UDC 665.63

P.Topilnytskyy, PhD, V.Romanchuk , PhD
(National University "Lvivska Polytechnica", Ukraine)

Chemmotological aspects of corrosion inhibitors used in automobile gasolines and aviation fuels production

Since gasoline and diesel fractions contain corrosive and aggressive components, it is necessary to protect the equipment from corrosion. The corrosion inhibitors based on vegetable oil and animal fat with di- and triethanolamine have been synthesized, nitrogen-containing corrosion inhibitors have been obtained, their physical and chemical parameters have been determined. It was shown that inhibitors on the basis of plant and animal raw materials, obtained under certain synthesis conditions, are able to protect the metal surface of oil refining equipment.

Gasoline and diesel fuels production is multi-stage process. At first, the gasoline and diesel fractions are produced at primary oil distillation plants. Then the gasoline is hydrogenated and direcred to catalytic reforming. The high octane gasoline component is obtained and mixed up with gasoline fractions of other processes. Thus the commercial gasoline is produced. The diesel fraction is hydroisomerized, cetane-additive additives are added and commercial diesel fuel is produced [1].

Since gasoline and diesel fractions contain corrosive and aggressive components, it is necessary to protect the equipment from corrosion.

It is well known that the most simple and relatively inexpensive method of protecting equipment is the use of inhibitors [2-4]. A corrosion inhibitor, introduced into an aggressive environment, inhibits the corrosive destruction of metals. There are number of requirements for inhibitors: to provide a certain maximum protective action at low concentration; be technological (do not derange the normal technological mode of the plants, do not impair the quality of products and the catalysts action); be economical; be resistant to redox processes; be non-toxic and environmentally friendly.

At present, a large number of corrosion inhibitors are known for the metals protection. Most of them are organic compounds of various classes that contain heteroatoms: nitrogen, sulfur, oxygen, phosphorus, silicon [5-7]. The use of natural materials as alternative corrosion inhibitors, plant raw materials in particular, is a promising direction in this area. The advantages of these materials: they are non-toxic, biodegradable, renewable, relatively cheap, easily available and environmentally friendly. These natural materials contain phytochemicals (tannins, alkaloids, amino acids, flavonoids, saponin phenols, *etc*.) and functional groups such as $–NH_2$, $–NR_2$, –SR and –COOH, which provide adsorption of these substances on the metal surface.

A number of researches have been carried out regarding the use of natural products as corrosion inhibitors. Chigirinets *et al*. [8] proposed to use rape-cake extract, macerating in the 2-propanol alcohol. Alarmal Mangai *et al.* [9] showed the corrosion inhibition effect of alkaloid extract part of the plant *Trichodesma indicum*

(Linn) R. Br. of Boraginaceae family. Extracts of *Funtumia elastica*, *Piper guineense*, *Telfairia occidentalis*, *Azadirachta indica*, *Hibiscus sabdariffa*, *Ocimum gratissimum*, *Chamaemelum mixtum*, *Nigella sativa*, *Wrightia tinctoria*, *Ipomoea triloba*, *Lupinousalbus*, *Tridax procumbens* and *Chromolaena odorata* [10-20] have been investigated for their inhibition effects on various metals. Animal fats can also be used as corrosion inhibitors [21].

The purpose of this work is to obtain nitrogen-containing substances from plant and animal raw materials and to investigate their inhibition effects in highly corrosive media.

According to literature data [6], the corrosion inhibitors based on unsaturated acids exhibit a greater protective effect compared with those on saturated acids. Therefore, we used vegetable oils with the highest content of unsaturated acids: corn, soya and sunflower oils (Table 1). In soya oil the total content of unsaturated acids is 77.0 %, in sunflower – 91.5 %, in corn – 80.5 %. For comparison we used coconut oil, in which the content of unsaturated acids is quite small (8 %), but there is a sufficient content of saturated lauric acid (48 %). All these products are the mixtures of glycerol and the corresponding acids. To extend the range of raw materials and to compare the protective properties we also studied beef fat, because it contains 51.0 % of unsaturated acids [22].

To obtain inhibitors, the fat or oil was loaded into a three-necked flask and di- or triethanolamine was added. The amount of di- or triethanolamine was calculated based on the ratio of components in the reaction and their molecular weight. The flask was heated to 393, 403, 413 or 423 K and stirred for 3–5 h.

Amines of fatty acids are formed due to the reaction of beef fatty acids with diethanolamine. During reaction of vegetable oils with diethanolamine we received amines of fatty acids and glycerin, which is a part of the corrosion inhibitor. When the acids interact with triethanolamine, esters are formed. The density, refractive index and protective corrosion effect were determined in the resulting products.

Investigation of inhibition effect was carried out by a gravimetric method, developed by Gajek *et al*. [5]. Quantitative evaluation of the inhibitor effect (at a certain concentration) on the corrosion rate is characterized by a protective effect Z:

$$Z = \frac{V_0 - V}{V_0} \cdot 100\% \qquad (1)$$

where V_0 – corrosion rate of a metal in a corrosive medium, $g/(m^2 \cdot h)$; V – corrosion rate of a metal after introducing the inhibitor, $g/(m^2 \cdot h)$.

Corrosion rate V is calculated according to Eq. (2):

$$V = \frac{\Delta m}{S \cdot \tau} \qquad (2)$$

where Δm – reduction of the metal plate weight due to corrosion, g; τ - the experiment time, h; S – surface area of the test plate, m^2.

A jet fuel–water system with a ratio of 1:2 (v/v) was used as a simulated corrosive medium. The water phase with density of 1.12 g/cm^3 contains magnesium chloride, calcium and sodium [5]. The temperature under which the corrosion was determined in all cases was 333 K, the experiment time 2 h, the inhibitors consumption 0.6 ml per 300 ml of corrosive medium.

The study of the inhibition effect by the gravimetric method was carried out using a metal plate made of steel St20.

3. Results and Discussion

The synthesis conditions and obtained results are presented in Tables 1 and 2. One can see from Table 1 that the density and refractive index of the resulting products change within narrow ranges.

Table 1

Synthesis conditions and indices of the inhibitors from mixtures of vegetable oil or beef fat and diethanolamine

Sample	Temperature, K	Time, h	Components ratio, w/w	n_D^{20}	ρ_4^{20}	*Z*, %
Beef fat/diethanolamine						
1	393	3	75/25	1.4867	0.9646	26.09
2	403	3	75/25	1.4866	0.9859	48.91
3	413	3	75/25	1.4866	0.9741	47.83
4	403	3	65/35	1.4865	0.9914	46.74
5	403	3	85/15	1.4865	0.9570	–22.39
6	403	4	75/25	1.4652	0.9771	74.66
7	403	5	75/25	1.4663	0.9781	64.88
Vegetable oil/diethanolamine						
8	403	4	(sunflower) 78/22	–	–	80.34
9	403	4	(soya) 78/22	–	–	54.26
10	403	4	(coconut) 74/26	–	–	43.62

The protective effect *Z* varies depending on the product used (fat or oils), the amount of added diethanolamine, synthesis time and temperature. Thus, when using diethanolamine in the amount of 25 % for 3 h at different synthesis temperatures, the protective effect of the samples 1-3 was insignificant 26–49 %. Moreover, the product obtained at the lowest temperature (sample 1) had the smallest effect. Sample 4, obtained under similar conditions (temperature 403 K, time 3 h), but with a higher content of diethanolamine (35 %), showed a protective effect, similar to the previous products (46.74 %). And sample 5 with 15 % diethanolamine did not protect the metal surface at all.

With the increase in the synthesis time to 4 or 5 h (samples 6 and 7) we observed the considerable increase in the protective effect (74.66 and 64.88 %, respectively). So, when using inhibitors based on beef fat with diethanolamine, the protective effect of the resulting products passes through the maximum at 403 K, further increase in temperature leads to a slight decrease in the protective effect. The increase in the synthesis time influences the protective effect of substances more significantly, but also passes through the maximum. The optimum time is 4 h. Increasing or decreasing the ratio of components from a stoichiometrically calculated one leads to the decrease in the efficiency. The excess acid or amine content does not have a positive effect.

If we analyze the efficiency of amines derived from oils, we observe the dependence of the product's efficiency on the total content of unsaturated acids in the virgin oil. The highest protective effect has the product based on sunflower oil and the smallest based on coconut oil.

Table 2

Synthesis conditions and indices of the inhibitors from mixtures of vegetable oil or beef fat and triethanolamine

Temperature, K	n_D^{20}	ρ_4^{20}	*Z*, %
Beef fat/triethanolamine 64.5/35.5 (w/w), time 3 h			
393	1.4813	1.0230	79.52
403	1.4804	1.0130	77.92
413	1.4817	0.9839	76.38
423	1.4764	0.9965	67.69
Refined sunflower oil/triethanolamine 69.3/30.7 (w/w), time 4 h			
393	1.4672	0.9684	9.46
403	1.4822	0.9757	37.77
413	1.4804	0.9839	40.92
423	1.4789	0.9758	80.31
Crude sunflower oil/triethanolamine 69.3/30.7 (w/w), time 4 h			
393	1.4785	0.9192	4.69
403	1.4786	0.9704	69.31
413	1.4772	0.9789	75.62
423	1.4834	0.9844	21.23
Corn oil/triethanolamine 65.3/34.7 (w/w), time 4 h			
393	1.4792	0.9754	11.77
403	1.4825	0.9814	68.46
413	1.4749	0.9829	49.21
423	1.4814	0.9854	33.08
Coconut oil/triethanolamine 67.0/33.0 (w/w), time 4 h			
393	1.4830	0.9400	45.69
403	1.4815	0.9580	70.08
413	1.4795	0.9750	47.85
423	1.4818	0.9800	66.15

When producing esters based on beef fatty acids and triethanolamine, the optimal synthesis temperature is 393403 K; the efficiency of esters is significantly higher than that of amines. In the case of the use of triethanolamine, the protective effects of all products increase. At the same time, the greatest protective effect (80 %) is observed for the inhibitor, obtained from refined sunflower oil at 423 K for 4 h. The inhibitor obtained from beef fat at 393 K for 3 h also shows a high protective effect (79 %). The product from crude sunflower oil slightly protects the metal surface; the highest protective effect was 75 % for the product obtained at 413 K for 4 h. The same synthesis conditions were found to be the best for the inhibitors based on corn oil. For the inhibitors based on coconut oil the synthesis temperature is lower (403 K) and time 4 h.

Table 2 shows the synthesis of fat and oils with triethanolamine, the indices and protective effect of the resulting inhibitors.

The protective effects of esters derived from different oils have different dependence on the synthesis temperature. For refined sunflower oil, the protective effect increases significantly with the increase in temperature to 423 K, for crude sunflower oil the maximum efficiency is achieved at 403–413 K, for corn oil – at 403 K. The same as for the inhibitors obtained from oils and diethanolamine, esters show greater or less effect at different content of unsaturated acids in triglycerides of oil. Different effect of the product obtained from refined and crude oils can be explained by different content of saturated and unsaturated acids in the oils, as well as by the presence of impurities in crude oil which become an ineffective ballast. At the same time, despite the lowest content of unsaturated acids in coconut oil (7 %), this inhibitor shows a fairly high protective effect – 70 %. The highest protective effect (80 %) was shown by the inhibitor synthesized from refined sunflower oil at 423 K for 4 h.

When comparing the protective effect of the resulting inhibitors, it can be argued that all products (amines and esters) derived from oils and animal fat exhibit protective properties.

Conclusions

So, we determined the most optimum conditions for obtaining highly effective inhibitors: synthesis time 4 h, and the temperature 403 K in the case of diethanolamine, and 423 K in the case of triethanolamine. The greatest protective effect was found for the inhibitor based on refined sunflower oil, and both di- and triethanolamine. The total amount of acids in this oil was 91.5 %, which confirms the greater efficiency of this product compared to those that have saturated acids. Thus, amines and esters of sunflower oil acids exhibit an equally high protective effect even in highly aggressive corrosive media.

References

1. Topilnytskyy P., Grynyshyn O., Machynskyy O.: Technologia Pervynnoi Pererobky Nafty i Gazu. Vyd-vo Lviv Polytechnic, Lviv 2014.
2. Topilnytsky P.: Chem. Chem. Technol., 2007, **1**, 45.
3. Shalaby H., Ravindranath K., Tanoli N., Al-Wakaa B.: Case Stud. Eng. Failure Anal., 2017, **9(C)**, 1. https://doi.org/10.1016/j.csefa.2017.04.004
4. Ormellese M.: Corrosion in Oil and Chemical Industry [in:] Wandelt K. (Ed.), Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry, Elsevier 2018, 145-154.
5. Gajek A., Zakroczymski T., Topilnytsky P., Romanchuk V.: Chem. Chem. Technol., 2012, **6**, 209.
6. Romanchuk V., Topilnytsky P.: Chem. Chem. Technol., 2010, **4**, 231.
7. Goyal M., Kumar S., Bahadur I. *et al*.: J. Mol. Liq., 2018, **256**, 565. https://doi.org/10.1016/j.molliq.2018.02.045
8. Chygyrynets' E., Vorobyova V.: Chem. Chem. Technol., 2014, **8**, 235.
9. Mangai A., Ravi S.: J. Chem.,2013, **2013**, 4.

http://dx.doi.org/10.1155/2013/527286
10. Raghavendra N., Ishwara Bhat J.: Res. Chem. Intermed., 2016, **42**, 6351. https://doi.org/10.1007/s11164-016-2467-1
11. Adindu C. *et al*.: Int. Lett. Chem., Phys., Astron., 2016, **68**, 24. https://doi.org/10.18052/www.scipress.com/ILCPA.68.24
12. Njoku D., Ukaga I., Ikenna O. *et al*.: J. Mol. Liq., 2016, **219**, 417. https://doi.org/10.1016/j.molliq.2016.03.049
13. Okafor P., Ebenso E.: Pigm. Resin Technol., 2007, **36**, 134. https://doi.org/10.1108/03699420710748992
14. Eddy N., Ebenso E.: Pigm. Resin Technol., 2010, **39**, 77. https://doi.org/10.1108/03699421011028653
15. Patel N., Jauhari S., Mehta G.: e-J. Chem., 2009, **6**, S189. https://doi.org/10.1155/2009/413421
16. Oguzie E., Iheabunike Z., Oguzie K. *et al*.: J. Dispers. Sci. Technol., 2013, **34**, 516. https://doi.org/10.1080/01932691.2012.682008
17. Oguzie E., Ogukwe C., Ogbulie J. *et al*.: J. Mater. Sci., 2012, **47**, 3592. https://doi.org/10.1007/s10853-011-6205-1
18. Oguzie E.: Corros. Sci., 2008, **50**, 2993. https://doi.org/10.1016/j.corsci.2008.08.004
19. Oyedeji O., Adeniyi B., Ajayi O., Konig W.: Phytother. Res., 2005, **19**, 362. https://doi.org/10.1002/ptr.1679
20. Aribo S., Olusegun S., Ibhadiyi L. et al.: J. Assoc. Arab Univ. Basic Appl. Sci., 2017, 24, 34. https://doi.org/10.1016/j.jaubas.2016.08.001
21. Pujar M., Miller A., Proroka M. et al.: J. Mater. Sci. Lett., 2000, 19, 1797. https://doi.org/10.1023/A:1006782020757
22. Evdokimov A., Fuks I., Shabalina T., Bagdasarov L.: Smazochnye Materialy. Heft i gaz, Moskva 2000.