

Research/Technical Note

Application of Plasma Erosion Technique for Faster Degradation of Coatings and Prediction of Their Durability

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Abstract: Assessment of durability of coatings is crucial for researcher especially for design of paints which would have service life warranty. As natural exposure takes several months for such studies, there is tendency today to use faster techniques like UV testers and Xenon arc weatherometers. Although these techniques are several times faster than natural exposure, it takes few weeks for coating chemist to observe any degradation. Among quicker techniques, plasma erosion is found to be useful one. Oxygen plasma produces extremely rapid degradation and few hours of exposure to plasma provides effects of several years of natural weathering. Advantages of the technique are speed and plasma equipments are cheaper than weatherometer. Results obtained with plasma erosion technique are found to have good correlation with results of exposure under Xenon arc source.

Keywords: Ionization, Excitation, Dissociation, Weatherometer, Degradation, Durability, Xenon-Arc

1. Introduction

Over the last three decades, the organic coatings industry has undergone rapid technological and structural changes. These changes have been induced by legislative actions such as restrictions pertaining to hazardous chemicals, toxic effluents and volatile organic compounds. Further changes have been induced by competitive and consumer pressures to produce environmentally and user friendly coatings without sacrificing ease of application, initial appearance or most importantly without significantly reducing the service life of the coating system. The consequence of these changes has been displacement of almost all previously commercially important well established coatings (largely high solvent coatings) by newer systems, the formulation and application of which are based on different chemistries and technologies. The issues surrounding paint durability are complex and often confusing. This is partially due to complexity of chemical reactions involved [1]. The principal factors causing the breakdown of paint and polymer systems are ultraviolet radiation from the sun, moisture and temperature. [2] Other factors include atmospheric pollution, dust, wind and microbiological factors like algae, fungi.

Data for use in service life prediction can be generated from three sources

- 1) Short term laboratory based exposures – It includes exposure of specimen to UV / Xenon arc sources, condensation testers,
- 2) humidity chambers and salt fog testers.
- 3) Long term in-service or outdoor exposures – This is natural exposure and includes subjecting specimen to outdoor different environment mainly in coastal weather having humid conditions with moderate temperature and tropical weather conditions – dry and high temperature variations. Attempts are made by researchers to accelerate these outdoor exposure conditions [3].
- 4) Fundamental mechanistic studies

The purpose of accelerated weathering is to shorten the time required to determine the effects of weathering on paints [4]. At present generating a reliable performance histories for a new coating requires an extensive in-service or out-door exposure program. Attempts at avoiding this task, by employing various forms of short term laboratory-based aging tests. Alternatively, creating a performance history from

results of in service exposures requires long exposure times and yield results which have limited reproducibility since the weather never exactly repeats itself. Therefore various attempts have been made by several researchers to use analytical techniques which are used in materials science for assessment of degradation of coatings. These include use of thermogravimetry (TGA), radiotracer technique [5] and electron impedance spectroscopy (EIS). Analytical techniques like infra-red spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) are used for evaluation of chemical changes during degradation. [6]. Apart from this, some researchers have used simulation models for prediction that can be used to aid development of formulation of paints [7].

Attempt is made here to explain a laboratory techniques which uses plasma to predict service life of coatings.

2. About Plasma

A plasma is a partially ionised gas consisting of equal numbers of positive and negative charges and a different number of unionised neutral molecules. When a gas is subjected to a D. C or radio frequency (R. F) potential at reduced pressure this is usually accompanied by glow which is known as glow discharge. The words glow discharge and plasma tend to be used synonymously, although glow discharges are not perfect plasmas but for the purposes of this text they will not be differentiated. The characteristic glow of these plasmas is due to electronically excited species producing optical emission in the ultraviolet or visible regions of the spectrum and is characteristic of the composition of the glow discharge gas. For example argon gives a bright blue colour and air or nitrogen gives a pink colour that is due to excited nitrogen molecules.

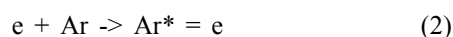
2.1. Ionisation

In the context of plasma enhanced chemistry reactors, the plasma is created in a vacuum chamber which contains a constant flow of a gas at reduced pressure which is typically in the order of 1 mbar. This gas is exposed to a radio frequency (RF) potential which results in the partial ionisation of the gas. In the ionisation process, a bound electron in an atom is ejected from that atom. For example, the ionisation of an argon atom is expressed as follows:



2.2. Excitation

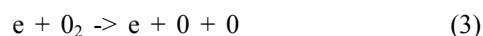
A less dramatic transfer of energy allows the electron the jump to a higher energy level within the atom. This process is known as excitation. The excited state of an atom is conventionally shown by an asterisk:-



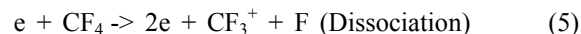
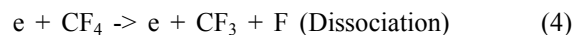
2.3. Dissociation

A further process which can occur is the dissociation of a

molecule. If oxygen, for example, is the gas subjected to the RF potential, the oxygen molecule can be dissociated into two oxygen atoms whereas a monatomic gas such as argon cannot be dissociated at all:-



A normal result of dissociation is an enhancement of chemical reactivity since the products are usually more reactive than the parent molecule. Dissociation may or may not be accompanied by ionisation, for example:-



2.4. Summary

The effect of exposing a gas to the RF potential at reduced pressure, a plasma is created which contains active species, for example, in the case of oxygen, atomic oxygen. Oxygen radicals will oxidise organic molecules more readily than oxygen molecules. So typically organic binder can be converted to carbon dioxide, carbon monoxide and water at room temperature, rather than elevated temperatures and furthermore the oxidation is more controllable.

2.5. Reactors

There are many types of reactors available. The barrel reactor used in this study is a cylindrical container which can be evacuated. The RF power, usually at 13.56 MHz frequency is applied to the system via internal or external electrodes by capacitive or inductive coupling. This type of reactor is used for the plasma ashing process and also for the plasma etching process.

Recently a novel design of barrel plasma reactor is reported where the electrodes and rollers are one end mounted around the barrel i.e., the biased and earthed electrodes are incorporated into the rollers that are used to rotate the reactor [8]. With advances in technology, plasma reactors with better control on etching or erosion process would be available in future.

2.6. To Conclude

It can be stated that oxygen plasma produces extremely rapid degradation and few hours of exposure e.g. to several years of natural weathering [9]. Advantages of the technique are speed and much cheaper than weatherometer. It was mentioned in a study carried out by Paint Research Association, UK (PRA) that plasma erosion technique (PET) can be used to study degradation of coatings in faster way. Drawback of direct plasma system is that it exposes substrate between two electrodes. Therefore deterioration of coatings is not only caused by radical species but by also by ions, electrons, highly reactive atoms and UV rays present in plasma. Therefore it is necessary to optimize conditions especially by placement of plasma generating zone so that selectively oxygen radicals can be beamed on coating surface. [10]

3. Experimental

3.1. Coating Systems

Coating systems taken for studies were white exterior water based emulsion paints of different pigment volume concentrations (PVC). Paint of high PVC is economical paints

Table 1. Details of paints exposed to plasma.

Paint	Pigment volume concentration	Binder system	Durability
Exterior emulsion paint A	65	Acrylic polymer	2 years
Exterior emulsion paint B	45	Styrene-acrylic copolymer	5 years
Exterior emulsion paint C	40	Styrene-acrylic copolymer	7 years

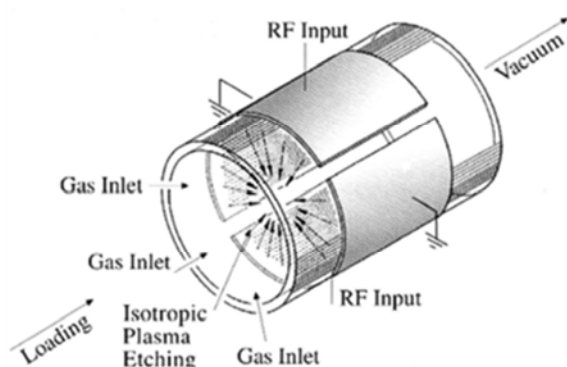


Figure 1. Plasma barrel reactor.

3.2. Application

Paints were applied on glass plate of size 6 x 8 cm by brushing after thinning to application viscosity by water and 3 coats of paints were applied. Paints were allowed to dry under ambient conditions in dust free environment. Care was taken to apply new coat 8 hours after earlier coat.

3.3. Conditions of Exposure

Paint films on glass plate were subjected to plasma barrel

$$\% \text{ Weight loss} = \frac{\text{Weight of paint before plasma exposure} - \text{Weight of paint after plasma exposure}}{\text{Weight of paint before plasma exposure}} \quad (6)$$

Extent of discolouration of paint which includes fading and yellowing was determined after plasma exposure.

For assessment of discolouration, total colour difference, whiteness index and yellowness index were measured using Macbeth colour computer under following conditions:

System of colour measurement – CIE

Source – Xenon flash lamp

Illuminant – D65 (Artificial sunlight)

Geometry of spectrophotometer – Diffuse/ 8 degree

Standard observer – 10 Degree

Mode of measurement– specular included

Total colour difference (dE) was measured taking paint film before exposure as reference and using following equation:

$$dE = \sqrt{dL^2 + dA^2 + dB^2} \quad (7)$$

Where

and is less durable in exterior environment.. Paints of low PVC and medium PVC were also taken to cover different range of paints. More details are given in table 1. Paints durability of these paints is already established from performance of these paints in natural exposures.

reactor Polaron model from Quorum Technologies, UK. Schematic of barrel reactor is shown in figure 1. Various conditions of exposure used are given in table 2. In plasma exposure, only two variables were controlled – energy of plasma and time of exposure.

Table 2. Conditions used in plasma exposure.

Sr. No.	Energy of Plasma	Time of exposure
1	40 W	2 Min
2	40 W	8 Min
3	40 W	30 Min
4	40 W	60 Min
5	100 W	60 Min

3.4. Observations

It was found that plasma exposure at 100 W energy for one hour is required to carry out sufficient degradation of organic binder.

Exposure at 40 KW energy for one hour was able to distinguish paint films based on their expected service life but difference in parameters measured was narrow. Exposure at low plasma energy and for shorter duration did not cause enough degradation of binder to arrive at conclusion and establish correlation. Loss of binder in these paint systems was determined by determining weight loss after plasma exposure.

dL is color difference in terms of lightness/darkness.

dA is colour difference in terms of redder/greener

dB is colour difference in terms of yellower/bluer

Whiteness index (WI) is measured by using following equation;

$$WI = L - 3 b \quad (8)$$

Where L and b are CIE coordinates corresponding to lightness/darkness and yellow/blue tone.

Yellowness index (YI) is calculated by using following equations:

$$YI = 100 (1.3013 X - 1.1498 Z) / Y. \quad (9)$$

Where X, Y, and Z are the CIE Tristimulus values

Properties like chalking, loss in sheen could not be assessed accurately due to small area of paint film subjected to plasma.

For following cases, definite trend was observed between expected life and properties.

1. Weight loss of paint film was found to be decreasing with plasma energy in order of increasing expected life.
2. Colour difference is found to be decreasing in order of increasing expected life.
3. Whiteness index was found to be increasing in order of increasing expected life.
4. Yellowness index is found to be decreasing in order of increasing expected life.

These results indicated that plasma had caused less degradation of more durable paints.

The observations are given below in table 3 and figure 2.

Table 3. Change in parameters of paints after plasma exposure.

Parameter	Paint A	Paint B	Paint C
Weight loss at 40w 60min	6.35	2.42	1.44
Weight loss at 100 W 60 mins	6.2%	4.7%	2.6%
Total colour difference at 40w 60min	1.2	1.1	0.8
Total Colour difference at 100 W 60 mins	1.7	1.1	0.7
Whiteness index at 40 W 60 mins	68.2	80.9	81.0
Whiteness index at 100 W 60 mins	69.2	77.8	81.0
Yellowness index at 40 W 60 mins	12.8	9.6	9.5
Yellowness index at 100 W 60 mins	11.9	10.4	9.7

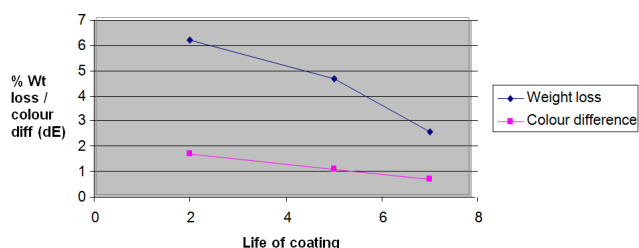


Figure 2. Graph of weight loss and colour difference of paints exposed to plasma at 100 W/1 hour.

3.5. Exposure to Xenon Arc Source

Exposure to Xenon arc sources is well established method for accelerated weathering and is used conventionally to

Table 4. Comparison of results of paint degradation after plasma & Xenon arc exposure.

Type of exposure	Parameters	Paint A	Paint B	Paint C
Exposure in Xenon arc weatherometer for 2000 hrs	Ratings of resistance to chalking	R=6	R = 8	R=9
	% loss of sheen	44.3	10.4	Nil
	% weight loss	6.2%	4.7%	2.6%
Exposure to plasma at 100 Watt energy for one hour	Total Colour difference DE in CIE system	1.7	1.1	0.7
	Whiteness Index	69.2	77.8	81.0
	Yellowness index	11.9	10.4	9.7

There was no significant deterioration found up to 1000 hrs of exposure under Xenon-arc source but later on degradation started more in paint A followed by B & C. In order to get clear differentiation, readings of chalking resistance and sheen (gloss at 85 deg glosshead) were recorded after 2000 hrs of exposure. Resistance to chalking was assessed using ASTM method and was rated on scale of 1-10 (1 – poor 10 – best). Chalking ratings are indicative of loss of organic binder due to degradation. Change in colouristic parameters are also

accelerate principle environmental factors in coatings industry. It is also specified by several standards like ASTM. It brings down requirement of exposure in natural conditions for paints from few years to few thousand hours. Good correlation of Xenon arc exposures to exterior natural exposures are reported [11]. In order to assess correlation between well accepted Xenon arc exposure and Plasma exposure technique, these paint systems were subjected to Xenon arc weatherometer after application of two coats on asbestos panels.

Schematic of Xenon arc weatherometer is shown in figure 3. It consists of Xenon lamp which is used to give illumination similar to natural sunlight after passing through Boro filters. The instrument has provision of spraying water at pre-determined interval to simulate rain. Paint panels are placed on rack which is kept rotating for ensuring homogenous exposure.

Details of exposure conditions used are given below:

Method – ASTM G 26

Instrument – Ci 35 Atlas weatherometer

Filters – Boro (inner & outer)

Cycle of exposure - 102 min UV cycle followed by 18 min rain cycle

UV irradiance level - 0.5 Watt/nm at 340 nm

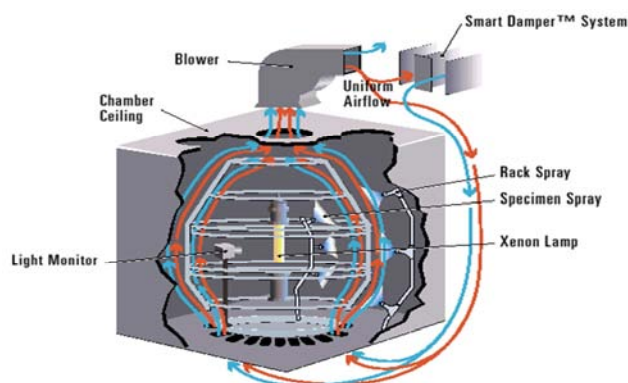


Figure 3. Xenon arc weatherometer.

indicative of degradation of overall paint systems which include chemical changes in pigments.

Results of degradation of paints after plasma and xenon arc exposure & are given in table 4. It is seen that degradation of less durable paint A is faster in both Plasma reactor and Xenon-arc weatherometer. More durable paints B and C also show similar trends. These results therefore clearly indicated good correlation of paints degradation between plasma exposure and exposure under xenon arc source.

4. Conclusion

Plasma Erosion Technique is found to be quick method for assessing durability of water based exterior emulsion paints with respect to certain properties like weight loss and discolouration. However it would require further optimization of conditions of plasma exposure to assess other properties after degradation. There was good correlation observed between exposure in xenon-arc weatherometer and plasma chamber. Plasma exposure technique can be of used to quickly shortlist coatings during designs & development stage as present techniques of accelerated exposures require several weeks for assessment of degradation. Plasma barrel etchers are relatively cheaper in cost and easier to operate.. Plasma erosion technique requires more study for different type of coating systems so that it can become part of national and international standards in future. However from limited study carried out so far it appears that this technique can act like supportive technique rather than competitive one for predicting durability of exterior coatings.

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