

## EVALUATION OF PROTECTIVE COATINGS FOR GAS PIPELINES

S GURUVIAH, V CHANDRASEKARAN, V GANESA SARMA AND E NALINI

Central Electrochemical Research Institute, Karaikudi 623 006

### ABSTRACT

Mild steel pipelines carrying coke oven (CO), blast furnace (BF) and mixed gases in steel plants are prone to attack by certain constituents of the gas. The rate of corrosion of the internal surface of a gas pipeline can be combated by applying a suitable internal protective coating to the pipeline. In this paper, various types of protective schemes (developed and commercial) were applied on sand blasted mild steel panels and the coated panels were evaluated by capacitance or resistance measurements and immersion tests in various electrolyte and gas condensates. It was shown that the following protective schemes gave good performance in all the tests. 1. Zinc-sodium silicate + epoxy TiO<sub>2</sub> 2. Zinc-rich epoxy + epoxy TiO<sub>2</sub> 3. Zinc-rich + black finish (com) 4. Zinc-rich epoxy + coal tar epoxy.

### INTRODUCTION

Mild steel pipelines carrying coke oven (CO), blast furnace (BF) and mixed gases in steel plants are prone to attack by certain constituents of the gas [1-3]. The nature of the problem is rather complex and varies to some extent from one plant to another depending on factors such as the quality of coal and various process and design aspects. The eventual failure of the pipelines usually results from two main causes: (a) chemical attack of the pipe steel by certain agents present in the gas and condensate, and (b) erosion of the pipe steel by solid particles present in the gas travelling at high velocity. These two processes can take place either simultaneously or successively, thereby making the second process easier. It is generally found that newly installed pipelines show the first signs of damage and failure owing to internal corrosion after being in service for only about 3-4 years. Once the leaks occur, the plant is forced to have a shut-down for necessary repair work which is hazardous as well as expensive. This also results in loss of production. The process of repair has to be repeated every time a leak appears and a time comes when it is necessary to replace the old pipeline with a new one which requires heavy capital expenditure. If the problem can be controlled and the rate of corrosion minimised, the plant will benefit by having a fewer shut-down, elimination of expensive and dangerous repair work, greater productivity, and longer life of the pipelines requiring no replacement for an extended period.

The rate of corrosion of the internal surface of a gas pipeline can be controlled by one or a combination of the following measures: (a) by controlling the process parameters (b) by removing the corrosion constituents from the gas and (c) by applying a suitable internal protective coating to the pipeline. Among these, the application of coating [4-5] is the commonest method of providing protection against corrosion. Coatings can either be of the barrier type or the inhibitive type. Those of the former type separate the environment from the metal surface and afford protection by virtue of their high ionic resistance which retards movement of ions, thereby reducing corrosion currents. Coatings of the latter type contain dispersed inhibitive pigments in the coating material itself or in the primer. These pigments may contain either salts of metals or metal particles. Those containing salts of metals have a passivating effect and those containing metal particles afford cathodic protection.

### EXPERIMENTAL

**1. Capacitance and resistance measurements:** The Universal Bridge B 224 (Wayne Kerr Company Limited, England) can measure resistance in the range of 10  $\Omega$  to 1000 M  $\Omega$  and capacitance in the range of 0.1 picofarad to 10 microfarad with 0.1% accuracy. To carry out measurements at different frequencies, an RC oscillator (Toshniwal Bros., Bombay) was used as an external source. The cell set up used was as follows:

Three cylindrical glass tubes, 2.5 cm diameter  $\times$  5 cm height, was placed in different portions of the steel plates coated with paints (5  $\times$  7.5 cm), edges sealed with araldite and the tubes filled with various electrolyte and gas condensate up to a height of 3 cm. A platinum foil, 1.5 cm<sup>2</sup> with a stem introduced into the solution, was used as the electrical lead for the measurement of capacitance and resistance of the varnish coating. The capacitance and the resistance were measured by making the set up (between the steel plate and the platinum foil) as one arm of the bridge. Measurements were made daily for 20 days at frequencies 1 KHz. Measurements were made at three portions of the steel plate and values obtained at the portions which gave the most consistent values were plotted.

**2. Immersion tests:** Various electrolytes were kept separately in different beakers and the painted panels in duplicate with and without scratch were immersed in the electrolyte for 1 to 4 months. Observations were made periodically and at the end of experiments the panels were taken from the electrolyte and the paint was removed by sharp knife and the surfaces of the panels were examined.

Electrolytes used for study were: (a) 3% sodium chloride (b) 3% sodium sulphate (c) 1% (W/W) sulphuric acid (d) coke oven gas condensate (e) blast furnace gas condensate (f) mixed gas condensate and (g) carbon dioxide saturated water containing sulphide.

The M S panels of size 5  $\times$  7.5 cm were sand blasted and the paint coating was applied with an interval of 24 hours. The paint scheme consists of primer coat plus finishing paint and thickness is of the order of 100-125  $\mu$ . The coating was applied by brush.

**3. Set up for gas corrosion studies :** The set up for the study of gas corrosion consists of gas generation unit and a gas circulation chamber. The CO<sub>2</sub> gas and CO<sub>2</sub> gas containing 1.2 to 2.4 g/cu.m. of H<sub>2</sub>S with moisture were passed through the exposure vessel using blowers assembly. The painted MS panels were kept inside the gas for a period of 200 hrs. At the end of the test the specimen was taken out and the observation was made.

The following paint schemes were employed on MS and used for capacitance/resistance measurements, immersion tests and exposure in the gas corrosion set up.

- a. Calcium chromate/iron oxide primer in epoxy polyamide plus chlorinated rubber MiO (commercial)
- b. Calcium chromate/iron oxide primer in epoxy polyamide + epoxy TiO<sub>2</sub>
- c. Zinc-ethyl silicate + -do-
- d. Zinc-sodium silicate + -do-
- e. Zinc-rich epoxy primer + -do-
- f. -do- + chlorinated rubber MiO (commercial)
- g. -do- + epoxy TiO<sub>2</sub> (commercial)
- h. -do- + coal tar epoxy (commercial)
- i. Zinc-rich primer + black finish (commercial)

Table I : Measurement of capacitance and resistance of painted panels at 1 KHz frequency  
Final value after 65 days

No paint scheme	Thickness (microns)	Resistance (1 × 10 <sup>6</sup> ohm)		Capacitance (PF)	
		Initial	Final	Initial	Final
<b>Coak oven gas condensate :</b>					
1. Zinc rich epoxy (D) + AC coat (C)	137.5	33.3	11.10	40.00	56.00
2. Zinc rich (C) + black finish (C)	100.0	722.0	100.00	3.48	5.30
3. Zinc rich epoxy (D) + epoxy TiO <sub>2</sub> (D)	112.5	100.0	100.00	2.00	3.00
4. Zinc rich epoxy (D) + undercoat 64 (D) + finished coat 66 (D)	162.5	50.0	9.00	30.00	51.00
<b>Blast furnace gas condensate :</b>					
1. Zinc rich epoxy (D) + AC coat (C)	137.5	50.0	16.60	27.00	39.00
2. Zinc rich (C) + black finish (C)	100.0	166.0	4.50	4.00	9.50
3. Zinc rich epoxy (D) + Epoxy TiO <sub>2</sub> (D)	112.5	100.0	100.00	2.00	3.00
4. Zinc rich epoxy (D) + undercoat 64 (D) + finished coat 66 (D)	162.5	50.0	12.00	20.00	35.00
<b>Mixed gas 1:1 condensate :</b>					
1. Zinc rich epoxy (D) + AC coat (C)	137.5	33.3	11.28	40.00	55.00
2. Zinc rich (C) + black finish (C)	100.0	166.0	1.00	2.70	5.50
3. Zinc rich epoxy (D) + epoxy TiO <sub>2</sub> (D)	112.5	100.0	100.00	2.00	3.00
4. Zinc rich epoxy (D) + undercoat 64 (D) + finished coat 66 (D)	162.5	25.0	5.00	40.00	60.00
<b>3% Na<sub>2</sub>SO<sub>4</sub> solutions :</b>					
1. Zinc rich epoxy (D) + AC coat (C)	137.5	50.0	25.00	30.00	40.00
2. Zinc rich (C) + black finish (C)	100.0	250.0	22.00	4.00	100.00
3. Zinc rich epoxy (D) + epoxy TiO <sub>2</sub> (D)	112.5	33.3	14.25	43.00	52.00
4. Zinc rich epoxy (D) + undercoat 64 (D) + finished coat 66 (D)	162.5	33.3	8.00	30.00	51.00

D = Developed at CECRI; C = Commercial

## RESULTS AND DISCUSSION

The resistance and capacitance values of painted panels measured in gas condensate and electrolytes are given in Table I. The paint scheme contains zinc-rich as primer coat. All the four paint schemes in Table I showed high resistance values even at the end of 65 days. The rate of change of resistance was not rapid. Similarly the increase in capacitance with time was not much. Hence all the four systems which showed high resistance and low capacitance values gave very good protection to the substrate. In all the four paint schemes the primer paint zinc-rich epoxy was developed in the Institute. In the case of paint scheme 4, the primer and the undercoat and finishing paint was developed in the Institute. The final resistance value and capacitance for both developed and commercial paints are nearly equal.

Table II gives the resistance and capacitance values in 3% NaCl solution for nine protective schemes. It is seen from Table II that a very high resistance value was obtained in all the paint schemes except the paint scheme No. 1 in 3% NaCl solution.

Similarly the capacitance value of all the paint system increases slightly and the value also was low except paint scheme No.1, in 3% NaCl. The capacitance and resistance values for all the nine paint schemes were measured in CO<sub>2</sub>-saturated water containing sulphide solution. The resistance value was high in all the paint schemes except No.1. Similarly the capacitance value was low and the increase was also slight except paint schemes 1 and 6. It is seen from the measurements that all the paint schemes showed good performance in CO<sub>2</sub>-saturated water containing 100 ppm of sulphide.

Table II : Resistance and capacitance of painted panels in 3% NaCl at 1 KHz

No.	Paint system	Thickness (microns)	Final value after 30 days			
			Resistance $\times 10^6$ (ohms)		Capacitance (PF)	
			Initial	Final	Initial	Final
1.	Calcium chromate/iron oxide primer + (D) Chlorinated rubber MiO (C)	200	0.9	0.7	320.0	360.0
2.	Calcium chromate iron oxide + epoxy TiO <sub>2</sub> (66) (D)	250	10.0	10.0	2.8	3.0
3.	Zinc ethyl silicate + epoxy TiO <sub>2</sub> (66) (D)	250	10.0	3.3	3.0	5.0
4.	Zinc sodium silicate + epoxy TiO <sub>2</sub> (66) (D)	250	100.0	25.0	36.0	55.0
5.	Zinc rich epoxy + epoxy TiO <sub>2</sub> (66) (D)	225	100.0	10.0	5.0	20.0
6.	Zinc rich epoxy + chlorinated rubber MiO (C)	175	10.0	1.0	100.0	200.0
7.	Zinc rich epoxy + epoxy TiO <sub>2</sub> (C)	250	20.0	16.0	32.0	33.0
8.	Zinc rich + black finish (C)	250	1.0	1.0	2.8	3.0
9.	Zinc rich epoxy + epoxy coal tar (C)	225	50.0	10.0	40.0	50.0

C = Commercial; D = Developed.

The observation was made at the end of 50 days on painted panels immersed in various electrolytes. All the paint schemes performed well except a few changes at edges and discoloration in gas condensation test. From the immersion test it is seen that zinc-rich epoxy + epoxy TiO<sub>2</sub> paint schemes, both commercial and developed, performed well in 1% H<sub>2</sub>SO<sub>4</sub> immersion test. The surface was examined after removal of paint. The surface was bright in all the paint schemes. In the case of 3% NaCl immersion tests, a few paints based on chlorinated rubber showed white rust at scratches; otherwise the paint remains in tact. No appreciable change was noticed in the case of painted panels exposed to CO<sub>2</sub>/H<sub>2</sub>S atmosphere for 100 hours.

Various types of paint schemes were evaluated. It is seen from the results that all the paint schemes with zinc-rich as a first coat showed good performance. The primer coat zinc-rich paint gives barrier protection as well as galvanic protection to steel surfaces. The top coat used for the study was (1) epoxy TiO<sub>2</sub>, (2) epoxy-coal tar, (3) chlorinated rubber paint and (4) commercial finishing paint. The permeability of the corrosive ion like H<sub>2</sub>O and Cl<sup>-</sup> is low in the case of epoxy medium than chlorinated rubber paint. Hence the resistance value obtained was very low in the case of chlorinated rubber paint scheme than epoxy paint scheme. Hence the paint scheme based on zinc-rich plus epoxy showed good performance in all the tests.

## CONCLUSION

The various paint schemes were evaluated by immersion tests and electrochemical tests using various electrolytes and gas condensates. The following gave good performance in both the tests:

1. Zinc-sodium silicate + epoxy TiO<sub>2</sub>
2. Zinc-rich epoxy + epoxy TiO<sub>2</sub>
3. Zinc-rich primer + black finish (commercial)
4. Zinc-rich epoxy + coal tar epoxy (commercial)

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## REFERENCES

1. J.W Graves and E.H Sullivan, *Mater Prot*, **5** (1966) 33.
2. A.K Lahiri (Ed), *Corrosion in Steel Plants*, Corrosion Advisory Bureau, Jamshedpur (1967).
3. J.W Chilver, *Corrosion Technol*, **11** (1964) 11.
4. E Escalante and W.P Iverson, *Mater Perform*, **17** (1978) 9.
5. R.L Davis, *Mater Prot* **6** (1967) 40.