Industrial Production of Acetal-Based Corrosion Inhibitors

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Abstract: Summary of researching results of practical application of 1,3-diheterocycloalkanes as new highly-efficient corrosion inhibitors is presented herein, made by Ufa State Petroleum Technological University and Research Institute of Fine Chemicals and Agents headed by Professor D.L.Rakhmankulov. The relevance of the problem studied is stipulated by possibilities in application of petrochemical intermediate products and waste to get multifunctional corrosion inhibitors. Researching of corrosion inhibitors with the use of acetics is demonstrated to be made in two directions: tailor-made synthesis of corrosion inhibitors of acetal type using cheap and available petrochemical stock; making corrosion inhibitors with increased protection properties and improved processing quality by blending with other substances. Under the pilot studies the process flow diagram for making industrial synthesis is proposed, and efficient operating conditions for the reaction enabling to get the best results to increase the output of the desired condensate (i.e. efficient corrosion inhibitors) are defined. Standard processing unit for making corrosion inhibitors by blending is engineered and proposed to be implemented and that was installed in some enterprises of the Republic of Bashkortostan.

1. Introduction

A problem of metal equipment protection against corrosion is one of the most important for safe operation and reliability thereof if exposed to corrosive media [1].

One of the most efficient ways in metal protection against corrosion is application of inhibitors, i.e. compounds decreasing the corrosion rate in various conditions and media at small concentrations thereof in aggressive environment. Metal protection against corrosion by the inhibitors by Rosenfeld [2, 3] is based on properties of some separate chemical compounds or mixtures thereof to decrease the corrosion rate or fully deactivate it, if they are added in small quantities to the corrosive media.

As a rule, the inhibition method is marked by high economic efficiency, easy industrial implementation with no changes in previously accepted process flow diagram, and usually requiring no extra funds for realization thereof, and no additional equipment to be installed [4, 5, 6].

There are many processes in chemical, petrochemical, oil-refining, metallurgical and other industries where metal parts of technological equipment come into contact with highly corrosive media, therefore, the area of inhibitors application is wide enough. The corrosion inhibitors are widely used for production, transportation and refining of oil and gas, for protection of power-generating equipment, in both industrial and household water supply, in systems for cooling industrial equipment and vehicles (combustion engines), for pickling of metals, etc. In the last few years the inhibitors were applied in rocket engineering, volatile inhibitors are now widely used for protection of engineering items against atmospheric corrosion, the inhibitors are actively added to lubricants, oil, petrol,
hydraulic fluid and emulsions [2, 7, 8, 9, 10, 11, 12].

Although there are many methods and means of inhibiting in petrochemical industry, a lot of problems in production engineering and industrial application of the inhibitors are not thoroughly studied yet. There are thousands of chemical compounds inhibiting the corrosion processes, however no theoretical approaches in selecting the chemical compound structure demonstrating maximum protective efficiency in certain conditions are provided yet up to now. Moreover, even for optimum “inhibitor – metal protection” system, there are no approved technologies in making inhibitors from cheap and available raw stock that would be of relatively low cost and similar to both domestic and foreign-made inhibitors by a number of properties thereof. A majority of reagents used for the protection of metal against corrosion in petrochemical industry are obtained from expensive and less accessible chemical and petrochemical products, therefore they are basically applied in certain separate facilities. At the same time many by-products and petrochemical waste possess some properties that are peculiar to compounds demonstrating high inhibiting ability in corrosive media.

2. Current corrosion inhibitor technologies

As theoretically it is impossible to make a universal (unique) corrosion inhibitor to be effective in any “corrosive medium – metal” system, a great number of reagents is to be developed. This problem is more pressing considering several climatic zones in Russia when many highly efficient inhibitors lose their technological and protective properties at low temperatures [1, 13].

Similar situation is with problems related to reduction of power consumption under operation of inhibitor protection installations, methods and ways of inhibitor applying during the repair period, control technologies for inhibitor protection efficiency in active pipelines, etc.

As rational solving of technological problems for inhibitor protection of metal equipment against the corrosion enables not only to significantly increase the life cycle of industrial facilities but to environmental stabilization in regions with the developed oil-gas and petrochemical industries, it is obvious that researching in this direction is an urgent scientific and technological challenge [14].

The corrosion inhibitors are known to be the basic chemicals. Nowadays there are varieties of formulations but not all of them may be applied for the equipment protection due to some nonconformities with technical characteristics and cost thereto. Availability of quite cheap and accessible raw stock is to be considered when making new efficient corrosion inhibitors. Application of individual compounds as the corrosion inhibitors is related to major technological, economic and other problems. Therefore, as a rule the inhibitors are of complex blend including an active component and different special admixtures and agents. The inhibitor formulations are compounded with various petrochemical waste and intermediate products without affecting the protective properties thereof thereby enabling solving the problems of cost, availability of raw feed for inhibitor synthesizing and waste utilization.

As a rule, the corrosion inhibitors consist of many components and are obtained by mixing thereof: active base, viscosity controller, solidifying point, stabilizers, etc.

One of the ways for practical application of 1,3-diheterocycloalkanes is using thereof as metal corrosion inhibitors. Ufa State Petroleum Technological University together with Research Institute of fine chemicals and agents (NIIReaktive) headed by Professor D.L.Rakhmankulov for more than 25 years have been engaged in researching and analyzing reactivity of such compounds, thereby monographs and a great number of reviews and over 1000 scientific papers have been published both in Russian journals and abroad, and over 1000 author’s certificates and patents have been obtained under the results thereof [12, 13,15, 16].

As both theoretical and experimental researching made by us have demonstrated that new prospective corrosion inhibitors being the chemical compounds containing heteroatoms (O, S, N) with lone pairs of p-electrons are of greater interest, much attention in the paper was paid thereto. In this regard, the compounds of linear and cyclic acetics as well as heteroanalogs thereof were of more importance, as they may be easily synthesized in either laboratory conditions or on industrial scale from cheap and accessible raw stock. Besides, some acetics are produced domestically. A number of
oxygen-, sulfur- and nitrogen-containing compounds are found in many intermediate products and petrochemical waste as the main component therein. The particular attention is given to acetals as they may be of any given structure with good purity and high yields as per the Prins reaction or by acetalization, thereby being extremely valuable as the model object to study the effect of the chemical compound structure upon the inhibiting ability thereof.

Over 300 compounds of this grade were synthesized and tested by us. Varying the character, nature and size of the substituent, the efficient corrosion inhibitor for steel to be affected by many corrosive media was found [17, 18, 19].

Individual acetals and heteroanalogs thereof possess extremely high protective effect, aftereffect time and excellent technological properties (low density, solidifying point, etc.). However, the cost thereof is much higher than that of industrially applied inhibitors. Therefore, corrosion inhibitors with the use of acetals were studied in two directions:

a) tailor-made synthesis of corrosion inhibitors of acetal type using cheap and available petrochemical stock;

b) making corrosion inhibitors with increased protection properties and improved processing quality by blending with other substances [12, 13, 20].

When making tailor-made synthesis of acetals enabling to get substituted 1,3-dioxanes from available and relatively cheap olefins and aldehydes, the Prins reaction is of the most interest [15].

4,4-dimethyl-1,3-dioxane is produced from isobutylene and formaldehyde on large industrial scale, however, the application thereof as the corrosion inhibitor is limited due to high volatility. Styrene and α-methylstyrene are preferred among other olefins, with 4-phenyl-1,3-dioxane and 4-methyl-4-phenyl-1,3-dioxane to be obtained therefrom, accordingly [15].

These compounds possess high protective effect. Besides, the cost for pure 4-methyl-4-phenyl-1,3-dioxane is just a bit higher than the cost for the inhibitors applied. However, application of pure 4-methyl-4-phenyl-1,3-dioxane is impossible in climatic conditions of the Volga region, Urals and West Siberia due to high solidification point (≈40°C).

Considering high inhibiting property of 4-methyl-4-phenyl-1,3-dioxane and formaldehyde, as well as relative simplicity of the processing technology, Academician Rakhmankulov D.L. together with his students made an attempt to get the inhibiting composition not from pure 4-methyl-4-phenyl-1,3-dioxane, but from the reaction mass, i.e. condensation products of α-methylstyrene and formaldehyde without isolating pure 4-methyl-4-phenyl-1,3-dioxane.

The process flow diagram for making synthesis in industrial conditions was proposed and efficient operating conditions for the reaction enabling to get the best results to increase the output of desired condensation reaction products were defined under the pilot studies [20].

Comparative laboratory studies of the proposed inhibitor and known corrosion inhibitors have indicated that the developed reagent is possessing high protective effect and sometimes even exceeds the corrosion inhibitors being used nowadays by technological indicators thereof, and it may be recommended for industrial application.

Now preparation of the corrosion inhibitors by blending is considered to be the most interesting one in achieving the best protective effect. The corrosion inhibitors for any “corrosive medium – metal protection” system may be obtained in such a way. However, the essential condition therewith is that substances containing atoms with lone pairs of p-electrons should be the inhibitor base [20, 21].

Standard technological installations for the corrosion inhibitors developed under the researching were installed in “Ufareaktiv” enterprises, pilot plant of the Institute of petroleum refining and petrochemistry at the Academy of Science of the Republic of Bashkortostan and Sterlitamak petrochemical plant. This installation is simple in operation and enables making a number of multicomponent corrosion inhibitors [11].

3. Results
Perspectives for development of the corrosion inhibitors technologies may be defined under thorough analysis of preparation and application thereof, thereby enabling to efficiently provide for strong
renovation of the whole national economy of the Russian Federation in successful solving of priority government problems of high-tech and social development of the country.

4. References

[1] Rakhmankulov D L, Bugai D Ue, Gabitov A I et al 2007 Corrosion Inhibitors Vol. 4 Theory and practice of corrosion protection of oil-field equipment and pipelines (M: Chemistry) P 300

[2] Rozenfeld I L 1977 Corrosion inhibitors (M.: Chemistry) P 350

[3] Rozenfeld I L 1980 Scientific and practical achievements in making and applying the corrosion inhibitors in CMEA countries Protection of metals 16 3 pp 227-236

[4] Ivanov Ye S 1986 Corrosion inhibitors for steel in acidic media (M. Metallurgy) p 175

[5] Reshetnikov S M 1986 Inhibitors against acid metal corrosion (L.: Chemistry) P144

[6] Kuznetsov Yu I 2002 Current state of the theory of metal corrosion inhibitors Protection of metals V.38 2 P 122

[7] Kuznetsov Yu I 2004 Physico-chemical aspects of corrosion inhibition in aqueous solutions Successes of Chemistry V.73 1 pp 79-93

[8] Kuznetsov Yu I 2015 Advance in science of corrosion inhibitors Corrosion: materials, protection 3 pp 12-23

[9] Kuznetsov Yu I 2016 Organic corrosion inhibitors. Where are we now? Part 1 Adsorption Review Corrosion: materials, protection 3 pp 25-40

[10] Kuznetsov Yu I, Chirkunov A A, Semiletov A M 2019 Progress in inhibition of metal corrosion and outlook in application thereof in petrochemical branch Corrosion: materials, protection 11 pp 1-18 DOI: 10.31044 / 1813 - 7016–2019–0–11–1–18

[11] Gabitov A I, Rohnik L Z 2009 Development of optimum structure highly effective multicomponent inhibiting compositions by methods of mathematical planning experiment Bashkir Chemical Journal V.16 3 pp 113-115

[12] Gabitov A I 2019 Petrochemical Compound-Based Corrosion Inhibitors IOP Conference Series: Earth and Environmental Science: Vol. 272 022081

[13] Gabitov A I 2019 Application of Petrochemical Heterocyclic Compounds as Corrosion Inhibitors IOP Conference Series: Earth and Environmental Science: Vol. 272 022082

[14] Kuznetsov Yu I 2015 Advance in science of corrosion inhibitors Corrosion: materials, protection 3 pp 12-23

[15] Rakhmankulov D L et al 1975 Chemistry and technology of 1,3-dioxacycloalkanes Technology of organic substances. Results of science and technology V.5 (M.: VINITI) P 288

[16] Vildanov F Sh, Zlotsky S S, Latypova F N, Mazitov R M, Udalova E A, Shavshukova S Yu, Rakhmankulov D L 2009 a prominent scientist and architect of science and education (M.: Inter) P 488

[17] Bugai D E, Gabitov A I, Zlotsky S S, Rakhmankulov D L 1989 Complex mechanoelectrochemical approach to making stress metal corrosion inhibitors Abstracts of the USSR Academy of Sciences. 305 4 pp 887-889

[18] Bugai D E, Gabitov A I, Bresler I G, Rakhmankulov D L, Paushkin Ya M 1990 Applications of quantum chemical protection indices of corrosion inhibitors under explanation of protection mechanism Abstracts of the USSR Academy of Sciences 314 2 pp 384-386

[19] Gabitov A I 1998 The achievements and tendencies in the theory and practice of corrosion protection (Ufa: Reactive) P 122

[20] Rakhmankulov D L, Bugai D E, Gabitov A I et al 2005 Corrosion inhibitors V.3 Principles of technology for making domestic corrosion inhibitors (M.: Inter) P 346

[21] Sevastianov A A, Korovin K V, Zotova O P, Solovev D B 2018 Features of the Geological Structure and Estimation of the Extraction Potential of the Sediments of the Bazhenov Formation in the Territory of Khanty-Mansiysk Autonomous Okrug IOP Conference Series: Materials Science and Engineering 463 Part 1, Paper № 022004. [Online]. Available: https://doi.org/10.1088/1757-899X/463/2/022004