EXPERIMENTAL EVALUATION OF INHIBITORS VCI 629, VCI 368 AND VCI 365 MANUFACTURED BY CORTEC CORPORATION

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June 26, 1992

OBJECTIVE:

To evaluate the corrosion protection properties of Cortec inhibitors so as to promote their application in the West Siberian oilfields and refineries of Russia.

SUBJECT AND METHODOLOGY OF EXPERIMENTS

1.1 Subjects of testing

Carbon steel was utilized for the purpose of testing. Chemical composition of steel was as the following:

C	-	0.22%
Mn	-	0.48%
Si	-	0.17%
Cr	-	0.30%
Ni	-	0.30%
S	-	0.05%
P	-	0.04%

The following inhibitors were tested: VCI-629, VCI-368, and VCI-365.

1.2 Methodology of testing

- Testing for protection against general corrosion
- Testing for protection against stress corrosion cracking
- Electrochemical testing of the inhibitors
- Testing of technological properties of the inhibitors

1.2.1. Corrosion testing

Rectangular shaped samples of carbon steel were utilized for corrosion testing. Dimensions of samples: 50 x 20 x 2mm. Tests were performed in the following corrosion mediums:

a) NACE TM-01-77 standard. Solution of NaCl 50g/l + CH_3 COOH 5g/l + H_2 S in distilled water. pH of solution 3.0-4.0
b) Simulation of corrosion aggressive medium of Samotlorskoye oil field (brine water). Solution of NaCl 17g/l + $NaHCO_3$ 0.6g/l + CaCl 0.2g/l + MgCl 0.2g/l. PH of solution 6.5
c) Simulation of aggressive medium of Samotlorskoye oil field with mentioned above chemical composition of brine water plus heptane additive - crude oil products simulation. Ratio brine solution to water 10:1.

The NACE TM-01-77 solution - procedure (a) -test samples were placed into glass ampoules. The corrosive solution was added into the ampoules and the ones were sealed. The ampoules were placed into the oven and conditioned for 24 hours. Temperature of the oven was maintained at 50° C. After 24 hours of the test ampoules were opened and corrosion products were washed out of the samples. The samples were dried in the desiccator with CaCl and checked for weight loss. The tests in Samotlorskoye oil field solution - procedure (b) and (c) - were performed according to standard. Special apparatus were used to perform the testing (Fig. 1). Conditions of the test: velocity of liquid flow - 1m/s, temperature - 25°C, duration of the test-6 hours. After testing, the samples were removed from the apparatus and corrosion products were washed out with water and acetone. Samples were dried in a desiccator with CaCl and checked for weight loss on electronic balances (0.0001g).

Inhibition ability was evaluated under two test variations of an inhibitor utilization:

1. An inhibitor was added directly to aggressive medium in the concentration of 200mg/l.
2. A steel sample was conditioned in the inhibitor over a 2 hour period in order to allow the inhibitor to form a protective film on the steel surface. After conditioning, the sample was transferred to aggressive media with an inhibitor additive - 200mg/l. According to this procedure "post-action inhibition effect" was determined. The inhibition coefficient - γ , and protective action of the inhibitor - Z , were calculated according to the following formulas

$$\gamma = \rho_o/\rho_1 \qquad Z = [(\rho_o - \rho_1)/\rho_o)] \times 100\ \%$$

where, ρ_o - rate of corrosion / qm^2hour / in aggressive medium

ρ_1 - rate of corrosion in aggressive medium with inhibitor

1.3 Electrochemistry

Kinetics of electrode processes were studied in the potentiodynamic regime of measurements, with utilization of potentiometer PI-50-11 and programmer PR-8. Polarization curves were taken using a cylindric carbon steel electrode (diam. 2mm, height 8mm) placed into an electrochemical glass cell with a subdivision of anodic and cathodic spaces. An AgCl saturated electrode was used to evaluate the protective properties of VCI-365. Deaerated model solutions (a) or (b) were used in the cell. A potential scan rate of ImV/s and a temperature of 25 °C were used. The impedance measurement method was used to evaluate the protective properties of VCI-365. The measured impedance characteristics were: active resistivity, Ra, and differential capacity, Cd, and the change of these characteristics with time and frequency. Impedance measurements were performed using an a.c. bridge with a frequency interval from 0.21 to 50 kHz. The working electrode was a steel sample coated with VCI-365 and immersed in a corrosive. A platinum electrode was used as a reference.

1.3.1 Stress accelerated corrosion tests complex

Complex of stress accelerated corrosion tests contained the following procedures:

- Corrosion cracking induced by dynamic/static stress test.
- Corrosion fatigue evaluation.
- Evaluation of hydrogen diffusion through steel membrane.

1.3.2 Stress corrosion cracking evaluation.

Generally, two methods are utilized in world practice to measure effectiveness of inhibitors in prevention of SCC processes:

- Estimation of threshold stress utilizing long term corrosion durability curves.

σ - $\log \tau_F$ where, δ - stress, τ_f - time to failure (cracking)

- Estimation of relative sensitivity of steel to stress cracking utilizing tensile stress applied on a steel sample with constant low rate of the sample deformation. Traditionally, SCC of steel is investigated using a method of static tensile deformation. But this method takes a long time (30 days) to accomplish and gives significant deviation of test data. Therefore, the low rate of deformation of steel specimens was used during the evaluation of the inhibitor's effectiveness. The test was performed using cylindric steel specimens (Fig. 2a) and specially designed experimental cell filled with corrosive medium. (Fig.3).

This assembly was installed in to a tearing machine and deformation was 2 x 10'V[1]. Specimen failure relative contraction ψ % and relative elongation δ % were measured. The corrosive medium was prepared according to the NACE TM-0177 standard. The major characteristics for evaluation of inhibitor protective action were the coefficient of protection (Kp) and the coefficient of corrosive medium effect (β).

$$Kp = \frac{\Psi_1 - \Psi_c}{\Psi_a - \Psi_c} \times 100\% \qquad \beta = \frac{\Psi_a - \Psi_c}{\Psi_a}$$

where,

ψ_a – relative contraction in an air medium
ψ_c – relative contraction in corrosive medium.
ψ_i – relative contraction in inhibited corrosive medium

The static load tension applied to cylindric specimens (Fig. 2a) method was utilized to evaluate the long term corrosion strength of steel. Induced stress in the sample was calculated according to the following formula: $\delta = 4P/\pi d^2$ where P - load, N; d - diameter of the specimen. Duration of the test was 720 hours. As the characteristics of tendency of steel to be subjected to SCC 1 - threshold stress and f- time to failure were evaluated. The test was performed in corrosive media (NACE TM-01-77) with continuous sparging of H_2S in to solution.

Fig. 1 Apparatus for evaluation of the inhibitors in Samotlorskoye corrosive medium. 1- U- shape vessel; 2- heater; 3- corrosive medium; 4- mixer; 5- sealed gear box; 6- electromotor; 7- heat exchanger; 8- sparger; 9- steel specimens; 10- stand.

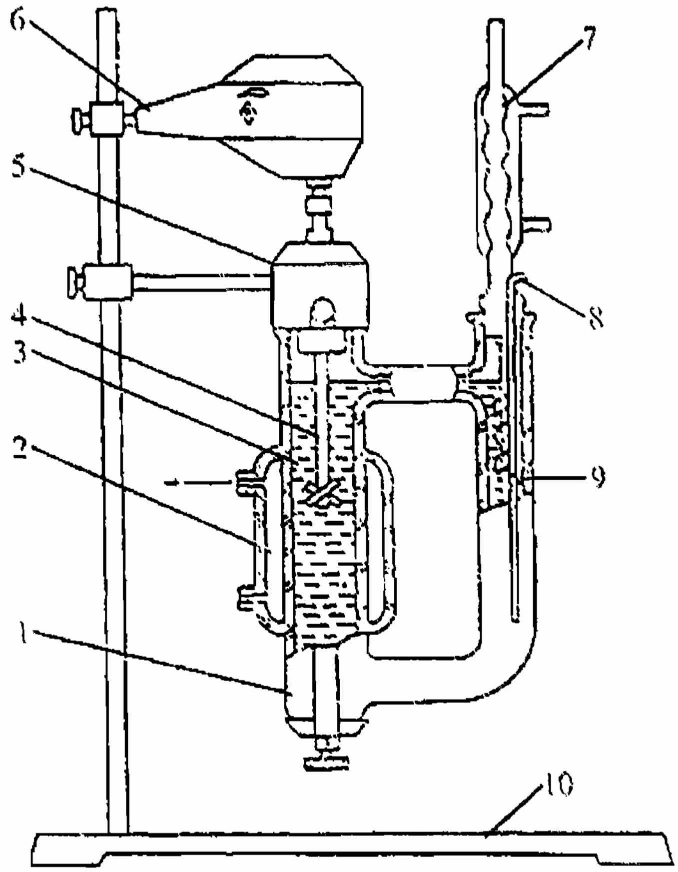


Fig.2 Specimens for evaluation SCC (a) and corrosion fatigue (b)

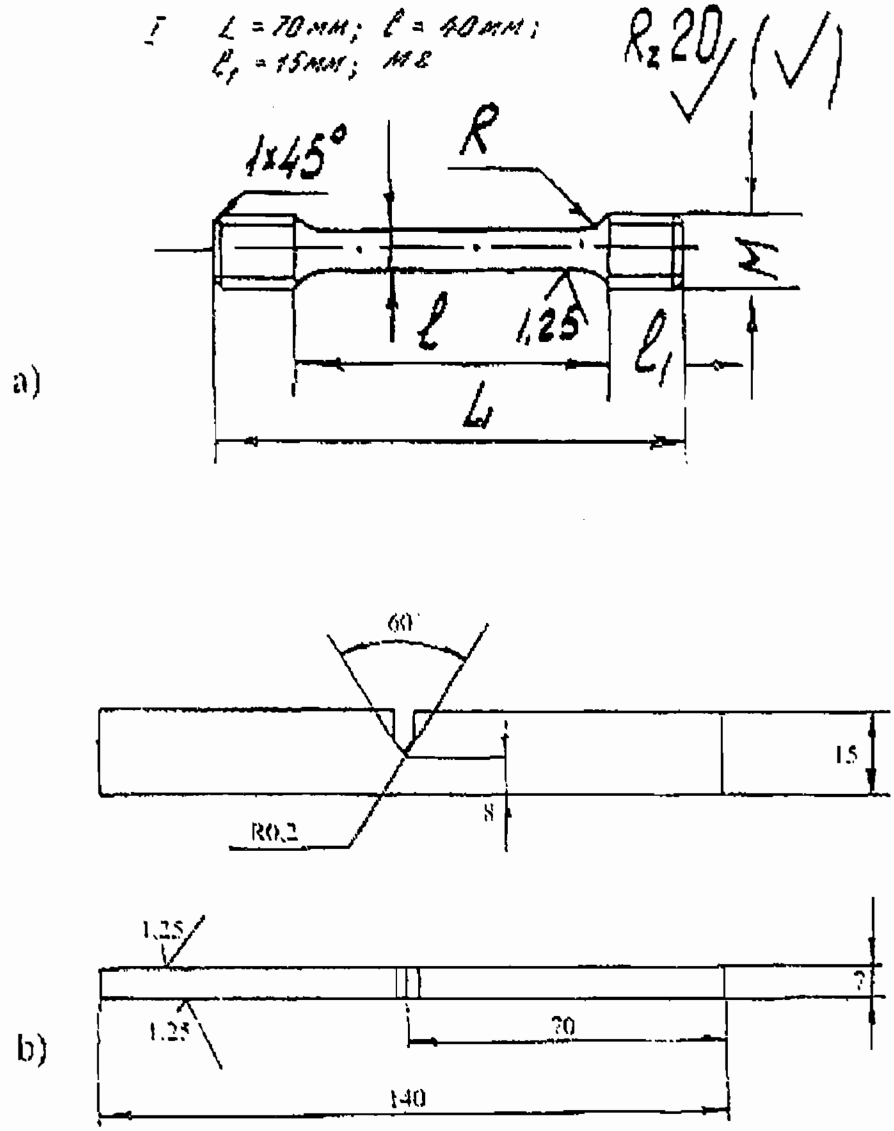


Fig. 3 Apparatus (cell) for testing of SCC.
1 - specimen; 2 - sealing collar; 3 - ring; 4 - housing; and 5 - connector.

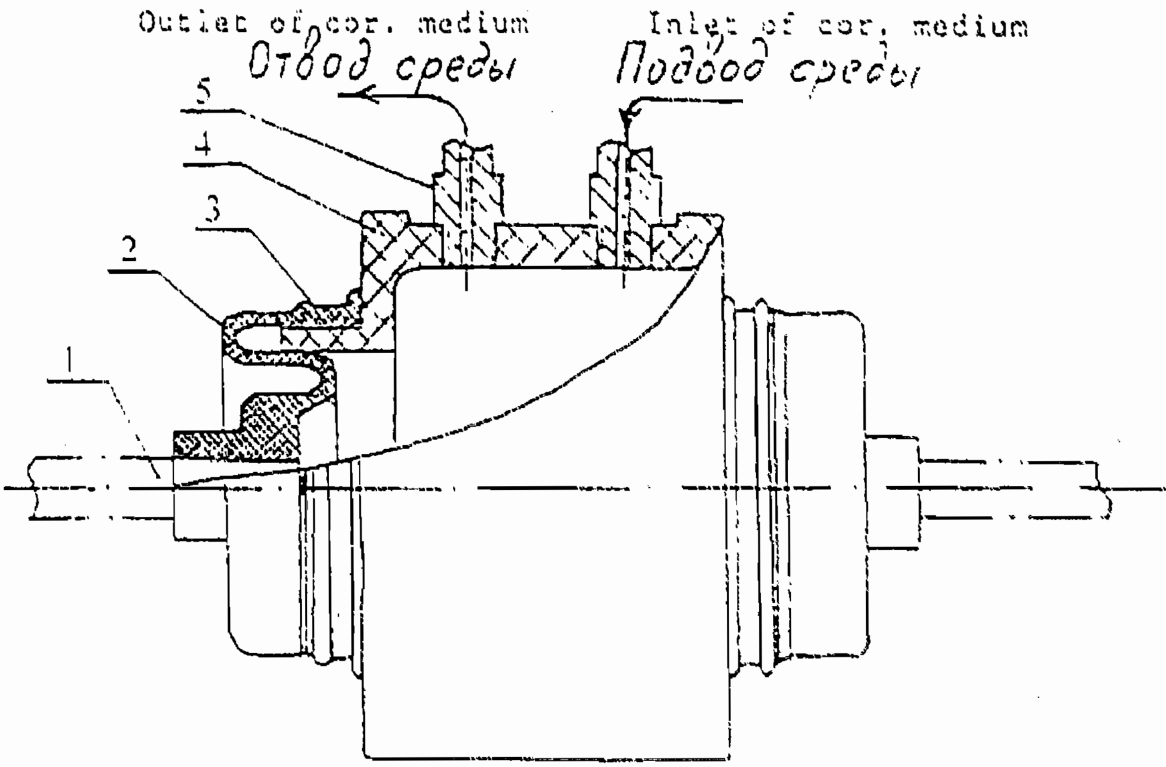


Fig. 4 Diagram of tension of carbon steel under rate of deformation
1 - air; 2 - corrosive medium; 3 - inhibited corrosive medium.

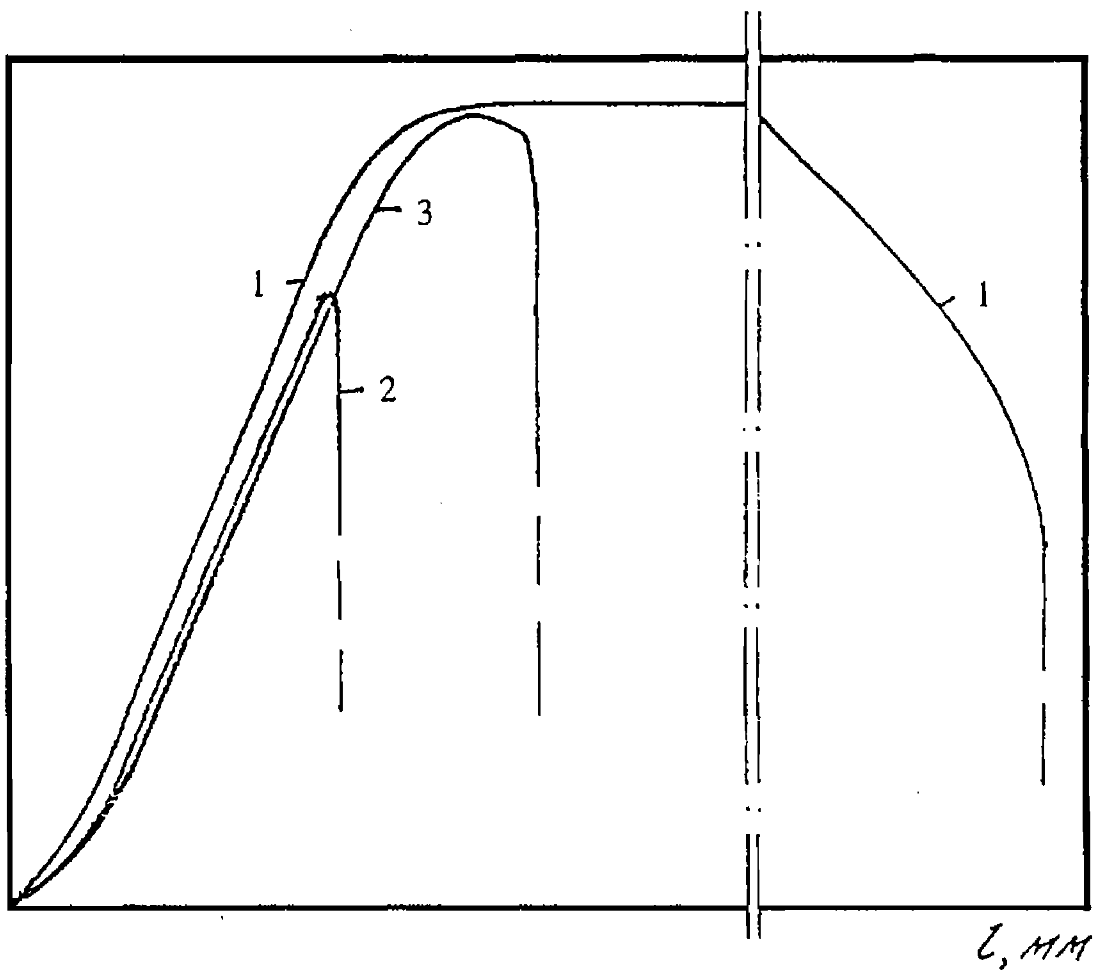


Fig. 5 Apparatus for low-cycle fatigue testing

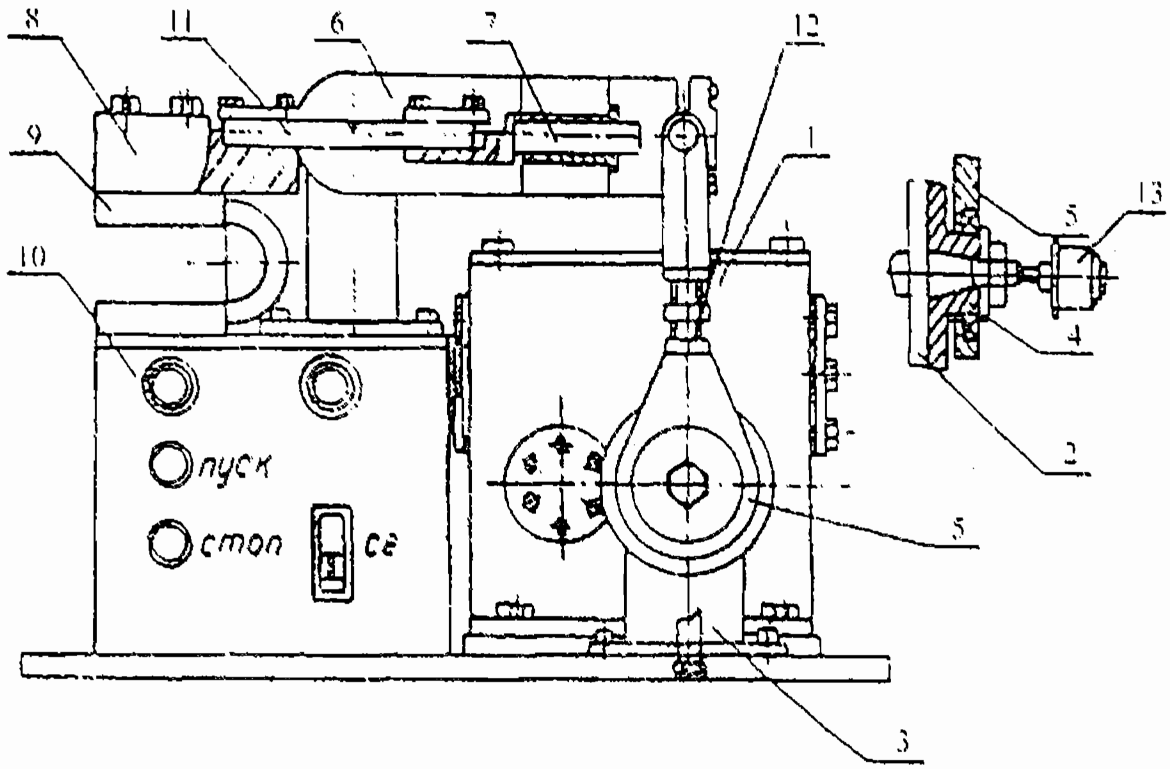
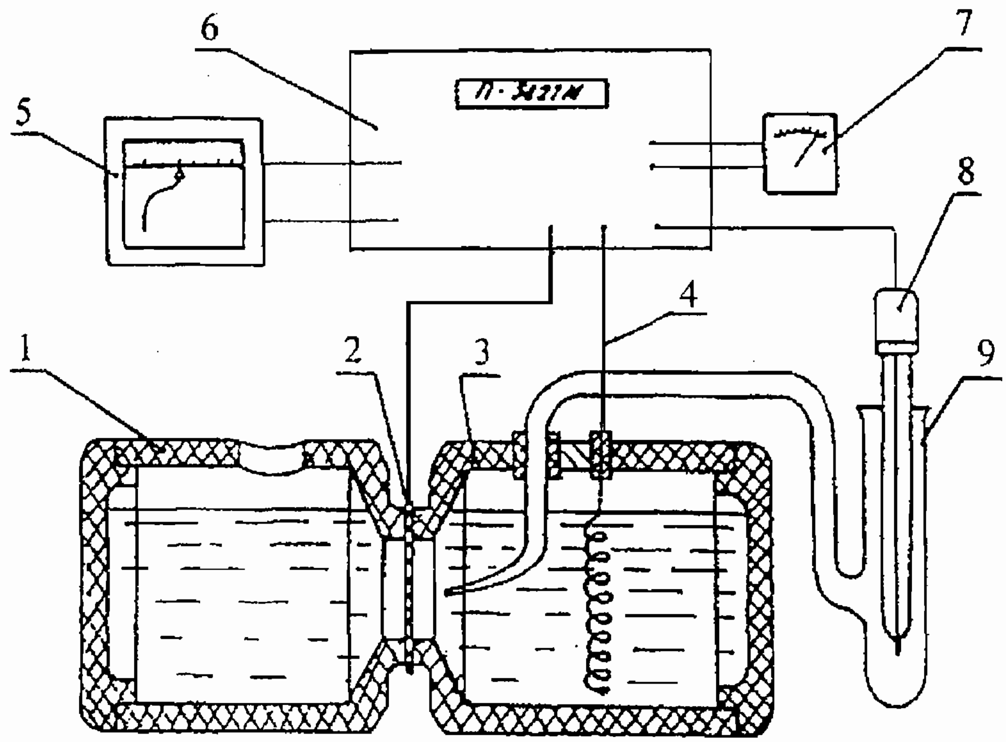


Fig. 6 Testing cells for evaluation of hydrogen diffusion through steel membrane. 1 - cell; 2 - specimen-membrane; 3 - measurement cell; 4 - platinum electrode; 5 - potentiometer-recorder; 6 - potentiometer; 7 - microampermeter; 8 - reference electrode; 9 - electric switch.



2 Experimental Results of the Tests

2.1. Effectiveness of CORTEC inhibitor protection of carbon steel submerged in a corrosive medium. (A) Simulation of NACE standard and (B) Samotlorskoye oil field brine water medium.

Table 1 shows the results of the test for carbon steel submerged in a corrosive medium (NACE standard), according to test procedure 2 (steel preconditioned in inhibitor for 2 hours).

Inhibitor	Concentration, Inhibitor in Test solution mg/l	Rate of corrosion ρ g/m² Inhibition coefficient γ Protection action - Z%		
		ρ	γ	Z
No inhibitor		1.19		
VCI-629	50	0.033	36.1	97.2
	100	0.027	44.07	97.7
	200	0.039	30.5	96.5
VCI-368 solut. In heptane	50	0.63	1.88	47.1
	100	0.143	8.35	88.0
	200	0.019	62.6	98.4
Olazol	50	0.0265	44.9	97.7
	100	0.038	31.3	96.8
	200	0.0165	71.9	95.4
SNPH-6301	200	0.11	10.75	90.7

It can be concluded from table 1 that the two most effective inhibitors are VCI-629 and Olazol. It should also be mentioned that VCI-629 is more effective in lower concentrations. VCI-368 showed the best performance, out of all tested inhibitors, under concentration of 200 mg/1. Table 2 shows data of the reflected effectiveness of the inhibitor's protection when procedure 1 was used (steel without conditioning in the inhibitor solution, before immersion in NACE test medium). The concentration used for of all inhibitors was 200 mg/1 in solution.

Inhibitor	p	Y	Z
No Inhibitor	1.19		
VCI-629	0.09	13.2	92.4
VCI-368	0.234	5.08	80.33
Olazol	0.054	22.0	95.5
SNPH-6301	0.113	10.5	90.5

It can be concluded from results presented in table 2, that the effectiveness of protection without preconditioning in inhibitor solution is significantly lower. VCI-629 was again superior to other Cortec inhibitors' properties. The conclusion that VCI-629 has the best adsorption characteristics and therefore best protection properties can be drawn from tables 1 and 2. After conditioning steel in the concentrated solution of VCI-629, a dense protective film forms on the metal surface. This film of the inhibitor offers good protection during further operation of steel structures in corrosive environment. After corrosion tests, the steel surfaces treated with VCI-629 appeared to be uniform without pittings and local corrosion.

Table 3 shows the results of tests of inhibitors effectiveness in a corrosive medium, simulated a composition of Samotlorskoye brine water were given. Apparently, that corrosivity of NACE media and Samotlorskoye brine water is close to the same (rate of corrosion 1.19 g/m^2 hour and 1.09 g/m^2 hours respectively). However, the effectiveness of the inhibitors in Samotlorskoye brine water was significantly less than in NACE medium. It may be explained by the fact that presence of H_2S in NACE medium causes a synergistic effect of protection. Without preconditioning the steel, effectiveness of the inhibitor's action did not exceed 50%. However, if a film of protection already exists on the metal surface (after conditioning of steel in the inhibitor), the protection action is significantly increased. The best inhibitors in this case are VCI-368 (Z=93.5%) and VCI-629 (Z=81-85%).

Table 4 presents the results of tests in a corrosive medium simulating the presence of brine water and hydrocarbons in Samotlorskoye oil field. As it can be seen, it is the most aggressive medium out of all tested. The same tendency of an increase in protection with metal preconditioning in inhibitor can be seen. After formation of inhibitior film on the metal surface, the coefficient of protection for VCI-629 Z=96.8% and for VCI-368 Z=90-91%.

Table 3. Protection properties of the inhibitors in the brine water of Samotlorskoye oil field.
T=25 C, velocity of liquid flow 1m/s.

Inhibitors concentration 200 mg/l in solution. + with preconditioning; - without preconditioning

Inhibitor	Preconditioning with inhibitor	ρ	γ	Z
No Inhibitor		1.09		
VCI-629	+	0.165	6.6	84.9
	-	0.84	1.3	22.1
VCI-368 sol. In heptane	+	0.071	15.3	93.5
	-	0.955	1.13	11.7
Olazol	+	0.204	5.34	81.3
	-	0.615	1.76	43.1
SNPH-6301	+	0.424	2.57	61.1
	-	0.515	2.1	52.4

Table 4. Protection properties of the inhibitors in the corrosive medium (brine water + hydrocarbons) of the Samotlorskoye oil field.

Inhibitor	Preconditioning withinhibitor	ρ	γ	Z
No Inhibitor		1.40		
VCI-629	+	0.045	31.1	96.8
	-	0.99	1.41	29.1
VCI-368 sol. In heptane	+	0.14	10.0	90.0
	-	0.25	5.6	82.1
Olazol	+	0.128	10.93	90.9
	-	1.02	1.37	27.1

SNPH-6301	+	0.129	10.85	90.8
	-	0.403	3.47	71.2

It therefore, can be concluded, on the bases of performed corrosion tests, that Cortec inhibitors VCI-629 and VCI-368 provide effective protection with Z=85-97%. VCI-629 shows superior inhibition properties if compared to other tested Cortec products.

2.2 Effect of Cortec inhibitors on stress corrosion cracking, corrosion fatigue, and hydrogen embrittlment of carbon steel in a corrosive medium.

Table 5 presents the results of stress corrosion cracking test of carbon steel coupons applied with low rate of deformation stress in corrosive medium (NACE TM-O1-77). The carbon steel used in the test had the following characteristics of durability: σ_1 =440 Mpa, σ_2 =331 Mpa. Relative elongation - δ and relative contraction - Ψ were shown in table 5. The data presented in table 5 is calculated as the arithmetic mean of 3-5 measurements. As it can be seen from the data, carbon steel is very susceptible to HiS induced brittleness - coefficient of medium effect is 0.94; time to failure decreased by 3.7 times. The inhibitors significantly increased the durability of steel and its resistance to SCC. Presence of VCl-629 in solution boosted protection of steel against SCC by more than 30%. According to Russian standard 39.0147103.324-88 inhibitors that offer this degree of protection can be recommended for industrial experimental application. Inhibitor VCI-368 is less effective (coefficient of protection - 20%). The same tests were performed in the corrosive medium simulated Samotlorskoye oil field conditions. The results proved the effectiveness of VCI-629, which showed coefficient of protection of 32%.

Table 5. SCC of steel in NACE corrosive medium. Rate of deformation $2*10^{-6}$ s^{-1}
Inhibitor concentration 200 mg/1 in solution

Inhibitor/ medium	τ_F	Ψ%	δ%	K_p	β
Air	52	58.3	16.6		
NACE Medium	14	3.3	2.8		0.94
VCI-629	28	22.7	8.1	35.3	0.61
VCI-368 in Heptane	28	13.5	6.3	18.5	0.77
Olazol	30	21.8	7.J	33.6	0.62

Where,

- τ_F - time to specimen failure
- Ψ - relative contraction of the specimen
- δ - relative elongation of the specimen
- K_p - coefficient of protection
- β - coefficient of medium effect

Table 6 presents the results of tests of the inhibitors effect on SCC, under static loading of steel specimens. Under static loading, carbon steel in the corrosive medium (NACE standard) is also susceptible to SCC. Under the stress of (0.9-0.5) time to failure for the steel specimens was less than 720 hours. According to NACE TM-01-77 standard this steel can be characterized as very susceptible to SCC. Failure pattern for the steel is brittle cracking. In the presence of inhibitors the durability of steel significantly increases. Such inhibitors as VCI-629, VCI-368 and Olazol are effective in protection of steel against SCC. After 720 hours of testing under (0.9-0.5) σ_t applied stress, no signs of failure were observed on steel specimens. Comparative analysis of SCC data under static tension stress and under dynamic tension stress allow us to suggest VCI-629 and Olazol as the best products for application in the corrosive mediums containing H_2S.

Table 6. SCC under static stress.
Inhibitor concentration 200 mg/1 in solution

Inhibitor/ Medium	Stress, σ Mpa	Time to failure, τ_F h	Pattern of failure
NACE medium	298 (0.9)	85	Brittle
	231(0.7)	197	Brittle
	166 (0.5)	350	Brittle
VCI-629	298	>720	No failure
	231	>720	No failure
	166	>720	No failure
VCI-368 sol. In heptane	298	>720	No failure
	231	>720	No failure

Olazol	298	)720	No failure
	231	)720	No failure

Table 7 results represent the effect of inhibitors on low-cycle fatigue. Low-cycle fatigue tests on steel specimens in the air atmosphere did not show any signs of failure after 50,000 cycles, and sometimes after 10^5 cycles when under applied stress. However, the results also show that all inhibitors significantly improve performance of steel in corrosive medium by increasing the number of cycles before failure. The best of all tested inhibitors were VCI-629 and Olazol. These products increased time until failure by 2 times.

Table 7. Effect of inhibitors on low-cycle fatigue. Inhibitor concentration 200/1 in solution.

Loading frequency 0.17 Hz.

Inhibitor/ Medium		±σ , Mpa		N	
Air		198	(0.6)	>5* 10^4	Failure was not observed
		168	(0.5)	>5* 10^4	
		135	(0.4)	>5* 10^4	
NACE medium		198	9370		
		166	12750		
		135	26050		
VCI-629		198	22750		
		166	28300		
		135	36550		
VCI-368	819		18860		
		166	22340		
Olazol		198	23310		
		166	30050		

Figure 7 shows the evaluation of the diffusion rate of hydrogen through a steel membrane immersed in a corrosive solution. The solution was prepared according to NACE standard TM-01-77. It can be seen that after 35-40 minutes of immersion, intensive diffusion of hydrogen through the steel membrane was observed in an uninhibited solution. As a result potential of passivated side of membrane dropped significantly to less noble values. In the solutions with inhibitive additive, almost no hydrogen diffusion was observed after 12 hours of testing. VCI-629 showed superior qualities when compared to other inhibitors in this test. Therefore, on the basis of the tests performed to evaluate the ability of inhibitors effectiveness on suppression of SCC and corrosion fatigue of carbon steel, VCI-629 was chosen as most effective and promising product. Effectiveness of VCI-629 may be compared to effectiveness of Olazol - inhibitor which is currently used for protection in West Siberia oil fields. VCI-629 is recommended for experimental application in Niznevartovsk oil field region.

2.3 Electrochemistry of carbon steel in corrosive solutions inhibited with Cortec inhibitors.

In Figures 8 & 9, potentiodynamic polarization curves for carbon steel in corrosive medium (NACE TM-01-77 and Samotlorskoye oil field) were represented respectively. As it can be seen from these figures all tested inhibitors effectively suppressed both anodic and cathodic processes. However, the inhibitors: VCI-629, VCI-368, Olazol have tendency to change steel potential to more noble values, which means that they affect mostly anodic processes. In corrosive medium (NACE TM-01-77) two inhibitors: VCI-629 and VCI-368 were most effective. High effectiveness of these inhibitors may be connected to adsorption of their molecules and formation of protective layer on metal surface. From Fig. 9, it can be concluded that in Samotlorskoye corrosive medium all inhibitors are very effective and their effectiveness is even higher than in the NACE solution. The best results were obtained usingVCI-629. From Fig. 10 it may be concluded that increase in concentration of VCI-368 in solution, especially in the presence of a preabsorbed film, leads to a significant shift of standard electrode potential to more positive values. The same effect was observed for VCI-629 polarization resistivity (Rp), which is the major characteristic of chemisorbed film, and has the highest value. This respectively reflects higher protective properties of this chemisorbed layer. Thus, electrochemical investigation proved the effectiveness and high protective properties of VCI-629 inhibitor.

Table 9. Electrochemistry

Inhibitor	Concentr.	NACE E,mV	NACE Rp, KOm/cm^2	NACE Z	Samotlorskoye E	Samotlorskoye Rp	Samotlorskoye Z
No inhibitor		-428	0.25		-510	0.92	
VCI-629	50	-303	5.5	99	-190	13.0	99
	100	-364	3.4	99	-90	25.0	99
	200	-286	6.5	99	-58	70.0	99
VCI-368	50	-324	5.0	99			
	100	-336	5.0	99		3.0	99
	200	-345	5.8	99		3.5	99

where, E - standard electrode potential, mV
Rp - polarization resistivity, KOm/cm^2
Z - coefficient of protection, %

Fig. 8

Potentiostatic polarization curves. Carbon Steel.
NACE TM-01-77 corrosive medium. + 200 mg/1 inhibitor.
1 - NACE medium; 2 - VCI-629; 3 - Olazol; 4 - VCI-368; 5 - SNPH-6301

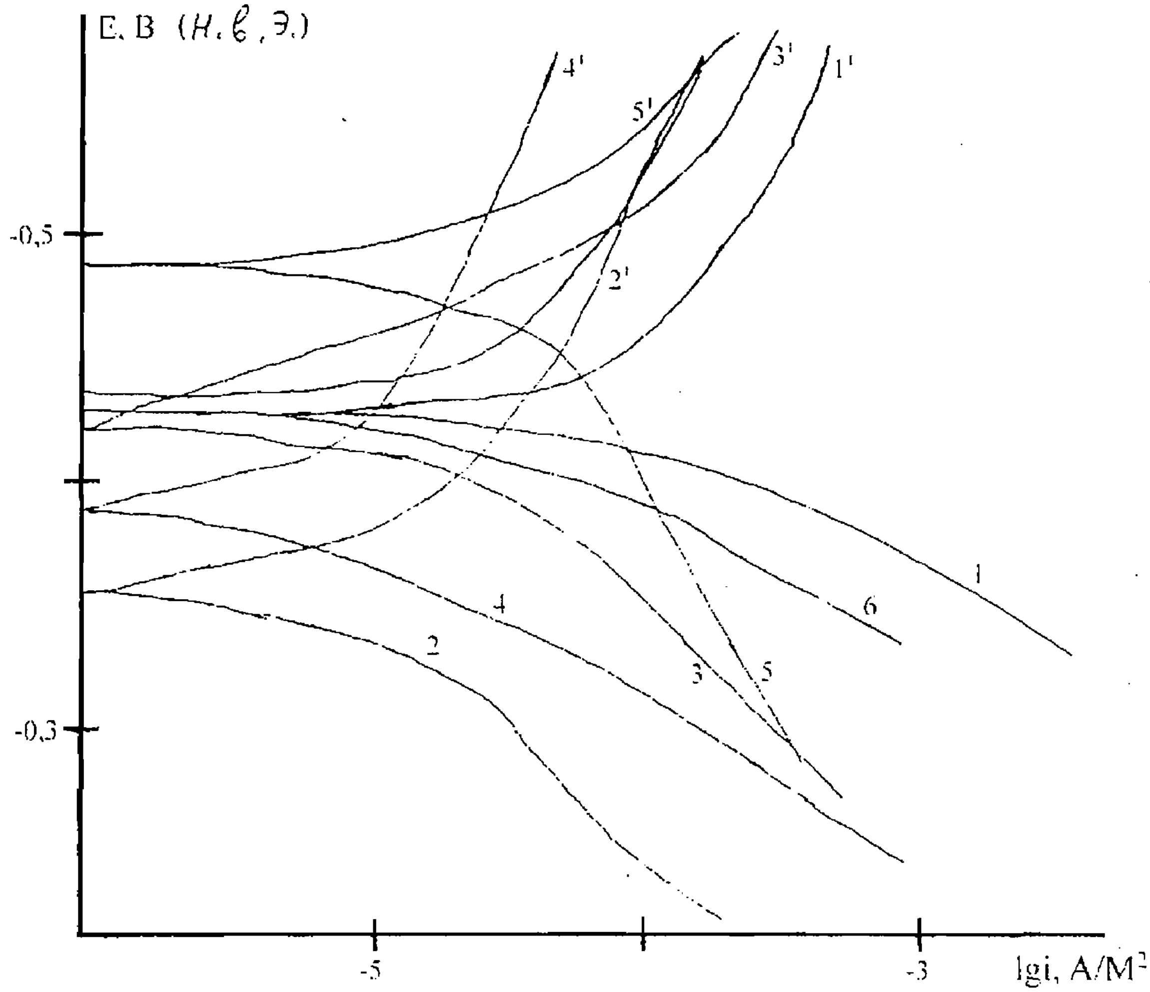


Fig. 9
Potentiodinamic polarization curves. Carbon Steel.
Samotlorskoye corrosive medium + 200 mg/l inhibitor.
1 - no inhibitor; 2 - VCI-629; 3 - VCI-368; 4 - Olazol; 6 SNPH-6301

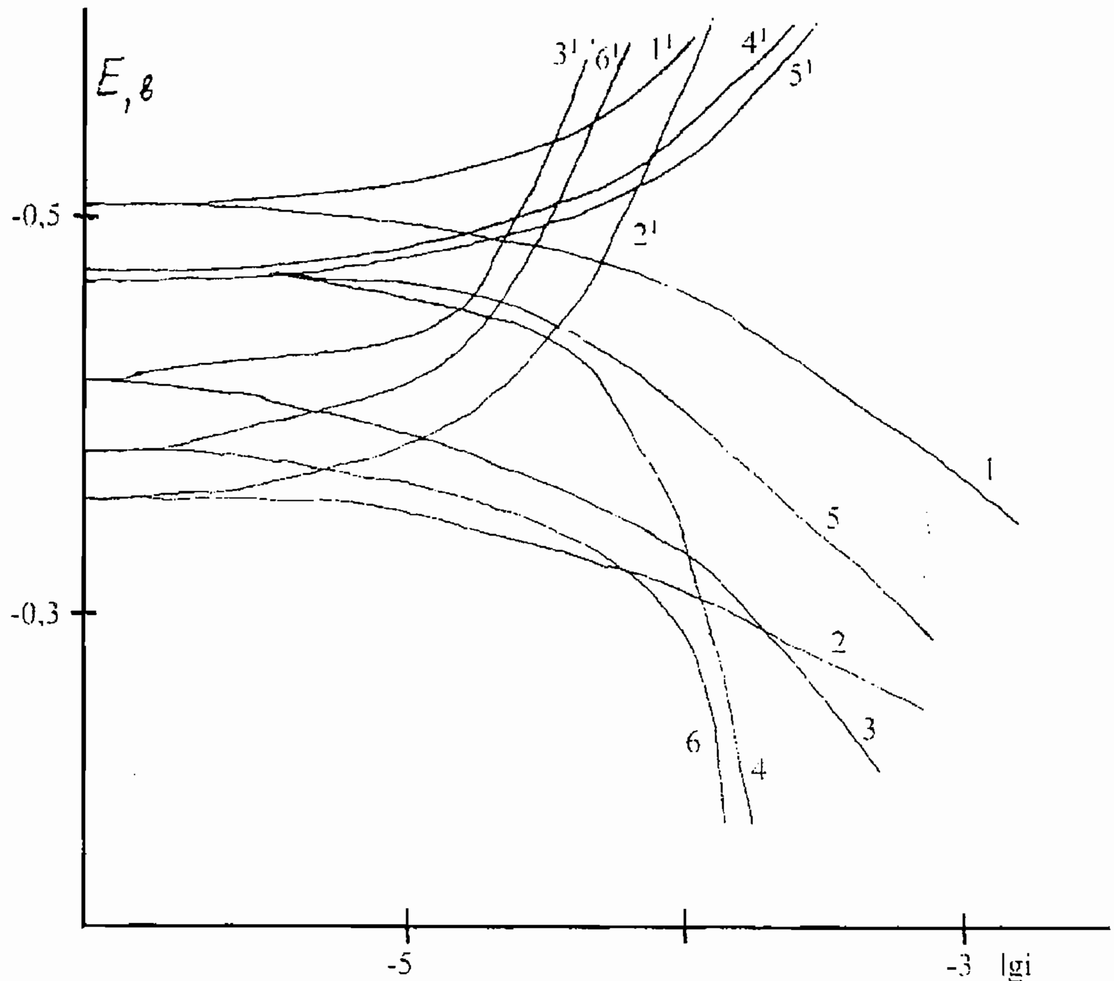


Fig. 10.
Potentiodynamic polarization curves.
Samotlorskoye corrosive medium. Carbon Steel.
Concentration of VCI-368 in solution: 1- 0; 2 - 50mg/l;
3- 100 mg/l; 4, 5 - 200 mg/l. 2, 3 - preconditioned specimens;
5 - specimen without conditioning.

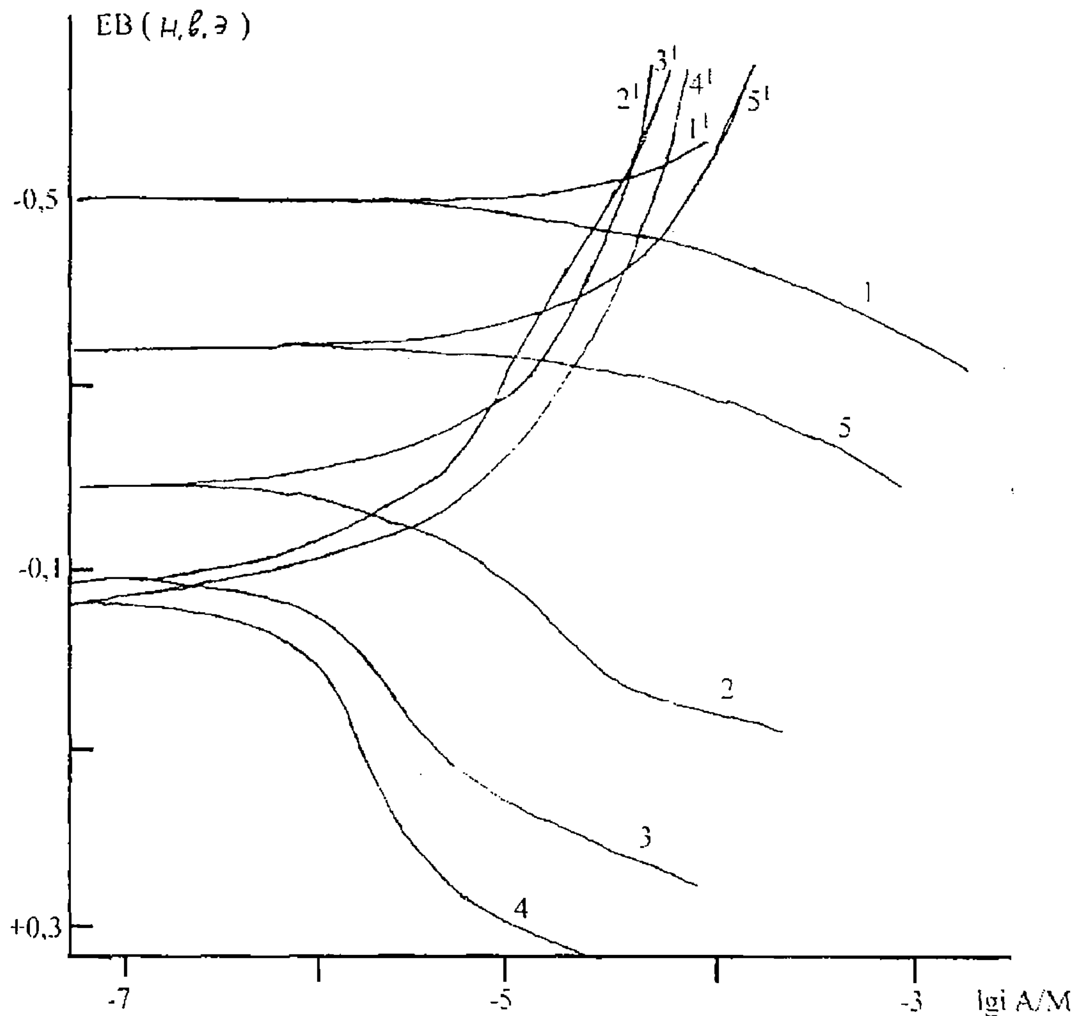


Fig. 11.
Potentiodynamic polarization curves. Carbon Steel.
NACE corrosive medium. Concentration of VCI-629 in solution:
1 - 0; 2- 50 mg/1; 3 - 100 mg/1; 4, 5 - 200 mg/1.
2,3,4 - preconditioned specimen. 5 - specimen without conditioning.