SYNTHESIS AND INVESTIGATION OF PROTECTIVE PROPERTIES OF
CERTAIN OXYETHYLATED NITROGEN COMPOUNDS

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Oxyethylated products are recommended for use as corrosion inhibitors for equipment used in the production, processing, and transportation of petroleum crudes and products, and also in the protection of steam condensate systems. These products manifest protective effects in solutions of salts, alkalis, and acids. Also reported is the use of oxyethylated derivatives as atmospheric corrosion inhibitors [1, 2].

These products vary considerably with respect to dispersibility in water, crude oil, and other media, but in any case their inhibiting effect is based on shielding of the protected metal surface as a result of adsorption inhibitor molecules.

The compounds used as corrosion inhibitors may be products from the condensation of olefin oxides with various compounds such as amines, amides, alcohols, or phenols.

In the work reported here, we investigated oxyethylated derivatives of caprolactam and benzotriazole. The ethylene oxide was condensed with the nitrogen compound at 40-70°C in the presence of sodium hydroxide as a catalyst in water in the case of the caprolactam, or or water—alcohol in the case of the benzotriazole at atmospheric pressure; the ethylene oxide was fed into the solution at approximately 12 liters/h.

We synthesized derivatives of caprolactam with an ethylene oxide:caprolactam ratio from 1:1 to 12.5:1, and derivatives of benzotriazole with a ratio from 1:1 to 28.5:1. The molecular weight of the caprolactam derivatives varied from 145 to 682, the benzotriazole derivatives from 161 to 1385. The respective refractive indexes n_D^{20} were 1.4960-1.4712 and 1.5450-1.4600. The oxyethylated derivatives of caprolactam had higher surface activities in comparison with the derivatives of benzotriazole. For 0.1% aqueous solutions of the caprolactam derivatives, the surface tension was in the range $(70.8-16.5) \cdot 10^{-3}$ N/m. All of the oxyethylated derivatives of caprolactam and benzotriazole were insoluble in water, whereas the benzotriazole derivatives has a very limited solubility.

We investigated the inhibiting properties of the oxyethylated products in aqueous salt solutions. In these tests we determined the degree of protection of U10 steel (KhGT17) [similar to W1 tool steel], M3, copper and S1 lead. Metal specimens were held in the corrosive medium in the presence of 0.01 M of the inhibitor for a period of 10 days at 18°C. The corrosion test results are presented in Tables 1 and 2.

These data indicate that the caprolactam itself does not prevent the corrosion of steel or lead and gives only slight protection of copper. The benzotriazole protects copper, although a darkening of the copper surface is observed as a result of formation of a complex; the benzotriazole does not protect steel but does not aggravate the corrosion, and it does not prevent lead corrosion. The introduction of oxyethylene groups into the caprolactam and benzotriazole imports protective properties for steel, but there is no clear relationship between the degree of oxyethylation and the degree of steel protection. For copper, the oxyethylated derivatives of benzotriazole are somewhat poorer in protective properties than the original product. It should be noted, however, that the introduction of the oxyethylene group at the pyrrole nitrogen, even though it does lower the level of copper protection, at the same time prevents complexation with the copper and darkening of the copper surface. The caprolactam derivatives are considerably less effective on copper than are the benzotriazole derivatives. The introduction of oxyethylene groups into the benzotriazole molecule up to a 15:1 ratio improves the protective properties of the products for to lead; with higher contents of the oxyethylene groups, the protection decreases. This sort of phenomenon is also chatacteristic for the caprolactam derivatives (in this case, the maximum protection is obtained

TABLE 1

Ethylene oxide: caprolactam ratio	Protection, %		
	U10 in 6 N Na$_2$SO$_4$	M3 in 6 N NaCl	S1 in 0.1 N Na$_2$SO$_4$
Caprolactam	Corrosion	32	Corrosion
1:1	29	26	44
2:1	31	39	54
5:1	39	39	54
6:1	40	39	80
8:1	44	41	93
10:1	19	24	72
12:1	12	14	49

TABLE 2

Ethylene oxide: benzotriazole ra	Protection, %		
	U10 in 0.5 N NaCl	M3 in 6 N NaCl	S1 in 0.1 N Na2 SO4
Benzotriazole	0	100*	Corrosion
1:1	10	97	25
2:1	20	—	29
4:1	25	93	49
6:1	37	96	59
8:1	—	98	79
13:1	40	100	95
15:1	42	98	77
20:1	60	93	59
28,5:1	75	90	49

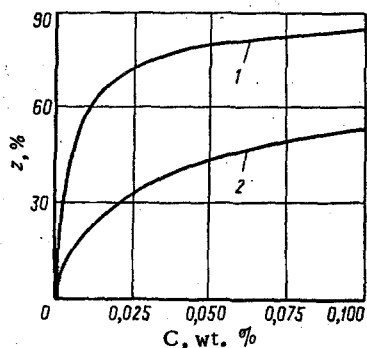*Darkening of copper surface was observed

Fig. 1. Degree of protection Z of U10 steel by benzotriazole derivative with 28.5 degree of oxyethylation, as a function of its concentration C under conditions of hydrogen sulfide corrosion: 1) in 3% aqueous NaCl solution; 2) in same medium, saturated with H$_2$S.

at an 8:1 ratio). The evident explanation for this behavior is that an increase in the content of oxyethylene groups above the level of 9 or 10 leads to "twisting" of the molecule into a helix, resulting in a decrease in capability of the molecule for being sorbed on the metal surface and a corresponding decrease in the degree of shielding of the metal surface by the inhibitor. Also, the concentration of 0.01 M for compounds with such a degree of oxyethylation is apparently above the critical micelle concentration; and it is known that the

formation of micelles also leads to a decrease in the capability of molecules for being sorbed on metal surfaces.

We also investigated the protective properties of the benzotriazole derivatives with a 28.5 degree of oxyethylation in aqueous 3% NaCl solutions saturated with hydrogen sulfide, with U10 steel specimens. An analysis of the data presented in Fig. 1 provides grounds for stating that in the medium saturated with hydrogen sulfide, a synergistic effect is observed (a reinforcement of the protective properties of the inhibitor) as the result of the action of the H_2S. This explains the noncoincidence of curves 1 and 2.

Thus, the oxyethylated derivatives of caprolactam and benzotriazole manifest a rather high level of anticorrosion efficiency, and they can be recommended for the corrosion protection of metals in aqueous media.

LITERATURE CITED

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KINETICS OF CO OXIDATION ON SOLID PROMOTER IN
REGENERATION OF CRACKING CATALYST

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In the modern stage of development of the catalytic cracking process, the most widely used technology of catalyst regeneration includes controlled oxidation of CO in a fluidized bed in the presence of a soild promotor. A solid promoter of CO oxidation, designated KO-9, has been developed at VNII NP [1]. Tests in semicommercial [2] and commercial units have demonstrated the high efficiency of this promoter in catalytic cracking systems.

We have investigated the kinetics of CO oxidation on the solid promoter in a micropilot unit, which includes a gradientless quartz reactor in the form of a sphere ($22 \cdot 10^{-6}$ m^3) with a vibrofluidized catalyst bed [3]. The studies were performed under steady-state conditions (the composition of the gas phase in the reaction zone was time-invariant), by passing a model mixture of gases $CO + O_2 + N_2$ through a vibrofluidized bed of regenerated KMTs-R catalyst mixed with the solid promoter KO-9. The characteristics of the support used in preparing the promoter were reported in [1].

The influence of the partial pressures of oxygen (P_{O_2}) and carbon monoxide (p_{CO}) on the CO oxidation rate was investigated at 600°C with an absolute pressure of 0.10-0.15 MPa in the system. The reactor was charged with cracking catalyst (2 g) mixed with the promoter (0.2 mg). This particular weight of catalyst was selected so as to ensure vigorous mixing of the gas and uniform distribution of the promoter through the volume of the reaction zone; another factor in the selection was the need to eliminate, so far as possible, the "background" due to oxidation of CO on the surface of the cracking catalyst.

Model mixtures of the gas were fed to the reactor at a rate of $(2.1-2.3) \cdot 10^{-6}$ m^3/sec (residence time 8.7-9.5 sec). The composition of the original gas mixtures was varied in such a manner that the partial pressure of one of the components in the reaction zone remained constant, while the partial pressure of the second component varied over the range of values realized in commercial practice. In the course of these studies, we performed six series of experiments, in three of which p_{O_2} was held constant (0.0042, 0.0085, or 0.018 MPa), and in the other three p_{CO} was held constant (0.002, 0.0052, or 0.012 MPa).

The experimenatlly determined rates of CO oxidation on the solid promoter as a function of p_{O_2} (with p_{CO} = const) or as a function of p_{CO} with p_{O_2} = const) is illustrated by the curves in Figs. 1 and 2. The CO oxidation rate R_p (kmoles/kg·sec) in the gradientless