Storage Tank Protection Using Volatile Corrosion Inhibitors

BORIS A. MIKSIC, FNACE, ALLA Y. FURMAN, AND MARGARITA A. KHARSHAN, *Cortec Corp.*

Research and fieldwork show that vapor phase corrosion inhibitors (VpCIs) can be used to protect the bottoms of aboveground storage tanks. The performance of VpCIs in these applications was confirmed by several corrosion and electrochemical methods. Their use in conjunction with cathodic protection is also discussed.

Volatile corrosion inhibitors, or vapor phase corrosion inhibitors (VpCIs), belong to the organic group of inhibitors. The vapors adsorb on the metal surface and suppress metal dissolution and reduction reactions. These affect anodic and cathodic processes. Organic amines and carboxylates are typical examples of this class. VpCIs have moderately high vapor pressure and can prevent corrosion without being applied directly to the metal surface.[1-3]

With VpCIs, the volatilized molecules can migrate to hard-to-reach spaces. When it reaches the metal, the VpCI attaches to it. Vapor pressure is a critical parameter in VpCI effectiveness. The most favorable range of pressure is 10^{-3} to 10^{-2} Pa at room temperature. Insufficient pressure leads to the slow establishment of the protective layer; if the pressure is too high, VpCI effectiveness is limited to a short time.[1-3]

Corrosion protection of fuel storage tanks is important because failures are costly and can cause contamination of the environment. Corrosion protection has been provided by VpCI technology for single- and double-bottom aboveground storage tanks (ASTs). Since 1986, there have been many cases where VpCIs have been used to protect storage tank bottoms. For single-bottom tanks, VpCIs have been added to the sand on which storage tanks were positioned, and for double-bottom tanks, in the space between bottoms (interstitial space [Table 4]).

Different application methods were developed for the protection of new and used tanks. Gandhi[4] has reported the results of applications. According to Gandhi, VpCIs were used to protect AST bottoms by mixing VpCI powder with gravel and sand. Corrosion was monitored over a two-year period. It was later confirmed that the VpCI protected the bottoms of those tanks against corrosion for more than 15 years after application. A special dispensing system for this application was developed. For new tanks, after a sub-base of sand and gravel is spread, VpCI powder is applied at the rate of 10 to 20 kg/100 m² (2 to 4 lb/100 ft²). It is mixed into the base with hand tools. The tank bottom is then laid out and fabricated as normal.[4]

When tanks are being refurbished and new bottoms plates are welded in, VpCIs are spread under the plate. Another approach is to inject a 5% solution of VpCI in the under-bottom of the storage tanks. For installation of new double-bottom tanks, VpCI powder is spread at the rate of 1 to 2 kg/10 m² (2 to 4 lb/100 ft²). The second bottom is then welded in place. For protection of existing tanks, VpCI

FIGURE 1

Setup of outdoor investigation of VpCI performance.

powder should be carefully blown into the voids to provide uniform distribution. Alternately, VpCI solution may be pumped into the voids and either left there or drained.[4] In another case, a VpCI slurry was used for corrosion protection of 17 large-diameter double-bottom ASTs. This was done in the 2000 to 2001 time frame. Measurements indicate good corrosion protection and no significant depletion of the inhibitor. VpCI slurry was injected into interstitial space. The space was filled with the VpCI slurry and held full for ~60 days. The telltale pipes were then uncapped and the slurry was allowed to drain to the level of the telltale pipes. Cathodic protection (CP) was also applied to the bottoms.
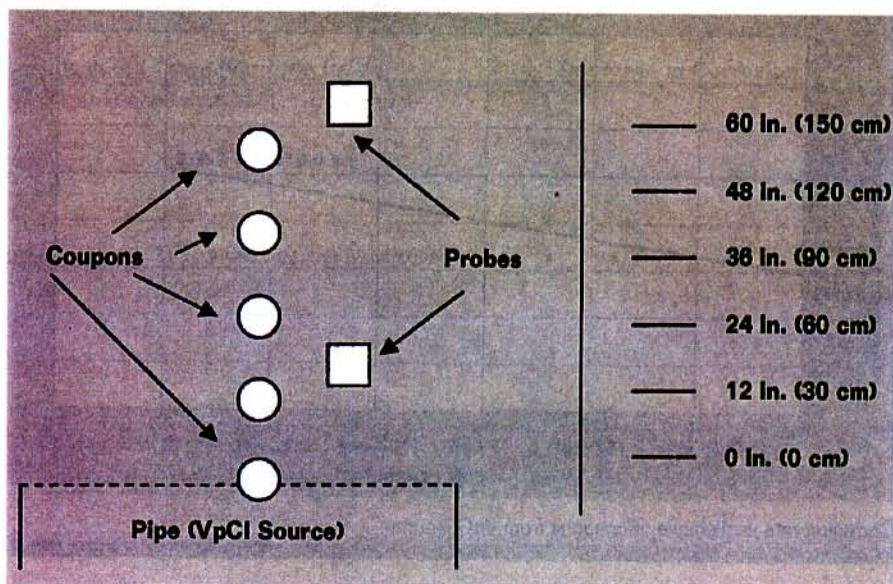
Experimental Procedures

OUTDOOR EXPERIMENT

An experiment was performed to find the maximum distance of VpCI action. At ground level, a box space filled with sand was prepared. A plastic pipe with slots, which contained the corrosion inhibitor, served as the VpCI source and was buried at a depth of 1 ft (0.3 m) in the sand; preconditioning was accomplished over a 30-day period. After this, the test coupons were placed in the sand box at distances from the pipe, ranging from 0 to 60 in. (0 to 150 cm), at a depth of 3 to 5 in. (7.5 to 10.5 cm) (Figure 1).

The corrosion rate was determined according to the formula:[5]

$$\text{Corrosion rate (mils/y)} = (K \times W) / (A \times t \times \Delta) \qquad (1)$$

where K = constant, 3.45×10^6; W = weight loss (g); A = area of the metal coupon (cm²); t = time (h); and Δ = density of the metal (g/cm³).

INDOOR EXPERIMENT
Sand Test

Two corrosion inhibitors, a VpCI and a conventional anodic inhibitor, were tested in the presence of CP. The results were compared to control data—samples under CP but without corrosion inhibitor.

The mixture consisted of playground sand: 70.0%; tap water: 29.4%; sodium chloride (NaCl): 0.3%; and VpCI: 0.3%.

Plastic containers were filled with this mixture. Pre-weighted carbon steel (CS) panels (SAE 1010), 5 cm by 9 cm, and zinc (99.9% pure), 1 cm by 5 cm, were inserted into the sand, 10 cm apart. In each container, steel and zinc panels were electrically connected. The current between steel and zinc panels was measured by an A.W. Sperry Multimeter DM-8600[†]. After 12 days, panels were removed from the sand and their weight loss was determined (Table 1).

Electrochemical Evaluation

The combination of the VpCI and CP was studied using the following methodology: An EG&G Potentiostat "Versastat" with software 352 SoftCorr 111[†], three electrode electrochemical cells, a saturated calomel electrode (SCE) as a reference, high-density graphite as a counter electrode, and CS SAE 1018 working electrodes.

Based on normal practice,[6] a cathodic potential of −900 mV (SCE) was applied to the CS electrode and the current corresponding to this potential was measured.
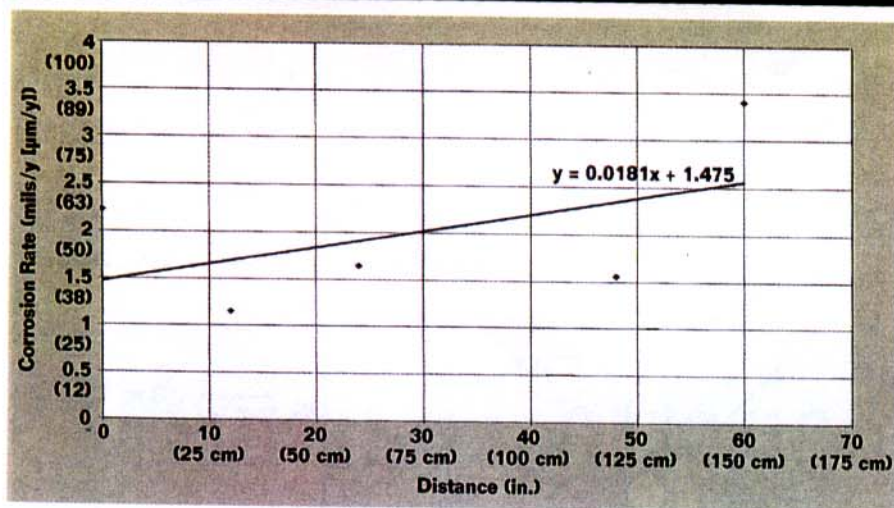
[†]Trade name.

TABLE 1

CORROSION RATE OF ELECTRICALLY CONNECTED CS AND ZINC

Product	Zinc Weight Loss (g)	CS Weight Loss (g)	Current in Zinc-Steel Circuit (mA)
VpCI	0.5	<0.01	131.7
Conventional anodic inhibitor	1.3	0.1	137.5
Control[(A)]	0.7	0.03	135.0

[(A)]Inhibitor was not added to sand.

FIGURE 2

$y = 0.0181x + 1.475$

Corrosion rate vs distance of coupons from VpCI source.

Corrosion rates were measured before application of the VpCI and then each two weeks after application until the rate stabilized. Table 4 presents the results of this field application.

Results
OUTDOOR TEST

The coupons situated closer to the VpCI source experienced a lower corrosion rate than those further away (Figure 2). For example, the corrosion rate of the coupon placed at a distance of 48 in. (125 cm) from the VpCI source is lower than that of the coupon located at the distance of 60 in. Apparently, under the described conditions, the VpCI migrates through the sand in inverse proportion to distance.

INDOOR TEST
Sand Test

Table 1 presents the results of this test. It shows that the presence of the corrosion inhibitor affects the corrosion rate of zinc and steel. In the test using a conventional corrosion inhibitor, the corrosion rate of the zinc sacrificial anode was nearly twice that of the control sample, and the corrosion rate of steel was about three times that of the control sample, to which no inhibitor was added. With VpCI, a lower corrosion rate of electrically connected zinc and steel was exhibited.

Electrochemical Evaluation

The results presented in Table 2 were obtained in 3% NaCl solution with and without inhibitor added. Electrochemical potential of the working electrode made from CS SAE 1018 was –900 mV vs CSE.

TABLE 2

POTENTIOSTATIC TEST

Product	Current at –900 mV (µk/cm³)
0.5% VpCI	22.9
0.5% conventional corrosion inhibitor	38.80
Control (3% NaCl)	27.2

To evaluate the difference in the behavior of different inhibitors applied in combination with CP, potentiodynamic polarization curves and corrosion potentials of zinc and CS were measured. All electrochemical measurements were conducted in 3% sodium chloride (NaCl) electrolyte; corrosion inhibitors were added at a concentration level of 0.5 wt%. The scan rate of the potential in potentiodynamic studies was 0.5 mV/s.

FIELD APPLICATION

Whited[7] described the reduction in corrosion rate achieved by the application of VpCI technology for the corrosion protection of the underside of the upper bottom on a double-bottom tank and on a single-bottom tank with a high-density polyethylene secondary containment liner.

The results of the treatment were measured by electrical resistance (ER) corrosion rate probes.

For this experiment, VpCI slurry was prepared by mixing 600 lb (272 kg) of VpCI powder with 900 gal (3,407 L) of water. A manifold assembly was built to allow flow of the slurry into telltale pipes. The distribution of the slurry during application was controlled.

TABLE 3(A)

CORROSION POTENTIAL OF CS SAE 1018 AND ZINC IN 3% NaCl SOLUTION CONTAINING CORROSION INHIBITORS

Product	E_{corr} mV, CS	E_{corr} mV, Zinc	Difference in the Electrochemical Potentials of CS and Zinc (mV)
0.5% VpCI	–515	–995	480
0.5% conventional corrosion inhibitor	–360	–795	435
Control (3% NaCl)	–535	–995	460

(A)Obtained from the polarization curves.

APPLICATION OF VpCI TO A DOUBLE-TANK INTERSTITIAL SPACE

Date	Probe No.	Calculated Corrosion Rate (mil/y)	Decrease in Corrosion Rate (%)
		Original corrosion rate after 13 days (control)	
12/16/04	P1	21.2	—
	P2	16.5	—
	P3	28.5	—
	P4	17.3	—
		Corrosion rate 21 days after inhibitor installation	
1/6/05	P1	12.4	42
	P2	9.5	42
	P3	10.7	62
	P4	5.9	66
		Corrosion rate 56 days after inhibitor installation	
2/10/05	P1	7.0	67
	P2	3.9	76
	P3	9.4	67
	P4	4.8	72

These results indicate that the current, which corresponds to a potential of -900 mV, depends on the type of the inhibitor in solution. When added to the solution, VpCI inhibits the cathodic reaction and subsequently lowers the level of current at a given potential. With a conventional anodic inhibitor, the opposite results are observed.

Data presented in Table 3 indicate that corrosion potentials of CS and zinc in 3% NaCl electrolyte containing VpCI are close to those of the control. This is attributed to the film-forming mechanism of corrosion protection of VpCI inhibitors. According to this mechanism, adsorption of VpCI on the metal does not cause a shift of corrosion potential because the mechanism affects anodic and cathodic reactions. The data also show that the difference in the electrochemical potentials of CS and zinc remain sufficient for use of the zinc as an effective anode in the test setup. The conventional anodic corrosion inhibitor in the system affects the corrosion potentials of the metals in a way that an electrical connection with zinc will not polarize CS to the cathodic potential sufficient for its protection.[6,8-9]

FIELD TEST

The data presented in Table 4 show that application of VpCI gradually reduced the corrosion rate. After 56 days, the reduction reached 67 to 76% of the initial corrosion rate.

Conclusions

1) Tests and experience indicate that VpCIs provide effective corrosion protection for single- and double-bottom storage tanks. The corrosion rate of CS protected by a VpCI is two to three times lower than unprotected steel. VpCI can be applied, in powder form or as a slurry, by mixing it with the sand used for the installation of the tanks.

2) VpCI provides protection to the metal located within 1 m of the VpCI source.

3) According to the test data, a VpCI is compatible with CP and, when used in combination with it, reduces the protective current required. This can also reduce electric power usage by the rectifier.

4) Not all types of the inhibitors can be used in combination with CP. Film-forming and cation-active types of inhibitors have a better chance for successful use with CP than anodic inhibitors.

References

1. G.H. Koch, M.P.H. Brongers, N.G. Thompson, Y.P. Virmani, J.H. Payer, "Corrosion Costs and Preventive Strategies in the United States," FHWA-RD-01-156 (McLean, VA: FHWA, 2002).

2. B.A. Miksic, "Use of Vapor Phase Inhibitors for Corrosion Protection of Metal Products," CORROSION/83, paper no. 308 (Houston, TX: NACE International, 1983).

3. B.A. Miksic, "Some Aspects of Metal Protection by Vapor Phase Inhibitors, Journal-Anti-Corrosion, Methods & Materials," Sawell Publications 3 (1975): p. 5.

4. A. Gandhi, "Storage Tank Bottom Protection Using Volatile Corrosion Inhibitors," Supplement to MP 40, 1 (2001): pp. 28-30.

5. T. Whited, "Corrosion Slowed on Tank Bottoms. Vapor Corrosion Inhibitors Used to Mitigate Corrosion Rate of a Double-Tank Interstitial Space," Pipeline & Gas J. (June 2005): pp. 49-50.

6. NACE RPO675-88, "Control of External Corrosion on Offshore Steel Pipelines" (Houston, TX: NACE).

7. NACE RPO169-96, "Control of External Corrosion on Underground or Submerged Piping Systems/ Section 6," Criteria and Other Considerations for Cathodic Protection (Houston, TX: NACE).

8. H.G. Byars, Corrosion Control in Petroleum Production, TPC Publication 5, p. 181 (Houston, TX: NACE).

9. ASTM G 31-72, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (West Conshohocken, PA: ASTM).

BORIS A. MIKSIC, FNACE, is president and chief executive officer of Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. A NACE member for more than 30 years, he received the NACE 2004 F.N. Speller Award for lifetime achievements in the field of corrosion engineering, is a NACE Fellow, and his company received a NACE Distinguished Organization Award in 2004.

ALLA Y. FURMAN has a Ph.D. and is a senior corrosion engineer at Cortec Corp.

MARGARITA KHARSHAN has a Ph.D. and is a laboratory director at Cortec Corp. **MP**