

Role of Organic Compounds as Corrosion Inhibitors for Metals and Alloys in Acidic Media – A Review

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Abstract

Corrosion control of metals and alloys is technically, economically, environmentally and aesthetically important. There are several ways for the protection metals and alloys from corrosion. One of most accepted option is to use inhibitors for protecting metals and alloys against corrosion. Many organic compounds having polar atoms such as N, O, S and P etc. have been extensively used for protecting various metals and alloys against corrosion. These organic compounds are adsorbed on the metal surface by these polar atoms and protective films are formed. The effects of various inhibitors on the corrosion of different metals and alloys in different acidic medium have been included in the present review.

Keywords: Corrosion, Inhibitors, Alloys, Metals, Polar.

I. INTRODUCTION

Corrosion is a phenomenon of universal interest. The word corrosion is derived from the Latin word *corrodere* which means to eat away. Thus corrosion may be defined as the slowly eating away of any material by the surrounding environment. Corrosion may also be considered as deterioration of a material or its properties because of its reaction with its environment. According to this general definition, decay, damage and deterioration of materials other than metals such as ceramics, plastics, wood, rubber etc. may also be called corrosion. However, since metals and alloys have and will undoubtedly continue to be the engineering materials of major concern, the corrosion term applies, in general to metals, alloys and other metallic materials.

Corrosion is a common cause of anxiety for metal users throughout the world since a long time. However, it was only in the sixties that the significance of corrosion was recognized in an economical context. It is expected that 1/4th part of the total production of metals and alloys go waste due to corrosion. Technological and economic consequences of the wastage of metals and alloys by corrosion cannot be ignored now. It is

possible to avoid about 30% loss due to corrosion if suitable measure are taken to control corrosion. Corrosion causes disastrous damage to metals and alloys structures causing economical consequences in terms of repair, replacements, product losses, safety and environmental pollution. Due to these harmful effects corrosion is an undesirable phenomenon that ought to be prevented (1).

There are several ways of preventing corrosion. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with the aggressive environment is one among the acceptable practices used to reduce or prevent corrosion. A corrosion inhibitor is a chemical substance which when added in small amounts to a corrosive environment, decreases and in some cases completely prevents the destruction of metals in corrosive media. Corrosion inhibitors are commonly added in small amounts to acids, cooling water, steam and other environments either continuously or intermittently to prevent serious corrosion. An inhibitor useful for a particular corroding system may not be effective for other corroding systems. Corrosion control by inhibitors in many cases, is found to be more suitable and has many advantages. A remarkable feature of the use of inhibitors to protect machinery, apparatus and structures against corrosion is the simplicity and cheapness of this method. A considerable lengthening of the service life of machinery is obtained with inhibitors, and in a number of cases the parts can be made out of ordinary alloys rather than enriched alloys.

Different types of organic compounds have been used as corrosion inhibitors and a partial account of them can be found in reviews by Putilova and others (2-5). Organic compounds containing N,S,O,P,As,Si etc., are known to act as inhibitors for corrosion of metals and alloys. Adsorption is the basis of inhibition mechanism, according to which inhibitors are adsorbed on the metal surface forming a protective layer. The inhibiting action exercised by organic compounds on the dissolution of metallic materials is normally attributed to interactions by adsorption between the inhibitor and the metal

surface. With every passing year corrosion inhibitors becomes increasingly important for the protection of metals and alloys in diverse branches of technology and economy. It can be stated without exaggeration that during recent years corrosion inhibitors not only have become a new independent mode of protection but also have altered significantly many classical protective media such as oils, greases, polymeric coatings, break fluids etc. Majority of the compounds or species used as corrosion inhibitors are organic in nature. An enormous number of organic compounds have been studied in their capacity as corrosion inhibitors for various metals and alloys in different acid solutions as corrosive media, by many workers. A brief review of the work done about organic inhibitors for corrosion protection of metals and alloys by various workers have been presented here.

II. H₂SO₄ SOLUTION AS MEDIUM

Antropov and his co-workers (6) carried out systematic studies of individual organic compounds as corrosion inhibitors, as well as studies of their mechanisms of action. The nitrogen containing compounds in the pyridine series considered included the following: pyridine, 2-picoline, 2,4,6-toluidine, aniline, ethyl aniline etc. Compounds of this series slightly inhibit the corrosion of iron in sulphuric acid solution. Quaternary salts of pyridine bases also manifest an inhibiting effect for zinc in 1N H₂SO₄. The protective properties of halides of substituted ammonium were investigated by Miskirdrh yan et al. (7). Of the compounds studied by them, the most effective in 6N H₂SO₄ were benzylallylamine hydrochloride, allylpiperidine hydrochloride, allylbenzylamine hydrobromide and triallylamine hydrobromide. The good protective properties of these compounds were attributed to the heightened adsorbptivity of iodine and bromine in comparison with chlorine. These compounds also show the protective properties at higher temperatures, indicating that the inhibitors act according to chemisorptions mechanism.

The protective properties of sulphur containing compounds in dilute sulphuric acid were investigated by Balezin et al. (8). They reported a rate of corrosion of steel in 0.2N H₂SO₄ as 1.4 mm/year at 20^oC. With a temperature rise of 10^oC the rate increases by a factor of approximately 2.5, to 9.1 mm/year at 40^oC, to 25 mm/year at 50^oC and to 60 mm/year at 60^oC. In the presence of an inhibitor the corrosion rate can be reduced to 0.3 to 0.8 mm/year. Of individual sulphur containing compounds, derivatives of 2-mercaptoimidazole were found to have the best protective properties. The optimum inhibiting effect

was for unsaturated compounds mixed with granulated 2-mercaptobenzimidazole. A mixture of propargyl alcohol with 2-mercaptobenzimidazole lowered the corrosion rate of iron by a factor of 200 to 400 at 50^oC and by a factor of 500 to 1000 at 70^oC. In the opinion of the authors, if this mixture is used in 0.2N sulphuric acid at 60^oC, carbon steels can be employed as structural materials for equipments.

Grigoryev (9) reported the decrease in the critical anodic current density for 18Cr-9Ni steel in solutions of sulphuric acid upto 14.3M, working with acrylic acid, maleic acid hexamethylenetetramine, aminophenol and dicyandiamide at various concentrations. He found that the critical anodic current density depended on the additive concentration, and gave an interpretation of the results obtained on the basis of the theory of the adsorption of organic molecules on the metal surface.

Mayanna and Setty (10) studied the kinetics of the dissolution of copper single crystal planes in areated 0.1N H₂SO₄ solution with various concentrations of benzotriazole. They concluded that benzotriazole acts as cathodic inhibitor at low concentration and as anodic inhibitor at high concentrations. At 7.5X10⁻³M, benzotriazole inhibits the corrosion to a maximum extent. The inhibition is more on the (100) plane than on the (110 or (111) plane of copper single crystal. Copper form a film with benzotriazole which brings mechanical passivity.

Corrosion protection properties of azoles (11), amines (12) and pyridine and its derivatives (13) towards the corrosion of 70/30 brass in sulphuric acid solution are reported by Chaudhary et al. The inhibitive efficiency of azoles for the corrosion of α -brass has been found to decrease in the order: 2-mercaptobenzothiazole > benzotriazole > benzimidazole. All the three azole compounds used were mixed inhibitors and inhibitive action is due to the formation of a protective complex film mainly with copper metal ions on the surface of the alloy. All the amine compounds studied show a poor efficiency and are anodic inhibitors. Pyridine, 2-picoline, 3-picoline and 4-picoline were also reported to decrease the corrosion rate of brass in 1% H₂SO₄. The inhibitive efficiency of these compounds may be arranged in the following order: 2-picoline > 4-picoline > 3-picoline > pyridine. The relative inhibitive efficiencies of these compounds are dependent on the relative position of N and -CH₃ group in the pyridine ring and the effective electron density which affects the surface adsorption characteristics. Malachite green, congo red, crystal violet, alizarin and methyl orange along with benzotriazole (14) have been reported to provide better protection from the corrosion and dezincification of

63/37 brass in 1% H₂SO₄ solution than in the presence of benzotriazole only. The inhibiting effect of pyridine, piperidine and 3-picoline on the corrosion of metallic glasses in 0.1M sulphuric acid solution are also reported (15). All the three compounds acted as mixed inhibitors and obey Langmuir adsorption isotherm.

Chaudhary and Chaturvedi investigated the inhibitive action of some azoles (16) and hexamethylenetetramine (17) towards the corrosion of mild steel in sulphuric acid solution. The effectiveness of the investigated azole compounds was found in the order: 4-amino-5-ethyl-3-mercapto-1,2,4-triazole > 4-amino-3-mercapto-5-ethyl-1,2,4-triazole > 4-amino-5H-3-mercapto-1,2,4-triazole. Low values of heat of adsorption is reported for all the azoles studied. Hexamethylene tetramine inhibited the corrosion rate with higher activation energy than that of the uninhibited system. It acts as a mixed inhibitor.

Chaudhary and Singh studied the inhibitive action of some azoles (18-20) and some other organic compounds containing nitrogen and sulphur (21-23) towards the corrosion of 304 stainless steel in 1.0M sulphuric acid. The inhibitive efficiency increases with the increasing concentration of azoles and decreases with increase in temperature from 20 to 40°C. All the studied azoles acted as cathodic inhibitors. DL-methionin was found to be very good inhibitor towards the corrosion of 304 stainless steel in 1.0M sulphuric acid solution. It acted as a mixed inhibitor and obey Langmuir adsorption isotherm equation. Out of dithiazone and thiosemicarbazide, dithiazone is a highly efficient inhibitor while thiosemicarbazide affords less efficiency towards the corrosion of 304 stainless steel. 2-Aminobenzene arsonic acid has been reported to be very effective inhibitor and acted as a mixed inhibitor.

Gurmeet Singh and Jha (24) studied the inhibitive action of resorcinol and pyrogallol for the corrosion of mild steel in 1.0N sulphuric acid solution. They reported that these compounds are predominately anodic inhibitors and inhibition efficiencies up to 82% can be obtained. The inhibition was assumed to occur via chemisorptions of the additive molecules. It was concluded that iron oxide and hydroxide were found on the surface when treated with resorcinol, whereas only iron oxide is found on the surface when treated with pyrogallol.

III. HCL SOLUTION AS MEDIUM

Hackerman et al. (25, 26) have compared the adsorption characteristics and inhibition efficiencies of 4-ethylpyridine with those of polyvinylpyridines having different degrees of polymerization. The authors have

shown that adsorption of the polymers takes place through several points of the molecule and that of the surface area of the metal inhibited in solutions of hydrochloric acid containing polyvinylpyridine is considerably greater than the area physically covered by the adsorbed molecules.

Nottes (27) has proposed the use of acetylene derivatives as inhibitors in petroleum refineries. The efficiency of 3-diethylamino-1-propyne, 3-dimethylaminobutyne, 3-benzylaminobutyne, 3-isopropylaminobutyne, 5-diethylamino-4-pentyn-2-ol and other compounds with a triple bond between carbon atoms were studied by him in solutions of hydrochloric, acetic and formic acids. This type of substances combines all the best inhibiting characteristics of the acetylenic derivatives with those due to the presence of nitrogen functions in the molecules, while the presence of hydroxyl groups affects their solubilities.

Kaesche and Hackerman (28) have investigated the inhibition of several aliphatic and aromatic amines on pure iron corroding in 1N hydrochloric acid. These authors observed in thirteen out of fourteen cases, that the inhibition was both anodic and cathodic but predominantly anodic. The exception was methylamine which acted only cathodically.

Klyuchnikov et al. (29) reported the results of protective properties of products of condensation of formaldehyde with amines. The compounds provided a good inhibiting effect. The most effective compounds in 7N HCl proved to be n-anisidine and n-aminophenol. With a rise in temperature the inhibiting effect of products of condensation of formaldehyde with amines is markedly increased, indicating an adsorption-chemical mechanism of action for these.

Desai and Rana (30) showed that sulphur containing organic compounds, benzyl thiocyanate and furfural are exceptionally effective suppressors of the corrosion of copper in hydrochloric acid solutions. Furfural afforded protection to copper at all concentrations of HCl, the efficiency being 90-98%. The amounts of furfural required to bring about efficient inhibition in dilute acidic solutions is greater than that required at higher concentrations of HCl solutions. According to the authors, the resin forming tendency of furfural appears to be responsible for the inhibiting power. Furfural have also shown very good properties in inhibiting corrosion of brass, aluminium and aluminium alloys (31). Its action must be connected with the tendency to form resinous products.

Fremier et al. (32) reported α - alkenylphenones as a new class of corrosion inhibitors for steel in strong HCl. It was found that when formulated with small amounts of surfactants, α - alkenylphenones provide excellent protection for oilfield steel in contact with strong HCl (up to 28%). The protection levels are similar to, and sometimes superior to those provided by alkynols.

Chaudhary et al. (33) have reported the inhibitive effect of 2-picoline, 3-picoline and 4-picoline on the corrosion behaviour of aluminium alloys in one percent hydrochloric acid. The inhibitors were found to retard the corrosion by predominantly acting on local cathodes although they were also partially effective on the anodes. Subramanyan et al. (34) have studied the protection properties of benzoic acid and its derivatives for the corrosion of steel in hydrochloric acid. It was found that the efficiency of corrosion inhibition was in the order: thiosalicylic acid > o-amino benzoic acid > p-amino benzoic acid > salicylic acid > benzoic acid > phthalic acid > nitro benzoic acid. The maximum inhibition efficiency shown by thiosalicylic acid is attributed to sulphur atom and also to the electron density at the benzene nucleus. Adsorption of the organic compound over the metal surface is considered to be responsible for inhibition.

IV. HNO₃ SOLUTION AS MEDIUM

Putilova et al. (35) studied the effect of carbamide and thiocarbamide on the corrosion of copper in nitric acid. These inhibitors have proved to be effective at a concentration of 25 mili mol/litre. The proactive effect in 5N HNO₃ is quite good and lasts for 5 days. Hydroxylamine hydrazine and phenyl hydrazine also exhibited protective properties. However, in concentrated solutions (6N to 9N) these compounds readily decompose and lose their protective properties.

Singh et al. (36) investigated to assess the inhibitive efficiency of benzoic acid and its hydroxy and nitro derivatives for 1060 and 3003 aluminium alloys in 20% nitric acid. They found that the parent compound, benzoic acid, was poor inhibitor with inhibition efficiency of the order of 16 to 20%. The inhibition efficiency exhibited by nitro derivatives of the benzoic acid are much higher as compared to that of benzoic acid. Hydroxybenzoic acid gives the maximum inhibition efficiency among all the compounds used by them. This enhanced efficiency may be advocated on the line that the adsorption of the inhibitor molecule take place via the hydroxyl group as well as through the delocalized π -electrons of the phenyl ring situated parallel to the electrode surface. This results in a greater surface area projected by the compounds on the metal surface, which causes greater protection.

Chaudhary et al. have investigated various organic compounds as corrosion inhibitors for many metals and alloys in different acid medium. They used o-, m-, p-tolyl thioureas (37), 1[(5-mercapto)-1,3,4-thiadiazolyl]-3-o-tolyl(38), p- toluidine, p-anisidine, p- chloroaniline, p-amino benzoic acid and p-phenetidine (39) for the corrosion of 1060 aluminium in nitric acid solution. It was observed that p-tolyl thiourea was more efficient than its other two isomers at all the three temperatures studied. All the three tolyl thioureas were found to be of mixed type of inhibitors. 1[(5-mercapto)-1,3,4-thiadiazolyl]-3-o-tolyl was found to be satisfactory inhibitor and not useful for longer duration of exposure. In the case of para substituted aromatic amines, p-amino benzoic acid showed maximum efficiency and the efficiency decreases in the following order: p-amino benzoic acid > p-anisidine > p-phenetidine > p-toluidine > p-chloro aniline.

Inhibitive effects of some azoles (40) such as 2-mercaptobenzothiazole, sulphathiazole and 1,2,3-benzotriazole and substituted urea (41) compounds for corrosion of aluminium in nitric acid have also been reported. Azoles were found to be most effective at 200 ppm concentration. At 250 ppm concentration, the inhibition efficiency of the compounds decreases, which is probably due to the formation of corrosion promoting species like S²⁻ and HS¹⁻.

V. CONCLUSIONS

Acid solutions are widely used in industries and some of most important fields of applications are acid pickling, chemical cleaning and processing, ore production and oil well acidification. Metals like iron, copper, aluminium etc. and their alloys being used in a wide range of acid environments. Organic compounds have been found to be very effective corrosion inhibitors for the protection of various metals and alloys from corrosion since long time. Though organic compounds proved to be very good inhibitors along with easy to use and also cheaper. However, the use of organic compounds as corrosion inhibitors is associated with the problem of creating environmental pollution and many of them are toxic in nature also. Therefore, recently the use of plants extract as corrosion inhibitors has been increasing rapidly as they are eco friendly and need of present world.

REFERENCES

- [1] J.Buchweishajja, Photochemicals as green corrosion inhibitors in various corrosive media-a review, Chemistry Department, College of Natural and Applied Sciences, University of Dares, Salaam.
- [2] I.N. Putilova, S. A. Balezin and V. P. Barannik, Metallic Corrosion Inhibitors, Pergamon Press, p. 30 (1960).
- [3] P Hersch, J. E. Hara, A. Robertson and S. N. Southerland, J. Appl. Chem. 11, 246 (1961).

- [4] G.Trabanelli and V. Carassiti, *Advances in Corrosion Science and Technology*, Vol. 1, Plenum Press, N. Y. (1970).
- [5] J. Bregman, *Corrosion Inhibitors*, Macmillan, N. Y. (1963).
- [6] L.I. Antropov and I. S. Pogrebova, *Izdat, VINITI, Moscow*, 2, 27 (1973)
- [7] S.P. Miskidzh yan, *Zashchita Metallov*, 2, 700, (1970).
- [8] S.A. Balezin, I. N. Putilova and V. P. Barannik, *Zashchita Metallov*, 4, 385 (1968)
- [9] V.P. Grigoryev, *Protection of Metals*, 1, 245 (1965)
- [10] S.M. Mayanna and T. H. V. Setty, *Corrosion Science*, 15, 627 (1975)
- [11] Pushpa Gupta, R. S. Chaudhary, T. K. G. Namboodhari and B. Prakash, *Brit. Corros. J.*, 17, 136 (1982).
- [12] Pushpa Gupta, R. S. Chaudhary, T. K. G. Namboodhari and B. B. Prasad, *J. Electrochem. Soc. India*, 32, 27 (1983)
- [13] Pushpa Gupta, R. S. Chaudhary, T. K. G. Namboodhari and B. Prakash, *Brit. Corros. J.* 17, 193 (1982).
- [14] Pushpa Gupta, R. S. Chaudhary, T. K. G. Namboodhari, B. Prakash and B.B. Prasad, *Corrosion*, 40, 33 (1984).
- [15] R.S. Chaudhary, T. K. G. Namboodhari, I. B. Singh and A. Kumar, *Brit. Corros. J.*, 24,273 (1989).
- [16] R.K. Chaturvedi and R. S. Chaudhary, *Corros. Prevention and Control*, 37, 26 (1990).
- [17] R.K. Chaturvedi and R. S. Chaudhary, *CHEMICON 90*, IT, BHU, Varansi.
- [18] A.Singh and R. S. Chaudhary, *J. Electrochem. Soc. India*, 44, 77 (1995).
- [19] Abhay Singh, *International Journal of Engineering Science and Computing*, 6, 8 (2016)
- [20] Abhay Singh, *Imperial Journal of Interdisciplinary Research*, 2, 11 (2016)
- [21] A.Singh and R. S. Chaudhary, *The Transactions of the SAEST*, 30, 104 (1995)
- [22] R.S. Chaudhary and A. Singh, *Bulletin of Electrochemistry*, 12, 585 (1996)
- [23] A.Singh and R. S. Chaudhary, *Brit. Corros. J.*, 31, 300 (1996).
- [24] Lakhan J. Jha and Gurmeet Singh, *The Transactions of the SAEST*, 26, 158 (1991).
- [25] R.R. Annand, R. M. Hurd and N. Hackerman, *J. Electrochem. Soc.*, 112, 138 (1965).
- [26] R.R. Annand, R. M. Hurd and N. Hackerman, *J. Electrochem. Soc.*, 112, 144 (1965).
- [27] E.G. Nottes, *Proceedings of 2nd European Symposium on Corrosion Inhibitors, Annali Univ., Ferrara*, p. 507 (1966)
- [28] H.Kaesche and N. Hackerman, *J. Electrochem. Soc.* 105, 4 (1958)
- [29] N.G. Klyuchnikov and G. L. Nemchinova, *Zashchita Metallov*, 7, 484 (1971).
- [30] M.N. Desai and S. S. Rana, *Proceedings of 2nd European Symposium on Corrosion Inhibitors, Annali Uni., Ferrara*, p 849 (1966).
- [31] M.S. Desai and S. M. Desai, *Proceedings of 2nd European Symposium on Corrosion Inhibitors, Annali Uni. Ferrara*, p 863 (1966).
- [32] W.W. Frenier, F. B. Growcock and V. R. Loop, *Corrosion*, 44,590 (1988).
- [33] P.N.S. Yadava, R. S. Chaudhary and C. V. Agarwal, *J. Electrochem. Soc. India*, 32, 235 (1983).
- [34] N.Subramanyan, S. Venkatakrishana Iyer and V. Kapali, *The Transactions of the SAEST*, 15, 251 (1980).
- [35] I.N. Putilova, S. A Balezin and V. P. Barannik, *Metallic Corrosion Inhibitors*, Pregamon Press, N. Y., p 31 (1962).
- [36] C.Chakrabarty, M. M. Singh and C. V. Agarwal *Corrosion*, 39, 481 (1983)
- [37] R.S. Chaudhary, D. D. N. Singh, P. N. S. Yadava and C. V. Agarwal, *J. Electrochem. Soc. India*, 28, 169 (1979).
- [38] D.D. N. Singh, R. S. Chaudhary and C. V. Agarwal, *J. Electrochem. Soc. India*, 28, 241 (1979).
- [39] R.S. Chaudhary, D. D. N. Singh and C. V. Agarwal, *J. Electrochem. Soc. India*, 27, 91 (1978).
- [40] D.D. N. Singh, R. S. Chaudhary and C. V. Agarwal, *Indian J. of Tech.* 18, 392 (1980).
- [41] D.D. N. Singh, M. M. Singh, R. S. Chaudhary and C. V. Agarwal, *Electrochim. Acta*, 26, 1051 (1981).