

# Performance of black pigments incorporated in interpenetrating polymer network (IPN)

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Received 2 January 2004; received in revised form 13 December 2005; accepted 1 February 2006

## Abstract

Interpenetrating polymer network (IPN) in which two different resins (epoxy and silicone) are not miscible as such with each other is made to do so by using cross-linking agents and catalyst. IPN possess good improved mechanical, chemical, heat and corrosion resistant properties than individual resins. Incorporation of black pigments like graphite, silicon carbide, carbon black and acetylene black has enhanced these properties because of their shape, size, acid and salt solution resistance, conducting nature and heat stability property. Flake structured graphite and hexagonal structured silicon carbide pigments in IPN protect the mild steel structures from corrosive and high temperature atmosphere for longer duration than the other pigments.

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**Keywords:** Black pigments; Interpenetrating polymer network (IPN); Heat resistance; Corrosion resistance; Impedance measurements

## 1. Introduction

High temperature corrosion is a big problem in chemical industries like petroleum, fertilizer and rocket launching vehicles. To overcome this problem, metal modification is mostly done. The developmental work is to protect the metal surface from high temperature corrosion by using heat resistant paint based on silicone resin incorporated with ceramic and metallic pigments [1]. IPN formulation is recommended for high performance coating to protect these structures. IPN are novel type of polymer hybrids and possess excellent physico-chemical properties. In this study IPN is prepared from epoxy and silicone resin with polyamidoamine as hardener. Epoxy resin is well known for its chemical resistance and also useful as a maintenance coating [2]. The silicone resins are mainly used for protecting the metal surface from high temperature corrosion [3]. Combination of these two resins has a better protective character for metals in high temperature as well as in highly corrosive environment.

Black pigments are ideal for heat resistant applications, for their heat dissipating property. Carbon black, graphite and silicon carbide powders are used in this study. The corrosion

resistance properties and thermal resistance behaviour of these coatings are discussed.

## 2. Experimental

Two types of IPN were prepared from baking type silicone, air drying silicone, epoxy resin and polyamidoamine hardener. Four types of black pigments such as graphite, silicon carbide, carbon black and acetylene black were incorporated in each resin and IPN to formulate 20 coatings. The compositions of the coatings are given in Table 1. Thus formulated coatings were applied on sand blasted surface and dried for 7 days and the baking type coatings were baked in an air oven at 453 K (180 °C) for 15 min. After complete curing the coatings were subjected to the following tests.

### 2.1. Mechanical properties

Thickness of the coated panels was measured by using Electrophysik, micro test Gb type 641. The scratch resistance of the coatings were carried out as per the ASTM specification D3359 using Erichsen model 259/1. Abrasion resistance of the coated panels were tested as per the ASTM standard D4060 for 1000 g load weight of 1000 cycles, using Taber abrasion tester model 503 (Table 2).

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Table 1  
Composition of black coatings

System	1	2	3	4	5
A	Si <sub>1</sub> Gr	Si <sub>2</sub> Gr	EpGr	IPN <sub>1</sub> Gr	IPN <sub>2</sub> Gr
B	Si <sub>1</sub> SiC	Si <sub>2</sub> SiC	EpSiC	IPN <sub>1</sub> SiC	IPN <sub>2</sub> SiC
C	Si <sub>1</sub> CB	Si <sub>2</sub> CB	EpCB	IPN <sub>1</sub> CB	IPN <sub>2</sub> CB
D	Si <sub>1</sub> AB	Si <sub>2</sub> AB	EpAB	IPN <sub>1</sub> AB	IPN <sub>2</sub> AB

Si<sub>1</sub>, air drying silicone; Si<sub>2</sub>, baking type silicone; Ep, epoxy polyamidoamine; IPN<sub>1</sub>, IPN<sub>2</sub>, inter penetrating polymer network 1 and 2; Gr, graphite; SiC, silicon carbide; CB, carbon black; AB, acetylene black.

## 2.2. Chemical resistance properties of the coating

The chemical resistance properties of the coated panels were tested in 3 wt.% sodium chloride solutions and 2 vol% sulphuric acid solutions for 15 days (Table 3).

## 2.3. Accelerated salt spray test

The coated panels were exposed in the salt spray chamber, where 5 wt.% of sodium chloride solution was atomized by the compressed air to create a fog. This test was conducted as per ASTM specification B117 for 500 h (Table 4).

## 2.4. Heat resistance test

This test was carried out according to the ASTM specification D2485. The failure of the coating was assessed visually by colour change, chalking, blistering, cracking and peeling off (Table 5).

Table 2  
Mechanical properties of the coating on mild steel panels

System	Thickness (μm)	Scratch hardness	Taber abrasion wear index $I = ((A - B)1000)/C$
A <sub>1</sub>	40 ± 2	4B	100
B <sub>1</sub>	40 ± 2	4B	100
C <sub>1</sub>	40 ± 2	5B	70
D <sub>1</sub>	30 ± 2	5B	60
A <sub>2</sub>	40 ± 2	4B	100
B <sub>2</sub>	40 ± 2	4B	100
C <sub>2</sub>	40 ± 2	5B	70
D <sub>2</sub>	30 ± 2	5B	70
A <sub>3</sub>	30 ± 2	5B	20
B <sub>3</sub>	30 ± 2	5B	20
C <sub>3</sub>	30 ± 2	5B	20
D <sub>3</sub>	20 ± 2	5B	20
A <sub>4</sub>	30 ± 2	5B	30
B <sub>4</sub>	30 ± 2	5B	10
C <sub>4</sub>	30 ± 2	5B	10
D <sub>4</sub>	20 ± 2	5B	10
A <sub>5</sub>	30 ± 2	5B	30
B <sub>5</sub>	30 ± 2	5B	10
C <sub>5</sub>	30 ± 2	5B	10
D <sub>5</sub>	20 ± 2	5B	10

5B, 0% area removed; 4B, less than 5% area removed; I, wear index; A, weight of panel before abrasion (mg); B, weight of panel after abrasion (mg); C, number of cycles of abrasion (1000).

Table 3  
Chemical resistance behaviour of the coatings on mild steel substrate

System	Immersion in 3% NaCl solution		Immersion in 2% H <sub>2</sub> SO <sub>4</sub> solution	
	Failure (days)	Type of failure	Failure (days)	Types of failure
A <sub>1</sub>	4	B	4	B and R
B <sub>1</sub>	2	B	2	B and P
C <sub>1</sub>	4	R	4	B and P
D <sub>1</sub>	3	R and B	2	P
A <sub>2</sub>	3	R	6	P
B <sub>2</sub>	2	B	2	B
C <sub>2</sub>	4	R	4	B and P
D <sub>2</sub>	4	R	2	B, P and R
A <sub>3</sub>	12	R	10	B and P
B <sub>3</sub>	9	B	10	B and P
C <sub>3</sub>	6	R	4	EC and R
D <sub>3</sub>	7	B	4	B
A <sub>4</sub>	14	B	15	B
B <sub>4</sub>	14	B	11	B
C <sub>4</sub>	7	R	6	P
D <sub>4</sub>	9	R	2	B
A <sub>5</sub>	15	B	15	B
B <sub>5</sub>	15	R	12	B
C <sub>5</sub>	7	B	4	EC and R
D <sub>5</sub>	9	R and B	3	B

B, blister; R, rust; P, peeling off; EC, edge corrosion.

## 2.5. Electrochemical impedance measurements

These measurements were carried out with PAR model 6310 system in frequencies from 10 KHz to 10 mHz and the applied signal amplitude was 10 mV. The electrochemical cell used for this study is a three-electrode system consists of coated panel as

Table 4  
Performance of coated panels in salt spray chamber

System	Tolerance limit (h)	Types of failure
A <sub>1</sub>	90	R and B
B <sub>1</sub>	50	R and B
C <sub>1</sub>	42	R
D <sub>1</sub>	60	R and B
A <sub>2</sub>	50	R and B
B <sub>2</sub>	48	R
C <sub>2</sub>	40	R and EC
D <sub>2</sub>	80	R and B
A <sub>3</sub>	340	R and B
B <sub>3</sub>	340	R and B
C <sub>3</sub>	120	R and EC
D <sub>3</sub>	100	B
A <sub>4</sub>	450	EC
B <sub>4</sub>	400	EC
C <sub>4</sub>	150	R
D <sub>4</sub>	200	R and B
A <sub>5</sub>	500	EC
B <sub>5</sub>	500	EC
C <sub>5</sub>	180	R
D <sub>5</sub>	200	B and R

B, blister; R, rust; EC, edge corrosion.

Table 5  
Heat stability performance of coated panels

System	Observation
A <sub>1</sub>	Slight change in gloss, colour is not changed up to 753 K (480 °C), above this temperature chalking is observed
B <sub>1</sub>	Slight change in gloss, colour is not changed up to 753 K (480 °C)
C <sub>1</sub>	No change in colour and gloss up to 643 K (370 °C)
D <sub>1</sub>	No change in colour and gloss up to 643 K (370 °C), above this temperature colour and gloss changed
A <sub>2</sub>	No change in colour and gloss up to 753 K (480 °C), above that minute cracks are observed
B <sub>2</sub>	No change in colour and gloss up to 753 K (480 °C), above that minute cracks are observed
C <sub>2</sub>	No change in colour and gloss up to 698 K (425 °C), above that chalking is observed
D <sub>2</sub>	Slight change in colour and gloss up to 588 K (315 °C), above that formation of cracks are observed
A <sub>3</sub>	No appreciable colour and gloss change up to 478 K (205 °C), above that colour change followed by chalking is observed
B <sub>3</sub>	No appreciable colour and gloss change up to 478 K (205 °C)
C <sub>3</sub>	No colour change, gloss reduced to some extent up to 533 K (260 °C), above that chalking is observed
D <sub>3</sub>	No colour change, gloss is observed up to 533 K (260 °C)
A <sub>4</sub>	Colour and gloss is not changed up to 643 K (370 °C), above that gloss and colour changed
B <sub>4</sub>	Colour and gloss is not changed up to 643 K (370 °C)
C <sub>4</sub>	No change in colour and gloss up to 588 K (315 °C), above that chalking is observed
D <sub>4</sub>	No change colour and gloss up to 588 K (315 °C)
A <sub>5</sub>	No appreciable colour and gloss change up to 698 K (425 °C), above that cracks are seen on the surface
B <sub>5</sub>	No appreciable colour and gloss change up to 698 K (425 °C)
C <sub>5</sub>	No colour change, but slight reduction in gloss is observed up to 588 K (315 °C) afterwards chalking is observed
D <sub>5</sub>	No colour and gloss change up to 588 K (315 °C), above that colour change, followed by peel off of the coating from the substrate is observed

working electrode, a platinum foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in 3 wt.% sodium chloride solution as electrolyte. The impedance measurements were done periodically after 1 h, 7 and 15 days duration. The resistances obtained from the Bode plot are given in Table 6.

### 3. Results and discussion

The thickness per coat of graphite, silicon carbide and carbon black incorporated silicone coatings are  $40 \pm 2 \mu\text{m}$  and that of acetylene black pigmented coating is  $30 \pm 2 \mu\text{m}$  (Table 2). This reduction in coating thickness for acetylene black is due to the fine particles of acetylene black which has good hiding power than the other pigments. Epoxy and IPN with graphite, silicon carbide and carbon black pigmented coatings has the thickness of  $30 \pm 2 \mu\text{m}$  present, whereas the acetylene black incorporated coatings in epoxy and IPN exerted  $20 \pm 2 \mu\text{m}$  thickness per coat. The scratch hardness values indicate that all the coatings have better adhesion over mild steel substrate. The coatings with graphite and silicon carbide pigment in silicone resin have

Table 6  
Charge transfer resistance values derived from the Bode plot of impedance studies

System	Charge transfer resistance ( $R_t$ ) ( $\Omega \text{ cm}^2$ )			
	1 h	1 day	7 days	15 days
A <sub>1</sub>	$1 \times 10^6$	$1 \times 10^5$	$1 \times 10^4$	$3 \times 10^2$
B <sub>1</sub>	$5 \times 10^4$	$2 \times 10^4$	$2 \times 10^3$	$5 \times 10^2$
C <sub>1</sub>	$2 \times 10^3$	$7 \times 10^2$	$4 \times 10^2$	$3 \times 10^2$
D <sub>1</sub>	$3 \times 10^5$	$8 \times 10^4$	$6 \times 10^3$	$4 \times 10^2$
A <sub>2</sub>	$4 \times 10^4$	$2 \times 10^3$	$1 \times 10^3$	$9 \times 10^2$
B <sub>2</sub>	$5 \times 10^6$	$2 \times 10^5$	$1 \times 10^3$	$8 \times 10^2$
C <sub>2</sub>	$1 \times 10^5$	$4 \times 10^3$	$2 \times 10^3$	$1 \times 10^2$
D <sub>2</sub>	$7 \times 10^7$	$8 \times 10^5$	$2 \times 10^3$	$4 \times 10^2$
A <sub>3</sub>	$6 \times 10^7$	$5 \times 10^5$	$4 \times 10^5$	$3 \times 10^5$
B <sub>3</sub>	$1 \times 10^6$	$3 \times 10^5$	$9 \times 10^4$	$8 \times 10^4$
C <sub>3</sub>	$9 \times 10^4$	$7 \times 10^3$	$5 \times 10^3$	$3 \times 10^3$
D <sub>3</sub>	$1 \times 10^8$	$5 \times 10^5$	$9 \times 10^3$	$9 \times 10^3$
A <sub>4</sub>	$6 \times 10^6$	$8 \times 10^5$	$1 \times 10^6$	$1 \times 10^6$
B <sub>4</sub>	$5 \times 10^8$	$8 \times 10^7$	$5 \times 10^6$	$2 \times 10^5$
C <sub>4</sub>	$2 \times 10^4$	$4 \times 10^4$	$4 \times 10^4$	$2 \times 10^4$
D <sub>4</sub>	$2 \times 10^6$	$8 \times 10^4$	$5 \times 10^4$	$2 \times 10^3$
A <sub>5</sub>	$4 \times 10^6$	$5 \times 10^6$	$6 \times 10^6$	$5 \times 10^6$
B <sub>5</sub>	$2 \times 10^8$	$2 \times 10^6$	$5 \times 10^5$	$2 \times 10^5$
C <sub>5</sub>	$5 \times 10^4$	$3 \times 10^4$	$3 \times 10^4$	$2 \times 10^4$
D <sub>5</sub>	$2 \times 10^5$	$1 \times 10^5$	$9 \times 10^4$	$5 \times 10^3$

slightly lower adhesion on the surface which may be due to the size and shape of the particles, which is different from the other two pigments. The spherical shaped fine particles of acetylene black readily incorporated into the resin produce good adhesion over the steel surface. The scratch hardness exhibited by these four pigments in epoxy and IPN are in 100% range. These coatings produce strong Vander walls forces on the surface and so the adhesion between the coating and the surface is very strong. The abrasion resistance of the silicone resin with graphite and silicon carbide incorporated coatings suffers high weight loss, which may be due to poor wetting properties of silicone resin [4] in the formulation. The other formulation shows optimum level of weight loss, as these coatings have very good cohesive force between pigment and the binder followed by good adherence on the substrate.

Chemical resistance behaviour of the coatings (Table 3) indicates that the silicone-based coatings protect the surface comparatively for lesser duration than the epoxy resin based formulation. This is mainly due to the poor wetting property of the silicone resin followed by inherent pore formation which leads to the formation of loose rust on the surface in sodium chloride and sulphuric acid solutions. The black pigment incorporated IPN coatings are not affected in 3% sodium chloride solution for 15 days. This suggests that the IPN does not allow the permeation of corrosive ions into it. Further the flaky and hexagonal structured graphite and silicon carbide pigments reduce the micropores on the surface and protect the surface for longer duration than the acetylene black and carbon black pigmented IPN composition. IPN with black pigments in the coated panels in 2% sulphuric acid solution exhibit similar behaviour. This chemical resistance studies strongly indicate that the formation

of IPN from the silicone and epoxy resin considerably increase the protective behaviour of these coatings in neutral as well as acidic environments.

The salt spray performances of the coatings are similar to the chemical resistance character (Table 4). System incorporated with graphite and silicon carbide show better result with carbon black and acetylene black. This is mainly due to the flake structured graphite and hexagonal structured silicon carbide completely blocks the pores and reduces the penetration of corrosive ions into it [5]. Acetylene black pigmented IPN protects for reasonable period better than the carbon black pigmented IPN in salt spray chamber. This may be due to the organic nature of the pigment followed by very good hiding property. The type of failure noticed in acetylene black pigmented coatings is blistering followed by rust formation, whereas in the case of carbon black pigmented systems, flash rust is directly formed at the pore site and then spreads all over the surface. This indicates that the excess pigmentation may lead to insufficient binder to form film over the surface.

Table 5 indicates the heat stability performance of the black pigments incorporated coatings. Graphite and silicon carbide pigment incorporated in silicone resin and IPN protect the surface above 698 K (425 °C) for a longer duration than the other systems. But both these pigments in epoxy resin will not tolerate the temperature above 478 K (205 °C). This clearly indicates that the maximum heat tolerance limit of epoxy resin is 478 K (205 °C). But the acetylene black and silicon carbide incorporated into epoxy coating withstands up to 533 K (260 °C). This may be due to these spherical and crystalline shaped pigments which have good hiding over the surface and do not allow the shrinkage of the binder present in it for certain period in this temperature. All the pigments in IPN perform well in high temperatures when compared with epoxy resin. The graphite and silicon carbide incorporated coatings perform well in high temperatures irrespective of binders (except epoxy resin). This is mainly due to the particle to particle contact of the pigments, which readily conduct the heat on the surface and withstand at high temperature quit a long duration. The acetylene black incorporated coating is completely turned into white after 588 K (315 °C). This is due to the oxidation of acetylene black at higher temperature and the carbon present in the molecule is converted into carbon dioxide. Once the white colouration occurs on the surface, further increase in temperature leads to peel off the coating from the substrate. The carbon black pigmented coatings are also stable up to 588 K (315 °C) in IPN, above that temperature chalking is observed. This is due to the exposure of the excess pigment present in the coating above that particular temperature. This high temperature study indicates that the formation of IPN from silicone and epoxy resin considerably improve the heat resistance behaviour of epoxy resin and also for silicone resin.

Bode plots of impedance diagram of graphite pigmented air drying and baking type silicone coatings on steel surface in 3 wt.% of sodium chloride solution for different durations are shown as Figs. 1 and 2. The charge transfer resistances exerted by the pigmented coating has decreased with duration (Table 6). At the initial stage, the resistances of the coatings are moderately

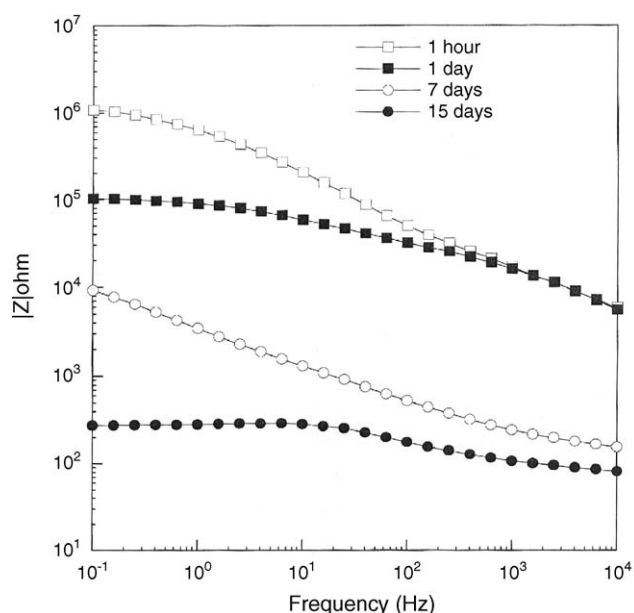


Fig. 1. Impedance diagram for graphite pigment incorporated silicone (air drying) coating on steel substrate in 3 wt.% NaCl solution.

in higher order. But with duration it decreases enormously and reached  $10^2 \Omega \text{ cm}^2$  within 15 days duration. This shows that the coating prevented the passage of the corrosive ions in the initial stage as barrier. After 1 day the barrier layer presented on the surface is degraded and the graphite pigment is exposed in the electrolyte. The graphite is a good conductor of electron and so it protects the surface as an electron conductor for some period. Thereafter, the coating lost particle to particle contact and so pore formation followed by corrosion process takes place and the failure of the coating is noticed. The impedance behaviour of epoxy-graphite pigmented coating (Fig. 3). The resistance of this system is in higher order. That is in the order

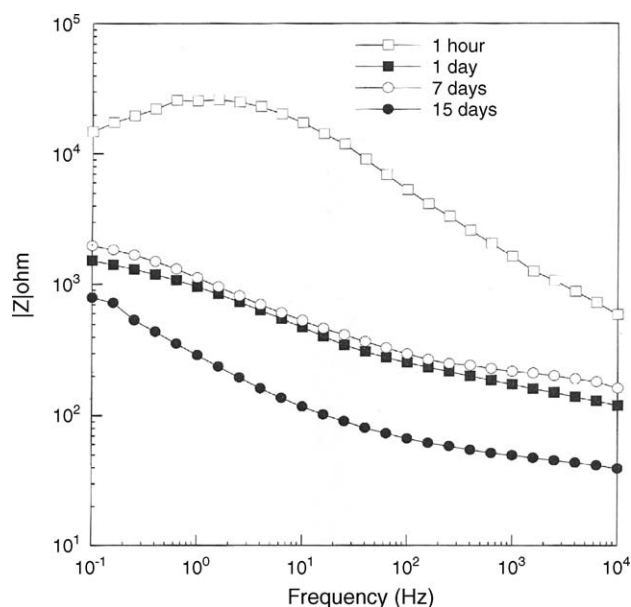


Fig. 2. Impedance diagram for graphite pigment incorporated silicone (baking type) coating on steel substrate in 3 wt.% NaCl solution.

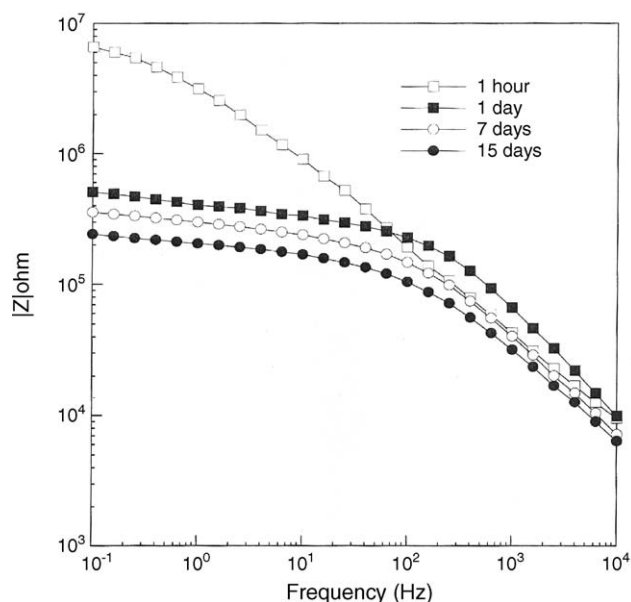


Fig. 3. Impedance diagram for graphite pigment incorporated epoxy polyamidoamine coating on steel substrate in 3 wt.% NaCl solution.

of  $10^7$ – $10^5 \Omega \text{ cm}^2$  for the period of the study. This diffusion controlled system is already explained by several authors [6,7] and so this system protects the surface as a barrier mechanism. Figs. 4 and 5 indicate the impedance behaviour of graphite in IPN<sub>1</sub> and IPN<sub>2</sub> for different durations. The resistance produced by the system through out the period of the study is nearly constant, that is in the order of  $10^6 \Omega \text{ cm}^2$ . This behaviour of the coating indicates that this coating do not allow the diffusion of electrolyte into it. The resistance produced by the coating is mainly dependent up on the surface phenomena such as surface toughness, defects, and water absorption. The exploration of the complexity of the reaction taking place on the surface is very

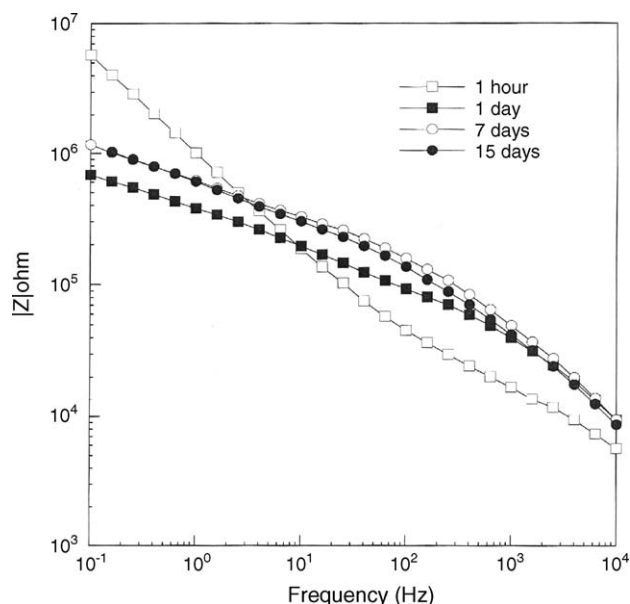


Fig. 4. Impedance diagram for graphite pigment incorporated IPN1 coating on steel substrate in 3 wt.% NaCl solution.

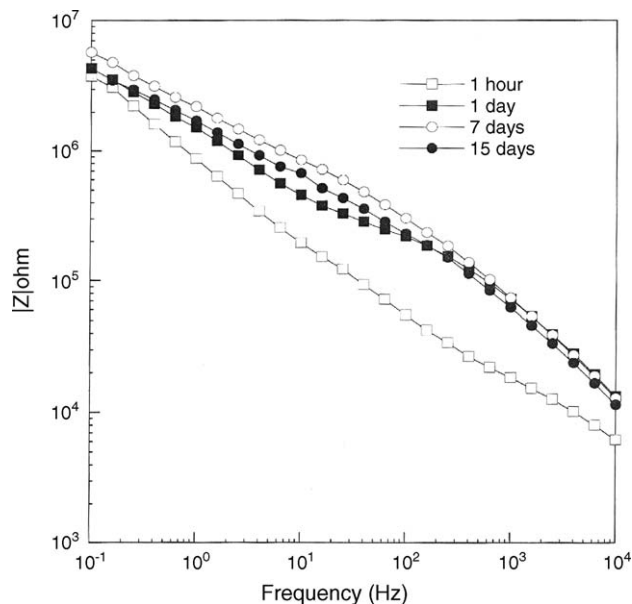


Fig. 5. Impedance diagram for graphite pigment incorporated IPN2 coating on steel substrate in 3 wt.% NaCl solution.

difficult. The graphite incorporated IPN is performing well and produce high resistance in 3 wt.% sodium chloride solution.

Resistance produced by the silicon carbide pigment incorporated silicone resins are in low range (Table 6). Initially this resistance is moderately higher order but after 1 day it is decreased to the range of  $10^3 \Omega \text{ cm}^2$ . This diffusion controlled reaction is explained by the initial barrier protection followed by pore formation leads to failure of the coating. The resistance exerted by the silicon carbide pigmented epoxy resin is in protective order, but after 7 days this resistance is reached  $10^4 \Omega \text{ cm}^2$ . This pigment incorporated IPN coatings produce higher resistance in the range of  $10^8$  and  $10^6 \Omega \text{ cm}^2$  initially, but after 15 days, this resistance decreases to  $10^5 \Omega \text{ cm}^2$ . This shows that these coatings produce the resistance in protective side [8]. This high resistance exerted by these coatings is due to the better protective property of the IPN and the fine dispersion of the silicon carbide pigment in it.

Resistance produced by carbon black and acetylene black pigmented silicone, epoxy and IPN systems in sodium chloride solution. Carbon black pigmented coating gives very low resistance in these resins and IPN media. This low resistance offered by the carbon black pigmented coating is evident because it is being extremely fine in particle size, tend to form aggregates through normal inter particle attraction and these aggregates may be attached to other aggregates or other primary particles to form larger units known as “agglomerates”. This may lead to the formation of pores on the surface and easily allow the penetration of corrosive electrolyte and lead to early failure of the coating. The acetylene black incorporated coatings produced higher resistance in the initial stage in the order of  $10^7$  and  $10^6 \Omega \text{ cm}^2$ , etc. But after 7 days these resistance is decreased to  $10^4$  and  $10^3 \Omega \text{ cm}^2$ . This shows that the coatings have an excellent protective capability at the initial stage in capacitive way, but later diffusion controlled reaction dominates to lead the failure of the



coating. Further this early failure may due to the low thickness of the coating that is 20  $\mu\text{m}$ . The IPN with acetylene black pigment may protect the surface for longer duration if the thickness of coating is in the order of 40  $\mu\text{m}$  range.

#### 4. Conclusion

The high temperature resistance test of black pigments incorporated in silicone, epoxy and IPN coatings are stable at 693 K (420 °C). The chemical resistance and salt spray experiments indicate that the graphite and silicon carbide incorporated epoxy coatings and IPN are suitable for sodium chloride environment. The impedance measurements suggest that the graphite and silicon carbide incorporated epoxy and IPN coatings extend conduction as well as barrier protection to the steel substrate for longer duration than the other black pigmented coatings. The acetylene black pigment in IPN coating above 40  $\mu\text{m}$  protects the substrate from sodium chloride solution. Flake structured

graphite and hexagonal structure silicon carbide pigments in IPN protect the steel structure for longer duration from corrosive as well as in high temperature environments.

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