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**CORROSIVE NATURE OF CERTAIN MEDIA IN THE
PRODUCTION OF PETROLEUM ADDITIVES**

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

11 September 1972

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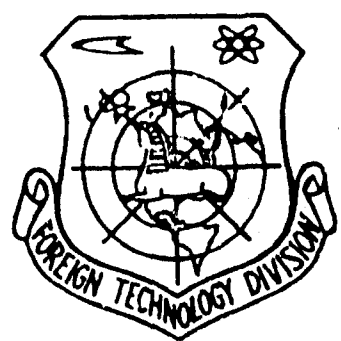
FOREIGN TECHNOLOGY DIVISION



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by

G. A. Allakhverdiyev, A. M. Kyazimov, et al.



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13. ABSTRACT

A 37% aq. HCHO soln. was the most corrosive medium for an oil additive (INKhP-21) prepd. by condensing an alkylphenol with HCHO and NH₃ at 96 to 98°. The corrosiveness was increased by the presence of HCO₂H (ph 2.7). Carbon and stainless steel were corroded at 3 mm/year and 0.01 g/m², resp. in 1% HCO₂H soln. NH₄OH inhibited corrosion during additive production. Carbon steels were corroded at 0.1 and 0.4 to 0.5 g/m² in the liq. and vapor phase, resp., of the condensation products during drying, due to the presence of water, HCO₂H, and other evapn. products at 120°. [AP1138120]

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В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й я	<i>Й я</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

CORROSIVE NATURE OF CERTAIN MEDIA
IN THE PRODUCTION OF PETROLEUM
ADDITIVES

G. A. Allakhverdiyev, A. M. Kyazimov,
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The production of petroleum additives is of great importance to the improvement of the working properties of lubricating oils.

However, the use and separation, during the individual stages of synthesis, of a number of substances which display a highly corrosive nature, causes the destruction of the equipment and distribution lines of commercial facilities.

Corrosion in the production of an additive which possibly is not so great as to cause destruction of the equipment can, however, facilitate the contamination of the synthesized additive with the corrosion products which, considering modern-day demands for high-quality additives and lubricating oils, is intolerable.

Corrosion in additive production processes has not been studied thoroughly nor has it been sufficiently discussed in the literature. Investigations have been conducted only into the behavior of certain steels during the production of alkylphenol [1], and also the corrosive condition of equipment and distribution lines of commercial facilities in certain Soviet petroleum additive plants.

Acquainting ourselves with the corrosive condition of the equipment in both experimental and industrial facilities has once again affirmed the necessity of studying corrosion in the production of additives for the purpose of devising effective anti-corrosion measures and electing the most stable and economically feasible materials for equipment and pipeline construction.

→ The This paper presents the results of experiments on the anti-corrosion resistance of certain structural materials during condensation of alkylphenol with formalin and ammonia with the subsequent settling and drying of the condensation product, which are technological processes for INKhP-21 additive; the synthesis method and production techniques for this additive are given in [2, 3].

Condensation takes place at 96-98°C at atmospheric pressure and mixing for two hours. Then, the condensation product settles out of the aqueous layer in the same reaction vessel and is fed to the drying tower ($p = 60 \text{ mm Hg}$, cm , $t = 120^\circ C$).

The condensation process occurs in a rather complex medium: owing to the chemical condensation reaction taking place, the content in the system of certain of the components decreases and the concentration of the others increases to a certain degree which naturally complicates the possibility of correctly estimating the corrosive nature of individual components during the process. Therefore, for the purpose of establishing the causes which have an effect on corrosion, it is advisable also to study the effect of the individual components and sample mixtures of these components on the durability of steels.

Corrosion experiments were conducted using laboratory apparatus (Fig. 1) modeled after that used in industry.

Steel samples, prior to testing, were subject to grinding, having been carefully degreased with ethyl alcohol, then held in

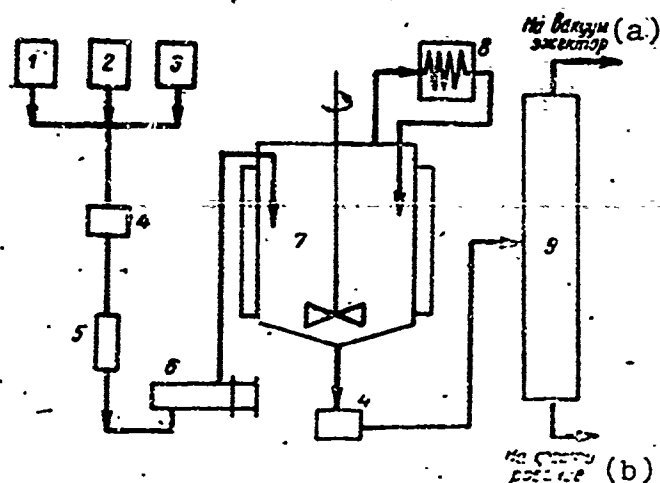


Fig. 1. 1, 2, 3 - alkylphenol, formalin, aqueous ammonia vessels; 4 - pumps; 5 - mixer; 6 - heat exchanger; 7 - condensation reactor; 8 - reflux condenser; 9 - drying column.
KEY: (a) To vacuum ejection; (b) To flotation.

a desiccator for 24 h over freshly-roasted calcium chloride, and weighed on special scales during the vapor-gas and liquid phases of condensation.

A comparison of the results (Tables 1, 2) showed that of all components of the condensation process the most aggressive was technical formaline (37% aqueous formaldehyde solution).

Table 1.

Steel brand	Rate of corrosion in various media $\text{g/m}^2 \cdot \text{h}$					
	Formalin		Aqueous ammonia		Alkylphenol	
	¹ p	² zh	p	zh	p	zh
St. 3	1.820	1.910	0.081	0.065	0.102	0.150
K20	1.310	1.803	0.051	0.040	0.110	0.123
St. 20	2.162	2.214	0.102	0.100	0.130	0.160
16GS	1.623	1.720	0.030	0.035	0.085	0.900
1Kh13	0.241	0.271	0.000	0.000	0.018	0.005
0Kh13	0.213	0.171	0.000	0.000	0.020	0.006
2Kh13	0.271	0.252	0.000	0.000	0.021	0.008
Kh17	0.152	0.103	0.000	0.000	0.015	0.002

¹p - vapor gas phase; ²zh - liquid phase

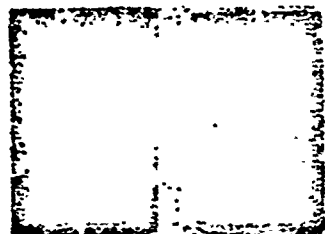
Table 2.

Steel brand	Rate of corrosion in various media, g/m ² ·h									
	Formalin + Aqueous Ammonia		Alkylphenol + Aqueous Ammonia		Alkylphenol + Formalin		Condensation		Drying	
	P	zh	P	zh	P	zh	P	zh	P	zh
St. 3	0.011	0.011	0.001	0.0015	2.100	1.213	0.500	0.525	0.450	0.190
K20	0.012	0.011	0.002	0.001	1.615	1.050	0.480	0.540	0.415	0.106
St. 20	0.012	0.013	0.002	0.003	2.200	1.340	0.495	0.56	0.480	0.205
16GS	0.011	0.000	0.001	0.001	1.542	1.180	0.370	0.420	0.32	0.096
1Kh13	0.000	0.000	0.000	0.000	0.180	0.210	0.090	0.150	0.025	0.007
OKh13	0.000	0.000	0.000	0.000	0.165	0.140	0.100	0.170	0.016	0.005
2Kh13	0.000	0.000	0.000	0.000	0.210	0.152	0.12	0.130	0.024	0.008
Kh17	0.000	0.000	0.000	0.000	0.136	0.129	0.07	0.09	0.009	0.002

The rate of corrosion for various brands of carbon steels in formalin (as well as in the liquid and vapor-gas phases) was 1.6-1.8 g/m²·h.

In this medium brand OKh13, 1Kh13, 2Kh13, and Kh17 stainless steels were the most durable.

Kh18N10T, OKh22N5T, Kh17N13M2T steels in formalin (and also in other media) did not lose even so much as their metallic luster, while OKh13, 1Kh13, 2Kh13, and Kh17 steels tarnished and were coated with noticeable corrosion spots mainly on the sample faces. Carbon steel samples were coated with a loose and easily removed layer of dark-grey condensation products in the liquid phase (b) and brown rust spots in the vapor-gas phase (a) (Fig. 2).



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Following removal of the corrosion product, corrosive damage of a uniform nature was detected on the surface of carbon steel samples.

In alkylphenol, all stainless steels had excellent durability. The rate of corrosion for carbon steels in alkylphenol relative to their corrosion in formalin was insignificant - 0.15 g/m^2 .

Steels tested in a 25% aqueous ammonia solution did not sustain any corrosive damage.

The low level of durability for carbon steels in formalin, apparently, is explained by the presence of acids (HCOOH) [4] in the formalin which in turn can be explained by the rather low pH of the solution ($\text{pH} = 2.7$).

The presence of formic acid in the solution gives the latter a rather noticeable aggressive nature in relationship to certain structural steels [5]. Thus, for example, it has been shown that in a 1% solution of formic acid, carbon steels are subjected to corrosion at a rate of 3 mm/year. For OKh17T, OKh22N5T, and Kh18N10T steels this indicator of corrosion is on the order of 0.01 g/m^2 .

It was discovered that the medium of the condensation process itself becomes less aggressive than the formalin solution.

In order to explain the reasons for the slow down in corrosion under these conditions, we conducted tests in sample mixtures by pairing the individual condensation reagents.

As a result, we established that the basic factor causing the slow down of the corrosion process is the aqueous solution of ammonia since the mixture of alkylphenol and formalin with aqueous ammonia solutions do not exhibit aggressive properties in relationship to either stainless or carbon steels.

Carbon steels in an alkylphenol formalin mixture are subject to corrosion at almost the same rate as when in formalin alone.

Stainless steels Kh17, 0Kh13, 1Kh13, and 2Kh13 both in formalin and during the condensation process undergo corrosion at a noticeably slower rate.

The rate of corrosion for carbon steels in the liquid phase of condensation products during drying did not exceed 0.1 g/m^2 although in the vapor-gas phase these steels corroded at a rate of $0.4\text{--}0.5 \text{ g/m}^2$ which, it is clear, is explained by the presence of water vapor, HCOOH , and other products which evaporized during drying, and also by the relatively high temperature (120°C).

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