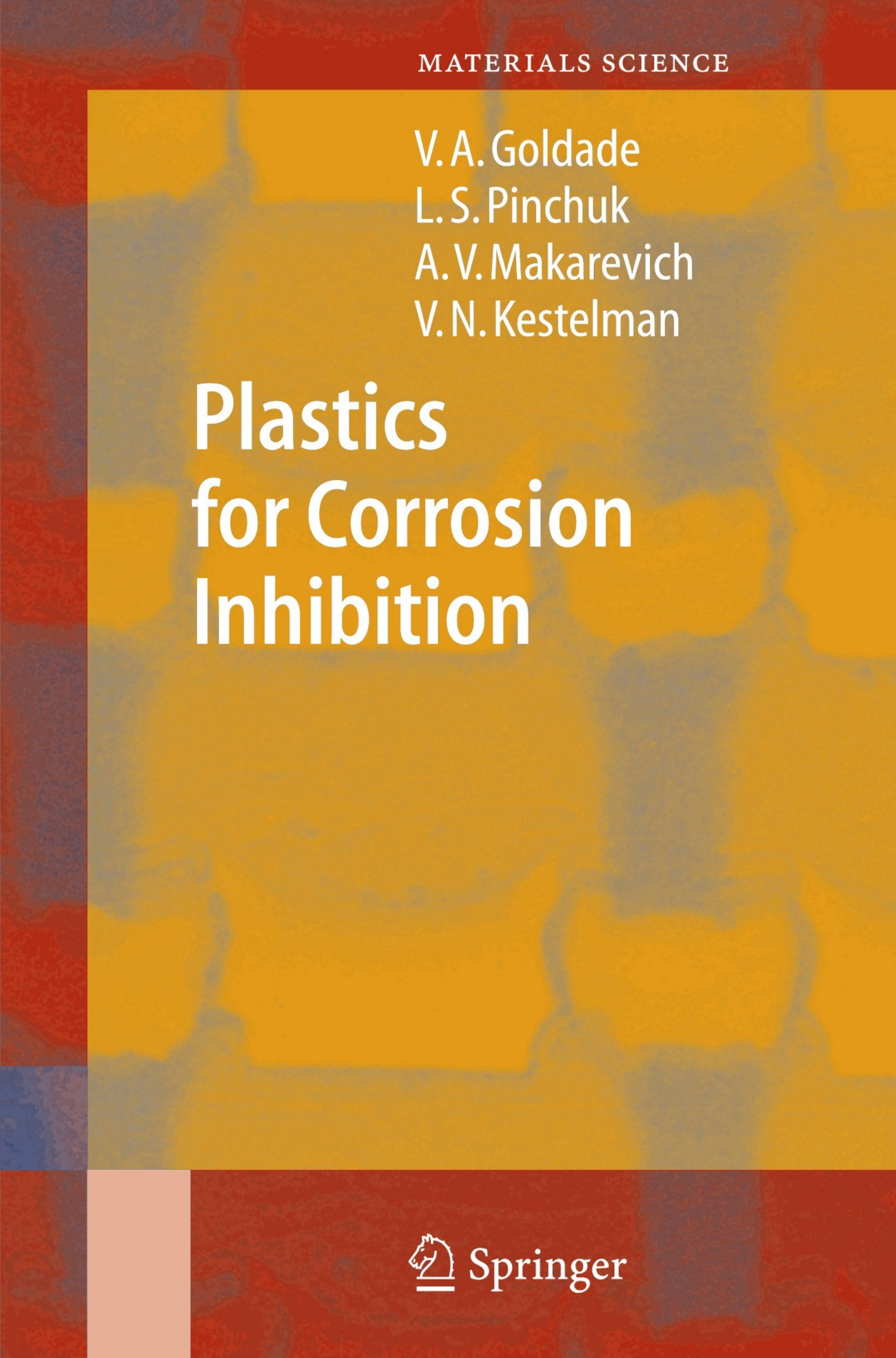

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L. S. Pinchuk
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Plastics for Corrosion Inhibition

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Prof. Victor A. Goldade
Prof. Leonid S. Pinchuk
Dr. Anna V. Makarevich
Metal Polymer Research Institute
National Academy of Sciences of Belarus
32a Kirov St.
246050 Gomel, Belarus
E-mail: vgoldade@tut.by

Prof. Vladimir N. Kestelman
KVN International
632 Jamie Circle
King of Prussia
PA 19406, USA
E-mail: kvnint@earthlink.net

Series Editors:

Professor Robert Hull
University of Virginia
Dept. of Materials Science and Engineering
Thornton Hall
Charlottesville, VA 22903-2442, USA

Professor R. M. Osgood, Jr.
Microelectronics Science Laboratory
Department of Electrical Engineering
Columbia University
Seeley W. Mudd Building
New York, NY 10027, USA

Professor Jürgen Parisi
Universität Oldenburg, Fachbereich Physik
Abt. Energie- und Halbleiterforschung
Carl-von-Ossietzky-Strasse 9–11
26129 Oldenburg, Germany

Professor Hans Warlimont
Institut für Festkörper-
und Werkstofforschung,
Helmholtzstrasse 20
01069 Dresden, Germany

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Preface

One of the key problems of failure-free operation of machinery is prevention of corrosion. The global scale of modern production makes this problem even more critical. At the beginning of the 21st century industrial contamination and the corrosion-active nature of the environment reached a level such that corrosive damage of materials became commensurate with their production volume and expenditure on anticorrosion protection of machines became comparable with investments in basic production. Anticorrosion techniques changed from being an auxiliary service to industrial enterprises into a developing, scientifically intensive and generously financed branch of production.

Polymers occupy a very specific place amongst anticorrosion techniques. Polymers combine good chemical resistance with impermeability to different media and unusual deformation characteristics. The main principle of their application as anticorrosion means is the creation of a tight barrier that insulates metal machine parts or constructions from corrosion agents. The advantages of polymers allow the creation of such a barrier at minimal cost, providing protection of the working machines from corrosion, combining their manufacture with preservation and decreasing the cost of anticorrosion. This is one of the main reasons why world production of polymer materials increased by almost 50% in the past decade.

Films and coatings are the simplest and most economical type of polymer anticorrosion elements. Their specific material consumption (the ratio of the element's mass to the protected metal hardware volume) is 5 to 20 times less than that of any other kind of polymer anticorrosion means. Application of polymer film elements meets the demands of economy of hydrocarbon raw materials resources, which are restricted and not renewable. Specialization of films and coatings to their fields of application in anticorrosion protection influenced their production technologies and design of the technological equipment. Almost all modification methods, including filling, plastification, gluing, orientation stretching and the effect of physical fields, are used for polymer formation. During recent decades there has been a significant increase in the production of anticorrosion films and coatings based on high-tech, multifunctional and comparatively cheap thermoplastics such as PVC, ethylene copolymers with vinyl acetate, high-molecular PE and conducting polymers (organic metals). The list of anticorrosion film elements has broadened and includes multilayered, shrinking and stretching films, those with regulated adhesion, damping air layers as well as gas-filled (foamed) and liquid-filled plastics.

The global production of polymer films and coatings is now approaching stable growth. Behind the stabilization or decrease of the production of traditional engineering materials (cast iron, steel and nonferrous materials) is generally recognized and convincing proof of the increasing role of anticorrosion polymer film elements in industrial production.

The corrosion-active nature of the environment in combination with frictional effects can initiate the most dangerous type of corrosion damage – corrosion-mechanical wear of metals. Wear by friction alone presents an acute problem for machinery. To solve this problem, large capital investments are spent on the repair of machines and production of spare parts. The cost of the working machines is constantly being reduced due to depreciation. The efficiency of the majority of machines is far below 50% because of, first of all, losses due to friction. Corrosion-mechanical wear of metals significantly aggravates the tribological problem. It is sufficient to consider the following examples.

Worn out internal combustion engine (due to wear caused by friction and high-temperature corrosion) increase contamination of the environment by 25–30%. Depressurization of industrial apparatus with movable seals greatly increases the danger to staff as well as for the environment. It is socially very important to increase the lifespan of implanted endoprostheses containing friction joints operating in chemically active biological fluids. The application of antifrictional polymer materials enabled a decrease in the acuteness of the tribological problem.

The efficiency of polymer materials as an anticorrosion mean of protection of metal parts from corrosion can be significantly raised by modification of polymer binders using corrosion inhibitors for metals. In this case it becomes possible to realize both the barrier and inhibition mechanisms for metal protection from corrosion in the anticorrosion element. Anticorrosion polymer elements as a source of electric field can hamper corrosion processes and corrosion-mechanical wear of metal parts by the electrochemical mechanism. Realization of the barrier, inhibition and electrochemical mechanisms of anticorrosion protection with the help of polymers not only allows a profound improvement in the anticorrosion protection of metal parts but comes close to the creation of “smart” anticorrosion plastics and anticorrosion systems.

Today, mechanical engineering has at its disposal a broad range of polymer materials containing contact and volatile corrosion inhibitors, as well as inhibitor complexes. Inhibited plastics are more efficient means of protecting metals against corrosion than traditional polymer materials. Their composition, molding procedures and design of technological equipment for the treatment of inhibited polymers are commonly patented. Meanwhile, eminent scientific and commercial centers worldwide investigate the issues of scientific development, production and applications of these materials. Significant expense on this research is quickly recouped as a result of abated corrosion damage. The methodology and technological concepts of developing inhibited polymer films, coatings and structural plastics and the assimilation of polarized polymer elements into anticorrosion systems are discussed in the present book. A special chapter is devoted to inhibited engineering materials such as glues, sealants, plastic carriers of corrosion inhibitors, inhibited plastic containers and microencapsulated corrosion inhibitors (CI).

The production and application of inhibited plastics affect many aspects of ecology. Polymer modification by various CI results in the emission of considerable amounts of toxic substances. Up to 85% of inhibited polymer films and plastic containers are intended for one use only and become industrial and domestic waste. Recycling or annihilation of these materials are serious technical problems complicated by the necessity to collect waste and other management problems. Nevertheless, the efficiency of anticorrosion techniques depends heavily on the solution of these problems. A number of countries in the world have adopted long-term programs for the recycling of polymer wastes, increased the funding of extraction of valuable components and elaboration of low-waste plastic technologies.

The statistics of the global production and consumption of anticorrosion materials bears witness to the fact that inhibited polymer materials are one of most promising approaches to decrease the losses from metal corrosion. Their production and application technologies are related to non-traditional fields of processing polymer materials and many of their specific characteristics are not reflected in technical literature, for various reasons. These questions are described in this book devoted to the means of anticorrosion protection of metals. The authors hope that the book will be of interest to professionals engaged in the spheres of protecting metals from corrosion, materials science, plastics processing technology and engineering ecology.

The authors express their gratitude to Prof. A.S. Neverov and Ph.D. I.V. Tsarenko for valuable ideas concerning modification technologies of polymer films by metal corrosion inhibitors, to S.Ya. Liberman and E.I. Parkalova for industrial use of the technology of inhibited plastics and to S.V. Zotov and L.S. Pushkina for their help in the preparation of this book.

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V.A. Goldade
L.S. Pinchuk
A.V. Makarevich
V.N. Kestelman

Contents

List of Abbreviations

AFM	atomic force microscopy
AKOR *(CI trademark)*	mineral nitrated oil
ATet	5-aminotetrazole hydrate
ATR	aatenuated total reflectance
ATr	3-amino-1,2,4-triazole
BMEA	benzoate of monoethanolamine
BMP *(CI trademark)*	neutralization product of urea-sulfated mineral oil
BTA	benzo-1,2,3-triazole
CAC	cyclohexylamine chromate
CEVA	copolymer of ethylene and vinyl acetate
CFD	copolymer of formaldehyde with 1,3-dioxolane
CI	corrosion inhibitor
CM	composite material
CTD	copolymer of trioxane with 1,3-dioxolane
DEL	double electric layer
Dichan	dicyclohexylamine nitrates
DMSO	dimethyl sulfoxide
DOP	dioctyl phthalate
DSC	differential scanning calorimetry
DSMO	*(CI trademark)*
DTA	differential thermal analysis
EIS	electrochemical impedance spectroscopy
ESCD	efficient surface charge density
FO	fuming-oxides
G-2 *(CI trademark)*	hexamethylenimine m-nitrobenzoate
GRM *(CI trademark)*	tar of vegetable oil and inedible fats
HDPE	high-density polyethylene
IFHAN-1 *(CI trademark)*	1-diethylamine-2-methylbuthanone-3
IFHANGAZ-1 *(CI trademark)*	dialkylaminoacrylonoitryle + dialkylamine
INHAM	inhibited antifrictional materials
IPF	inhibited polymer films
IRS	infrared spectroscopy
KSK *(CI trademark)*	sulfated acidic tar

LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
M-1 *(CI trademark)*	salt of cyclohexylamine and SFA
M1–P–M2	metal 1 – polymer – metal 2 systems
MNI-3 *(CI trademark)*	oxidized petrolatum
MNI-7 *(CI trademark)*	oxidized ceresin
MO	mineral oil
MPC	maximum permissible concentration
MPE	metal-polymer electret
MPJ	metal-polymer joint
MSDA-1 *(CI trademark)*	salt of dicyclohexylamine and SFA
MTet	5-methyltetrazole
NDA	nitrate of dicyclohexylamine
NG-203 *(CI trademark)*	oil solution of potassium sulfonate and oxidized petrolatum
PA	polyamide
PAni	polyaniline
PAN	polyacrylonitrile
PC	polycarbonate
PE	polyethylene
PET	polyethylene therephtalate
PFR	phenol-formaldehyde resins
PHC	polyheterocyclic compounds
PhTet	5-phenyltetrazole
PI	polyimide
Pl	plasticizer
PMMA	polymethyl methacrylate
PP	polypropylene
PPl	pentaplast (penton) – [poly-[3,3-bis-(chlormethyl)oxetane]
PPy	polypyrrole
PS	polystyrene
PTFCE	polytrifluorinechlorine ethylene
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	polyvinyl acetate
PVAL	polyvinyl alcohol
PVB	polyvinyl butyral
PVC	polyvinyl chloride
PVDC	polyvinyliden chloride
PVF	polyvinyl formal
PVFE	polyvinyl formal ethylal
RH	relative humidity
SB	sodium benzoate
SCC	stress corrosion cracking

SFA	synthetic fatty acid
SEM	scanning electron microscopy
SIM *(CI trademark)*	condensation product of alkenyl succinic anhydrate and urea
ST	selective transfer
Tet	tetrazole
Tr	triazole
TSC	thermally stimulated current
TSD	thermally stimulated depolarization
UHMWPE	ultrahigh molecular weight polyethylene
Ukramin *(CI trademark)*	a product of neutralizing fatty acids by monoethanol amine
VCI	volatile corrosion inhibitors
VITAL *(CI trademark)*	a mixture of potassium and triethanolamine salts of unsaturated fatty acids of tall oil
VNH-5 (*CI trademark*)	benzo-1,2,3-triazole subjected to heteroalkylation
VNHL-20 *(CI trademark)*	dimorpholinephenyl-methane
VNHL-49 *(CI trademark)*	N-cyclohexylphenylimine
WI	wear inhibitors
XPES	X-ray photoelectron spectroscopy
XSA	X-ray structural analysis

1 Design Principles of Plastics Containing Metal Corrosion Inhibitors

Design of plastics incorporating corrosion inhibitors (CI) presents an intricate scientific and technical problem. Knowledge from different scientific domains, including materials science, physical chemistry, electrochemistry, physics of dielectrics, physics of polymers, plastics processing technologies and tribology, is necessary to solve the problem. This interdisciplinary problem challenges the specialists in various fields with unexpected results. Any solution will have a profound commercial impact since: (i) polymers are used in the majority of products in combination with metals, (ii) contacts of metals with other materials either in the atmosphere or technical media are a potential hotspot for corrosion and, (iii) inhibited plastics have proved to be the most efficient means of eliminating corrosion available today.

Plastic containing CI is in its essence a composite material. Inhibitors and special additives, which also have a function regulating physical-chemical interactions between the polymer and inhibitor, are spread within the polymer component of the composite at a given degree of cohesion with the polymer. Compatibility of the CI with the polymer binder should not be too high as the inhibitor would not be released from the composite. In the case of low compatibility the release rate of the inhibitor will be too high and the life of the plastic as an inhibitor carrier would be unacceptably low.

Production of such composite materials encounters a serious technological obstacle in the low thermal stability of both polymers and CI. Moreover, there is always a danger of impairing the inhibitor's properties during joint thermo-mechanical processing with the polymers, in which the inhibitor loses its volatile components when heated to the polymer softening point. Therefore, technological procedures for combining polymers and inhibitors are, as a rule, at the level of inventions and often constitute the "know-how" of the developers of the inhibited plastics.

These materials are highly efficient as a means of corrosion inhibition due to their ability to realize almost all inhibition mechanisms of metal corrosion, namely: the barrier mechanism connected with the impenetrability of polymers for most corrosion media; the inhibition mechanism induced by a specific action of the inhibitors on the corrosion process kinetics; the protecting mechanism related to the effect of the polarizing charge formed in the plastic upon distribution of electrode potentials within the corrosive system, among others. Due to the diversity of these mechanisms the methods for estimating efficiency of plastics containing CI often results in incommensurate results. The methodology of selecting test methods for inhibited plastics involves a number of factors; the key is approximation of the testing scheme to the real operation conditions of an article along with simplification and acceleration of the experiment.

Materials of the considered class are used in corrosion-proof goods in the form of films, coatings and structural products. The films are commonly used in packaging, the coatings are used for protection of machinery and buildings with large specific area, and the structural products are predominantly used in fIt follows from equation It follows from equation riction joints operating in hostile media. The form of inhibited plastics depends on their processing technique, structure and characteristics.

The present chapter, which is *per se* an introduction to this book, is devoted to the topics above.

1.1 Underlying Notions

As the subject of the present book lies at the junction of several sciences, it will be expedient to give some principle terms to be used in further narration. There are three groups of terms related to metal corrosion, composite materials and tribology.

1.1.1 Corrosion of Metals

Metal corrosion is a physical-chemical interaction between a metal and a medium leading to degradation of service properties of the metal and the medium or a technical system they constitute. A chemical reaction between a metal and a medium, or their components, at their interface lies at the base of metal corrosion.

The mechanism for metal corrosion depends, first of all, on the type of hostile medium. *Gas corrosion* occurs in metal contact with an active gas. A layer of solid corrosion products (scale) is formed on the metalware surface in dry oxidative gases at elevated temperatures. Metal corrosion in electrolyte solutions, even if the solution is in the form of a thin film on a metal surface, follows the reaction

$$\mathrm{M} + \mathrm{Ox} = \mathrm{M}^{z+} + \mathrm{Red}\ , \tag{1.1}$$

where M is the metal, Ox is the oxidant particle, Red is its reduced form; Ox acquires a charge $+ze$, and Red acquires a charge $-ze$ (where e is the electron charge). In the majority of cases this reaction follows the electrochemical route, i.e. an atom M and a particle Ox are not in direct contact but the electrons are transferred from M to Ox through M's conduction zone (Fig. 1.1).

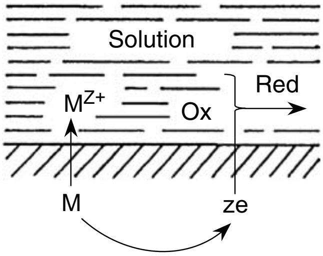

Fig. 1.1. Scheme of electrochemical corrosion mechanism of metals [1]

Electrochemical corrosion of metals follows the scheme indicated in Fig. 1.1 in two reactions, i.e. anodic dissolution of the metal and cathodic reduction of the oxidizer:

$$\mathrm{M} = \mathrm{M}^{z+} + ze\ , \tag{1.2}$$

$$\mathrm{Ox} + ze = \mathrm{Red} \tag{1.3}$$

These reactions are totally independent but interrelated through electric neutrality of the metal-electrolyte solution system.

Metal corrosion is a spontaneous process accompanied by a decrease in Gibbs' energy in the corrosion system. The Gibbs' energy varies in metal corrosion in a similar way to in any other spontaneous chemical reaction. Thermodynamic instability of the metal in contact with an electrolyte solution is judged from the magnitude of its electrode potential. Let us consider its mechanism.

Transfer of charge carriers from the metal to the electrolyte solution as well as movement of ions in the electrolyte are hampered by the corrosive system. The electrolyte solution induces the formation of a surface layer in the vicinity of the metal electrode surface consisting of spatially separated positive and negative charge carriers, which is called a double electric layer. Spatial separation of charges is always accompanied by a potential difference, therefore the double layer exerts a perceptible influence on the rate of electrode processes. The double layer consists of two parts: a compact layer and a diffusive layer (Fig. 1.2).

The compact, or Helmholtz, layer is the closest to the surface, in which the charge distribution and potentials change linearly with distance from the electrode surface. The potentials change exponentially when the more diffused outer Gouy–Chapman layer is formed.

The corroding metal potential is inconstant since it is affected by corrosion factors varying in time. As soon as the electrochemical corrosion becomes stationary, the electrode potential acquires a constant value E_{corr}. Once the stationary potential or the corrosion potential has stabilized, velocities of the anodic (1.2) and cathodic (1.3) reactions on the electrode equalize. E_{corr} measured in standard conditions relative to some standard reference electrode

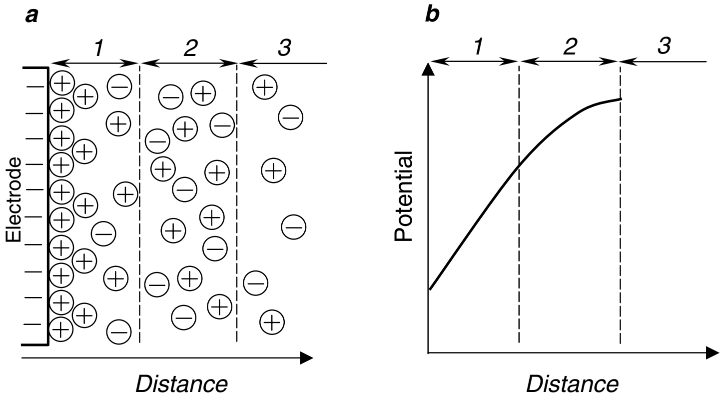

Fig. 1.2. (**a**, **b**) The double layer. Distribution of ions as a function of distance from the electrode behaving as an anode (**a**) and variation of potential with distance (**b**) for the model shown. (1) Helmholtz layer, (2) Gouy–Chapman layer, (3) bulk solution

is called the standard electrode potential E_0. Metals are placed according to ascending electrode potentials in Table 1.1 [2,3].

The electric current passing through the corrosive system changes the electrode potential. *Polarization* is the deviation of the electrode potential from the equilibrium state when electric current is passed through the electrode-electrolyte solution interface. The unequal rates at which separate stages of the total electrode process are running are the reason for this polarization. The polarization is called concentration polarization when an insufficient amount of the reacting substance is fed to the electrode surface and its concentration near the electrode is less than its volume content in the corrosive system. The polarization is called electrochemical polarization when the limiting stage of the electrode process turns out to be the charge transfer through the electrode-solution interface (Fig. 1.2). There are also the anodic and cathodic polarization depending on the electrode potential bias for direct current passage. The phenomenon that counteracts the electrode polarization is called *depolarization*. Polarization can be lowered or averted by adding special substances called depolarizers.

It is convenient to use polarization diagrams, sometimes called Evans' diagrams, to forecast metal corrosion. These are the graphs of electrode potential versus the logarithm of current or the logarithm of current density [4]. One such diagrams is presented in Fig. 1.3. Metal M corrodes in acidic solution, in which hydrogen atoms are reduced. The inhomogeneous structure of the metal promotes the formation of anodic and cathodic areas on its surface. The point of intersection of the anodic and cathodic curves corresponds to the maximum density of the corrosive current i_{corr} on the abscissa axis and to corrosive potential E_{corr} on the ordinate axis.

Table 1.1. Standard potentials of electrode reactions of metals in aqueous medium at 25°C

Electrode Reaction	E_0, V	Electrode Reaction	E_0, V	Electrode Reaction	E_0, V
$Li^+ + e^- = Li$	−3.045	$Zr^{4+} + 4e^- = Zr$	−1.53	$Sn^{2+} + 2e^- = Sn$	−0.136
$Rb^+ + e^- = Rb$	−2.925	$Ti^{3+} + 3e^- = Ti$	−1.21	$Pb^{2+} + 2e^- = Pb$	−0.125
$K^+ + e^- = K$	−2.925	$V^{2+} + 2e^- = V$	−1.18	$W^{3+} + 3e^- = W$	−0.11
$Cs^+ + e^- = Cs$	−2.923	$Mn^{2+} + 2e^- = Mn$	−1.18	$Bi^{3+} + 3e^- = Bi$	+0.226
$Ca^{2+} + 2e^- = Ca$	−2.87	$Nb^{3+} + 3e^- = Nb$	−1.10	$Sb^{3+} + 3e^- = Sb$	+0.24
$Na^+ + e^- = Na$	−2.714	$Zn^{2+} + 2e^- = Zn$	−0.763	$Re^{3+} + 3e^- = Re$	+0.30
$La^{3+} + 3e^- = La$	−2.52	$Cr^{3+} + 3e^- = Cr$	−0.74	$As^{3+} + 3e^- = As$	+0.30
$Mg^{2+} + 2e^- = Mg$	−2.356	$Ga^{3+} + 3e^- = Ga$	−0.53	$Cu^{2+} + 2e^- = Cu$	+0.340
$Am^{3+} + 3e^- = Am$	−2.32	$Fe^{2+} + 2e^- = Fe$	−0.44	$Cu^+ + e^- = Cu$	+0.520
$Pu^{3+} + 3e^- = Pu$	−2.07	$Cd^{2+} + 2e^- = Cd$	−0.402	$Hg_2^{2+} + 2e^- = 2Hg$	+0.796
$Np^{3+} + 3e^- = Np$	−1.86	$In^{3+} + 3e^- = In$	−0.342	$Ag^+ + e^- = Ag$	+0.799
$Be^{2+} + 2e^- = Be$	−1.85	$Tl^{3+} + 3e^- = Tl$	−0.336	$Rh^{3+} + 3e^- = Rh$	+0.80
$V^{3+} + 3e^- = V$	−1.80	$Mn^{3+} + 3e^- = Mn$	−0.283	$Pd^{2+} + 2e^- = Pd$	+0.987
$Al^{3+} + 3e^- = Al$	−1.67	$Co^{2+} + 2e^- = Co$	−0.277	$Ir^{3+} + 3e^- = Ir$	+1.000
$Ni^{2+} + 2e^- = Ni$	−0.257	$Mo^{3+} + 3e^- = Mo$	−0.20	$Pt^{2+} + 2e^- = Pt$	+1.19
$Ti^{2+} + 2e^- = Ti$	−1.63	$Ge^{4+} + 4e^- = Ge$	−0.15	$Au^{3+} + 3e^- = Au$	+1.52

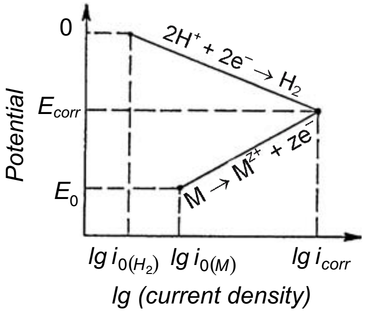

Fig. 1.3. Evans' diagram

The parameters necessary to construct the diagram are usually measured by the potential. The instrument automatically maintains the desired potential between the working and reference electrodes by passing the appropriate current between the working and counter electrodes. This current is controlled, and the potential of the working electrode is measured.

The corrosion process rate and mechanisms depend upon internal and external factors. The innternal factors are the nature of the metal, its chemical composition, structure, electrode surface state, and the presence of residual stresses. The external factors are chemical composition of the corrosive medium, and conditions of the process, including temperature, pressure, flow velocity. The competing effects of these factors determine which direction of the corrosion process dominates.

Anodic dissolution of metals may run together with formation of oxides, hydroxides and hydrogen ions. Typical cathodic processes of metal corrosion are electrochemical reduction reactions of hydrogen (hydrogen depolarization), oxygen (oxygen depolarization) or oxygen-containing ions.

The metal can enter into interactions with environment components and form compounds that are stable to corrosion during anodic dissolution. *Passivity* is the thermodynamic state of reaction in metals at which their corrosion retards abruptly. The transfer of a metal into the passive state is called *passivation,* and the layer formed on the metal electrode surface is called the passivating layer. Oxide and salt passivation of metals are distinguished by the composition of passivating layers.

M. Pourbaix [5] has devised a compact summary of thermodynamic data of potential – pH diagrams related to corrosion behavior of any metal in water. These diagrams are now available for most common metals. Diagram (Fig. 1.4) shows specific conditions of potential and pH under which the metal either does not react (immunity) or is able to react to form specific oxides or complex ions. These data indicate the conditions under which diffusion-barrier films may form on the electrode surface. The diagram outlines the nature of stoichiometric compounds into which any less stable compounds

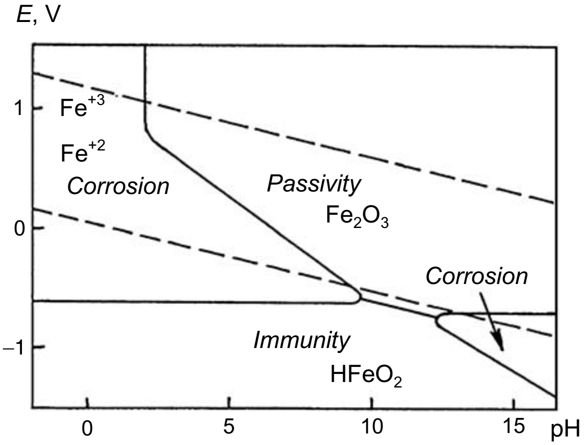

Fig. 1.4. A simplified Pourbaix' scheme for iron at 25°C

may transform whenever equilibrium is achieved. Pourbaix' diagrams describe the equilibrium state of a metal when immersed in an acid or alkali.

Corrosion inhibitors are substances whose introduction in small amounts into a corrosion system (aggressive medium, polymer coating, lubricating or packing material, etc.) produces noticeable corrosion abatement in metals. CI are subdivided into adsorption and passivating CI by their action mechanism. The former protect metals by affecting the kinetics of the electrode corrosion processes. The latter promote the formation of an oxide or other films on a metal product to transfer the metal into the passive state.

Metal corrosion is classified by the type of the hostile medium and conditions at which it runs. Some aspects of atmospheric, marine, underground and biological types of corrosion are considered in this book. Heterogeneity of a metal or medium, specific conditions of oxidizer supply and withdrawal of corrosion products, which do not intrude into the equipotential state of the corroding metal surface, may bring about the areas where either anodic or catholic reactions dominate. *Local corrosion of* metals without passivation may mean the intensive local dissolution of the metal in anodic regions. *Crevice corrosion* is local corrosion of metals in a structure having holes and narrow clearances. The electrolyte solution contacting open areas of a metal structure gains limited mass exchange with the solution trapped in the voids and clearances. The main reason for crevice corrosion in atmospheric conditions is moisture condensation on the article surface. In liquid media there is a hampered access of O_2 and removal of corrosion products from the gaps, where the latter leads to violation of metal passivity. As a result, the electrode potential of the metal in a clearance shifts to the region of negative values. Hence, a galvanic element appears in the article, experiencing crevice corrosion with a potential difference of 0.5–0.75 V. In the element, the metal in the clearance acts as an anode and the metal on the open surface of the article as a cathode. Formation of such galvanic elements results in corrosive-mechanical failure of metals in friction joints, which is called mechano-chemical wear.

1.1.2 Composite Plastics

Composite materials are multiphase systems consisting of two or more components that preserve their structure and properties within the composite formulation.

The present work is devoted to polymer composites whose *matrix*, i.e. uninterrupted component within the composite structure, consists of a polymer material. The matrix imparts a given shape to the composite product, distributes mechanical loads in the material and protects other components from external effects. The matrix material predetermines the range of working temperatures, resistance to corrosion, electrical properties, aging regularities of the composite, as well as processing technique of the composite into articles.

The materials under study are filled composites, which means that the matrix contains dispersed *fillers* – particles of organic or inorganic solid matter, liquids or gases. The filler particle size varies in a wide range. A distinct feature of a composite is the presence of heterogeneous inclusions visible without a microscope. These components tend to become finer as the technology perfects and may reach 1 µm in size, necessitating a microscope to identify them. By the end of the twentieth century there is a new trend in manufacturing of composite materials in which particles of nanometer size (10^{-9} m) are used. A large portion of the volume of these fine particles occupies the surface layer, so their properties differ from those of the constituent substance, especially in the macrovolume. Surface phenomena play a paramount role in technological operations of manufacturing a composite consisting of nanoparticles [6]. A *nanocomposite* is a composite material whose components have the dimensionality of colloidal particles (10^{-9}–10^{-7} m).

Classification of composites by the phase inclusion size bears a philosophical aspect: how small should a component in the matrix be not to make the term "composite material" so universal as to include in fact all materials? Interatomic distances in molecules and crystals are of $1.5 \cdot 10^{-10}$ m dimensionality, distances between iterative elements of the crystalline structure are 10^{-10}–10^{-9} m, while the size of the smallest intermolecular voids in polymers is 10^{-8} m. Note that mean nanoparticle size (plastic pigments are 10^{-8}–10^{-5} m in size, the diameter of monocrystalline fibers or whiskers is 10^{-7}–10^{-5} m, glass microspheres are 10^{-6}–10^{-4} m) is commensurate with parameters of monolithic simple materials. This means that in the totality of engineering materials, nanocomposites occupy a place at the boundary between composite and simple materials.

Particles of the dispersed phase can be spread within the matrix randomly, although they commonly tend to arrange in a certain order (Fig. 1.5).

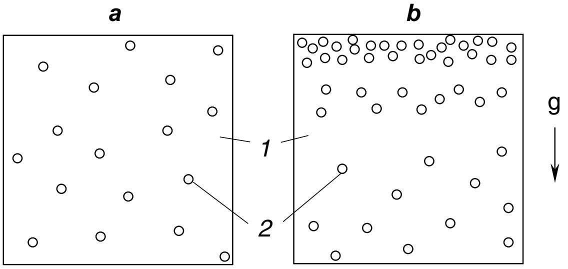

Fig. 1.5. Structural schemes of dispersion-filled composites: (**a**) isotropic, (**b**) anisotropic. (1) matrix, (2) dispersed phase

When the particles are chaotically scattered, the materials are called *isotropic*, i.e. their properties are identical in all directions. When the particles are distributed evenly within the matrix at a concentration gradient g (g – the vector indicating the direction of fastest change of particle concentration in the matrix), the composite is *anisotropic* and its properties depend upon the direction. The purpose of manufacturing isotropic composites is to place a respective component exactly in the site where properties of the composite article are to be realized most fully.

Formation of the composite is accompanied by mechanical, physical and chemical interactions of the components. This leads to phases and interfaces between them. Interfacial interactions of components are a function of their thermodynamic, kinetic and mechanical compatibility.

Thermodynamic compatibility is a property of the composite matrix and other components to be in the state of thermodynamic equilibrium at temperatures corresponding to its formation regimes or the operation conditions of the material.

Kinetic compatibility is a property of the composite components to be in a metastable equilibrium state (as opposed to a stable one) regulated by electric interactions between the components, by conditions of adsorption, diffusion or chemical reactions between them. Components that are compatible in a thermodynamic sense (temperature, pressure and ambient effects) might become incompatible kinetically, which can lead to the release of one of the components from the matrix.

Mechanical compatibility is reached if deformation characteristics and heat-expansion coefficients of components (which can be compatible neither thermodynamically nor kinetically) are similar, so that the composite integrity will not be disrupted during operation and mechanical properties will remain stable.

Thus, the components form an integral composite material when they are interrelated through mechanical, physical and chemical bonds. The mechanical bonds arise under the action of friction forces when the components become engaged mechanically via the natural or purposefully created asperities on contacting surfaces. These bonds define the properties of polymer overcoats on metal parts as well as triboengineering characteristics of metal-polymer friction joints. Physical bonds are the result of molecular interactions on the surface layers of components. Gravitation, electrostatic and magnetic interactions of the composite ingredients belong to physical bonds. Chemical bonds represent joining of atoms and ions of different contacting components into molecules and crystals. The work needed to break a chemical bond is much larger than that to disrupt physical intermolecular bonds.

Among the advantages of the composites is the possibility of assembling them from required components via the necessary type of links. The term "design of compounds" used in engineering means the choice of the form and dimensions of the compound with allowance for the magnitude and time of the load action, part configuration and material strength. This term in materials science will justify speaking about design composites with preset type of binder and other components, their distribution within the matrix, matching of the technological procedures using the mechanical, physical or chemical bonds and, bearing in mind their strength and stability, with account of operation conditions, the cost of and specific demands made of the composites.

Composition optimization is the process of selecting the best correlation of componential concentration in the composite. The best composition meets the optimum criterion, which is the qualitative index expressing the threshold of composite efficiency. It assists in comparing the alternative compositions, aimed at choosing the best one. Optimization of the composition is based on experimental determination of its characteristics through testing samples of various compositions. Optimization of the manufacturing technology of composites embraces numerous factors, requiring a creative approach. the most reliable optimization is the fabrication of samples of an optimum composition proceeding from all alternatives of the technology. Testing of such samples and comparison of their technical and economic characteristics can be the basis for selecting an optimum technology. This path is, however, time consuming and requires significant expenditure. The composite processing technology is usually chosen on the basis of experimental results and the availability of traditional production equipment.

Modern trends in the design of composite materials presuppose the development of intelligent or smart composites [7]. These materials adapt to service conditions either through varying their charge state or physical-chemical structure, or regulation of this adaptation degree by a feedback system [8]. The principle of operation of such smart materials is illustrated in Fig. 1.6.

This material contains structural elements functioning as [9]: (i) a sensor – a sensitive element or a meter responding to ambient variations; (ii) an actuator – a structure with which the material exerts an effect on the environment; (iii) a processor – structural element controlling the actuator functions based on signals incoming from the sensor. Material 2 contains structures

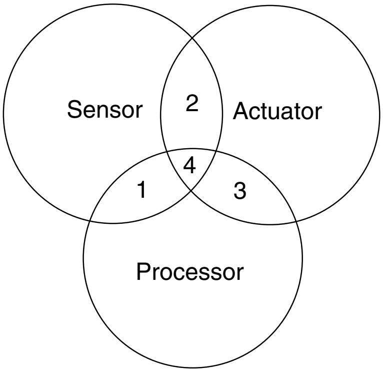

Fig. 1.6. Scheme of smart material structure. (1) adaptive structure, (2) controlled, (3) active, (4) intelligent structure

functioning as a sensor and actuator simultaneously. This controlled material may influence the environment in the form of mechanical loading, electrical or magnetic field, etc. Material 3 combines the functions of the processor and actuator. This active material is programmed to respond to variations in the environment properties. The majority of polymer packaging films containing CI belong to this group. Material 1 is fit with structural elements serving as a sensor and processor. This is an adaptive material able to adapt to varying ambient conditions. Intelligent or smart material 4 incorporates the elements functioning as a sensor, actuator and processor. Along with exerting an active influence of physical, chemical or biological nature upon the environment it also regulates its own activity, i.e. the level of this influence depending on the degree of variation of the environment.

Composite materials consisting of a few components, each of which is intended for individual functions within the composite, are optimum for imparting smart properties.

1.1.3 Friction of Inhibited Plastics

Tribology is a science studying friction, wear and lubrication, along with interactions of the contacting physical bodies during their mutual motion.

Friction is the resistance to relative movement of two contiguous bodies arising in the zones of their contact and is effective in the contiguous plane. The friction pair is a system of two elements whose contacting surfaces are moving relative to each other. One of the elements is a frictional material; the other is a counterbody (rider). The friction surface is a solid body surface participating in friction. Wearing is the process during which the material is separated from the friction surface and residual deformation is accumulated in the solid body being abraded that is exhibited in a gradual change of the body size and shape. Wear is the result of the wearing process. A lubricating material is fed to the friction surface to reduce wear rate and friction force. Lubrication is the effect of the lubricating material. Triboengineering is an applied sphere of tribology that represents the final stage of elaboration of the friction joint.

Mechanical energy generated by the movement of the contacting bodies is converted by friction into other types of energy, leadings to triboelectric and tribochemical phenomena.

In the case that the frictional material is a polymer belonging to the class of dielectrics, it becomes electrified byt friction. *Electrization* means the formation of excess and similar charges on the surface or in the bulk of the body participating in friction. High electrization of dielectrics is attributed to their low electroconductivity. When a polymer is rubbed against a metal, the electrization potential of the polymer part reaches its stationary value in a few seconds, after which it remains invariable. *Electrets* are dielectrics that preserve their electrization for a long time and are, in fact, analogues of a permanent magnet.

When metal parts rub in an electrolyte, it is possible to form short-circuit galvanic microelements (Fig. 1.7). Potentials ${}_1E_3$ and ${}_2E_3$ appear at the metal-electrolyte interface and contact potential difference ${}_1E_2$ in the contact sites of the parts. The electromotive force of these elements promotes electrode processes on the friction surfaces. The processes appear even though ${}_1E_3 = {}_2E_3$ because of the galvanic elements resulting from crevice corrosion in the friction zone.

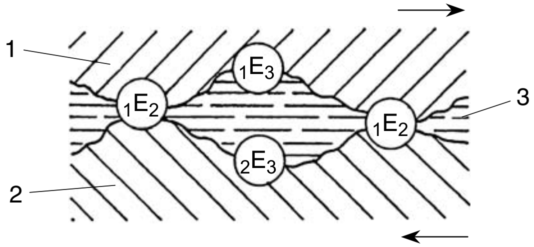

Fig. 1.7. Formation of galvanic elements in the contact of metal parts. (1) and (2) friction surfaces of metal parts; (3) electrolyte

Friction and corrosion mutually affect one another. Friction violates integrity of the passivating layers on the friction surface of metal parts. Movement of the friction surfaces relative to each other accelerates supply of corrosion matter to the freshly formed surface areas of the mechanical counterbody and removal of the products of electrode reactions. These stages of the electrode process are less intensive in static conditions and follow the mechanism of diffusion or convection. As can be seen, corrosion serves as a catalyzer of mechanical wear during metal friction in electrolytes. *Mechano-chemical* *wear* is the wearing of a material during friction accompanied by its chemical interaction with the environment.

Tribochemistry is a domain of chemistry that studies chemical and physical-chemical variations in solid bodies under the action of frictional energy. Wear of metal counterparts in polymer-metal friction pairs is far higher than in metal-metal pairs [10]. To explain this phenomenon the following model has been proposed [11]. Microasperities on the friction surface experience high-intensity impacts. A microasperity is transferred into an excited state called a triboplasma at the moment of impact. It is characterized by a high local temperature (above 10^4 K) and a short lifetime ($<10^{-7}$ s). Various physical processes leading to photon and electron emission take place in the triboplasma state of the microasperity. Energy accumulated on microasperities is not fully dissipated; a part of it remains in the surface layer and initiates chemical reactions on the friction surface. Free radicals are formed in the polymer-metal friction pair. These radicals are the products of macromolecular destruction and act as surfactants towards the metal counterbody [10].

Polymer-metal friction pairs are also characterized by frictional *transfer of material*. This implies the material displacement from the polymer part friction surface onto that of the metal counterbody. Macrotransfer is realized either as a fatigue detachment of polymer particles sticking to the counterbody or as galling, i.e. sticking of the viscous-flow fragments from the polymer surface layer, their extension and movement in the friction direction.

All the mentioned phenomena occur during friction of the polymer-metal pairs in electrolyte solutions, including crevice corrosion and formation of galvanic pairs in the friction zone, triboelectrization of the polymer frictional material and formation of electrets, superposition of the electrode potential of the metal counterbody and that of the polymer triboelectrization potential, tribochemical reactions yielding macroradicals and their interaction with the newly formed areas of the metal friction surface, as well as frictional transfer of the polymer material to the counterbody. Participation of the inhibited plastic in friction makes the situation still more complex due to liberation of CI in the friction zone and their effect on the kinetics of electrode processes, on lubrication and formation of fresh sites of passive films on the friction surface of the metal counterbody. The interrelationship between these processes is reviewed in Chap. 4.

1.2 Corrosion Processes in Metal-Polymer Contacts

Local corrosion of metals occurs because of many factors, the most critical of which are inhomogeneity of the metal phase and difference in composition of the corrosive medium, i.e. electrochemical heterogeneity on different areas of the metal surface.

The most widespread corrosion types are point corrosion or pitting, filiform, crevice, contact and intercrystalline corrosion. The highest danger for the metal-polymer system is presented by the crevice type of corrosion.

Crevice corrosion is often observed in clearances between metals and in places of loose contact between the metal and dielectric (including corrosion resistant materials). Passivating materials and alloys, such as stainless chromium and nickel-chromium steels, aluminum and magnesium alloys are most inclined to crevice corrosion [2,12,13].

Crevice corrosion starts because of hampered access of electrolyte and oxygen in the space of the clearance. This changes the pH of the electrolyte solution in the clearance, spurs the anodic and retards the cathodic processes. As a result, the metal electrode potential shifts to the negative with respect to the potential on the open surface. These processes bring about electrochemical microelements of the slot-open-surface type, in which the metal in the clearance serves as an anode [14].

Let us consider some peculiarities of local corrosion of metals in contact with polymers stimulated by changes (inhibition or acceleration) of corrosion processes at the metal–polymer interface. These changes can be attributed either to a limited velocity of movement of the substances participating in the corrosion process or to chemical and electrochemical effects of the polymer on the metal and their influence on the corrosive media activity.

1.2.1 Corrosion Specifics at the Metal-Polymer Interface

Abnormal local corrosion of metals in contact with plastics induced by formation of concentration elements [14] was related in the 1930s to specific properties of plastics. Indeed, plastics contain monomer remainders, stabilizers, plasticizers, and other corrosion-active components. For example, testing of metal screws screwed into a threaded polymer plate in a thermal humid chamber showed [15] that corrosion of the screws was caused by migration of ammonium, hydrochloric and acetic acids from the polymer material. Analogous results were obtained when studying aluminum corrosion in a closed volume containing emissions of enamels, lacquers and different plastics [16]. It was recognized for more than a century that rubber initiated corrosion of contacting metal parts. This is the reason for protecting metals in contact with rubber by applying special coatings.

A convenient model for studying crevice corrosion specifics at the metal–plastic interface turned out to be the “polymer coating on a metal substrate” system.

Anticorrosion properties of coatings are largely based on chemical resistance of the polymer used for the coating, its permeability for corrosive media and adhesion to the object being protected. One of the major criteria of the protecting durability is the coating continuity. Any defect on the coating may disable the article. The defects may occur because of technological conditions at coating formation, variations in the material properties under operation in hostile media, etc. A single defect on the coating does not impair its protective ability at once, and at the forefront in such conditions is the stability of adhesive bonds.

When a polymer is brought into contact with a low-molecular-weight liquid, it can adsorb onto the polymer surface, diffuse into its bulk and, finally, cause its swelling and dissolution. Named processes bring about in the first place changes in molecular interactions of the polymer, which affect itsphysical-mechanical, electrical and other properties. Corrosion resistance of the metal-polymer joints is affected significantly by electrochemical interactions between the components due to the presence of the areas of dissimilar electrode potential on the metal substrate [17]. Physical-chemical interactions between components of the metal-polymer system influence the two main factors that condition reliability and protective ability of the polymer coatings: firstly, penetrability of aggressive media initiating corrosion processes and metal failure, and secondly, physical-mechanical barrier properties and adhesive strength of the polymer coatings.

Delamination of the polymer coating under the action of aggressive media is accompanied by a shift of the substrate electrode potential into the region of negative values, so-called downgrading. Variation of the substrate potential at coating peeling proves that either the cathodic reaction of oxygen under the coating is retarded or the process of metal ionizing is accelerated [18]. It is possible to control both anodic and cathodic processes via regulation of the electrode potential of the metal substrate.

To investigate the coating adhesion stability one can use a method during which the coating delamination rate is recorded around a handmade point defect (puncture) reaching the substrate [19].

Kinetics of electrochemical processes in the electrode-coating-electrolyte systems has been examined by the potentiostatic method within the $\pm 4\,\mathrm{V}$ exponentiation range. The samples were polarized in a three-electrode electrochemical cell installed with a thermostat to maintain a constant temperature regime. The working electrode was a sample in the form of a metal (or graphite) plate with a one-sided coating.

The diagrams proving that the delamination kinetics of polymer coatings is dependent upon the potential value and sign are presented in Fig. 1.8. The difference in the location of minima on the curves corresponding to graphite and steel means that the delamination process is interrelated with redox reactions on the substrate surface inducing the formation and failure of oxide films. Thus, by alternating the substrate electrode potential, one can regulate the protective capability of the polymer coatings in electrolytes.

Moreover, corrosion processes may run on metals covered with varnish – and paint materials in an atmosphere and lead to the formation of numerous tortuous filiform areas of damage. This type of failure, called *filiform corrosion,* is a specific form of crevice corrosion. The filiform type of corrosion does not, as a rule, lead to metal failure but only impairs its appearance. Filiform

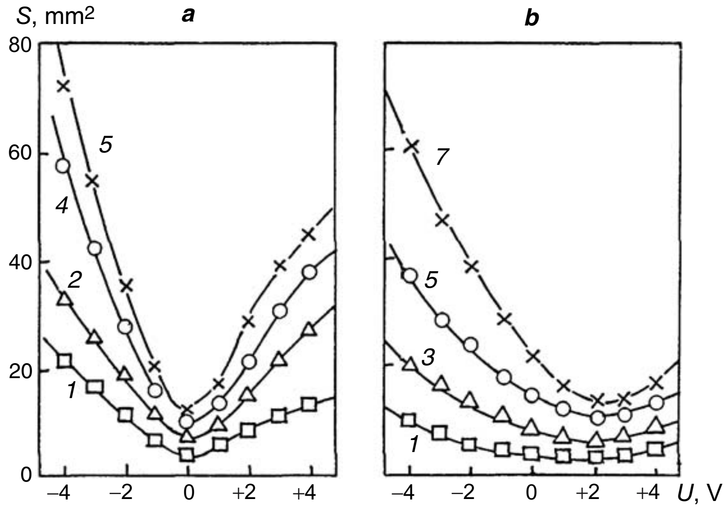

Fig. 1.8. Delamination kinetics of polyethylene coatings from graphite (**a**) and steel (**b**) substrates in a 5% solution of H_2SO_4 versus potential value U fed to the substrate and exposure time in electrolyte (numbers on curves indicate exposure time in hours)

corrosion on steels is exhibited as a network of 0.1–0.5-mm-wide thread-like corrosion products [2]. The color of the threads is typical of Fe_2O_3, while their heads are green or blue, which indicates the presence of the bivalent iron.

The filiform corrosion is induced by the generation of electrochemical elements of differential aeration in the corrosion system. The filiform corrosion usually occurs in a medium of high relative humidity (65–95%). At 100% humidity the threads widen and can swell the coating. Phosphating of the metal surface and priming with zinc chromate assists in diminishing the filiform corrosion, although not averting its emergence.

To combat the crevice corrosion one should seal gaps and clearances by metal materials not provoking corrosion of the basic material and apply electrochemical protection and corrosion inhibitors [13, 20].

1.2.2 Polymer Materials as a Source of Corrosion Agents

Comprehending corrosion as failure of materials under the action of the environment, it would be justified to relate this term to fracture of polymer materials under the action of ambient factors, including elevated temperatures, ionizing radiation, UV radiation, ozone, mechanical loads, chemical and biological matter.

However, the term “corrosion” is not accepted in relation to polymer materials. Such terms as aging, decomposition and destruction are used for characterizing polymer fracture under external effects, where the first term is used in the most analogous sense to “metal corrosion”. Usually, two types of processes are running during polymer aging: destruction and macromolecular cross-linking. Time makes the aging mechanism and the increase of intermediate and final products more complicated.

The aging reaction is often classified by the nature of its inducing agent and the character of its effect on macromolecules (thermal, oxidative, radiation, mechano-chemical). As a result of aging, polymer materials change their properties and composition. These changes are caused by physical-chemical reactions leading to the release of low-molecular-weight products, oxidation of macromolecules, formation of active fragments (macroradicals), macromolecular destruction and syneresis of liquid-phase components from the polymer composition. We will dwell upon just a few characteristic examples for different polymer classes out of the great variety of failure processes in polymer materials.

Destruction of macromolecules as a result of *chemical interactions* with the environment leads to the fracture of polymer materials with the formation of active components. Participation of individual macromolecules in destruction processes is dependent upon the amount of the constituent reactive groups. Introduction of substituents of different compositions into the polymer chain changes their stability in thermal oxidation reactions and in response to chemical reagents and moisture effects.

The presence of multiple bonds in the macromolecule backbone chain greatly reduces its resistance to external effects. Introduction of heteroatoms (nitrogen, oxygen, sulfur) impairs polymer resistance to chemical agents.

The polarity of macromolecules and the solvent determine the effect of organic solvents on polymer materials. Polymers containing polar groups are resistant to non-polar substances but can swell and be dissolved in polar substances. The polymer permolecular structure exerts a considerable effect on its stability under aging as well. Crystalline polymers dissolve slower than non-crystalline ones, which is due to different diffusion velocities of low-molecular-weight components in the crystalline and amorphous polymers.

A critical factor that influences significantly aging of polymer materials is *temperature*. The temperature effect leads to changes in the chemical structure of macromolecules and their permolecular packing. Destruction of a macromolecule is accompanied by formation of low-molecular-weight products like water, hydrogen chloride, carbonic oxide and other. The temperature effect in air results in a thermal oxidative destruction of macromolecules. More low-molecular-weight compounds are formed than in thermal decomposition in an inert gas or vacuum during thermal oxidative destruction of polyethylene. Thermal oxidative destruction is accompanied by formation of hydroxyl, peroxyl, carboxyl and ester groups. Saturated low-molecular-weight hydrocarbons along with unsaturated ethane-, ethylene-, propylene- and butane-type hydrocarbons, as well as carbon oxide, water, formaldehyde, fatty acids and ketones were found in the products of the polymer thermal oxidative destruction. This failure regularity is characteristic of other types of polymer materials as well.

Polymers containing halogens, including chlorine and fluorine, release highly active products like hydrogen halide and some other low-molecular-weight compounds during thermal oxidative destruction of polyethylene. For instance, the thermal effect in air on polyvinyl chloride leads to the release of hydrogen chloride, while the polymer sample changes icolor and becomes cross-linked. Polymer materials with side substituents (polyvinyl acetate, polyvinyl formal) decompose under heating in oxygen and release acetic acid, ketones and carbon dioxide. They form cyclic compounds, carbonic oxides, water and ammonium during fracture of polyamides. Decomposition of polybutylene terephthalate in air is accompanied by formation of carbonic oxides, terephthalic acid, acetic aldehyde and other low-molecular-weight compounds.

Silicone-organic polymers are more resistant to elevated temperatures. As a result of thermal-oxidative destruction, they release low-molecular-weight products like water and formaldehyde.

In fact all polymer materials release hydrogen during thermal-oxidative destruction.

Thermal-oxidative destruction of polymer materials is accompanied by the formation of corrosion-active components that may essentially change corrosion processes in the polymer-metal contact.

An important factor leading to alteration of polymer characteristics is the *mechanical effect*, e.g. milling, attrition, rolling, mixing or ultrasoound. It is possible to break atomic links by mechanical action to form active macromolecular fragments and release low-molecular-weight products. Mechanical destruction follows the radical, ionic or mixed mechanisms depending on the ambient composition. A specific fracture mode of polymer materials is *stress-induced aging*. The effect of mechanical stresses intensifies oxidation processes, thermal oxidative destruction and crack propagation in materials.

Photochemical effects on polymer materials activate macromolecules through the adsorption of energy quanta followed by their dissociation into active components. The activated molecules are capable of various interactions with other molecules.

Photochemical destruction of polymers runs together with formation of oxide compounds, low-molecular-weight and structurized products. These results in the generation of cracks on the surface of polyolefin articles, and their mechanical and dielectric properties are noticeably impaired.

As a result of photochemical destruction, the halogen-containing polymers split off low-molecular-weight products having analogous composition to those isolated during thermal-oxidative destruction. For example, as polyvinyl chloride breaks down, the release of hydrogen chloride is observed.

Polyimides show an increasing content of the monomer and raised brittleness under the effect of photochemical factors.

Splitting of hydrogen is observed under exposure of polymer materials to *ionizing radiation* along with formation of multiple bonds, release of low-molecular-weight hydrocarbons, destruction and cross-linking. Depending on the dominant process, polymer materials can be subdivided in their relation to ionizing radiation into two groups: (i) those in which the polymers form a spatial cross-linked structure, (ii) those in which the polymers are destroyed.

The ionizing radiation results in active macroradicals, oxide compounds and low-molecular-weight products. Thus, exposure of polyolefins in air is accompanied by generation of low-molecular-weight compounds and cross-linking. Fluorine is released under the action of ionizing radiation on polytetrafluoroethylene.

The corrosion-active products can be released from polymers together with technological low-molecular-weight additives like plasticizers and lubricants. Low-molecular-weight substances on the surface of polymer parts can enter into interactions with atmospheric oxygen, active components of the lubricating medium or dissolve in the working fluids, thus changing their composition and properties, particularly those that are corrosive.

Polymer materials can also breakdown under *the action of microorganisms.* Along with impairing the appearance, microorganisms worsen hygienic characteristics of materials based on polymers, lower their mechanical strength, wear resistance, dielectric and other properties. Products of microorganism vital functions released on the polymer surface change corrosion processes during the contact of biologically damaged polymers with metals.

Proceeding from the above, it can be concluded that polymers and compositions on a polymer base can become, under the action of operating conditions, the sources of products changing corrosion kinetics in the polymer–metal systems.

1.2.3 Polymer Effect on Electrochemical Polarization Kinetics of Metals

The efficiency of protecting systems based on polymers is conditioned largely by the barrier effect of polymer elements insulating metals from the environment. The electrochemical barrier, which is dependent upon the substrate polarization, can be far more efficient than the diffusion-mechanical one governed by the material permeability. It is feasible to attain a low rate of coating peeling and negligible corrosion damage of the substrate via its polarization even in the case of continuity violation of the polymer coating (crack, puncture).

It is recognized that once the barrier action of structural polymers is broken, they cannot impose any effect on metal corrosion in electrolyte solutions, although the linear-selective dissolving of the metal is attributed to specific properties of dielectrics in individual cases. Investigations of the polymer-wetting liquids are of high practical importance for forecasting electrochemical stability of metal-polymer systems.

The authors have studied the effect of polymer powders and films on corrosion rate of steels and their physical-chemical properties in aqua solutions of electrolytes. The experimental method was as follows.

One of two platinum electrodes was immersed into an NaCl solution (10^{-4} mol/l) to a fixed depth. The immersion depth of the second electrode was a variable factor. Kinetics of the second electrode potential variation towards that of the silver chloride was registered and compared to the case when a PVB powder was placed on the solution surface (dispersion degree 160–200 μm, powder layer density 4 mg/cm^2).

Application of polymer powders on the solution surface leads to the generation of an electrode potential gradient in solution depth (Fig. 1.9). The strongest reduction of the potential in time was recorded at a minimal (15 mm) distance of the electrode from the powder layer on the surface. With increasing immersion depth, the potential variation becomes less prominent and is not registered at 60 mm depth.

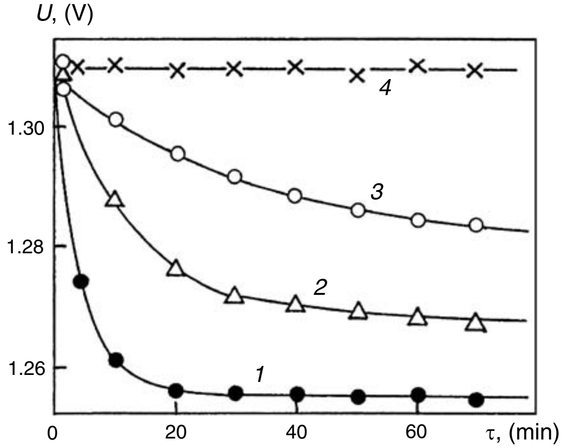

Fig. 1.9. Dependence of platinum electrode potential (U) in NaCl solution with PVB powder on its surface versus time (t) and immersion depth of the electrode (mm): (1) 15; (2) 30; (3) 45; (4) 60. Polarization current density is +0.1 mA/cm^2

Based on the known representations of the electrode processes, the derived data can evidently be related to a considerable change of the local depolarizer concentration in the vicinity of the upper electrode as compared to that at a certain depth; this is because of the polymer powders placed on the solution surface. This phenomenon can apparently be attributed to diffusion of water-soluble additives from the powder into solution as well as adsorption of the depolarizer on the polymer particles.

Potentials of the electrodes immersed into aqua solutions are changed significantly during cooling down to freezing in the presence of polymer powders on the liquid surface [21]. It was established that PE, PVB and PPl powders did not in fact change polarization kinetics in distilled water but their effect was perceptible in diluted aqua solutions of electrolytes (10^{-4} mol/l). The polarization stress varies insignificantly in more concentrated solutions (0.1 mol/l and higher) when a powder is placed on the electrolyte surface. This fact speaks in favor of the adsorption mechanism of the polymer effect on metal polarization in electrolyte solutions.

The contacting metals are subject to a specific effect due to the polymer materials. This effect should be considered during the design of anticorrosion metal-polymer parts and joints and when predicting their service parameters.

1.2.4 Permeability of Polymers to Electrolytes

One of the reasons for local corrosion at the metal-polymer interface is sorption of electrolytes by polymers and permeability of the polymer barrier towards electrolytes. Sorption of electrolytes (acid solutions, bases and salts) leads to essential variation in the service characteristics of the protecting polymer coatings and anticorrosion packaging films under mechanical loads. These variations under mechanical loads, especially in seals and friction joints, are much deeper and can affect mechanisms of contact interactions.

Transfer of aqua electrolytes in polymers has characteristics [22] that distinguish it from the transfer of other low-molecular-weight matter. The presence of water in the medium sorbed may result in formation of aqua associates and electrolyte in the polymer. Depending on the amount of sorbed water, the polymers are subdivided into three groups: (i) hydrophobic, i.e. slightly swelling in water (water concentration in the polymer below 0.5%), (ii) mildly hydrophilic (water concentration 0.5–10%), (iii) hydrophilic (water concentration above 10%). This subdivision is very conventional since the permeability mechanism depends not only on water concentration in the polymer but on the nature of their physical-chemical interactions with electrolyte ions and macromolecular active centers as well [23].

Hydrophobic polymers (polyolefins, polystyrene, polyethylene terephthalate, pentaplast, fluoroplasts) contain small amounts of polar groups in their macromolecular composition able to interact with water and electrolytes. To that extent, the permeability mechanism of electrolytes in hydrophobic polymers is similar to that of gases.

The comparison of permeability values of low-molecular-weight substances diffusing into hydrophobic polymers from water solutions to those from the dry gaseous phase (e.g., HCl, NH_3, CO_2, SO_2) showed that these values were commensurate, providing that the vapor elasticity over the solution and its partial pressure in the gaseous phase were equal. It is believed that volatile electrolytes are transferred in hydrophobic polymers in the form of non-dissociated molecules devoid of hydrate shells.

It is important for hydrophobic polymers that their permeability to nonvolatile electrolytes is at least three orders of magnitude lower than that for volatile electrolytes. Low permeability for nonvolatile electrolytes is related to their low sorption by the non-polar polymers.

Liquid electrolytes display significant differences in permeability values. For instance, permeation of hydrogen chloride through polyethylene film when diffusing from concentrated hydrochloric acid is detected in a few minutes, whereas permeation of potassium chloride is not recorded even after three months. Permeation of nitric acid through fluoroplastic film is recorded in a few tens of minutes, while it is necessary to wait more than a year for sulfuric acid to be detected [22]. With increasing concentration of the electrolyte its permeation rises. Polymers whose electrolyte diffusion factor is $D < 10^{-17}\mathrm{m}^2/\mathrm{s}$ are considered to be practically impermeable. Polyolefins, fluoroplasts and polyesters are easily permeable to hydrochloric, hydrofluoric, nitric, acetic and fluorosilicic acids, and ammonium diffusing form aqua solutes. They are less permeable for sulfuric and phosphoric acids, salts and caustic alkali. Phosphoric acid easily diffuses into PVC as well. In this case [23], diffusion of the acid is conditioned by the presence of a plasticizer in the polymer.

The effect of technological additives on permeability of polymers is connected with variations in their sorption capacity, formation of defects and interactions of the electrolyte and additives. Impregnation of fillers improves, as a rule, permeability of polymers and intensifies clusterization of water and the penetrant. When polyethylene is filled by talc, HCl and H_2O clusters formed in the polymer can be observed in microscope. Water and HCl sorption increases proportionally to the volume content of talc up to 17% concentration. Further increase in talc concentration does not result in sorption growth because of filler particle aggregation in the polymer binder.

The permolecular structure of polymers exerts a perceptible effect on permeability. Thermoplasts whose structure is not spherulitic and materials with a coarse-spherulitic structure are highly permeable because of different development levels of the microcapillary system of permolecular formations.

Mildly hydrophilic polymers (weakly swelling in water) are characterized by a limited amount of polar groups in macromolecules. Their typical representatives are aliphatic polyimides (water absorption at room temperature is 2–12%), epoxy resins, collagen and polyester resins. Swelling, dilution and destruction processes take place in mildly hydrophilic polymers during sorption and electrolytic diffusion. During sorption, geometrical parameters of samples vary continuously in these systems and affect clearances, seals and tribojoints. Moreover, surface concentration of the electrolyte, water absorption, crystallinity degree and molecular mass (at chemical destruction) alsovary. Diffusion of electrolytes in polymers of the above class will be exemplified on PA [22,23].

Acid dissociates at low acid concentrations inside the polymer and its ions start to bond with the charged end groups of macromolecules. Concentration dependencies of the diffusion factor of the electrolyte and self-diffusion factors of individual ions can be explained by saturation of the bonding centers. As a result of the diffusing ions' interaction with the polymer polar groups (centers) this dependence is observed at the initial stages of sorption of the ionic mobility on the filling degree of the adsorption centers. The sorbed ions start to bond with polyamide end groups $–NH_3^+$ and $–COO^-$ with increasing electrolyte (acid) concentration in the polymer. Their electrostatic and chemical interaction with the macromolecule attenuates with further diffusion of ions. This results in an abrupt increase of the diffusion factor of the acid on transition through the critical region (equal concentration of the bound ions and binding centers).

Volatility of the electrolyte exerts an insignificant effect on permeability. The penetration depth of acidic solutions into epoxy resin diminishes as follows: $H_2SO_4 > HNO_3 > HCl$. The permeation depth of alkali is significantly (about ten times) less than that of the acids. The concentration dependence of the diffusion factor of an acid depends on its and the polymer's origins. Thus, with growing concentration of HCl in a solute its permeation depth grows too. The diffusion factor of H_2SO_4 in a polyester resin reduces at 60°C from $3 \cdot 10^{-7}$ to $4 \cdot 10^{-18}$ m^2/s as the acid concentration in the solute increases from 1 to 25%. Diffusion of H_2SO_4 into epoxy resin set by amine hardener is accompanied by binding and the permeation depth changes by more than a factor of 10 when the hardener content doubles.

The permeability of salt solutes (NaCl, KCl) in epoxy resins corresponds roughly to that of nonvolatile solvents: $10^{-15} – 10^{-19}$ $g/(m \cdot s \cdot Pa)$ in hydrophobic polymers.

Hydrophilic polymers contain a commensurate amount of hydrophilic and hydrophobic fragments in macromolecular composition, including proteins, some polyurethanes and acrylate copolymers. Water is a good solvent for hydrophilic polymers, and therefore it often violates the original structure of the polymer on sorption of aqua solutions. Non-polar fragments, due to their macromolecular flexibility on sorption of aqua solutions, can associate and form areas of elevated hydrophoby to hamper the electrolyte motion. Hydrophilic sections of the chain encircled by the solvent are responsible for the electrolyte transfer. The majority of polymers cannot form fully hydrophobic areas because their polar and non-polar sections in macromolecules are frequently varying.

Films of hydrophilic polymers are the traditional objects of research into electrolyte transfer in polymers. For a long period this process was described as diffusion of water molecules through pores in the films. Selectivity of membranes towards the penetrants was attributed to the presence of charges on the pore walls impeding diffusion of similarly charged ions.

In the 1960s the concept of electrolyte transfer was recognized as a process of diffusive penetrability consisting of sorption, diffusion in the polymer and desorption stages [24]. The main idea contends that the electrolyte should dissolve in the polymer matrix to exercise the transfer. Its concentration in the polymer is defined by the distribution constant of the electrolyte between the polymer phases and the contacting solution. By analogy with gas penetrability, the transfer of electrolytes can be characterized by the permeability ratio P

$$P = DK \ , \tag{1.4}$$

where D is the diffusion factor and K is the distribution constant.

In its physical sense the permeability ratio of electrolytes is the amount of a substance transferred per unit time through a unit surface of a polymer film of a unit thickness with the electrolyte activity in the outer solution equal to a unit. The dimensionality of the permeability ratio coincides with the diffusion factor since the distribution constant is a dimensionless quantity.

Since solubility of electrolytes in hydrophilic polymers essentially depends on the presence of water, an important characteristic of transfer is the volume fraction of water contained in the polymer [20]. Localized water inclusions, sufficient to solvate the electrolyte and raise its solubility, are formed in the polymer matrix. In the case of a high water concentration in the polymer, the concentration of the electrolyte in water can become equal to its concentration in the ambient solution.

The diffusion factor of the electrolyte is a function of water content in the polymer. To describe the dependence of the diffusion factor on the volume fraction of water in the polymer, the representation of the free volume theory is successfully used [25, 26]. Providing that the free volume of the swollen polymer is proportional to the volume fraction in water, a simple equation relating the diffusion factor of the electrolyte in the polymer D and water D_0 will be

$$\mathrm{Lg}\, D = \lg D_0 - K\,(1/H - 1) \ , \tag{1.5}$$

where H is the volume fraction contained in the water.

Equation (1.5) describes satisfactorily the experimental data. Penetrability of hydrophilic films of cellulose acetate towards NaCl increases sixfold from $H = 0.08$ to 0.56 when wetted [27].

Hence, polymer structure and properties change under the effect of sorbed electrolyte. Consequently, permeability of polymers towards electrolytes can be chosen as a critical factor visualizing the intensity of corrosion processes in the polymer–metal contact.

1.3 Components of Inhibited Plastics

Inhibited plastics are composite materials (CM) consisting of inhomogeneous components (phases) separated by interfaces. They contain thermoplastics or thermosetting plastics, or their blends as a matrix (binder) representing an uninterrupted component within the CM. The matrix adds the necessary configuration and continuity to CM, transfers and redistributes loads over the material and defines its major physical and chemical properties [28–31]. The polymer matrix of inhibited plastics is a carrier of the functional component, a CI, which protects conjugated metal parts from corrosion. The degree of CI binding with the polymer carrier depends on the thermodynamic compatibility of CI, the binder and other components as well as on the material structure. Both the micro- and macrostructure of CM can be varied within a wide range by altering their formulation and production process. The inhibited plastics contain, along with CI, ingredients that impart certain service characteristics and alleviate processing of the composites [32–34].

When choosing the components of inhibited CM, one should take into account:

- operation conditions and corresponding anticorrosion, deformation and strength, diffusive and other characteristics contributing to durability of the composite article,
- process behavior of components making possible their joined processing in the material,
- economical aspects, such as demands, anticipated production volume and scheduled service life, raw materials and their cost, available processes for using secondary materials and wastes, presence of special equipment and rigging and necessity of their retrofitting,
- social factors connected with conditions and safety of production and application of the material and its products, process impact on the environment and means of recycling industrial and domestic waste.

1.3.1 Binders for Inhibited Plastics

Plastics are materials based on polymers that are found in the plastic or viscous-flow state during processing into articles and are solid, glassy and/or in a crystalline state when they are final products [29, 30, 35].

The thermoplastic binder is chosen for the purpose of acting as an inhibited CM and is aimed at reaching the required service characteristics of the final product.

The range of plastics used as (matrix type) binders for inhibited CM is extremely broad and includes practically the whole list of commercial thermal and thermosetting plastics [36–45].

Thermoplastics are based on linear or branched polymers, copolymers or their blends that are reversibly transferred at heating into a plastic or viscoplastic state as a result of melting of the crystalline and/or softening of the amorphous (glassy) phase [29]. Inhibited CM based on thermoplastics are largely adopted in anticorrosion techniques. Most thermoplastics are produced at a large scale in petrochemical enterprises and are comparatively