NANO-COATINGS PROTECTIVE PROPERTIES IN AMINUM ENVIRONMENTS

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ABSTRACT

It is known that one of the methods for purifying gas fraction from hydrogen sulfide is amine treatment. Various types of amines are used to remove hydrogen sulphide, carbon dioxide and carbon dioxide from petroleum gases. The choice of specific amine depends on the needs of the process. Mono-ethanolamine (MEA) $(C_2H_4OH)\ NH_2$ and diethanolamine (DEA) (C_2H_4OH) 2NH are commonly used. Both are ammonia derivatives. To develop recommendations on the choice of material from which to make equipment for amine plants, comparative studies of corrosion resistance of traditionally used low-temperature carbon steel and nano-composite coatings obtained by electrodeposition method. The research have shown, that average corrosion rate on a standard sample (without coatings) is 0.9969 mm / year. Because of this, the frequency of changing equipment for cleaning oil from acidic components (hydrogen sulfide, carbon dioxide and carbon dioxide) on average is 1 time per two years. During the one year testing period nano-composition coatings showed protective efficacy when exposed to acidic corrosion / erosion. It should be noted that there is a likelihood of damage to the coating during mechanical action. It is established that the use of protective coatings leads to an increase in corrosion resistance 24-56 times, which indicates the expediency of their use in these operating conditions.

Keywords: nano-composition coatings, corrosion resistance, amine media, protective properties, carbon steel

INTRODUCTION

Special interest to composites and coatings has emerged last decades in connection with sharp growth of requirements to operational properties of the materials working in the conditions of corrosive medium, friction and deterioration. In this connection working out of effective and economic methods of nano-coatings reception, studying of processes of electroplating, as well as research of electrolytic coatings microstructure influence on its properties are the actual problems of modern materials science. Generally amine equipment are used for cleaning petroleum gases from hydrogen sulfide, carbon dioxide and carbon dioxide from petroleum gases. These substances must be removed because of their toxicity, corrosion and ability to pollute the environment. As a rule, amine plants are made of low-temperature carbon steel, while solutions of amine dissolve copper, bronze and most alloys turn into zinc or copper [1-5]. The weakest point of the amine system are the pipelines on the saturated amine line, often suffering due to intense corrosion. Iron sulphide (FeS) is formed on a metal surface under the influence of hydrogen sulfide. The stripper (amine regeneration column), which contains a lot of hydrogen sulfide and carbon dioxide, is the most corrosive [6-10]. Corrosion damage decreases at low temperatures. The average corrosion rate for conventionally used materials is 0.9873 mm / year. Therefore it is necessary to completely change the equipment once every two years.

The composition of petroleum gases include aliphatic hydrocarbons, hydrogen sulfide, carbon dioxide and other components. To neutralize them, amine solutions are used. Monoethanolamine (MEA) $(C_2H_4OH)\ NH_2$ and diethanolamine (DEA) $(C_2H_4OH)_2NH$ are commonly used. Each of them has its advantages and disadvantages. MEA can better purify fractions from hydrogen sulphide than DEA. However, MEA can combine with other substances such as CS_2 (carbon disulfide) and form salts that remain in the amine solution, and the presence of O_2 enhances the process [11-15]. Over time, these salts can form deposits, which leads to loss of amine solution and causes equipment corrosion. DEA, which is chemically weaker than MEA, does not form significant amounts of salts, therefore, the solution of DEA is lost less during the formation of salts. In addition, since the chemical bond between DEA and hydrogen sulfide is weaker than that between MEA and hydrogen sulfide, less heat is required to regenerate DEA to separate absorbed hydrogen sulfide and other acidic components, therefore, to remove acidic components, gases are treated with a solution of diethanolamine (DEA):

$$(C_2H_4OH)_2NH + H_2S \rightarrow (C_2H_4OH)_2NH_2HS \text{ – bisulfite}$$

$$2(C_2H_4OH)_2NH + H_2S \rightarrow \{(C_2H_4OH)_2NH_2\}_2S \text{ –sulfite}$$

$$(C_2H_4OH)_2NH + CO_2 + H_2O \rightarrow (C_2H_4OH)_2HCO_3 \text{ – bicarbonate}$$

$$2(C_2H_4OH)_2NH + CO_2 + H_2O \rightarrow \{(C_2H_4OH)_2NH_2\}_2CO_3 \text{ – carbonate}$$

$$COS + H_2O \rightarrow CO_2 + H_2S \text{ – carbon dioxide and hydrogen sulfide}$$

EXPERIMENTS

The composition of petroleum gases includes aliphatic hydrocarbons, hydrogen sulphide, carbon dioxide, etc. The average component composition of high and medium pressure gas is presented in Table 1. Hydrogen sulfide must be removed because of its toxicity, corrosiveness and the ability to pollute the environment. During combustion, SO_2 and S_2 are formed - potentially hazardous substances. One of the ways to purify the gas fraction from hydrogen sulphide is the amine treatment. To remove hydrogen sulphide, carbon dioxide and carbon dioxide from petroleum gases, various types of amines are used.

It is known that choice of a particular amine depends on the needs of the process. Typically, mono-ethanol-amine (MEA) $(C_2H_4OH)\ NH_2$ and di-ethanol-amine (DEA) $(C_2H_4OH)_2NH$ are used. Both are derived from ammonia.

Table 1- Average component composition of high and medium pressure gas

Name of components	Medium pressure gas from unit 200 (% weight)	High pressure gas from unit 200 (% weight)
Nitrogen	0.78	1.1
Carbon dioxide	4.5	6.38
Hydrogen sulfide	22.32	19.44
Mercaptan	0.01	0.0073
Methane	24.12	28.75
Ethane	14.36	12.9
Propane	19.36	15.8
Butane	4.61	3.54
Isobutane	2.32	2.12
Pentane	2.29	0.9
Isopentane	2.34	1.51
Hexane and above	2.87	3.37
Humidity of gas (% weight)	0.36	4.22
Density at 0 ° C (kg / m^3)	1.175	1.144

MEA can better clean fractions of hydrogen sulphide than DEA. However, MEA can be combined with other substances such as CS_2 (carbon disulfide) and form salts that remain in the amine solution, and the presence of O_2 enhances the process. Over time, these salts can form deposits, which leads to loss of amine solution and causes corrosion of the equipment.

DEA, which is chemically weaker than MEA, does not form significant amounts of salts, so the DEA solution is lost less when forming salts. In addition, since the chemical bond between DEA and hydrogen sulphide is weaker than the bond between MEA and hydrogen sulphide, DEA regeneration requires less heat to separate absorbed hydrogen sulphide and other acidic components; therefore, to remove acidic components, the gases are treated with a solution of diethylamine.

One of the methods of protection against corrosion damage of materials was the nanostructured composition coatings (nano-CEC) on chromium base. In order to evaluate the effectiveness of nano-CEC protective properties, it has been decided to test for corrosion / erosion resistance with corrosion obtaining samples. Samples are made of carbon steel ASTM A333 GR6:

Carbon,% wt. = 0.30 max.
Manganese,% wt. = 0.29 - 1.06 max.
Phosphorus,% wt. = 0.025 max.
Sulfur,% wt. = 0.025 max.
Silicon,% wt. = 0.10 min.

Obtaining of corrosion samples was made using electrodeposition technologies. Corrosion samples are pairwise installed on the first and third Y300 threads on the lines of the enriched amine. After the extraction of corrosion samples, a primary examination of corrosion samples was carried out, consisting of a visual and gravimetric assessment of the state of obtaining.

RESULTS AND DISCUSSIONS

The difference between the samples CC3112LP installed on Y300 from the CC3212LP previous ones consisted in the temperature of electrodeposition, and also the fact that a program was developed that provides for the installation and periodic extraction of samples for the survey. The location of the experiment is the fifth string U300, on which there are a sufficient number of low pressure fittings, which allow installing and removing corrosion samples without affecting the technological process.

a) б)

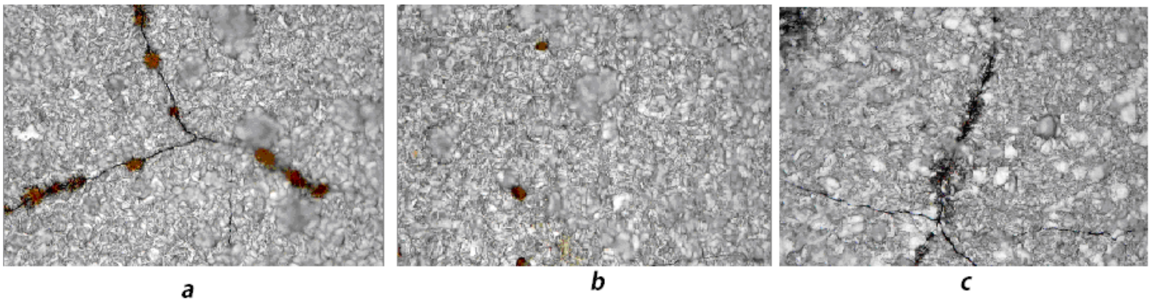
Fig.1. a) the corrosion sample CC3112LP, installed on U300 equipment b) the corrosion sample CC3212LP, installed on U300 equipment

Corrosive samples are installed on the fifth string of U300 on the line of enriched amine and a separation collection. As an indicator of corrosion-erosion resistance of obtaining in conjunction with the samples with the nano-CEC Cr-C, standard samples made of carbon steel ASTM A333 GR6 without coating are installed. Survey of the state of corrosion samples was conducted after 6 month, Fig. 2:

a) b) c)

Fig.2.a) corrosive sample CC03004LP (sample D875); b) corrosive sample CC03005LP (sample D896); c) corrosive sample CC03006LP (sample D888)

According to the data obtained during the examination of corrosion samples, corrosion rates were calculated, a visual and metrological evaluation of the electrodeposition obtaining state was made. On the surface of the corrosion-proof sample D875 with the electrodeposition pated by the technology of 2017 (position CC03004LP), there are no traces of mechanical and corrosion-erosive damage. The average deposition thickness, color and surface roughness have undergone changes. The corrosion rate on the standard sample D173 (without coatings) was 0.9969 mm / year, which is 32 times higher than on the D875 sample (with electrodeposition obtaining). On the figure 3 typical microstructure of corrosion defeats is shown.



а - 293К, б -303К, в – 313К

Fig. 3. Typical microstructure of corrosion defeats of the nano-CEC surfaces, obtaining by electrodeposition method

On the surface of the corrosion-proof sample D896 with the electrodeposition obtaining, performed on the (fig.3, b), there are no traces of corrosion-erosion damage. The geometric parameters of the sample are broken (a slight bend relative to the generatrix). On the lateral surfaces, there are traces of mechanical impact, which probably occurs when the sample is removed from the fitting. The average deposition thickness, color and surface roughness have undergone changes. Comparative analysis with the standard sample was not carried out, due to the lack of the possibility of installing the second sample at this position.

CONCLUSIONS

At the expiration of the test period, it was established that corrosion and corrosion erosion damage was not observed on the surface of corrosion samples with the electrodeposition obtaining under 303 K temperature. The average thickness of the obtaining, color and surface roughness did not undergo significant changes. In the zone of the partition between the base metal of the sample and the obtaining, the metalized coating isn’t peeled off.

On the surface of the corrosion-proof sample D888 with the electrodeposition spraying technology (position CC03006LP), there are no traces of corrosion-erosion damage. On the side of the sample, the damage increased to 11 mm. An initial stage of detachment of the coating on the surface from the side of the room is observed. The average thickness of the obtaining, color and roughness underwent changes. The corrosion rate on the standard sample D174 (without obtaining) was 0.84 mm / year, which is 24 times higher than on the D888 sample (with Electrodeposition obtaining).

During the 6 month testing period nano-coatings showed a protective efficiency when exposed to acid corrosion / erosion. It should be noted that there is a possibility of damage to the coating during mechanical impact.

It is established that the use of protective coatings leads to an increase in corrosion resistance 24-56 times, which indicates the expediency of their use in these operating conditions.

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