FOREIGN TECHNOLOGY DIVISION

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IN THE ROLE OF ACID CORROSION DECELERATORS

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UTILIZING WASTES OF THE SYNTHETIC RUBBER INDUSTRY IN THE ROLE OF ACID CORROSION DECELERATORS

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When manufacturing divinyl by catalytic decomposition of ethyl alcohol, synthetic rubber plants are using various wastes of complex composition, which can serve as decelerators of acid corrosion of certain metals. To these wastes belong so called 'foamy reagent (PR,) vat remains (KO,) and motor fuel (MT.) Below are given certain data about the composition of these wastes[1].

The foamy reagent (PR) is called a vat product, consisting after distillation of technical butyl alcohol from higher alcohols and hydrocarbons. In its composition are included 25 - 35% of higher

alcohols, 3 - 5% butyl alcohol, 25 - 30% hydrocarbons, and 30 - 35% heavy residue. From the higher alcohols in PR are contained mainly **hexyl** and in smaller amounts octyl alcohol and also unsaturated alcohols C_6 and C_8. In slight amounts are detected phenols (cresol and ethyl phenol,) as well as higher aldehydes (capronic and caprylic.)

In the synthetic rubber manufacturing process are also formed saturated and unsaturated hydrocarbons. Hydrocarbons with lower boiling points are not condensed, and are separated from divinyl during rectification in form of vat residues (KO.) Their basic fraction (35 - 45°C) **contains up to 40% of amylene** and the same amount of piperylene. In a higher boiling fraction (65 - 80°C) is contained hexylene and hexadiene (up to 70%) and **small** amounts of benzene, toluene and hexene. In composition of high boiling fractions are included diolefines.

Motor fuel (MT) represents a mixture of nonpolymerized hydrocarbons from the washed off vat residues.

In the work described below, carried out by the weight method at temperatures of from 0 to 80°C, within each 20°C, we investigated the retarding action of the following synthetic rubber industry wastes:

PR-on corrosive destruction of low carbon steel 08 in 1 and 7 percent solutions of sulfuric and hydrochloric acid solutions;

PR and KO-on corrosion of stainless steel 1KH18N9T in 1 and 7 percent of hydrochloric acid;

PR, KO and MT-on corrosion of copper in 3 percent nitric acid.

The vessels with acid solutions **were thermostated and provided**

with polished ball coolers. Steel and nickel samples for the experiment were cleaned with emery paper of various numbers, they were defated with alcohol and suspended, and copper samples were subjected to electropolishing.

The results of the experiment are given in table 1, an examination of which shows, that the investigated wastes appear to be sufficiently effective steel corrosion decelerators in solutions of sulfuric and hydrochloric acids, and also of copper in a nitric acid solution. In case of low carbon steel the effectiveness of PR rises with the increase in acid concentration, as well as with the rise in temperature. Especially effective is PR for a 7% solution of hydrochloric acid at 80°C, where the rate of corrosion of low carbon steel drops by more than 260 times (table 2.)

A considerably smaller effectiveness of PR in sulfuric acid in comparison with hydrochloric can be explained by the fact, that in H_2SO_4 solutions the surface of the metal is positively charged, and this weakens the inhibiting effect of organic cations[2].

On the basis of Kolotyrkin and Iofee[2-6] works, we assume, that the introduction into sulfuric acid solutions of halide ions leads to chemosorption of the later by surface iron atoms and to displacement of zero charge potential in direction of more positive values, as a result of which the surface of the iron acquires a negative charge. Since PR contains protophylic substances (alcohols, aldehydes,) given orgainic cations in solutions of acids, it is possible to consider the amplification of PR effectiveness when small amounts of potassium iodide

are added.

Table 1.
Corrosion losses of certain metals in acid media contained in the role
of inhibitors synthetic rubber industrial wastes

1 Кислота	2 Ингибитор и его концентрация вес. %	3 Скорость коррозии, г/м²·ч, при				
		0°	20°	40°	60°	80°
Сталь 0,8 STEEL 0,8						
H₂SO₄	5% ПР PR	0,36	1,27	4,41	7,41	9,09
»	То же ditto	0,50	1,78	6,55	14,05	19,65
»	5% ПР+0,1% KJ	0,18	0,27	0,64	1,82	4,73
»	То же ditto	0,14	0,18	0,27	0,46	0,73
HCl	5% ПР PR	0,18	0,45	1,18	2,45	4,91
»	То же ditto	0,27	0,73	1,82	4,09	9,55
»	2,5% ПР+0,5% арсенита натрия sodium arsenite	—	0,10	0,25	0,16	0,09
»	То же ditto	—	0,11	0,22	1,25	6,70
»	5% ПР+1,0% арсенита натрия sod. arsenite	—	—	—	0,09	—
»	То же ditto	—	—	—	0,27	—
Сталь 1Х18Н9Т Steel 1 Kh 18N9T						
HCl	5% ПР PR	—	0,035	0,068	0,14	0,41
»	То же DITTO	—	0,000	0,025	0,065	0,29
»	0,5% КО	—	0,113	—	—	6,159
»	То же DITTO	—	—	—	—	0,73
Никель Nickel						
HCl	2% ПР PR	—	—	—	0,40	—
Медь Copper						
HNO₃	5% ПР PR	0,00	0,18	748	982	3572
»	1% КО	0,30	0,27	256,0	1914,0	5922,0
»	5% МТ	0,40	1,60	10,61	1800,0	5380,0

KEY: 1) acid; 2) inhibitor and its concentrated weight. %; 3) rate of
corrosion, g/m²·hr at.

These assumptions were fully justified: additions of small amounts
of potassium iodide (0.1 weight percentage) has by many times increased
the effectiveness of PR (see table 1 and 2); at 80°C the inhibiting
effect of this composition was found to be in 7% of sulfuric acid
solution exactly 2200.

The effectiveness of foamy reagent in hydrochloric acid is
considerably increased by sodium arsenite additions in amounts of

0.5 to 1 weight percentage (see table 1 and 2.) It is interesting to mention, that during the introduction in 1% hydrochloric acid an admixture of 2.5% PR + 0.5% sodium arsenite the rate of steel 0.8 beginning with 40°C drops not only relatively, but also absolutely and at 80°C steel 08 in 1% HC1 becomes stable. As to 7% HC1, the effectiveness of the admixture here, beginning with a temperature of 40°C, decreases (fig. 1.)

Table 2.
Inhibitor effects of certain synthetic rubber industrial wastes for steel, nickel and copper in acid media

1 Кислота	2 Ингибитор и его концентрация вес. %	3 Ингибиторные эффекты при				
		0°	20°	40°	60°	80°
Сталь 08 *STEEL 08*						
1% H₂SO₄	5% ПР *PR*	3,92	5,83	6,46	13,36	38,61
7% »	То же *ditt.*	7,96	13,88	21,68	29,67	81,49
1% »	5% ПР+0,1% *PR* KJ	7,75	27,14	44,81	54,46	74,21
7% »	То же *ditt.*	29,26	135,71	520,15	915,04	2207,15
1% HCl	5% ПР *PR*	3,06	6,47	9,40	18,22	37,11
7% »	То же *ditto*	44,78	60,64	99,05	170,19	263,0
1% »	2,5% ПР+0,5% *PR* арсенита натрия *and alosnte*	—	17,30	42,56	302,25	2207,8
7% »	То же *ditto*		294,18	771,5	558,25	390,7
1% »	5% ПР+1% ар- *PR* сенита натрия *sod arp.*	—	—	537,3	—
7% »	То же *ditt*		—	2584,5	—
Сталь 1Х18Н9Т *Steel 1KЦ19Ц 9Т*						
3% HCl	5% ПР *PR*	—	5,8	10,0	14,5	18,0
7% »	То же *ditt*	—	—	28,8	32,7	35,6
1% »	0,5% КО	—	—	—	—	1,18
7% »	То же *ditt*	—	—	—	—	14,0
Никель *nickel*						
3% HCl	5% ПР *PR*	—	—	—	18,05	—
Медь *copper*						
3% HNO₃	5% ПР *PR*	—	177,0	2,0	3,8	2,1
3% »	1% КО	—	177,0	1,9	1,9	1,3
3% »	5% МТ	—	40,0	46,0	2,1	1,4

KEY: 1) acid; 2) inhibitor and its concentrated weight. %; 3) inhibitor effects at.

The low values of temperature corrosion coefficients ($\%/°C$) which are not conducted here because of lack of space, confirm the greater role of the diffusion factor in the steel corrosion process in solution of sulfuric and hydrochloric acids, inhibited by a PR addition, and about the high quality of the forming protective layer.
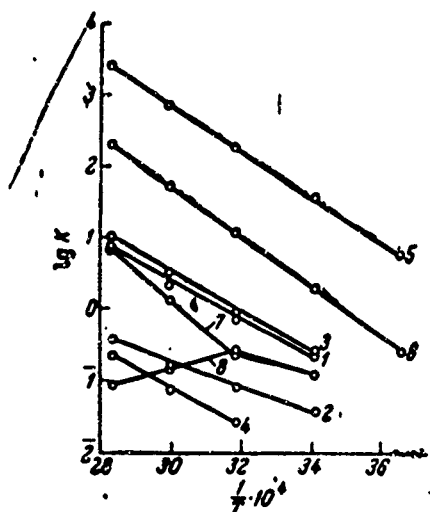

Fig. 1. Dependence of steel corrosion rate logarithm 1KH18N9T in hydrochloric acid solutions upon reverse absolute temperature $1/T\ 10^4$ (Curves 1-4 for steel 1KH18N9T; curves 5-8 for steel 08):

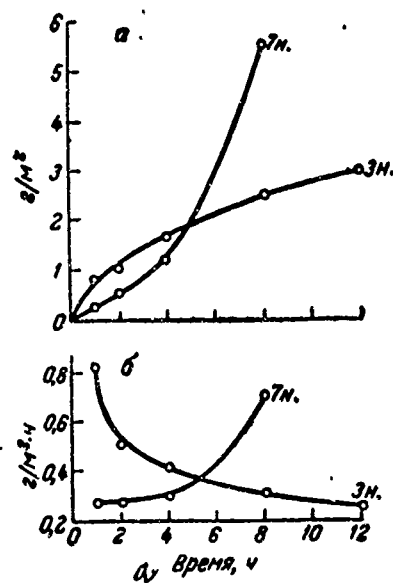| Curve	HCl	Decelerator
1	3%	—
2	3%	5 weight % PR
3	7%	—
4	7%	5 weight percentage PR
5	7%	—
6	1%	—
7	7%	2.5 weight % PR plus 0.5 weight % sodium arsenite
8	1%	ditto

Fig. 2. Corrosion dependence of steel 1KH18N9T upon time (a) and its speeds upon time (b) in 3% and in 7% hydrochloric acid solutions containing PR at 80°C. a-time hrs.

In this way PR and other compositions on its basis can be recommended in the role of cheap and effective decelerators at acid pickling of low carbon steel[7].

We also investigated the decelerating action of PR on corrosion

of stainless chrome nickel steel 1KH18N9T in hydrochloric acid solutions. It is known, that this type of steel appears to be a known structural material in chemical industry. But the area of its application is limited by the insufficient stability in solutions, containing chlor-ions. In essence, at present time there is generally no steel, sufficiently stable in hydrochloric acid solutions. Consequently the raise in stability of steel type 1KH18N9T is represented in an actual problem. As is evident from data in table 1 and 2, introduction of PR in a quite considerable measure increases corrosion stability of steel 1KH18N9T.

Data in fig. 1 show, that in 1% HC1, containing PR, steel 1KH18N9T is practically undisturbed, and in a 3% solution it is subjected to a certain smaller disturbance, but exceeding the rate of corrosion in a 7% solution. But this appears to be valid only for relatively short sections of time (up to 6 hrs,) and then the picture changes sharply. It is evident from fig. 1 that if in 3% HC1 the corrosion process of steel 1KH18N9T goes with damping in time, then in a 7% solution within 6-7 hours after beginning of corrosion the process obtains a violent development.

Less effectively protecting stainless steel from hydrochloric acids are vat residues (see tables 1 and 2.)

Wastes of synthetic rubber plants, in particular PR and KO, slow also down copper corrosion in nitric acid solutions, but these admix-tures appear to be effective only at low temperatures and low con-centrations of electrolyte-aggressor (see table 1 and 2.) And so, in

a 7% HNO$_3$ PR and KO reduce their effectiveness practically to zero (fig. 3.) The inhibiting effects of these admixtures are sharply reduced at electrolyte temperatures, exceeding 20°C. The foamy reagent slows down also the rate of nickel corrosion in hydrochloric acid solutions.

With respect to the mechanism of protective action of the invest-igated admixtures on the corrosion of steel it is possible on the basic of dependence $\lg K = f(1/T)$ and the facts of increasing the inhibiting effect with temperature to come to a conclusion, that the admixture components are chemoabsorbed by the surface of the metal. This process in a sulfuric acid solution is facilitated by introduction of iodine ions, capable of recharging the surface of steel. The retarding effect of PR and KO on the rate of copper corrosion in nitric acid can be explained by the disruptive effect of components of these admixtures on nitric acid, since the latter autocatalytically accelerates the corrosion process[8].
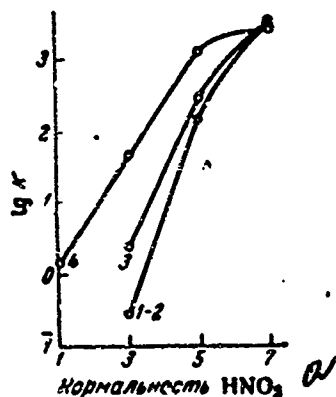

Fig. 3. Dependence of copper corro-sion rate logarithm in nitric acid solutions upon its normalcy at 20°: 1-HNO + 5 weight % PR; 2-ditto + 1 weight % KO; 3-ditto + 5 weight % MT; 4-without decelerator. a-normalcy of HNO$_3$

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