SCIENTIFIC AND PRACTICAL PROGRESS IN THE DEVELOPMENT AND APPLICATIONS OF CORROSION INHIBITORS IN THE COMECON COUNTRIES*

I. L. Rozenfel'd

UDC 620.193.01

Corrosion inhibitors are one of the most effective and economic means of protecting metals, machine parts, and equipment of the petroleum, gas, petrochemical, and chemical industries from corrosion. They can give a tenfold increase in the service life of equipment, prevent accidents, and in some cases permit equipment to be made of ordinary steels and alloys instead of stainless steels.

In the countries of the Council of Mutual Economic Aid (COMECON) much success has been achieved in developing a theory of protection of metals from corrosion by means of inhibitors, and in goal-directed synthesis of efficient inhibitors and their practical applications.

Scientific Progress

In addition to the classical mechanism of action of inhibitors, consisting in retardation of the kinetics of electrochemical reactions, in recent years it has been shown that metals can also be passivated by means of specific chemical compounds which accelerate the kinetics of the cathodic reaction. Being rapidly reduced, these compounds shift the potential of many metals beyond the passivation point. By varying the composition and structure of the compounds we can regulate the sign and magnitude of the charge on the reduced particles and thus retard or accelerate the kinetics of the cathodic reaction. Examples of the latter mechanism are afforded by the nitrobenzoates of amines, which are rapidly reduced (at up to 20 mA/cm^2) in neutral electrolytes, because the difficultly reduced NO_2^- anion is incorporated into the benzene ring where it loses its negative charge, and one of the two electrophilic substituents attaches itself to the benzene ring, withdrawing electrons from the reduced particle. Acquiring a positive charge, the nitro group becomes easily reduced on many metals, in particular iron, which has a negative charge on its surface.

By regulating the electron density at the reaction center we can also enhance the adsorption of organic compounds in metals in acid electrolytes. In particular it has been shown that the higher the electron density at the nitrogen atom of amines and their derivatives, the more effective is the inhibitor. As a measure of the electron density at the nitrogen atom we can take the ionization potential, because first ionization involves detachment of one of the electrons of the unshared pair.

In this connection, in recent years in various COMECON countries extensive research has been conducted into the influence of the structures of organic compounds on their inhibiting properties. It has been shown that the protective properties of organic compounds in acid media depend to a large extent on the Hammett and Taft constants, which determine the electron density at the reaction center. Quantitative relations have been derived between these parameters and the protective properties of the compounds. Much attention has been paid to adsorption processes. It is assumed that adsorption of organic substances involves exchange of water dipoles, oriented with their negative ends toward the metal, for molecules of the organic substance, which are oriented with their carbon chains toward the interface. The π-electron interaction has been examined, and attention has been paid to its important role in the adsorption of organic amines.

*Presented in 1978 to a symposium of corrosion specialists of the COMECON countries and Mexico.

Institute of Physical Chemistry, Academy of Sciences of the USSR. Translated from Zashchita Metallov, Vol. 16, No. 3, pp. 227-236, May-June, 1980. Original article submitted May 15, 1978.

There has been further development of the theory of electrocapillary phenomena in application to the problem of inhibition of corrosion media. It has been shown that surfactants reduce the surface tension in proportion to the quantity of adsorbed substance. Inhibitors of the anionic type (halide ions) are adsorbed more strongly at positive potentials, and inhibitors of the cation type (pyridine and aniline derivatives) at negative potentials. In some cases a correlation has been found between the capability of organic compounds to reduce the surface tension and their ability to reduce the corrosion of metals. In particular, it has been shown that the surface activity of amines varies in the same degree as the inhibiting action of these compounds in acid corrosion of iron. The inhibiting action of substances containing $-NH_2$, $=NH$, $\equiv N$ or $\equiv NR^+$, NR^+_4 as their sole functional group is correlated with their ability to reduce the surface tension of mercury. Precision determinations of the amounts of inhibitors adsorbed on metal surfaces reveal that they are often fractions of a monolayer. Clearly it is sufficient merely to block the active centers in order to bring the metal into the passive state.

An important achievement of the COMECON scientists was to discover and investigate the effect of synergism, i.e., enhancement of the inhibiting properties of one substance by another. Organic cations formed in electrolytes on account of the reaction of protonation of many inhibitors do not always display a protective effect. They usually protect those metals which are negatively charged, and are poorly adsorbed on a surface of like charge. However, if the organic cation is accompanied in the electrolyte by an anion-active substance (I^-, Br^-, Cl^-), the inhibiting action of the organic compounds is sharply increased. The explanation is that the anion-active substance, being adsorbed on the metal surface, creates a negative charge which promotes the adsorption of the positively charged organic cation.

Thus, sulfosalicylic acid reduces the hydrogen overvoltage and enhances the corrosion of steel in sulfuric acid, while tetrabutylammonium cations have a weak protective action; if both are present together in the electrolyte, they sharply increase the hydrogen overvoltage and reduce the corrosion rate by several orders of magnitude. The protective properties of pyridine and aniline derivatives are sharply increased when halide ions (Cl^-, Br^-, I^-) are added to the electrolyte. The ability of halide ions to increase the adsorption of organic substances is evidently universal for compounds present in the electrolyte in the form of cations. Such substances include amines and their derivatives, sulfoxides, sulfoamides, etc.

Synergism may also appear in the joint action of an inhibitor and hydrogen sulfide, which is itself a dangerous corrosion-active agent which accelerates general corrosion, hydrogen absorption, and stress corrosion cracking of steels. However, in the presence of hydrogen sulfide some organic substances display exceptionally high protective properties. Thus, in sulfuric acid, tetrabutylammonium sulfate does not have protective properties; however, if hydrogen sulfide is present in the electrolyte, even small amounts of tetrabutylammonium sulfate (0.0005 or 0.0025 mole/liter) reduce the corrosion rates of steel by factors of 96 and 750, respectively.

A new trend has developed in research on corrosion inhibitors — quantum-chemical calculations of the energy states of inhibitors in the adsorbed state. Computer calculations show that when adsorbed on iron, amines and their derivatives act as electron donors. They become positively charged, forming a peculiar barrier which hinders emergence of cations from the metal lattice into the solution. On the other hand, an anion of the MeO_4^{n-} type, acting as an electron acceptor, forms a strong chemical bond with the metal. Adsorption occurs via oxygen atoms, as shown by the marked increase in their negative charge. The charge on the metal atom of the anion is practically unaltered, refuting the formely held view that oxo anions are adsorbed by the agency of the central metal atom.

In some COMECON countries (USSR, Hungary, and Romania) much attention has been paid to research on the mechanism of hydrogen sulfide corrosion. Investigations of the kinetics of the electrochemical reaction have revealed that H_2S changes the hydrogen overvoltage and accelerates the process of ionization of iron atoms, i.e., corrosion. This is because, in electrolytes containing H_2S, hydrosulfide ions or hydrogen sulfide molecules are adsorbed on the surface of the metal. It is thought that, according to the pH, intermediate compounds $(FeHS^-)_{ads}$ or $(FeH_2S)_{ads}$ arise, and promote anodic solution. Ionization of these intermediate complexes is accompanied by regeneration of the hydrogen sulfide in the solution, giving rise to a continuous process even at low concentrations.

$$Fe+H_2S+H_2O \rightleftharpoons (FeHS^-)_{ads}+H_3O^+ \quad (1)$$

$$(FeHS^-)_{ads} \rightarrow FeHS^+ + 2e \quad (2)$$

$$FeHS^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O \quad (3)$$

The mechanism of acceleration of the cathodic reaction involves the formation of a negative ψ' potential owing to adsorption of sulfide ions on the surface of the metal. The point is that the surface compound $FeHS^-$ is an ionic dipole with its negative end turned toward the solution. This must reduce the overvoltage and promote discharge of hydrogen ions at the electrode. Moreover, discharge of hydrogen ions can occur at protonated sulfide ions $(H_3S^+)_{ads}$ or at intermediate complexes Fe(H—S—H), strongly promoting the discharge of hydrogen ions:

$$Fe+HS^- \rightarrow Fe(HS^-)_{ads} \quad (4)$$

$$Fe(HS^-)_{ads}+H_3O^+ \rightleftharpoons Fe(H—S—H)_{ads}+H_2O \quad (5)$$

$$Fe(H—S—H)_{ads}+e \rightarrow Fe(HS^-)_{ads}+H_{ads} \quad (6)$$

It is also thought that in some cases discharge of hydrogen ions occurs from H_2S molecules, since this is energetically more advantageous: The dissociation energy of the HS—H bond is much lower than that of the HO—H bond, and this may also be one of the causes of the decrease in the hydrogen overvoltage.

Concerning the mechanism of the stimulating action of H_2S on hydrogen adsorption in steels, the following considerations have been put forward: there are a number of known catalytic poisons, including H_2S, which hinder the electrochemical desorption of hydrogen from the surface of a metal or the reaction of molecule formation from ions

$$H_{ads}+H^+ \rightarrow \uparrow H_2 - e \quad (7)$$

$$H_{ads}+H_{ads} \rightarrow \uparrow H_2 \quad (8)$$

The more the desorption of atomic hydrogen is hindered, the higher is its concentration on the surface, and the more strongly does it tend to penetrate into the metal.

The above mechanism shows what paths we must follow to avoid hydrogen sulfide corrosion. Obviously, the most effective method is to replace the intermediate complex $(Fe—H—S—H)_{ads}$, which stimulates corrosion and hydrogen absorption, by another complex containing an organic radical. We must make use of its synergism with sulfide ions, which promote the adsorption of organic cations.

In research on corrosion inhibitors, a start has been made on the use of new physical methods of investigations such as ESCA (x-ray photoelectron spectroscopy), photoelectric polarization, and electroreflection, which have markedly raised the level of theoretical work. In particular, by ESCA the valence state of the inhibitor atoms in the adsorbed state was determined. It was shown that all the oxo anions except chromate ions remain in unreduced form during adsorption. Chromate ions change from the hexavalent to the trivalent state. In adsorption of inhibitors containing a common anion of the MeO_4^{n-} type we observe an increase in the bond energy ΔE_b of the electrons for the $Fe2P_{3/2}$ electrons, indicating that these inhibitors function as acceptors. During adsorption of oxo anions the passivating layer is of Fe_2O_3 in which part of the oxygen is replaced by oxo anions. Quantum-chemical calculations show that the strength of the bond between the oxygen and the iron then sharply increases.

Practical Results

Using the theoretical ideas discussed above, in the COMECON countries we have succeeded in synthesizing and industrially adopting a number of highly effective corrosion inhibitors for a wide range of purposes.

Volatile Atmospheric Corrosion Inhibitors

For prolonged storage, transportation, and protection of engineering products between operations, universal volatile inhibitors have been created; they afford protection from atmospheric corrosion in very varied climatic zones for over 10 years. These inhibitors are mononitro- and dinitrobenzoates of amines and can evaporate at a useful rate (vapor pressure 10^{-3}-10^{-7} mm) at room temperature (20-40°C). The essence of the method of protection is that in a closed space in which the products are kept (a container or a polyethylene sheath) a small

amount (50-100 g/m^3) of inhibitor is placed. It evaporates and saturates the space with its vapor, which is adsorbed on the metal surface and protects it from corrosion. To protect large articles and extended structures with large numbers of devices and electronic apparatus, to obtain rapid saturation of inaccessible parts by inhibitor vapor, inhibitors have been created with higher vapor pressures (tens of millimeters). These are amine derivatives. The effectiveness of heteroalkylated lower volatile inhibitors can be judged from the data in Tables 1 and 2.

As well as these inhibitors, for protection of metals from atmospheric corrosion the inhibitors VNKhL-20 and VNKh-1 have been developed; they also protect ferrous and nonferrous metals (USSR). In Czechoslovakia a volatile inhibitor has been created consisting of a composite of several chemical compounds. This inhibitor protects steel, chromium, and nickel, but does not affect copper or zinc. On the basis of this inhibitor a number of inhibiting papers have been developed and produced under the general name of "Svik" for the protection of ferrous and some nonferrous metals. In Poland the home-produced inhibitor paper "Lik," which contains a two-component inhibitor, is widely used in industry.

The volatile inhibitor "Korreks-11" and the inhibitor paper "Korrozal Papir" have been created and are used for long-term protection of metal articles in Hungary. In East Germany volatile inhibitors have been developed, and anticorrosion papers of marks A and B are produced. Mark B paper is intended for electrical engineering parts and protects ferrous and nonferrous metals (nickel, chromium, aluminum, copper, silver, cadmium, zinc, magnesium–aluminum alloys, and brass). In Romania, effective home-produced volatile inhibitors are also being developed and used.

Various methods have been developed for using volatile inhibitors: inhibitor papers; porous inhibited adsorbents — "Linasil', Linapon"; washing articles such as high-pressure spherical containers with alcoholic solutions of inhibitors; and sublimation and deposition of thin films of corrosion inhibitors on the surface of large articles such as power generation equipment, boilers, and waste gas heaters (USSR).

To use the last-mentioned method, portable hand-held equipment of the "revolver" type (Czechoslovakia) and stationary plants (Czechoslovakia, USSR) have been developed. Heated air is passed through silica gel or zeolite granules soaked in inhibitor (USSR, Czechoslovakia), or through special cassettes filled with inhibitor (USSR) which are placed immediately behind the heating elements. The air, now saturated with inhibitor vapor, passes to the article; on contact with the cold surface of the metal, the inhibitor is deposited on it, forming a thin film. In Czechoslovakia this method of preserving is denoted by a word rendered in Russian as "Aerozolirovanie" ["Aerosolization"].

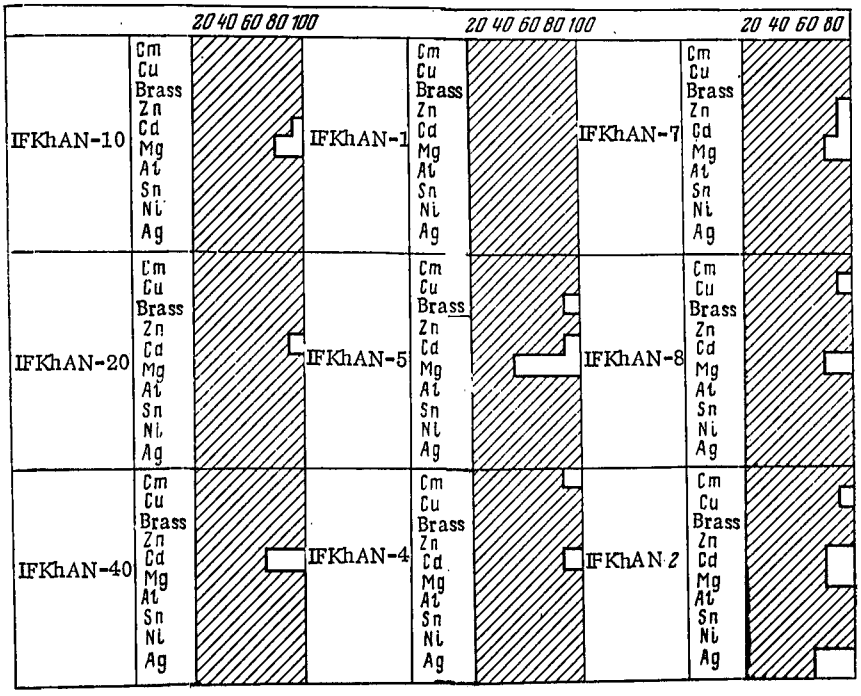
Inhibitors for Heat-Exchange Apparatus, Heating Systems, and Hydraulic Tests

In the COMECON countries a number of efficient inhibitors for corrosion protection of heat-exchange apparatus in chemical and petrochemical processes, compressors, motors, etc. have been developed. They include IFKhAN-12, Tasol, IFKhAN-21 (USSR), I-7 (Bulgaria), and Silenal S and Silenal PSN (Poland).

The Bulgarian I-7 is an original three-component composite (Z = 95%). The dose is 20-50 mg/liter, effective up to t = 60°C over a wide range of pH values (4.5-8). The effect lasts for 300-500 h. The protected system is first saturated with a 10% solution of I-7 for 2 h (C = 10 mg/liter). The next 5 g of inhibitor is added in a concentration of 50 mg/liter. Then 100 mg/liter is added from the seventh to the 55th hour. The applications are for protection of heat-exchange equipment, pipelines, and reservoirs with corrosion-active waters. The service life of the equipment is increased sixfold. The number of repairs is reduced, and the loss of products is cut down (with ecological improvements to the environment).

Silenal S and Silenal PSN (Poland). Silenal S (a two-component mixture) is a silicate inhibitor containing about 1% of the sodium salt of ethylenediaminetetraacetic acid (EDTA). Silenal PSN is a four-component mixture containing added zinc salts and sodium polyphosphate. Both inhibitors are used to protect open circulating cooling systems from corrosion. The dose is 200-300 mg/liter (40-60 mg/liter SiO_2). Silenal S is recommended for not-too-aggressive water — water-cooling and central heating systems — and Silenal PSN for aggressive waters; it reduces corrosion by a factor of 3-4.

TABLE 1



For protection of apparatus for high-pressure hydraulic testing against corrosion and stress corrosion cracking, inhibitors of the amine nitrobenzoate type (USSR) are recommended; their protective properties can be judged from the data in Table 3.

Inhibited Polymer Coatings

With the aim of corrosion protection of semifinished and finished engineering products during transportation and storage, nonadhesive inhibited polymer coatings have been developed; when finished with, they can easily be removed. Such coatings (KhS-596, AK 535, GF 570 RK, IS-1, ISM-3, S-1820, S-1802, KhP-1, and LSP) are used to protect metal structures, finished engineering products, and also for chemical machining of aluminum alloys and stainless steels (USSR, Czechoslovakia, Poland).

Inhibitors for the Oil and Gas Industry

In the COMECON countries we have created efficient inhibitors for protection of equipment in the oil and gas industry against general corrosion, hydrogen absorption, and stress corrosion cracking. Recently, special attention has been paid to finding inhibitors against hydrogen sulfide corrosion, since in the USSR we have discovered very rich gas fields containing up to 10% of hydrogen sulfide, and H_2S also appears in old oil wells owing to microbiological processes developing in the water pumped into the seam to maintain the pressure. The presence of hydrogen sulfide in gas and oil promotes hydrogen absorption by steels and stress corrosion cracking. We have found very effective inhibitors for the extraction, transport, and processing of gas and oil.

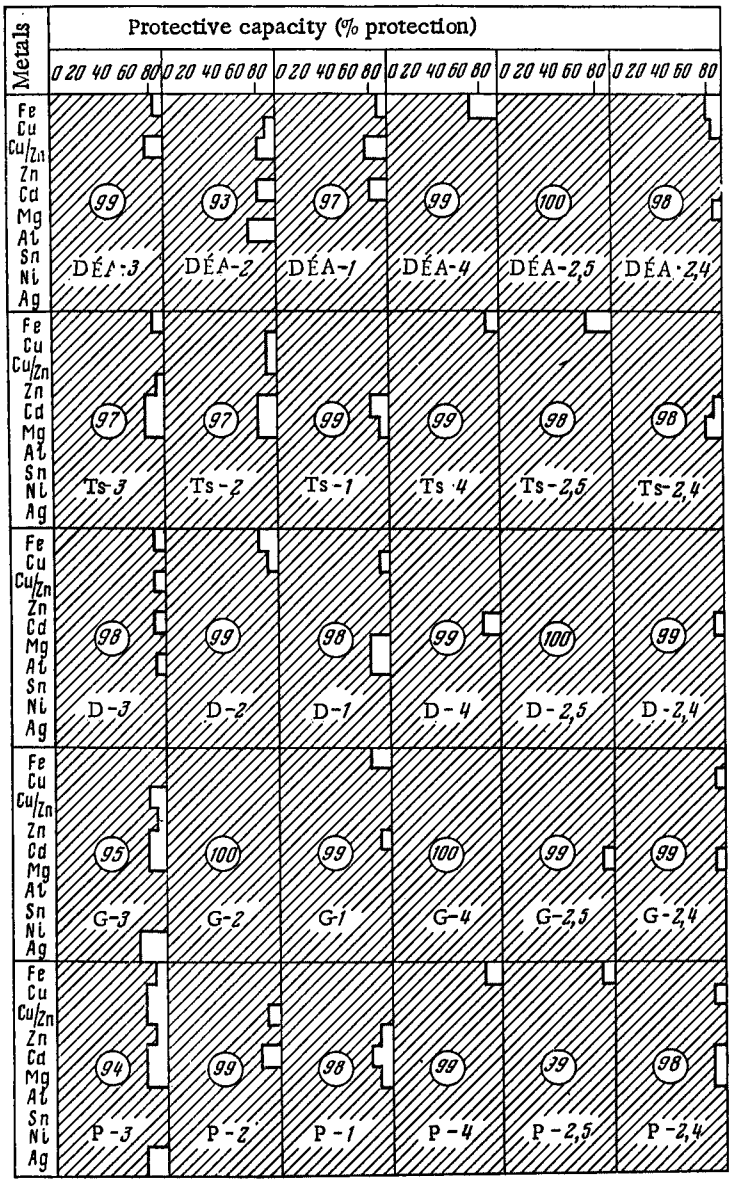
Inhibitors for Hydrochloric Acid Treatment of Oil and Gas Boreholes

The relatively high temperatures of deep boreholes (150-180°C) have made it necessary to seek high-temperature corrosion inhibitors with the aim of protecting the well equipment during hydrochloric acid treatment which is used to increase the oil and gas yield of the beds. The most effective inhibitors are acetylene compounds (giving protection up to 130°C). When they are mixed with nitrogen-containing inhibitors (BA-6, PKU, MG-130), protection from the action of hydrochloric acid on the equipment is achieved at 150-170°C.

Inhibitors for Extraction, Transport, and Processing of Gas Containing a High Hydrogen Sulfide Concentration

Unique inhibitors (IFKhANGAZ) have been developed for protection of gas field equipment from corrosion and stress corrosion cracking over the whole cycle of extraction, transport,

TABLE 2.



and processing of the gas. Their distinguishing feature is their universal nature: They can suppress general corrosion, hydrogen absorption, and stress corrosion cracking. They also prevent foaming and entrainment of absorbents used to remove hydrogen sulfide from the gas. In addition, they act as foam suppressors. Thus, it is unnecessary to use separate inhibitor and foam suppressant compounds. Inhibitors of the IFKhANGAZ type are also effective for oil wells and when the oil contains hydrogen sulfide. The protective and technological properties of IFKhANGAZ inhibitors are better than those of the best inhibitors on the world market.

Various methods have been developed for using IFKhANGAZ inhibitors. One of these is to pump the inhibitor into the borehole. As the gas emerges, the inhibitor is entrained with it, and thus protects the equipment from stress corrosion cracking. Another method is to use special pistons to spread viscous solutions of inhibitor on the interior surfaces of the pipes by which raw gas is fed to the sulfur removal plant. A third method is to add 25-20 mg/liter of inhibitors to the solutions used to remove hydrogen sulfide from the gas. The use of IFKhANGAZ inhibitors completely suppresses corrosion and stress corrosion cracking in the equipment, and can increase the output of the sulfur removal plant by 20-25% (USSR).

TABLE 3

Alloy	Time to failure, days	
	without inhibitor	with inhibitor
Steel ÉP-257	10	>90
Magnesium alloy MA2-1	20	>90

Inhibitor Compositions for Petroleum Gas Compressors

The compressors in general use are unsuitable for compressing petroleum gas containing hydrogen sulfide. These relatively rapidly go out of order owing to hydrogen absorption and stress corrosion cracking. In the USSR we have developed the first method of protecting compressors, designed for compressing gas containing up to 3% of hydrogen sulfide, from corrosion by means of a special inhibitor composition, IFKhANGAZ-K. Hydrogen probes show that in the presence of the inhibitor hydrogen absorption by the steel is completely avoided, and therefore also stress corrosion cracking of the individual elements of the compressors. The capability of these inhibitors to avoid stress corrosion cracking can be judged by results obtained in industrial tests (Table 4).

We see that without the inhibitor, after a short period (120 h) the metal loses much of its ductility and strength, whereas in the presence of the inhibitor the initial ductility and strength of the steel are preserved.

To protect compressors we need only small concentrations of the inhibitor. The consumption is about 2.5 kg of inhibitor per day for each compressor. This completely eliminates stress corrosion cracking, increases the stability of operation of the compressors, and improves their output. Compressors protected by IFKhANGAZ-K operate stably for a long time without stoppage, and it is unnecessary to build plants for purifying the petroleum gas from hydrogen sulfide or to make the compressors from special steels (USSR).

Inhibitors for Oil Refining

In Hungary, Poland, and Bulgaria, inhibitors have been developed for protecting oil refining and preparation plants from corrosion.

The inhibitor INS-A (Hungary) is a mixture of organic compounds containing nitrogen and sulfur. It emulsifies in water and dissolves in hydrocarbons. It is more effective in places where corrosion is due to H_2S, HCl, and CO_2 in conditions where water condenses. It retards corrosion in plants for processing oil in the vapor phase.

The inhibitor Petralin D4 (Hungary) is a mixture of organic compounds containing nitrogen. It emulsifies in water and dissolves in hydrocarbons. It dissolves easily in water in the presence of H_2S, CO_2, and HCl, and to a lesser extent in hydrocarbons. It effectively retards corrosion due to H_2S, HCl, and CO_2. It retards corrosion in oil refining plants in the gas and vapor phases.

Koren N-2 (Poland) is intended for protecting the upper parts of distillation columns and condensing and cooling systems (on the petroleum product side) made of low-carbon steels; it reduces the corrosion rate to 0.1 mm/yr (increasing the service life by a factor of 2-3).

TABLE 4. Influence of IFKhANGAZ-K Inhibitor on Mechanical Properties of Steel (industrial tests on compressor station)

Characteristics of specimen	Original specimens	Duration of tests (120 h)			
		without inhibitor	with inhibitor		
			S-1	S-2	S-3*
Strength σ_t, kg/mm^2	45,0	40,8	45,9	44,9	43
Rel. elongation δ, %	22,0	14,1	21,8	21,8	20
Rel. reduction ψ, %	64,1	39,0	66,4	64,0	64

*First, second, and third stages of gas compression.

It is produced in the form of a 10% solution in xylene. It has been adopted at all petroleum refineries.

Mak-4 (Bulgaria) is a copper—ammonia complex (carbonate) including an organic component. When fed to an oil desalting line, it quickly reacts with the aggressive agents present in the oil, forming alkali-metal salts and compounds which are stable at the rectification temperatures; these accumulate in the still residues. In addition, MAK-4 has antioxidant and detergent properties, and also prevents the formation of scale. It is used at the Burgas Petroleum Refinery.

It is fed in together with the caustic soda: MAK-4 inhibitor in the form of a 5-10% aqueous solution is fed to the oil desalting line at C = 8-10 mg/liter relative to the feedstock. At 7 m from its injection point, a 10% solution of alkali is injected at 20-40 mg/liter. In refining high-sulfur oil it is recommended that 2-4 mg/liter of film-forming inhibitor should be added to the slime lines.

Economic Effect

Experience of the use of corrosion inhibitors in COMECON countries shows that, according to their applications, an economic saving of 20,000-100,000 rubles is obtained per ton of inhibitor.

COLLECTIVE EXPERT ASSESSMENT OF PROMISING DIRECTIONS IN THE THEORY OF CORROSION AND PROTECTION OF METALS, AND COOPERATION BETWEEN MEMBER-COUNTRIES OF COMECON IN ITS DEVELOPMENT

L. I. Freiman, V. M. Novakovskii, and Ya. M. Kolotyrkin

UDC 620.193.01

A questionnaire has been addressed to 54 specialists from Bulgaria, Hungary, East Germany, Poland, the USSR, and Czechoslovakia on the present level and directions of development of the theory of corrosion and on the cooperation between the member-countries of COMECON in this field. By analyzing the replies, the authors elucidate and comment on the prevailing opinions on these questions.

In recent years, increasing use has been made of questionnaires addressed to experts in order to predict the development of science and technology. This method was included in the recommendations for forecasting in the COMECON group [1], and has been used, in particular, to assess the various courses for increasing the reliability of steel structures in hydrogenating media [2].

The aim of any questionnaire addressed to experts is to elucidate the spectrum of opinions, particularly the predominant opinions, and sometimes to find their "averaged" pattern. Of course, in scientific matters the predominance of some particular opinion does not guarantee that it is correct. Moreover, an inquiry made among specialists in a given field reflects, as it were, the "view from inside." It would also be very interesting to have a "view from outside," i.e., to find the opinions of specialists working in related fields of science and technology. To elucidate this it is necessary to overcome a whole series of organizational and technical difficulties. These circumstances reduce the value of questionnaires, but by no means render them worthless, because a statistically reliable knowledge of the prevailing opinions, irrespective of attitudes to them, is very important for solving a number of problems of science and scientific organization.

In our work, performed within the framework of the scientific—technical collaboration on Theme I, "Development of a Theory of Corrosion and Protection of Metals," in the COMECON

L. Ya. Karpov Scientific-Research Physicochemical Institute. Translated from Zashchita Metallov, Vol. 16, No. 3, pp. 237-249, May-June, 1980. Original article submitted October 31, 1979.