersion test, porosity.

تقييم تأثير الاهتزازات على معدل التآكل في طلاءات السيارات

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الخلاصة

في هذا البحث تم دراسة تأثير درجة الحرارة على معدل تآكل طلاء سبائك الألومنيوم AA6111 المستخدمة في هياكل المركبات تحت شروط الحالة السكونية وحالة الاهتزازات. منظومة اختبار الاهتزازات جمعت مختبريا واستخدمت لاختبار خمسة أنواع مختلفة من الطلاءات هي (EASI, Numix, Lesonal, DENSO and Polaron) في محلول (NaCl 5%) باستخدام طريقة اختبار الغمر. بينت النتائج ان الطلاء Lesonal اظهر أفضل حماية من التآكل، في حين اظهر طلاء DENSO قيم كبيرة من معدل التآكل، بينما الطلاءات الأخرى امتلكت قيم متوسطة. تم تطوير نموذج لتآكل الطلاءات لوصف عمليات التآكل الحاصلة عند السطح. بينت النتائج أن معدل التآكل في حالات الاهتزاز هو اكبر من حالة السكونية وايضا ان الاهتزاز يؤثر على معدل الحماية للطلاء.

الكلمات الرئيسية: الاهتزاز، اصباغ السيارات، سبيكة الالمنيوم AA6111، فحص الغمر، المسامية



1. INTRODUCTION

The AA6111 aluminum alloy was one of the premier types of aluminum alloys used for external automotive body panels. Favorable characteristics include good corrosion resistance, high strength stiffness to weight ratio which makes it the ideal candidate to respond to the weight reduction demand within the automotive industry **Jain, et al., 1998**. In the use of aluminum alloys for automotive bodies, the predominant problems are vibration and corrosion. There are many sources of vibration in vehicles including rotating parts of the vehicle engine, driveline, brakes, wind, tire contact patch and road surface **Singh, 2006**. Vehicle body normally suffers from the crevice, pitting and general corrosion. Crevice corrosion usually occurs when constricted gaps are filled with water. Narrow gaps are almost invariably formed between the metal components are welded together or onto members. Pitting and general corrosion mainly occurs in vehicles in large areas, such as doors and heads or engine cover. This coating plays a major role in the protection of the automotive body from corrosion. Various types of coating are used by automotive manufacturers to produce appearance enhancement and corrosion protection **Hugh, 1988**. Various techniques were used in evaluating the corrosion resistance of vehicle paints under various effects. One of the best methods incorporating static and vibration is immersion corrosion test. Immersion method is a non-electrochemical test method and applied to a wide range of conditions including static and vibrations. This method is allowing to assess the corrosion of coating materials and salts solutions **Narayanan, 2012**.

Limited researches have been reported to analyze the effect of vibrations on corrosion and aluminum that used in automotive bodies. **Textor, et al., 1995**, studied the corrosion problems of two types of aluminum alloy used in car body AlMgSi (for outer uses) and AlMg (for interior use). They showed that the proper selection of alloy and surface finishing technique is important in specific precautions during manufacture. **Azuma, et al., 1998**, studied the infiltration of sulfuric acid results from acidic rain on the automotive clear coat using the microscopic method. Their results show that two-dimensional distribution of sulfuric acid infiltration in the acrylic melamine cross section of clear coat. **Schulz, et al., 2000** simulated a new approach of the worst case of the weather conditions in harsh urban and industrial environments on automotive OEM coatings. Their results show that the coatings differ in the rate of degradation after an acid attack due to the difference in penetration of acid solution. **Siggelkow, 2002** studied the corrosion protection of the automobile body using two types of coatings: zinc-magnesium alloys and a thin organic coating. Their results indicated the thin organic coating gives the best corrosion protection. **Nagai et al., 2006** showed that using light metal materials and changing vehicle body structure, has been resulting in deterioration of the car body rigidity so that some elastic vibrations in the car body are easily induced. **Liew, et al., 2006** studied the linear and nonlinear vibration analysis of a three-layer coating-FGM-substrate cylindrical panel subjected to a temperature gradient across the thickness. The results showed that the vibration frequencies are significantly influenced by temperature change. **Lonyuk, et al., 2008** studied the mechanical properties of eight different coating systems for automotive applications. They observed delamination failure between the basecoat and primer for some coating systems and adhesive failures between the primer and substrate for others. **Whitehouse, 2010** described the mechanisms for corrosion in automobile bodywork and show the improvements in corrosion protection from significant advances in protective paint coating systems, material selection, and design. **Alizadeh, et al., 2016** investigated two types of failures delamination and coating damage accurse on an automotive coating system by an electrochemical



impedance spectroscopic method (EIS). They show that there was a good correlation between the results of image processing and the parameters extracted from EIS test. **Liza, et al., 2017** studied the overall corrosion performance of cars of different origins. Their results showed the overall corrosion ratings are categorized into 6 observation areas: exterior, under the hood, underbody, interior, perforation and functional.

The purpose of this paper is to study the effect of vibration process and temperature on the corrosion rate of AA6111 aluminum alloy coated with five different types of commercial paint based acrylic used in automotive bodies. To achieve this goal, vibration system provided by temperature controller collected in the laboratory and used for testing use immersion corrosion test method. The mechanism of acrylic paint corrosion is developed, discussed and illustrated.

2. EXPERIMENTAL

2.1 Types of Vehicle Paints

The automotive coating is a multilayer coating system. In vehicles, it generally consists of three coat systems: primer, base coat, and clearcoats. The primer is the first coat to be applied. The main functions of the primer are to act as a leveler and protector and to make the base coat easier to apply on the surface. The base coat is applied after the primer coat. This coat contains the visual properties of color. Base coat used in the automotive applications is commonly divided into three categories, solid, metallic, pearlescent colors. Clearcoat usually sprayed on top of a colored basecoat, the clearcoat is a glossy and transparent coating that forms the final interface with the environment **Streitberger, 2008**.

Most automotive paints compositions consist of acrylic with different types of additives by manufacture companies. The most common type of acrylic paint is latex. Acrylate has excellent properties such as the weathering and oxidation resistance and little tendency to absorb ultraviolet light. **Table 1** shows five different types of paints with manufacture company and sources which is being used in this study.

For analysis the following names are given for paints:

Model A: aluminum automotive epoxy primer + Easicoat E3 1K basecoat + 2K clear coat.

Model B: Numix primer 1K+ Numix base coat 1K + Numix clear coat.

Model C: Lesonal 1K Etch primer + Lesonal WB 93P based coat+ 2K HS fast clear 420.

Model D: 2K primer surfaces + D100 1K basecoat +2K Fast dry clearcoat.

Model E: 1K MS Acrylic primer + P-Acryl/C1 base coat + P-Acryl/C2 HS acrylic clear coat.

2.2 Materials and Sample Preparation

Specimens were cut from the plates AA6111 aluminum alloy of dimensions of 25 mm × 50 mm × 2 mm for the purpose of immersion testing. The specimens were prepared in the workshop of the College of Engineering at the University of Basrah. A hole was drilled in the middle of each specimen. A total of 75 coupons were processed for testing. Each specimen was coated with three layers (primer is applied to the surface first, then basecoat is painted and finally clear coat is applied). **Tables 2 and 3** show the chemical compositions and mechanical properties of the AA6111 aluminum alloy. **Fig.1** shows the shape and size of the specimens.



Table 1. Paint types and manufacture company.

No.	Paint type	Manufacture company	Origin
Primer			
1	Aluminum Automotive Epoxy Primer (2K Grey Automotive Epoxy Primer (Auto paint)	Guangzhou Huantong Paint Industry Co., Ltd	Chani
2	Numix primer 1K	National Paints Factories Co. Ltd.	UAE
3	Lesonal 1K Etch Primer	Autopaints Brighton part of Lesonal WB company	UK
4	2K primer surfaces (DENSO)	Foshan Shunde Himens Chemical Industrial Co., Ltd	Chani
5	1K MS Acrylic Primer	Polaron Boya Kimya Sanayi ve Ticaret AS (Polaron paints)	Turkey
Basecoat			
1	Easicoat E3 1k Basecoat Auto Paint	Guangdong Yatu Chemical Co., Ltd.	Chani
2	Numix Base Coat 1K.	National Paints Factories Co. Ltd.	UAE
3	Lesonal WB 93P Water Based tinter	Akzo Nobel Ltd Part of Lesonal WB company	UK
4	D100 1K Basecoat (DENSO)	Foshan Shunde Himens Chemical Industrial Co., Ltd	Chani
5	P-Acryl/C1 Base Coat Paint	Polaron Boya Kimya Sanayi ve Ticaret AS (Polaron paints)	Turkey
Clear coat			
1	2K clear coat (Easi Auto paint)	Guangdong Yatu Chemical Co., Ltd	Chani
2	Numix Clear Coat	National Paints Factories Co. Ltd.	UAE
3	2K HS Fast Clear 420	AkzoNobel Coatings Ltd part of Lesonal WB company	UK
4	2K Fast dry clear coat (DENSO)	Foshan Shunde Himens Chemical Industrial Co., Ltd	Chani
5	P-Acryl/C2 HS acrylic clear coat	Polaron Boya Kimya Sanayi ve Ticaret AS (Polaron paints)	Turkey

Table 2. Chemical compositions of AA6111 aluminum alloy for automotive body **Sakura, 2008.**

Alloy	Chemical compositions wt %							
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
AA6111	0.7-1.1	0.4	0.5-0.9	0.15-0.45	0.5-1	0.1	0.15	0.1



Table 3. Mechanical properties of aluminum alloy AA6111 for automotive body **Sakura, 2008.**

Alloy	Mechanical properties			
	Tensile strength MPa.	Yield strength MPa.	Young modulus GPa	Elongation %
AA6111	290	160	71	0.26

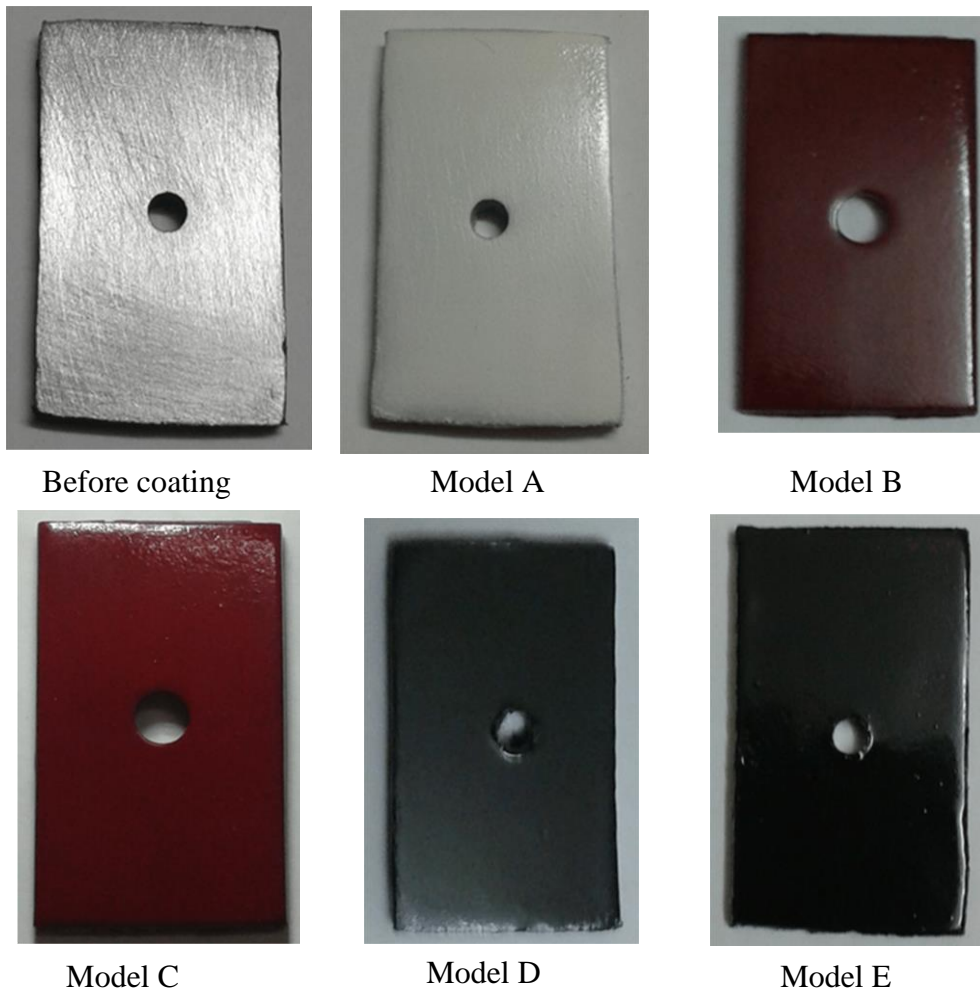


Figure 1. Photograph of the uncoated and coated specimens.

3. IMMERSION TEST METHOD

Fig. 2 shows a schematic diagram of apparatus used in the immersion test method. The equipment's of apparatus are collected laboratory according to **ASTM G32-03 amended, 2003 and Mayer, 2010**. The apparatus consists from VIBCO's vibrating test table (Model US-900, manufacture by VIBCO Inc. Co., USA) for generation vibrations and Digital hotplate heater (model SD300 manufactured by Bibby Scientific Limited, UK) to provide temperatures during the test. The specimens were suspended in beakers of 500 ml full by 5 % wt NaCl solution **ASTM B 895 – 05**,



2005 and the beakers are mounted on the plate of the heater during conducted corrosion immersion test. The immersion tests were conducted at atmospheric pressure. The test temperatures applied were 25 °C, 30 °C, 35°C, 40°C, 45°C, 50 °C, 55 °C and 60 °C for an exposure period of 15 days. The corrosion mass loss is measured for a set period of different time duration 1 day and for 15 days at the set temperatures.

The test specimens are removed from the solution and immersed in the cleaning solution to remove the oxidation films. The cleaning solution used consists of 50 g of sodium hydroxide mixed with 200 g of zinc dust in 1L of pure water. The mixture is boiled for 5 min at atmospheric pressure **Baboin, 2002**. The coupon is immersed in the cleaning solution for 1 min to remove the oxidation films and then the specimens were air-dried at room temperature. The specimen was weighed, and its mass weight was recorded. The mass losses due to corrosion process are determined by subtracting the weight of the cleaned specimen from the initial weight of the specimen. The corrosion rates in mm/year are calculated by assuming uniform corrosion over the entire surface of the specimen according to procedures of the **ASTM G31-72 standard**. According to this standard, the corrosion rates (C_r) are given by the following formula:

$$C_r = \frac{W * K}{\rho A t} \tag{1}$$

Where,

W: Mass loss in gm.

K = $8.76 * 10^4$ for (C_r) in (mm/year).

ρ : Mass density of aluminum in (kg/m^3).

A: total surface area of the specimen (m^2).

t: Time of immersion in (hr.)

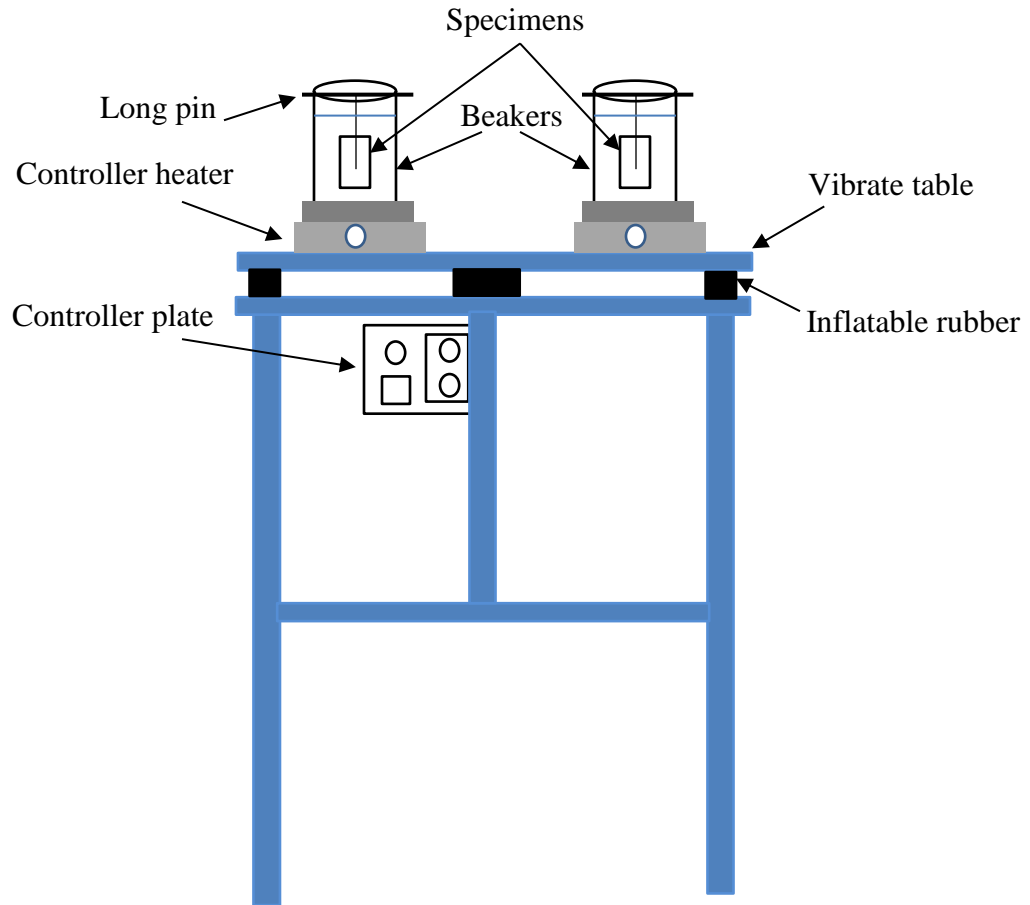


Figure 2. Schematic diagram for immersion test apparatus.

4. MEASURING POROSITY OF COATING

Porosity is a measure of the void spaces in a material or it is the portion of the material volume occupied by pore spaces. There are two types of porosity: surface porosity and subsurface porosity. The porosity of coating can be determined by known bulk density and practical density **Reymond, 1995**.

The bulk density of coatings is defined as a total weight of coating divided by total volume occupied. The bulk density was measured using direct weighing method (cylinder method). A cavity is made on the specimen for the coating material is sprayed on it. After spraying the coating ground to make this specimen strictly cylindrical. Given the size is known of the substrate, the volume of the coating can be calculated. After grinding, the specimens are weighted and the mass of coating is determined. Practical density is the volumetric mass of the solid coating. It differs from bulk density because the volume used does not include pore spaces. This type of density is given by coating manufacture companies. From known the practical density and bulk density, the porosity (ϕ) of the coating can be express by the following relation **Tushinsky, 2002**:



$$\phi = \left(1 - \frac{\rho_b}{\rho_p}\right) * 100 \% \quad (2)$$

Where,

ρ_b : The bulk density in g/cm^3 .

ρ_p : The practical density of coating in g/cm^3 .

Φ : The porosity of the coating as a percentage value.

5. RESULTS AND DISCUSSION

5.1 Static and Vibration Immersion Corrosion Test

Fig. 3 shows the values of the corrosion rates as a function of immersion time of five painted samples, immersed in 5 % NaCl solution for 15 days. The value of test vibration frequency was taken as 100 Hz with an amplitude of the frequency of 0.5mm for all test specimens during corrosion vibration tests. As indicated, the values of corrosion rate increases with the increase in time of immersion and there are increasing in the values of corrosion rate under the action of vibration compared to static case. This is because the increase of immersion time increases the values of corrosion reactions on the painted specimen surface, i.e., increased of the dissolution of the paints under the continuous attack of corrosive ions and agents of the solution to the surface of the painted specimen which could lead to the increased weight-loss with time. As well as the increase of the dissolution paints with increase immersion time allow to the chloric ions in the solution to the permit through paint films on the surface of samples tested and reached to aluminum alloy. This leads to the increase of the chemical reaction occurs at surface and under-paints surfaces, which increases the corrosion rate.

As indicated the corrosion rate increased under the action of vibration for five kinds of vehicle paints. However, the increase in the corrosion rate is not uniform. This trend is attributed to the fact that vibration contributes to the removal of the corrosion products from the immersed coated metal surface portions attacked by corrosion during tests and this lead to increase in the reaction at the immersion specimen surface. For static case, the corrosion products collected or oxides film initiated on the specimen surface act as a barrier between the specimen surface and the corrosive ions in the test solution which leads to reducing the chemical reactions and diffusion rates of ions and this reduces corrosion attack.

Fig. 4 shows the corrosion rate change with temperature for five types of coatings. As is evident from the figure, there is a significant change in the corrosion rate with the temperature changed. When the temperature is less than 25 °C, there are small increases in the corrosion rate, but when the temperature is higher than 25 °C there are magnify a sudden increase in the corrosion rate. This increase in corrosion rates continues until temperature 45 °C and then begins to increase with small values. Also, it is noted that the increases in corrosion rate as a result of the presence of vibrations are irregular. As well as that all the obtained curves are non-linear.

Increasing temperature will make the vehicle paint film absorb or evacuate water. At low temperature all acrylic paint films become brittle and this will make the paint film absorb or evacuate water. This water absorption increasing weakness of paints, i.e. the bonds between acrylic atoms and pigments becomes a weakness and this lead to increase degradation and losses of electrons during oxidation.

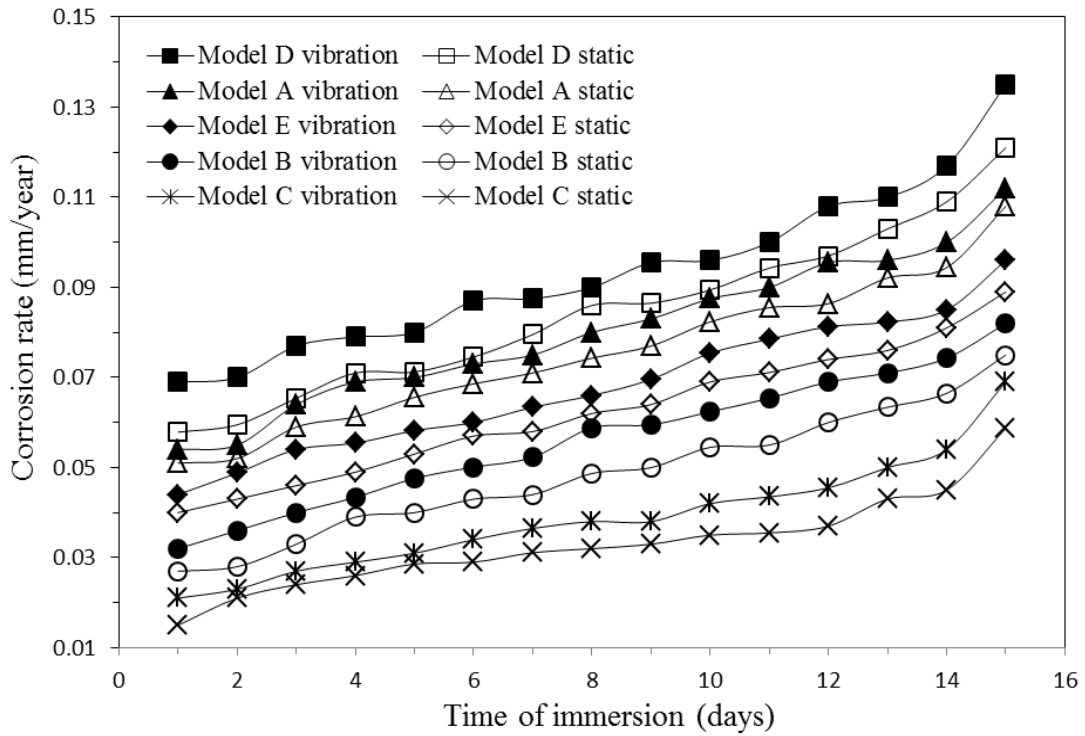


Figure 3. Corrosion rate vs. time for the five paints under static and vibration process.

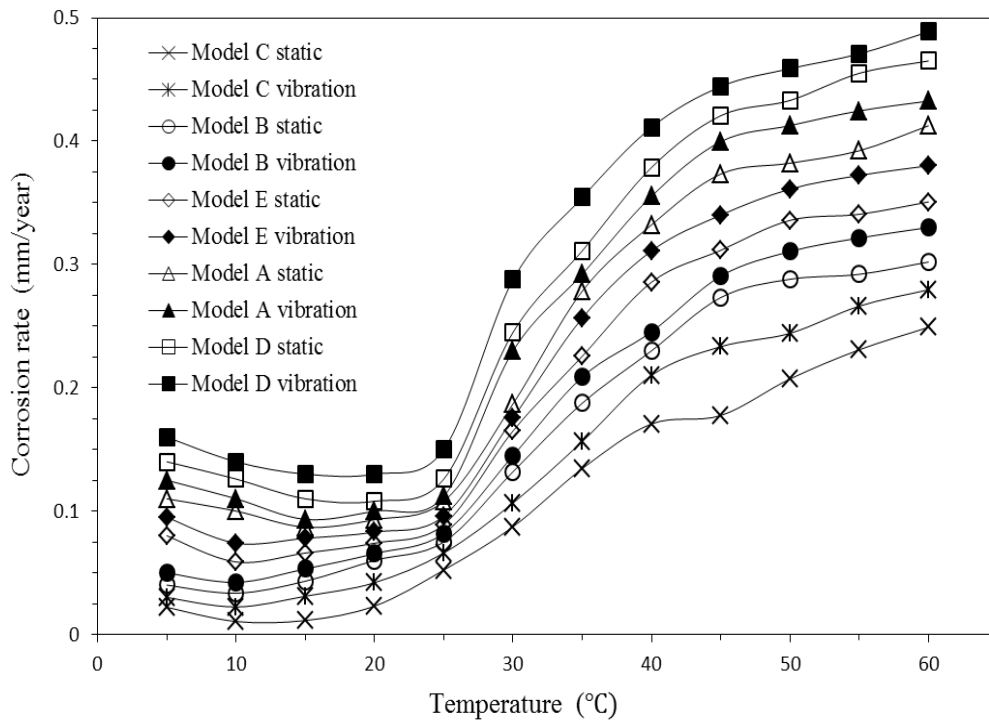


Figure 4. Corrosion rate vs. temperature for the five paints under static and vibration process.



Acrylic paint is an organic molecule that contains two types of carbon-carbon double bonds: allyl and vinyl. These two types of double bonds have different reactivities, vinyl bonds fully react and allyl bonds react at least to a certain degree. The vibrations can cause a bond to break and create free radicals. The free radicals on opposite ends of the broken bond can become so separated that they will not recombine.

Acrylic paints will be fragile at cold temperatures. The cold temperature also causes losing the bond between paint layers with the underlying surface and leads to flaking, chipping and peeling. Paint layers will form stress cracks painting on a rigid surface will help circumvent this weakness. An acrylic paint applied to excessively hot temperatures causes softness and often develop bumps, blisters, and other imperfections. The vibration enhanced and increase all the problems associated with the influence of temperatures.

The higher the temperature is, the higher the vibration frequencies of the atoms and molecules. A vibration frequency increase reduces or destroys the bonds between the atoms in the material of the paint; as a consequence, the deformations occurring inside and on the surface between of the paint-metal increase and the resistance to the corrosion oxidation process is reduced. Vibration leads to the reduced cohesion between the surface atoms of the aluminum material and paint coatings. Both vibration and temperature effect on the delamination of coatings. Since the collected corrosion products at the surface of the aluminum-coating surface, due to volume changes exerted by temperature or vibration, this leads to fracture and deformation at some points on the metal-coats interface which causes delamination of coatings.

Vibration influence of various properties of vehicle coatings especially porosity and diffusion. The porosity of the vehicle coatings, which is due to irregular voids, different additives, voids inside splats, reduces the corrosion resistance. As the vibration increases, it increases the diffusion rate of water and its impurities through porosities of coatings and this increases the corrosion rate. On the other hand, the increase of temperature causes the paint to extension and this increases the pore size of porosities and cavities of surface paint and with vibration process, this increases the diffusion through paints and increase the oxidation and reduction process. **Table 4** shows density given by manufactures companies, measured values and the porosity values calculated using **Eq.(2)**.

Table 4. Practical density, bulk density, and porosity of tested paints.

Paint models	Practical density (g/cm ³)	Bulk density (g/cm ³)	Porosity %
Model C	1.050	1.128	6.92
Model B	0.980	1.062	7.72
Model E	1.270	1.382	8.11
Model A	1.150	1.256	8.44
Model D	1.750	1.916	8.68

From **Table 4**, it's clear that the model C has a lower degree of porosity in the painted layer which has a value of 6.92 %, while that for model D paint is 8.68 %. Thus, it is clear that the corrosion resistance was determined by both the chemical compositions and paint properties especially its porosity level. Through the paint porosity; the chloride ions in water permeate through the paints



and reach the interface between paint and metal. When the water solution meets the contact part of a steel, the galvanic cell is formed and increase the reaction rate between molecular structures of paints and steel surface which contributes to increases the corrosion rates.

In order to explain the difference in effect between static and vibration on corrosion surfaces, a macroscopic analysis of surface were performed. A comparison in corrosion morphology between five painted specimen surface under static and vibration in the 5% NaCl solution after 15 days at 60°C are presented in **Fig. 5**. Visual inspection of immersed surfaces of the five models of coatings showed pits, cavities, gloss change, blistering and some damages on the surfaces. These pits and cavities are formed on the specimen surface due to local corrosion as a result of exposure of specimen surfaces to the corrosive ions present in the solution and this leads to the loss of coats at different points. It's clear from the surface microstructures of all five specimen surfaces shown in **Fig. 5**, the vibration increases pits and cavities on surfaces compared to that of the static case.

All painted coating surface have blisters initiated in coatings but model E have larger amount covered the surface after static corrosion test compared to other types. These blisters (lifting or disruption) of the paint coating are initiation at most times due to the formation of aluminum corrosion products under the paint surfaces. Sometimes this blister contains vapors, liquid, gas or crystals. These blisters, especially after vibration applied, can cause pinholes or cavities in the coatings. On the other hand bubbles within a paint, film appear as small blisters and may be found in parts of excessively thick paint films. These may be intact or broken to leave a crater.

Model D at static corrosion test show pits and cavities on the surface, but at the corrosion-vibration test, the surface shows more damages on painting surface due to the physical and chemical action of the solution on paints which effects directly by vibration process.

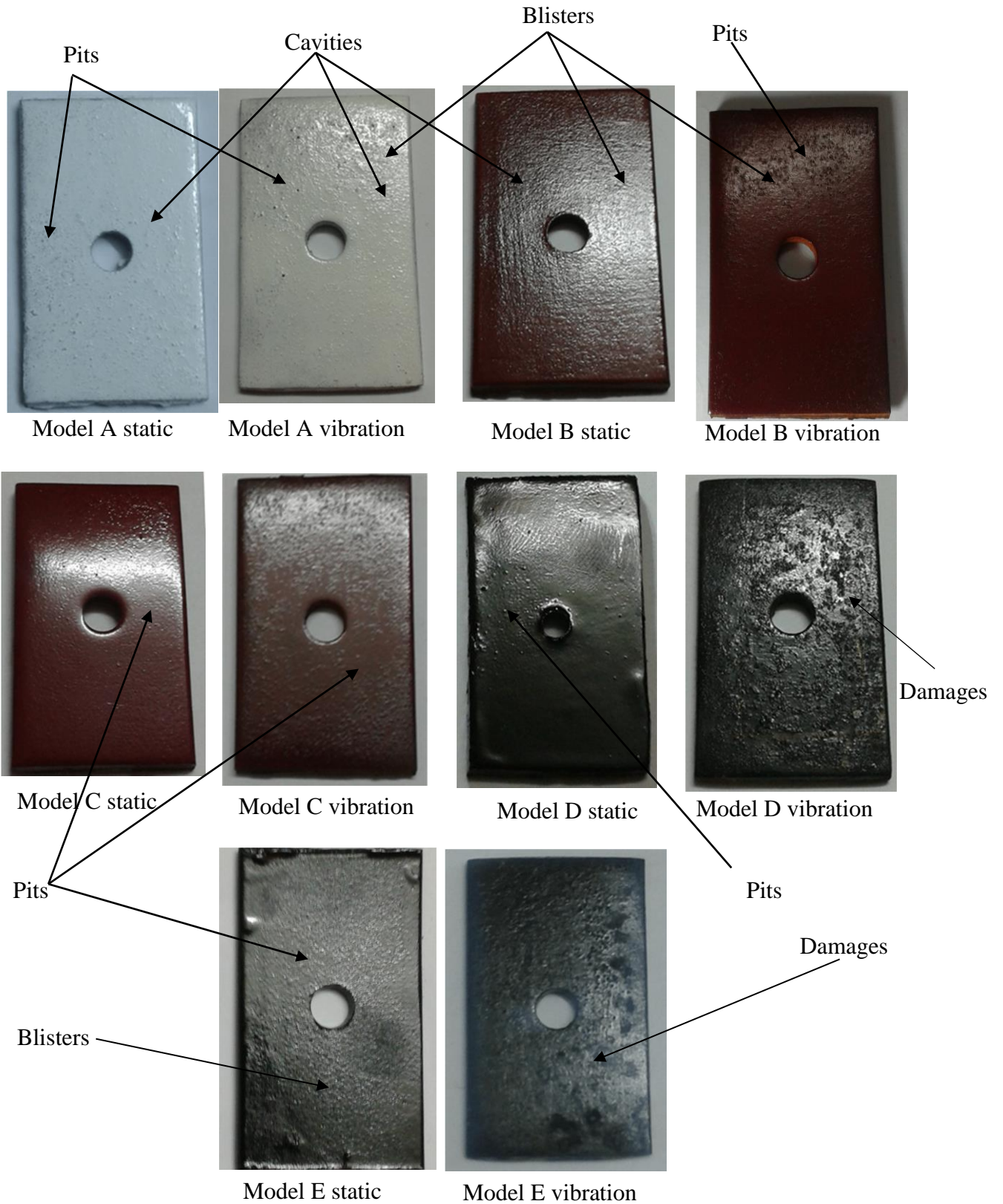


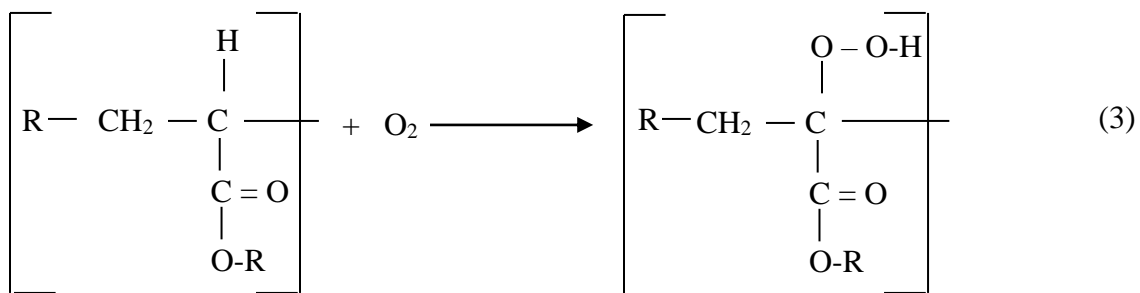
Figure 5. Surface morphology of five paints after test in 5 % NaCl solution at 60 °C.



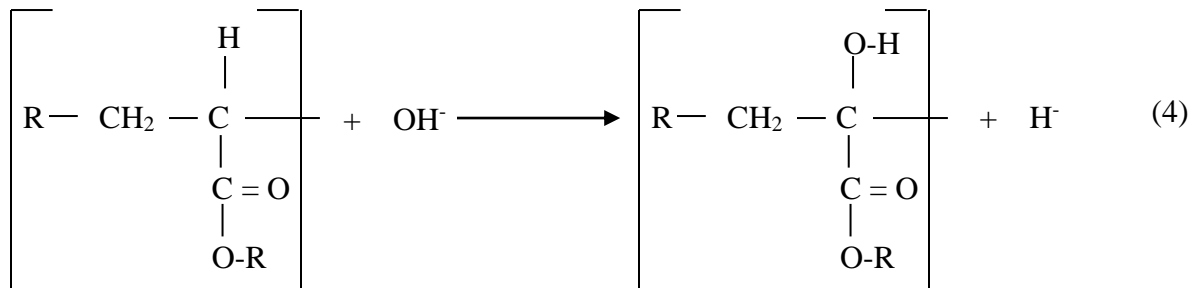
5.2 Mechanism of Acrylic Paint Corrosion

The mechanism of corrosion of acrylic paints starts by the reaction of water impurities and coating surface. The reaction occurs at the metal coating surface and in most time causes the initiation of pitting. The possible reactions occurring in the coating surfaces depend on the materials additives to coating and can be summarized as follows:

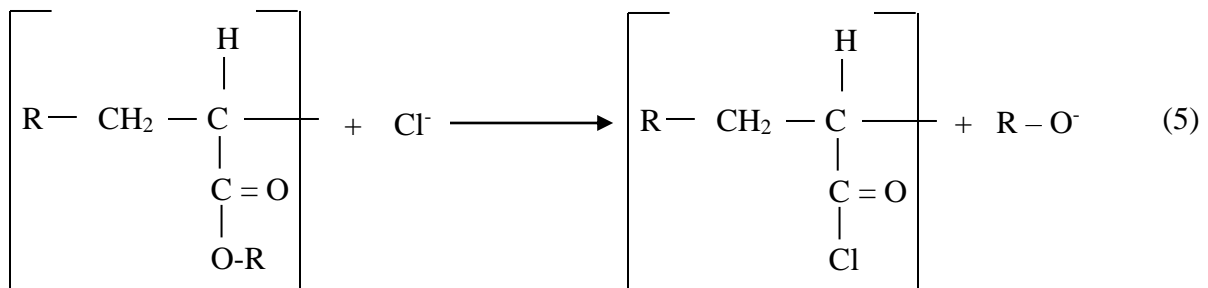
Acrylate paints react with the oxygen to form peroxy radicals (COO-) which has very low reactivity. These peroxy radicals tend instead to terminate polymerization through radical-radical recombination. Because the oxygen reacts slowly, oxygen inhibits the cure at the surface resulting in a tacky layer called the oxygen inhibition layer. The reaction between oxygen and acrylic paint can be given as:



The reaction between acrylic and hydroxyls ion from humidity or water can be represented by the following reactions:



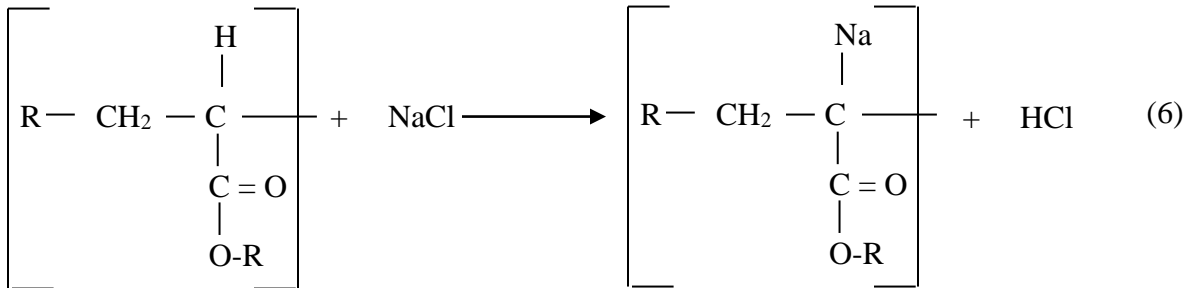
The reaction between acrylate and chloral ions can give as follows:





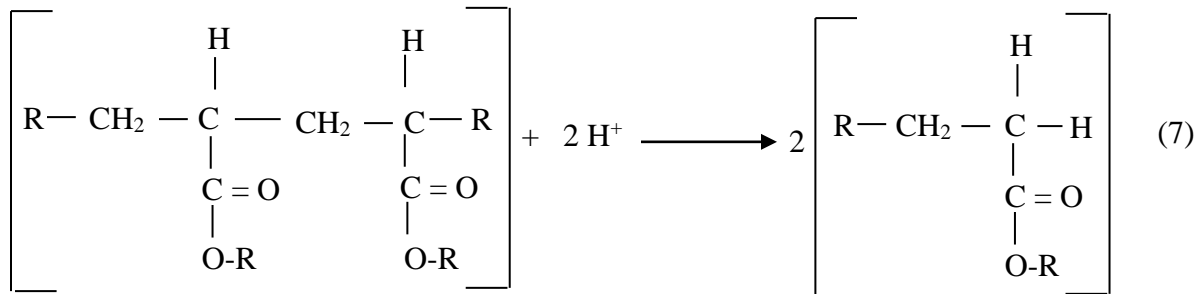
The result of reactions unsaturated carbonyl compounds. This compound will react violently with water producing acrylic acid while it will form anhydrides when reacted with sodium salts of carboxylic acids.

The reaction between acrylic and sodium chloride NaCl can be given by the following reactions:



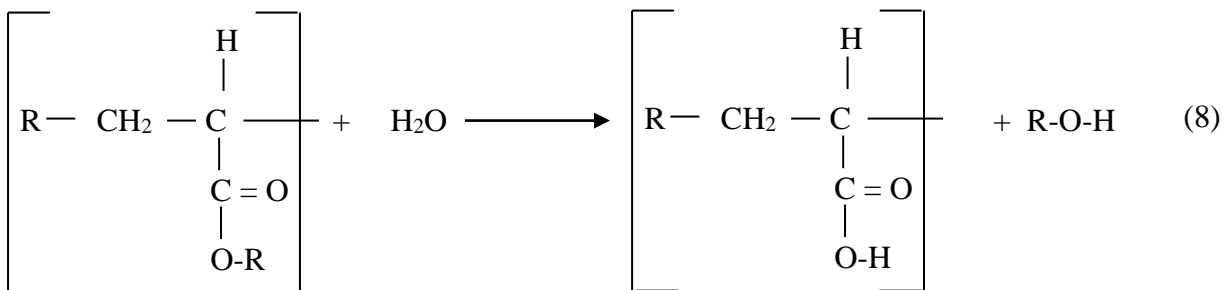
Sodium acrylics have the ability to absorb large amounts of water and lesser amounts of other liquid mixtures. Sodium acrylate is an anionic polyelectrolyte with negatively charged carboxylic groups in the main chain.

The reaction between acrylic and hydrogen ions can be given by the following reactions:



During reactions, electrons are transferred from acrylate paint to the solution, i.e., an oxidation process occurs together with a reduction process. During this reaction, the bond forces between acrylate coating components are broken and this causes loss of cohesion between coating components. The hydrogen ions are partitioning the acrylate monomer into two components, while in the other reactions, there are rearrangement instructions by entering new components to the paint and this weakens the bonds between molecular structures and reduces cohesion and enhances the corrosion rate.

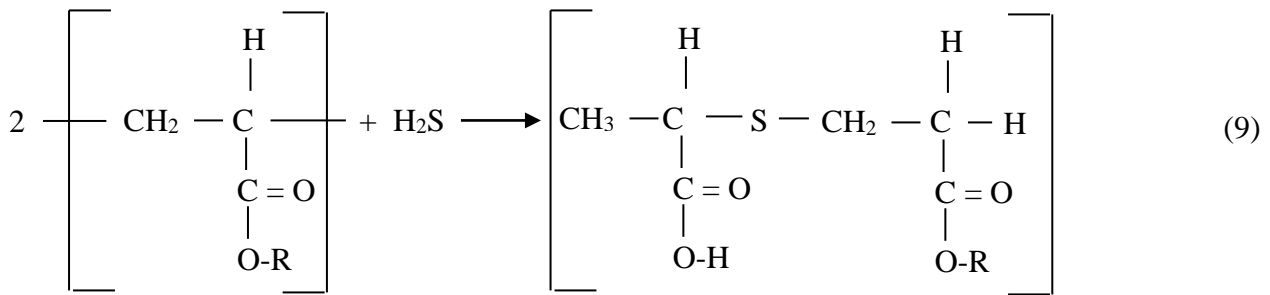
The general degradation of acrylic in water can be given by the following reaction:





In these hydrolytic degradations, various bridges are broken, creating various OH containing products. As result of this degradation, new linkages have less flexibility than the initial linkages are formed.

Various gases air can affect directly in acrylic paint degradation like SO₂ and H₂S produced in the polluted areas which are converted into sulfuric acids which makes the precipitates acidic. These acids when fall on the coatings catalyzes the hydrolysis reaction of the acrylic clear coat.



6. CONCLUSIONS

Based on the tests conducted, the conclusions of the paper can be summarized as follows:

- 1- Corrosion is dependent on vibration: as vibration increases, the corrosion rate increases.
- 2- The higher the temperature, the higher is the vibration frequency, and the higher is the corrosion rate of a material.
- 3- The vibration can accelerate the destruction of the passivation film on the coating surface and increase the activities of Cl⁻ ions.
- 4- The corrosion protection of paints is inversely proportional to porosities of paints i.e. that the porosity of model C lower than others paints and the model D has the largest value.
- 5- The vibration accelerates the destruction of the passivation film and increases initiation of pits at the metal surface.
- 6- Both higher and lower temperature increases corrosion rate of vehicle paint under the action of vibrations.
- 7- Microscopic inspection shows blisters, pits and cavities on specimens surfaces after the test.

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