CORROSION OF METAL CONSTRUCTIONS UNDER THE EFFECT OF POLYMERIC COATING CONTAINING-FLAME RETARDANT SYSTEMS

A.M.Dorfman, V.I.Mikhailov, V.I.Kodolov, V.I.Povstugar
(Izhevsk Mechanical Institute, Izhevsk 426069, Udmurt Republic, Russia)

ABSTRACT

Polyethylene flame-protected coatings are known to have good reliability, chemical resistance, insulating characteristics and prevent the metal form corrosion. In real use, however, there is a danger of damage or exfoliation of the coating resulting in a clearance between the coating and the metal. Atmosphere-induced washout of the coating components in this case stimulate their aggregation on the metal surface which may cause its corrosion. The possibility of reducing corrosivity of the polyethylene coating containing the product of interaction of polyvinyl alcohol and methylphosphonic acid as a flame retadant additive by means of heterocyclic amine is studied in the paper. To stimulate the corrosive processes on a metal coating interface corrosive and polarisation measurements have been performed. It has been found that the degree of extract coating corrosion is determined by the concentration of methylphosphonic acid facilitating anode and cathode processes. The introduction of heterocyclic amine into a flame-retardant polyethylene promotes the retardation of both electrode processes, its ifluence on the anodic process being greater. The inhibiting effect of heterocyclic amine is supposed to be connected with the appearance of an additional absorption potential. In this case the effectiveness of heterocyclic amine decreases with pH icrease and this may be connected with the concurrence in the adsorption of hydroxyl and amine on the surface of iron. The conclusion of the possibilty to use the inhibitors of acid corrosion for the decrease of flame retardant coating corrosivity has been made.

Key words: corrosivity, polarisation measurements, flame-retardant additive, heterocyclic amine, methylphosphonic acid.

INTRODUCTION

It is known that the diffusion of atmospheric moisture in the interphase metal/low flammable polyethylene containing as flame retardant additives the products of polycondensation of methylphosphonic acid (MP7 with polymers results in the washout of MP due to partial hydrolysis of flame retardant additive and metal corrosion rate icrease [1].

One of the way to reduce the metal corrosion rate in the presence of acids is to use corrosion inhibitors.

The aim of research was to compare the corrosivity on carbon steel of flame-protected polyethylene, containing as a corrosion inhibitor a heterocyclic amine (A), which improves at the same time the flame protection of the polethylene composition.

EXPERIMENTAL

Low density polyethylene 3-22 mass % flame-retardant additives (M) as a modifier derived from a) polyvinyl alcohol and b) MP at their mass ratio 1,0 : 1,3, has been taken for the research. As an inhibitor we used heterocyclic amine A, whose content in the composition was 10% of MP mass taken for the preparation of the flame-retardant additive.

The flame-protected composition was obtained by the mixture of components with the subsequent extrusion at 417-437K and by the pressing of samples to receive the film with a thickness of 0,5 mm.

The notation of the sample composition includes data a) on the presence of heterocyclic amine A, b) as well as on a qualitative composition of the flame-retardant additive and c) its content in the polymeric composition. As an example of the notation of the composition containing the heterocyclic amine A and 6 mass % M is PEMA-6; and as an example of the composition containing 22 mass % M is PEM-22. As working solution we used extracts 4.500 .g of flame-protected polyethylene in one litre of the starting solution (a) 30 mg/l NaCl + b) 70 mg/l Na_2SO_4.

Methods of preparation and analysis of working solutions, as well as polarization potentiodynamic and corrosion research have been described [1]. Factor of acceleration of electrode reactions γ calculated from the polarizational curves according to formula $\gamma = j/j_{st}$ where j_{st} and j is the current density in the starting and working solutions, respectively. Cathode current was determined at the potential $E_c = -0,7V$; and anode current - at $E_a = -0,2v$.

RESULTS AND DISCUSSIONS

1. It has been found that the behaviour of steel under test is characterised by the corrosion increase during of whole testing period.

Compared with the starting solution all the working ones except for the extracts PEMA-3 and PEMA-6 increase the corrosion losses of steel (Table), i.e., they are corrosive ones. pH and MP concentration

Table. Characteristics of extracts of flame-protected polyethylene composition

Extract	Concentration of MP, M x 10^4	pH	Corrosion losses of steel after 48 hour testing, g/m^2
Starting solution	0	5,85	2,80
PEM-3	4,73	3,58	2,90
PEMA-3	4,74	3,60	2,78
PEM-6	7,62	3,22	3,00
PEMA-6	7,60	3,21	2,82
PEM-11	15,13	2,81	4,32
PEMA-11	15,10	2,81	3,72
PEM-17	22,40	2,71	5,50
PEMA-17	22,31	2,71	4,07
PEM-22	27,65	2,65	6,44
PEMA-22	27,74	2,64	4,14

in the extracts of the samples PEM and PEMA, containing equal quantities of flame-retardant additives have similar values, which is the evidence of the homogeneous mechanism of MP extraction from the samples. However, in all cases the corrosivity of PEMA is lower than the corrosivity of PEM and this may be accounted for an inhibiting influence of heterocyclic amine A.

2. Fig. 1 illustrates some results of polarizational measurements. Anode curves in the starting solution are of the form typical of electrodes in the absence of the passivity phenomena and the diffusion limiting current in the cathode potential area (j_d) is conitioned by a slowed down diffusion of oxygen onto the electrode surface in a neutral salt solution[2]. Unlike the starting solution, the rate of both electrode reactions in the extracts of all flame-retardant polyethylene considerably increases. The comparison of these rates shows that in PEMA extracts they are in all cases lower than in PEM extracts which is caused by a specific influence of heterocyclic amine A. The processing of the experimental data polarizational measurements (Fig.2) showed that the acceleration of electrode processes in the exrtacts was proportional to theMP concetration in them. This effect is explained by the fact that with the appearance of MP in an agressive medium of the starting solution there appeares one more depolarizer - hydrogen ions. In polarisational measurements this results in the increase of j_d. The stimulation of the anode process is accounted for an increased solubility of the anode reaction products in the acidified medium of the electrolyte which decreases the overvoltage of the iron solubility.

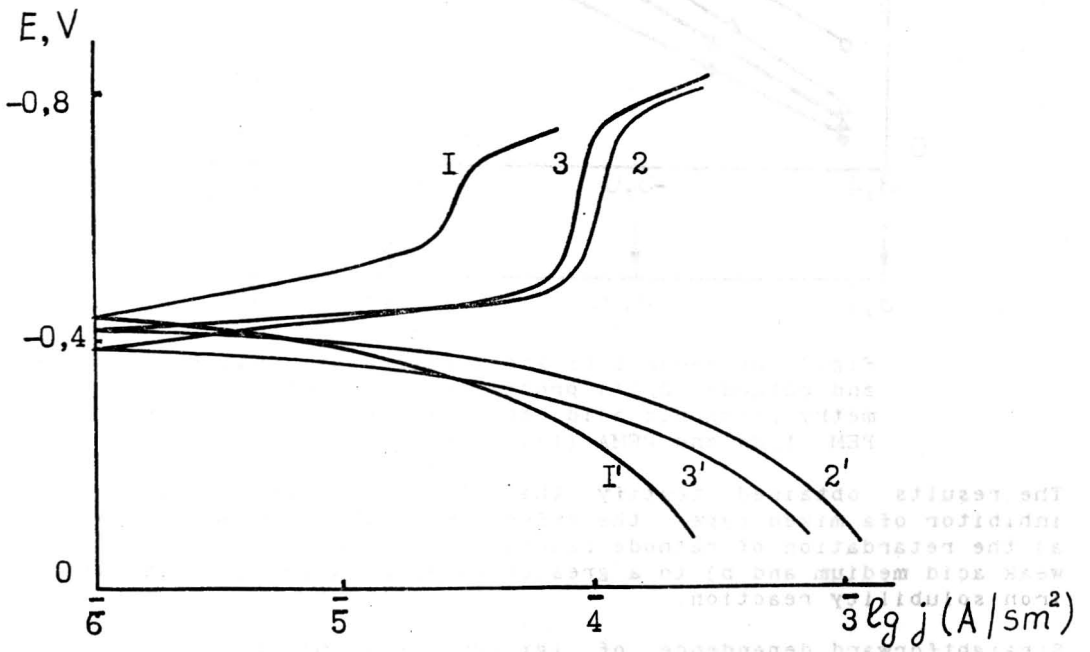

Fig. 1. Cathode (1-3) and anode (1'-3') polarization curves of carbon steel in working solutions. 1, 1'-starting solution; 2, 2'-extract PEM-22; 3-3'--extract PEMA-22.

Introduction of heterocyclic amine A into the flame-protected polyethylene promotes retardation of both electrode processes. But influence on the anode process is more evident.

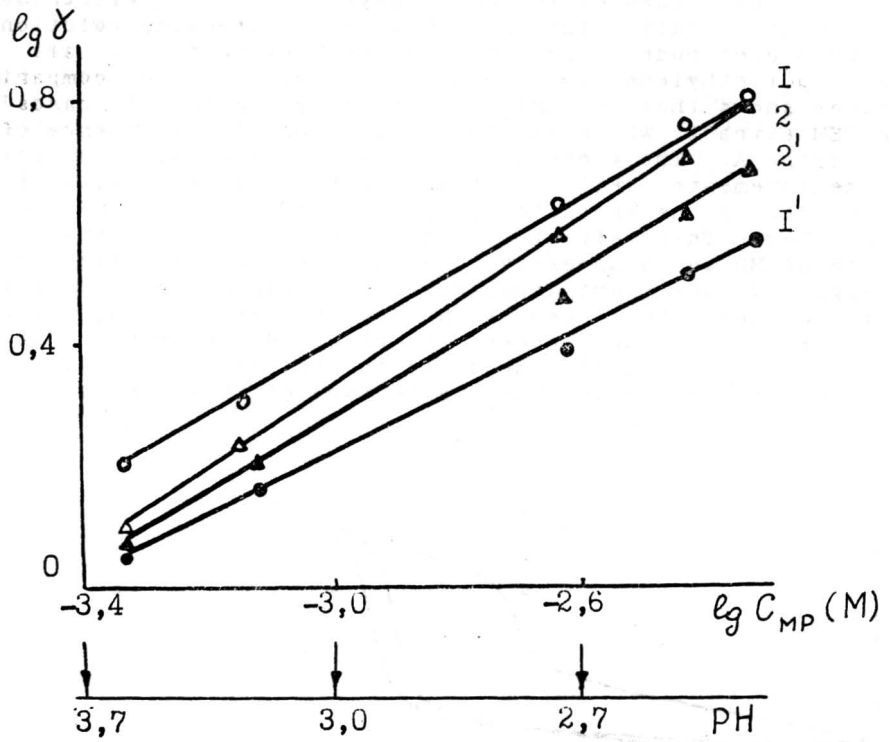

Fig.2. Dependence of acceleration of anode (1, 1') and cathode (2, 2') processes of carbon steel upon methylposphonic acid concentration (C_{MP}) in PEM (1, 2) and PEMA (1', 2') extracts.

The results obtained testify that the heterocyclic amine A is an inhibitor ofa mixed type, the effect of which is connected with a) the retardation of cathode reaction of hydrogen extraction in a MP weak acid medium and b) to a greater extent, with the retardation of iron solubility reaction.

Straightforward dependence of lgγ-lgC confirms the appearance of additional adsorption potential of heterocyclic amine A on a uniformly heterogeneous surface[3]. In this case the efectiveness of heterocyclic amine A with pH increase decreases. This may by associated with the concurrence in adsorption of hydroxyl or amine on the surface of iron.

Thus, the results presented show that the introduction of the corrosion inhibitors can greatly reduce the corrosivity of the flame-protected coating, increasing by this the reliability of its usage.

REFERENCES

1. Dorfman A.M., Michailov V.I., Semakina N.V. et al. Influence of fire-proofing components in polyethylene on steel corrosion, Metal Protection, 27 (1991), (6), 1045 (in Russian).
2. Scorchelletty V.V. Theoretical principles of metal corrosion. Chemistry, Leningrad (1973), 263 (in Russian).
3. Reshetnikov S.M. Inhibition of acidic metal corrosion. Udmurtia, Ishevsk (1980), 38 (in Russian).