ELECTRETS IN ENGINEERING
Fundamentals and Applications

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SPRINGER-SCIENCE+BUSINESS MEDIA, LLC

Library of Congress Cataloging-in-Publication Data

Kestelman, V. N. (Vladimir Nikolaevich)
Electrets in engineering : fundamentals and applications / by Vladimir N. Kestelman, Leonid S. Pinchuk, Victor A. Goldade.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-7923-7754-2 ISBN 978-1-4615-4455-5 (eBook)
DOI 10.1007/978-1-4615-4455-5
1. Materials. 2. Electrets. I. Pinchuk, L.S. (Leonid Semenovich) II. Goldade, V.A. (Viktor Antonovich) III. Title.

TA403.6 K47 2000
620.1'1297--dc21

00-040550

Originally published by Kluwer Academic Publishers in 2000
Softcover reprint of the hardcover 1st edition 2000

Printed on acid-free paper.

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PREFACE

Recently a new sphere in materials science has formed which subject is structure and properties of electret materials used in engineering, medicine, biotechnology and other branches. It is characterized by specific methods of experimental investigations based on recording charge transfer, polarization and depolarization of dielectrics and involves original techniques and physico-mathematical aids where notions that exist at the interface of several natural and technical sciences are concentrated. It embraces a vast area of applications mainly in engineering, instrument-making, electronics, medical technique, biotechnology, and etc., has a specialized technological base for electric polarization of dielectrics composed of uncommon technological methods, equipment and instrumentation.

Apparently, future fundamental investigations in the domain of electret materials science are to be developed at the interface of computer simulation, physics and physical chemistry of dielectrics. Elaboration of a model for electric polarization of solid media with uneven charge density distribution, complicated by surface phenomena, outer electromagnetic, heat, chemical and other effects, presents a grave methodological problem. The simulation of structures in which polarization follows diffusion mechanism of chemically active molecules or their fragments, and the development of calculation methods for polarized charge relaxation and regularities of dielectric nonlinear properties, are the most urgent objectives of current research. Success in bioelectret effect studies is anticipated to result in profound widening of natural science knowledge.

The results of fundamental investigations have found a wide area of technical applications. This includes all industrial branches from general engineering to microelectronics, medicine and biotechnology The development of nanotechniques for thin electret film production (Langmure-Blodgett technique) efficiently used in microelectronics, nonlinear optics and biotechnology, inspires hope that through commercial production improvements in technology, labor productivity and product quality will be attained. This confidence is rooted in experience obtained from rapidly developing computer and measuring facilities, communications, and other engineering branches, which roots are built from of advances in electret materials science.

Today's electret engineering includes multitude of microphones, telephones, sensors and many other systems without which man's life would be inferior. Fields of electret application stretch from household filter for running water to space vehicles, and from mebrane separating bacteria to endoprostheses. Engineering challenges to increase pressure, speed and temperature while simultaneously reducing machine mass are to a great degree supported by successes in electret materials science.

All natural processes including metabolism, rock formation, hydrological cycle, etc. are connected by the electret effect. The investigation of bioelectricity and geophysical fields promote a more comprehensive understanding of processes taking place in nature and outlines new prospects in their rational management.

Advances in electret techniques spur the expanded nomenclature of electret materials. Their creation encounters, as a rule, preconceptions towards feasibilities of these materials. Nevertheless, their production techniques, compositions and optimum variants of application are innovatory and competitive. A number of electret systems are referred to as smart ones, i.e., systems able to adapt to operation conditions and effect properties of conjugated parts, articles or components of technological process.

Thus, electrets are a vast class of promising materials showing wide prospects for applications in engineering, medicine and biotechnology, and indicating high level of a large group of engineering articles. The range of investigations in materials science has shifted to the creation of multifunctional materials involving those being physical field sources. Their role in technical progress is continuously growing.

With developing electret materials science and growing significance of electric polarization as a technological process, the activities connected with development and utilization of electret articles start to be specialized. The combination of specific for electret new systems of knowledge, methodology, tooling, specialized techniques and professional skills has led to formation of a special teaching course of electret materials science in educational institutions and public recognition of specialists in the field of electrets.

All aspects of electret application cannot be fully reflected here in a single book. Concepts which have not yet received universal recognition but adequately reflect contemporary trends in electret development, are disclosed by the authors along with traditional representations. The authors attempted to objectively show a number of viewpoints, even disputable ones and hope the present book will stimulate new investigations in the domain of electret effect application.

CHAPTER 1

ELECTRET EFFECT AND ELECTRIC TECHNOLOGIES.

First investigations of electret effects were undertaken at the beginning of the twentieth century by a Japanese physicist Eguchi in 1919 [1]. Theoretically the existence of electrets as a "permanently polarized dielectric" was forecasted already in 1892 by the British physicist Heaviside. An electret was produced by Eguchi by melting a mixture of carnauba wax, rosin and beeswax and cooling it to solidification in a static electric field. He has noticed that charges on the specimen surface immediately upon its formation were opposite in their sign to those of the adjacent electrodes. The charge was named by Eguchi a heterocharge. The electret can change its charge with time for the opposite. This one reached upon stabilization was named a homocharge.

It was supposed initially, that the electret effect was conditioned by "freezing" of the field-oriented dipolar molecules. After the field removal the remanent polarization and the related surface charge begin to slowly reduce with time. Later (in the 50-s) Gross has established, that along with polarized charges found in electrets there are charges involved from the outside during polarization. He has also shown that remanent polarization can emerge through both dipolar molecule freezing and space charge formation during ion and electron migration in electric field. In the 60-70-s Sessler, Perlman and others were studying the homocharge origin by examining kinetics of the charge carrier recombination in the electret traps.

The electret effect is generally described by the phenomenological theory which basic statements were formulated by Adams [2] and Swann [3]. The recent state of the phenomenological theory of electrets has been reported by Gubkin [4], Sessler [5] and other authors [6, 7]. The last digest of literature on electrets, charged and poled dielectrics and their application was given in [8].

When speaking about electrets we imply dielectrics which preserve electric charges of both or one sign for a long period. It can be asserted now, that electrets have been formed from practically all dielectric materials and the electret effect itself is a universal phenomenon like polarization or conduction. To produce the electret state it is necessary for a dielectric to have sufficiently deep trapping levels for electrons and adequately deep potential wells for ions and dipole molecules, while electric conductance of the material should not exceed $10^{-8} - 10^{-10}$ Ohm^{-1}cm^{-1}.

1.1. POLARIZATION OF DIELECTRICS

1.1.1. The main notions and terms.

One of the dielectric basic properties is its ability to polarize under the external electric field action. Polarization consists in violation of statically equilibrium distribution of charged particles in the substance and the appearance of the resultant electric moment different from zero.

The state of the effected by electric field dielectric can be described by two vector values: electric intensity **E** and polarization **P**.

Polarization **P** is a value characterizing qualitatively the phenomenon of dielectric polarization. It is equal to the limit of the ratio between the electric moment of some volume of a substance and this volume when it tends to zero. In the majority of cases polarization (of the so-called linear dielectrics) is proportional to electric intensity in a given point of a dielectric:

$$\boldsymbol{P} = \varepsilon_0 \chi \boldsymbol{E} \qquad (1.1)$$

where $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m is a dielectric constant; χ is dielectric susceptibility (dimensionless parameter). The product of $\varepsilon_0 \chi$ (absolute dielectric susceptibility) characterizes the dielectric ability to polarize. It is a scalar value for isotropic substances and tensor for anisotropic ones. The nonlinear ("active") dielectrics which include, in particular, segnetoelectrics have no proportionality between vectors **P** and **E**. Polarization by module equals to surface density of the dielectric bound charges.

$$P = \sigma_{bnd} \qquad (1.2)$$

Along with the mentioned **P** and **E**, one more electric value **D** is often introduced, which characterizes electric displacement (electric induction):

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} \qquad (1.3)$$

The substance ability to polarize is otherwise estimated by its relative dielectric permeability ε connecting the vectors of electric displacement and intensity through a simple relation:

$$\boldsymbol{D} = \varepsilon \varepsilon_0 \boldsymbol{E} \qquad (1.4)$$

(the word "relative" is usually omitted in this term).

The comparison of Eqs. (1.1), (1.3) and (1.4) shows the relation between dielectric permeability and susceptibility:

$$\varepsilon = 1 + \chi \qquad (1.5)$$

It is evident, that dielectric permeability could not be less than 1, so far χ for any substance, except for vacuum, is positive. For vacuum $\chi = 0$ and $\varepsilon = 1$.

From relations (1.1) and (1.5) it is seen that polarization is linearly connected with dielectric permeability

$$\boldsymbol{P} = (\varepsilon - 1)\varepsilon_0 \boldsymbol{E} \qquad (1.6)$$

It grows under the action of a fixed electric field with increasing ε. The value of ε of conventional dielectrics lies within the 1 - 40 limit.

When describing dielectric properties in an alternating electric field the notion of a complex, or generalized dielectric permeability is introduced to simplify the mathematical and physical interpretation:

$$\varepsilon^* = \varepsilon - i\varepsilon'' \qquad (1.7)$$

where ε'' is the dielectric loss factor, $i = \sqrt{-1}$.

To characterize a dielectric in an alternating electric field, it is important to assess the time of particles displacement or orientation under the field action, i.e. to know *relaxation time* τ which defines the polarization setting time. It is also customary to identify the time constant of dielectric polarization reduction upon external field removal as relaxation time τ. It is a time interval when the initial polarization magnitude reduces *e* times.

If $\tau \ll T$ (T is the period of electric field variation), then the dielectric polarization proceeds as in the constant field, because particles manage to follow the field variations. When $\tau \gg T$, i.e. under a high frequency field, polarization is not observed at all as far as the dielectric particles do not succeed to noticeably shift or swing during the half-period of the field variation. At $\tau \approx T$ polarization develops not fully because the displacing or orienting particles are lagging in their motion behind the varying electric field. In this case polarization and field intensity show a phase difference leading to dielectric losses.

Dielectric losses govern energy dissipation generated as heat under the applied to dielectric alternating field. Dielectric losses measure is the tangent of dielectric loss angle:

$$tg\,\delta = \varepsilon''/\varepsilon \qquad (1.8)$$

According to Debye there exist the following relations between ε, ε'' -- and the applied field angular frequency ω:

$$\varepsilon = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(\omega\tau)^2}; \varepsilon'' = \frac{\Delta\varepsilon \cdot \omega\tau}{1+(\omega\tau)^2} \qquad (1.9)\,(1.10)$$

where $\Delta\varepsilon = \varepsilon_{st} - \varepsilon_\infty$ (dielectric permeability increment), ε_{st} - static dielectric permeability, ε_∞ - dielectric permeability at an infinitely high field frequency.

Equations (1.9) and (1.10) are obtained under condition that all dielectric dipoles are similar, do not interact with each other and so are characterized by the same relaxation time τ. Nevertheless, real dielectrics, particularly polymers, feature a certain distribution of relaxation times described by the relaxation spectrum $\varepsilon(\omega)$ and distribution function $F(\tau)$. For symmetric function $F(\tau)$ we can use equation from [9]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(i\omega\tau)^{1-\alpha}}, \qquad (1.11)$$

where α is the parameter characterizing width of the relaxation time spectrum ($0 \leq \alpha \leq 1$). In this case the dependence $\varepsilon'' = f(\omega)$ in a wide range of the external field frequency is in the form of a circumference arc which center lies below the abscissa axis (the so-called Cole-Cole's diagram). A more general equation can describe polarization processes with asymmetric distribution function of relaxation time:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1+(i\omega\tau)^{1-\alpha}]^\beta} \qquad (1.12)$$

where β is the parameter taking account of the function $F(\tau)$ asymmetry. When $\beta = 1$, the function looks like (1.11). If $\alpha = 0$ and $\beta = 1$, it corresponds to Debye formulae (1.9) and (1.10).

Transfer of electric charges in a substance under the external electric field is characterized by *specific electric conductance* (conductivity) $\gamma = dj/dE$, where j - density of a current passing through a specimen, E - constant electric field intensity. The inverse value $\rho = 1/\gamma$ is called *specific electric resistivity*. Electric conductance is not a characteristic property of dielectrics as compared to polarization. So far, it is often neglected (especially when polarization phenomena are considered) taken equal to null. Such a dielectric is called an ideal one. However, in a number of cases the processes referred to dielectric conductivity should be taken into account, for example when examining dielectric losses.

Charge in dielectrics is transferred by ions, charged macromolecules associates or separate macromolecules in solution (molions), as well as by free and weakly bonded electrons. The total electric conductance is determined by concentration n_i, charge e_i and mobility μ_i of all kinds of carriers:

$$\gamma = \sum_i n_i e_i \mu_i \tag{1.13}$$

According to the physical origin of charge carriers we discriminate ion, molion (electrophoretic) and electron conductivity.

For ionic conduction the concentration and carrier mobility and, hence, specific conductance of dielectrics are exponentially dependent on temperature T. As for e.g., for the majority of ion crystals the dependence $lg\ \gamma = f(1/T)$ can be presented as a straight line.

Under relatively low T and E electron conduction of dielectrics also increases exponentially with the rising T. While under high field intensity (E = 10^6 - 10^8 V/m) pickup of electrons from the substance atoms and molecules, and electrons ejection from electrodes are observed. The conditioned by these processes additional electron conduction results in a considerable increase of the total electric conductance, being thus dependent on the field intensity. Specific conductance of different dielectrics in strong fields is satisfactorily described by the relation [10]:

$$\gamma = \gamma_0 \exp(\beta_i E^n) \tag{1.14}$$

where γ_0 is the pre-exponential factor, β_i - coefficients, and n is varying from 1/2 in Frenkel's theoretical equation [11] to 2 in the calculated relation, which takes account of the combined tunnel and thermal ionization of dopes.

1.1.2. Polar and nonpolar dielectrics.

Dielectric losses and ability to polarize is strongly conditioned by the dielectric nature and structure. At present it is used to divide dielectrics into two classes: *nonpolar* (neutral) and *polar* dielectrics (dipolar).

A molecule of a substance consists of particles with a certain electric charge, either positive or negative. The algebraic sum of all charges in a molecule equals zero and the substance of a large volume is electrically neutral. Spatial position of charges in molecules of different substances can be different. Gravity centers of the sums of molecular positive and negative charges can spatially coincide or not. In the first case we have a nonpolar molecule and the substance consisting of such molecules is also nonpolar. In the second case the molecule and the substance are polar even in the absence of the external electric field when molecules are electric dipoles with different from zero intrinsic electric moment.

The electric moment of a molecule is $p = q \cdot l$, where q is the total positive (or negative) charge, l is the dipole arm. In most cases the intrinsic electric moment of polar molecules makes up about 10^{-30} C·m because the electron charge $e = 1.6 \cdot 10^{-19}$ C and the arm $l \cong 10^{-10}$ m. The nonpolar substance molecules have $l = 0$, so far $p = 0$.

Monoatomic molecules (He, Ne, Ar, Kr, Xe) and those consisting of two identic atoms connected with a homopolar link (H_2, N_2, Cl_2, etc.) belong to nonpolar substances. The molecules of potassium iodide KI, a typical ionic compound, (with a heteropolar link) possess a relatively large constant electric moment $p = 23 \cdot 10^{-30}$ C·m. Aluminum iodide AlI_3($p = 16.5 \cdot 10^{-30}$ C·m) and tin chloride $SnCl_4$($p = 17.0 \cdot 10^{-30}$ C·m) are among those inorganic substances which display high p values.

Hydrocarbons are mostly nonpolar or weakly polar substances. Yet, if hydrogen atoms are substituted for halogen atoms or -OH, $-NO_2$ groups, asymmetric molecules are formed with $p > 0$.

Substances of the hydrocarbon composition, including polyethylene, paraffin, ceresine, polyisobutylene, polystyrene, uncured rubber, petroleum oils, etc. are practically nonpolar organic materials used in engineering. Dielectric losses in nonpolar polymers are characterized by $tg\delta = (1 - 3)10^{-4}$, specific conductance 10^{-17} - 10^{-18} $Ohm^{-1}cm^{-1}$ and dielectric permeability ε in the 2 - 2.5 range. $tg\ \delta$ maximums observed in the high or low frequency range applied to the dielectric field are often attributed to polarization of the random polar groups or the presence of crystalline regions and their melting. Along with the cited above polymers used as nonpolar dielectrics we can also name polytetrafluoroethylene (Teflon), poly - β -vinyl naphthalene and poly - α - methylstyrene. Heat-resistant polymers include polyphenyleneoxide, poly-n-xylylene and polyphenylene. They can preserve their properties of nonpolar polymers up to 180, 300 and 500°C, correspondingly. Polyimide-based nonpolar dielectrics are noted for their valuable correlation of high mechanical and dielectric properties in the -200 - +200°C interval.

Polar polymers are distinguished by a somewhat higher conductance as compared to nonpolar ones ($\gamma = 10^{-12}$ - 10^{-16} ohm^{-1}/cm^{-1} in the glassy state). The value of ε varies from 2.5 to 3 at $T < T_g$ and it reaches 4.0 - 12.0 for the highly elastic state of polymers. The $tg\ \delta$ values range from 10^{-3} to 10^{-2} away from the maximum region. Introduction of polar substitutes noticeably alters the polymer dielectric properties. Important factors are not only polarity (i.e. dipolar moment) of the introduced group, but how the constituent enters the monomeric unit as well. This is because polar groups can enter both the main chain of the polymer and its branches too. Strongly polar are polyvinylchloride, polyvinyl alcohol and its derivatives, phenol-formaldehyde resins, polytrichloroethylene and others.

1.1.3. Polarization mechanisms.

All dielectric particles able to move or orient under the applied electric field can be divided into two groups: elastically (strongly) bonded and weakly bonded. A quasi-elastic force hampers the elastically bonded particle bias from its equilibrium state, round which it accomplishes heat oscillations. Such forces appear under electric field action and bias of electron shell and nucleus in atoms, atoms in molecules, charged ions in crystals, dipolar molecules in molecular crystals.

The weakly bonded particles acquire several equilibrium positions. They can occur with a definite probability in each of these positions. The frequency of the particle displacement from one equilibrium position to another is defined by the height of the potential barrier between the equilibrium states and the dielectric temperature. When the external electric field is superimposed the energy of particles and the probability of their occurrence in the equilibrium states vary. As a result, asymmetry appears in the charged particles distribution, i.e., the dielectric polarizes.

We discriminate four main types of polarization: electronic, ionic, orientation and space-charge (Fig. 1.1).

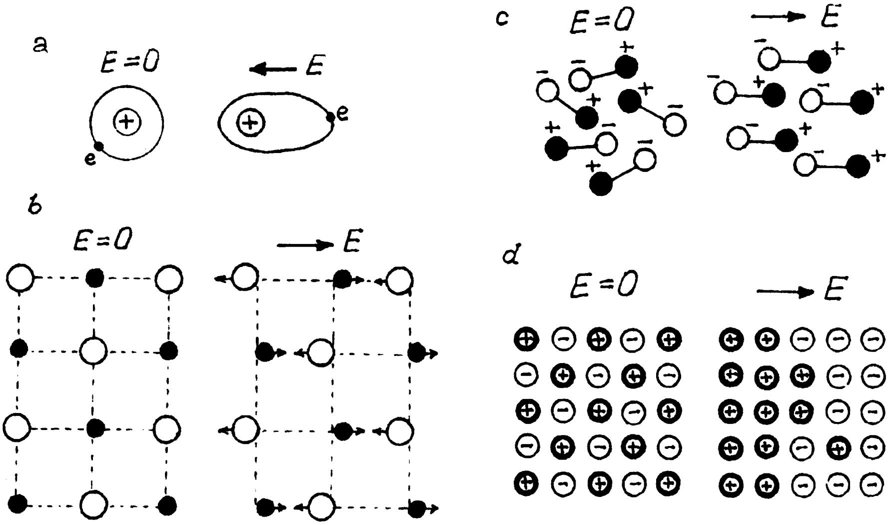

Fig. 1.1. Polarization mechanisms: electronic (a), ionic (b), orientation (c), spatial-charge (migration) (d).

Electronic polarization is caused by violation in symmetric distribution of electrons in atoms relative to their nuclei. Ionic polarization emerges due to shift in the positive and negative ion centers of gravity. Orientation polarization results from the field-stimulated orientation of molecules with the constant dipole moment. Space-charge polarization is observed when charge carriers are accumulated at the interface and grain boundaries in dielectrics with a heterogeneous structure (it is often called interlayer, migration or Maxwell-Vagner's polarization).

Polarization does not appear immediately upon electric field application. It is brought about with some delay, which is dependent on the relaxation time. The relaxation time increases for different polarization mechanisms in the following direction: electronic→ionic→orientation→space-charge.

According to the disclosed physical mechanism there are two forms of polarization (depending on the distance of particle displacement) and several kinds (depending on what kind of particle displaces) [12]. Polarization produced by elastically bonded particles is called elastic polarization and that of weakly bonded particles - relaxation or heat polarization (see Table 1.1).

Table 1.1.Characteristics of the main kinds of elastic and relaxation polarization of dielectrics

Elastic (deformational). Negligible shift of charged particles; strongly bonded dielectric particles.

Polarization type	Result of external field action	Relaxation time	Dielectrics types
Electron	Shear of electron orbits in atoms	10^{-15}-10^{-11} s	All dielectrics(to a certain degree); nonpolar dielectrics
Atomic (ionic)	Shift of atomic nuclei, emergence of induced dipolar moment	10^{-13}-10^{-11} s	Ionic crystals; nonpolar dielectrics
Elastic shift of dipolar molecules	A special case of atomic polarization involving variation of molecule-dipole	10^{-13}-10^{-11} s	Molecular crystal of dipolar molecules
Dipolar (orintational)	Directed orientation of polar molecules	from fraction to hundred seconds	Polar dielectrics containing charged defects forming quasidipoles (ceramics, alcali halogen crystals)

Ionic or electron	Orientation of quasidipoles formed by weakly bonded ions (electrons) via jumps from one equilibrium state to another	$\tau = \frac{1}{2\nu_0}\exp\left(-\right.$	Dielectrics with defective crystal lattice or contaminated (inorganic glasses, ion crystals with loose packing)

Relaxation (heat) Considerable shift of particles; formation of several equilibrium states; weakly bonded dielectric particles.

Polarization type	Result of external field action	Relaxation time	Dielectrics types
Space-charge (migration)	Charge carrier shift at a micro-distance; large polarization regions formation; considerable dispersion of electric energy	varies in a wide range	Dielectrics with a marked ionic or electron conductivity; semiconducting crystals with wide filled band
Domain	Orientation of domain electric moments; strong poling; considerable energy dissipation in alternating field	from 10^{-6} s to several h	Segnetoelectrics
Resonance	Dielectric losses due to resonance between applied field frequency and that of intrinsic electron oscillations, that of ions or active molecular groups.	10^{-9}-10^{17} s	All dielectrics including polymers in high field frequency

Elastic (deformation) polarization is characteristic of mainly non-polar dielectrics and is caused by the charge carrier bias relative to each other in the field direction. The most spread kind of elastic polarization is *electronic* one which results from elastic bias and deformation of electron shells with respect to dielectric atom nuclei. Electronic polarization can be called universal, because it is typical for all without exception dielectrics independently of any other coexisting types of polarization. A peculiarity of electronic polarization is its extremely short setting time (10^{-15} - 10^{-14} s). So, dielectric permeability of dielectrics with only electronic polarization is practically not dependent on frequency at alternating voltage.

Nonpolar dielectrics with only electronic polarization should hold the relation being the consequence of Maxwell's theory:

$$\varepsilon = n^2 \tag{1.15}$$

where n is the optical refractive index.

Table 1.2 lists the parameters of some nonpolar dielectrics in different aggregate states.

Table 1.2 Values of n^2 and ε for nonpolar dielectrics (at normal pressure and temperature)

Dielectric	Aggregate state	n^2	ε
Hydrogen H_2	Gas	1.00028	1.00027
Oxygen O_2		1.00054	1.00055
Nitrogen N_2		1.00060	1.00060
Ethylene $C_2 H_4$		1.00130	1.00138
Tetraform CCl_4	Liquid	2.13	2.24
Benzene $C_6 H_8$		2.25	2.28
Toluene $C_7 H_8$		2.25	2.39
Transformer oil		2.25	2.25
Paraffin	Solid	2.10	2.2
Amber		2.40	2.2-2.9
Polystyrene		2.52	2.3-2.6
Sulfur		3.69	3.8
Diamond		5.76	5.7

It is seen from the Table that the relation (1.15) is true for dielectrics which are considered to be nonpolar.

The other kind of elastic polarization is *ionic* one which is caused by elastic displacement of the oppositely charged ions as to equilibrium position in the electric field. Setting time of ionic polarization is longer as compared to electronic one and ranges from 10^{-13} to 10^{-11} s. Ionic polarization is characteristic of ionic crystals, for e.g., rock salt. Sometimes ionic elastic polarization is referred to as a special case of *atomic* polarization [12]. In fact, any molecule composed of separate atoms experiences redistribution of electrons between atoms, so far some atoms attain a more positive charge, when others a more negative. If an electric field is applied to such a molecule an induced dipolar moment is generated leading to atomic polarization.

Sometimes an *elastic displacement of dipolar molecules* takes place in molecular crystals on condition the molecules do not change their equilibrium orientation under the heat movement. If a dipolar molecule is elastically linked in the crystal lattice, then it elastically turns under the pair of forces in the electric field and changes its initial orientation.

On the whole, the processes of electronic and ionic polarization are identical and bear a deformation character. Along with the mentioned high velocity of polarization setting, it is important that elastic polarization is not connected with irreversible energy dissipation at low frequencies, i.e., it does not provoke dielectric losses.

Relaxation (heat) polarization combines several kinds of polarization related to inelastic displacements of charges in dielectrics. In case weakly bonded particles are the dipolar molecules of gases, liquids or solids orienting under electric field, then *dipolar (or orientation)* polarization arises in the dielectric. The weakly bonded ion (electron) relaxation causes *ionic (electronic) heat polarization* (in contrast to ionic and electronic elastic polarization).

Dipolar polarization is conditioned by the dominating unidirected orientation of dipolar electric moments. It is characteristic of a large group of polar dielectrics whose molecules possess dipolar moment even in the absence of external field. For dipolar orientation it is peculiar to overcome interacting forces of molecules which takes time and energy. Time of dipolar polarization setting (relaxation time) depends on the molecule size, substance viscosity and electric interaction between particles.

As compared to polar molecules the formed by weakly bonded ions and electrons quasi-dipoles change their orientation owing to ion and electron jump from one equilibrium position to another. Without electric field the ion (electron) chaotically changes its location and the dielectric as a whole does not acquire the dipolar moment. In electric field every charged particle of a quasi-dipole experiences an additional force which displaces the particles in a certain direction. That's why the dielectric polarizes.

Polarization of a dielectric containing relaxation particles of a certain kind (dipoles, ions, electrons) follows the exponential law. Energy model of relaxation polarization (by example of a weakly bonded ion) gives the following relation for the relaxation time:

$$\tau = \frac{1}{2\nu_0}\exp\left(\frac{U_0}{kT}\right), \qquad (1.16)$$

where ν_0 is the frequency of ions heat oscillations in equilibrium position, U_0 - potential barrier height between equilibrium positions. Thus, the higher the potential barrier and lower the temperature, the longer is the relaxation time.

Some inorganic dielectrics, particularly, ceramics, glasses, etc., show a *space-charge (migration) polarization* resulted from redistribution of charges in the dielectric bulk. The charge carriers (free ions and electrons) which provide the dielectric conductance in the constant electric field take part in this kind of polarization. Weakly bonded ions (electrons) do not reach electrodes during their motion at migration polarization, but attach at a distance from the initial center of heat oscillations. Current (the so-called absorption current) generated in the process of polarization decreases with time due to the forming space charges which create the oppositely directed electric field. Relaxation time of migration polarization could be much longer than that of ionic heat polarization and differs greatly for different dielectrics.

The migration space-charge polarization is typical for polymers with a sufficient amount of ions and takes place at above the glass transition temperature. Fast increment of dielectric losses in this region is caused by the rising conductance of the material [13].

Some types of crystals called segnetoelectrics obtain *domain polarization* under the electric field action. Segnetoelectrics are noted for their homogeneously polarized domains having a spontaneous kind of polarization arbitrarily emerging without any external effects. In the absence of electric field dipolar moments of domains are disordered. When the field is applied the domains start to orient in predominantly one direction leading to polarization of segnetoelectrics.

In the high-frequency range (10^9-10^{17} Hz) the dielectrics are characterized by a special type of polarization called *resonance polarization*. Its losses are conditioned by the resonance between the applied electric field frequency and natural oscillations frequency of the electrons, ions or active molecular groups. The resonance losses of electronic polarization have maximums in the IR, visible and UV spectra. Those of ionic polarization are commonly found in the IR region (sometimes in the lower frequencies).

In contrast to the majority of the low-molecular compounds with the only possible electric relaxation behavior, polar polymers are characterized by at least two maximums of dielectric losses. The low-temperature process *(dipolar-group polarization* or β-process) is defined by the motion of the smaller-size polar groups of different mobility. The high-temperature region of relaxation *(dipolar-segment polarization* or α-process) reflects the existence of a specific form of structural units mobility typical of only high-molecular substances, i.e., interrelated motion of chain segments not disturbing their inner conformation. These phenomena are discussed in detail elsewhere [13-15].

It is important to discuss one more phenomenon often accompanying dielectric polarization, although it can't be termed polarization in the generally accepted meaning of the word. This is *injected charge*. Its occurrence in dielectrics is treated as an "external" relaxational polarization [12]. Usual or "internal" polarization in its classical sense is the emergence of dipolar moment in a dielectric placed in electric field. As a result, bound charges of different signs appear on the surface: negative localize in the anode vicinity, while positive near the cathode. The involved electric field is opposite to polarization field in direction. In the case of injected charge the bound negative charge will be on the dielectric surface near the cathode, the bound positive charge will be found near the anode and thus formed field will have the same with the polarizing field direction. So, there is a formal similarity between the usual ("internal") remanent polarization and the injected charge. That's why the process of charge injection into a dielectric can be treated as an *"external" polarization*. The external remanent polarization occurs due to charge transfer from electrodes or interelectrode gaps into dielectrics followed by its fixing in the bulk traps.

1.2. ELECTRET PROPERTIES AND PRODUCTION.

1.2.1. The main types of electrets.

The present day electret effect concepts are based on dipolar polarization, charge displacement inside molecules or domains and the formation of spatial or surface charges. There exist two types of electrets (Fig. 1.2) distinguished by: i) *heterocharge* conditioned by electric polarization in the dielectric bulk due to dipolar orientation, ionic (or electronic) polarization and spatial charge displacement; ii) *homocharge* resulted from injection of charges of the same with electrode sign from electrodes into the dielectrics. The near-electrode space is characterized by charge exchange, so the formation of both heterocharge and homocharge proceeds simultaneously. The difference between the real or "free" charge σ_h (homocharge) and the remanent polarization **P** (bound heterocharge) represents the most important experimentally determined characteristics of electrets - the efficient surface charge density σ_{ef}.

There exist several methods of electret production. Most of them are based on the following procedure: a dielectric is placed in electric field and subjected to additional physical action which either reduces dipolar relaxation time or accelerates the charged particles migration. Depending on the type of physical action we discriminate thermo-, photo-, magneto-, radioelectrets and others. The electret state can occur in a dielectric even without the external field application, but, for example, from mechanical deformation (mechanoelectrets); during dielectric charging in corona discharge (coronaelectrets); at polymer heating in contact with unlike metals (metal-polymer electrets); at friction-induced electrification (triboelectrets). Electret effect is also peculiar to segnetoelectrics (segnetoelectrets) and living tissues (bioelectrets). By fixing the oriented in electric field dipoles and displaced ions using, for example, curing, chemoelectrets are obtained.

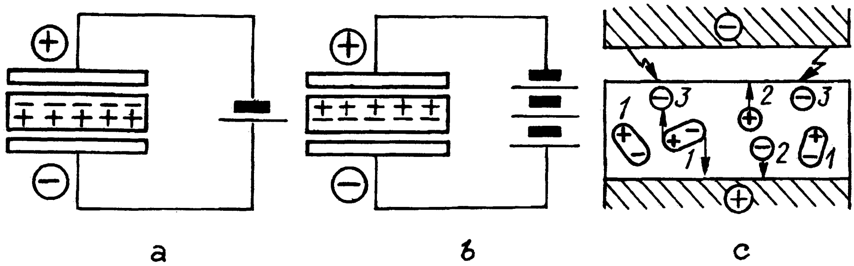

Fig. 1.2. Heterocharged (a) and homocharged (b) electrets; c - types of electret charges: 1 - oriented and orienting dipoles, 2 - shifted charges, 3 - injected charge carriers.

It is convenient to present *thermoelectret* (Fig. 1.3a) formation graphically (Fig. 1.4). The specimen is first heated to a T_p temperature, then the electric field is switched on and the specimen is endured for a certain time under T_p temperature, followed by a slow decrease down to room temperature. The polarizing time and temperature depend on the dielectric type. A noticeable effect is exerted on the formed electret characteristics by the polarizing field intensity. Depending on E_p value the electret acquires either hetero- or homocharge.

An indispensable and sufficient condition for the *metal-polymer electret* (MPE) formation is the polymer specimen heating in contact with the short-circuited electrodes made of unlike metals (Fig. 1.3b) [16]. Their thermal treatment regime is standard for the thermoelectret polarizing, i.e. endurance under T_p during time t_p, followed by slow cooling down to room temperature. The difference between the electrode metal potentials which form a pair of electrodes 1 and 2 serves as a polarizing field. It is characteristic of MPE to possess a homocharge, which means that the electret surface charge sign coincides with polarity of the corresponding electrode relative to the normal hydrogen potential.

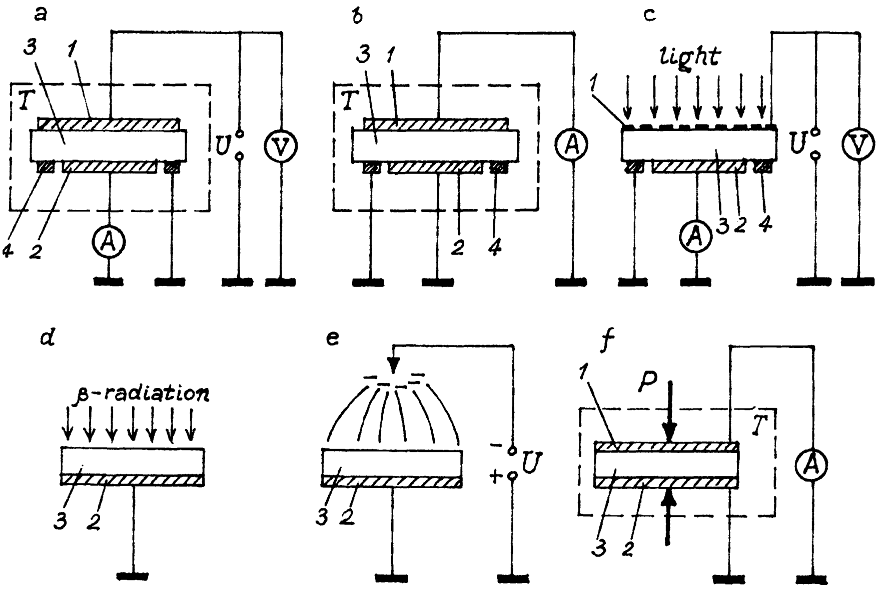

Fig. 1.3. Principal production schemes for thermal electret (a); metal-polymer electret (b); photoelectret (c); radioelectret (d); corona-electret (e); mechanoelectret (f): 1, 2 - electrodes, 3 - polarized dielectric, 4 - guard ring, *U* - power source, *A* - current meter, *V* - voltmeter, *P* – pressure

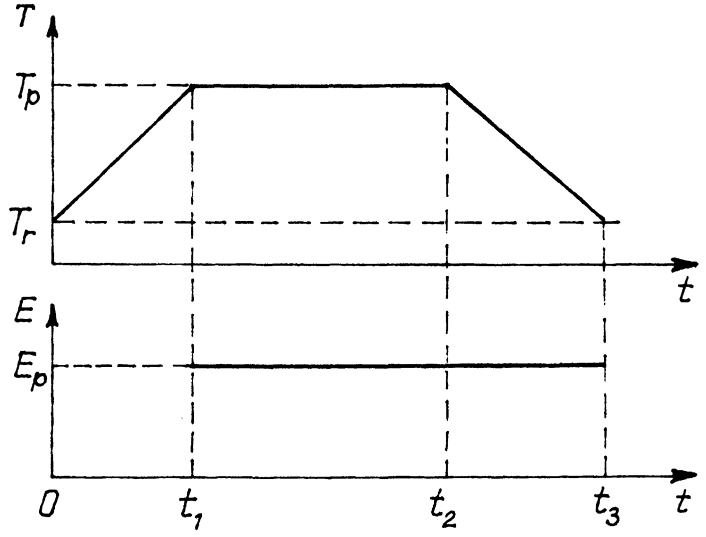

Fig. 1.4. A typical polarization regime for thermal electret production: T_p- polarization temperature, T_r - room temperature, *E*p - polarizing field voltage, t_1 - polarization onset time, t_2 – beginning of specimen cooling, t_3 - polarization termination, $t_p = t_3 - t_1$ - time of polarization.

When *photoelectrets* are made, (Fig. 1.3c), light serves as the heat source. Upper electrode 1 is made of a metallic grid or a semiconducting glass. The polarizing regime is the following: the dielectric in a strong electric field is exposed to light for a few minutes and upon light removal the voltage is switched off. It is typical for photoelectrets to possess only the heterocharge which diminishes with time. Photoelectret equilibrium charge is governed mainly by the polarizing field intensity. Light intensity and time of polarizing are related through the interchangeability law according to which the photoelectret charge value is in each moment defined neither by the light intensity nor polarizing time, but only by their product [17].

Radioelectrets are produced by exposing a dielectric to a beam of charged particles. This can be a beam of electrons, β- or γ-radiation. The principle diagram of set-up is similar to that for the photoelectrets production. For the case of radioelectret production without electric field the upper electrode is excluded (Fig. 1.3d). The electrons entering the substance retard and are captured in traps close to the irradiated side of the dielectric, thus forming a negative charge. The generated field induces the positive charge in the near electrode area of the opposite side.

Electroelectrets are produced just the same way as thermoelectrets, except for the thermal treatment. The polarizing field intensity is in this case higher than for thermoelectrets. Electroelectret charge is dependent mainly on the charge carrier injection.

To produce a *coronaelectret* the dielectric is placed in corona discharge field (Fig. 1.3e). One of the electrodes in this case is the ionized air-plasma, the specimen itself is placed in contact with the ground-metallic electrode and the injected charge carriers create homocharge in the electret.

Mechanical compression of specimens between heated plates results in the formation of *mechanoelectrets* (Fig. 1.3e). The emerged polarization decreases with time. In contrast to thermoelectrets, mechanoelectrets manifest a complex distribution of charges over the surface. This is because of simultaneous orientation and polarization in direction perpendicular to the plane of orientation.

Magnetoelectrets were first obtained in 1965 [18] by polymers heating to their softening in magnetic field of about 1 kA/m intensity. Study of magnetoelectrets is a comparatively new field of the physics and chemistry of polymers. Though the mechanism of their formation is not well understood, polarization is supposed to arise here due to changes in dielectric permeability of materials in magnetic field, caused by anisotropy of macromolecular magnetic properties. Surface density of magnetoelectret charge is composed of dipolar polarization, spatial charges and Maxwell-Vagner's polarization.

Table 1.3 illustrates production regimes and the initial charge surface densities for some types of electrets.

Table 1.3. Electret charges and production regimes

Electret type	Material	Thickness mm	T_p, °C	t_p, min	E_p, kV/cm	σ_{ef}, nC/cm^2
Themo-electrets	$MgTiO_3$	1.0	300	480	50-80	8-15
	CaF_2	1.2	190	300	10	up to 50
	PVC	0.4	70-130	6	10	up to5
	PS	0.025	120	30	30	5-7
	PA-6	1.6	200	80	25	5
MPE (eletrode) Cu-Al	PVB	0.2	134	65	-	15
	PS	0.3	140	85	-	7
	PA-6	0.5	220	80	-	8
Radio-electrets	Borosilicate glass$^{1)}$	17.5	20	-	-	up to 90
	Carnauba wax$^{2)}$	2	20	-	5	up to 40
	PETF$^{3)}$	0.01	20	-	-	140
	PTFE$^{3)}$	0.01	20	-	35	88
Mechanoelectrets	PC$^{4)}$	0.7	190	60	-	4.15
	PETF$^{4)}$	0.7	196	60	-	1.2

$^{1)}$ exposure to electron beam with 2 MeV energy;

$^{2)}$ β-radiation by a source of ^{90}Sr ($8 \cdot 10^4$ Gy dose);

$^{3)}$ γ-radiation by a source of ^{60}Co (300 Gy dose);

$^{4)}$ up to 10 MPa pressure

1.2.2. Two types of electret charges.

It is peculiar for electrets to maintain a lasting coexistence of charges of different signs on the opposite sides, although with time surface charge varies (Fig. 1.5). The analysis of experimental data suggests three cases: i) electret heterocharge decreases with time (down to zero or some constant magnitude); ii) heterocharge drops to zero, transfers to homocharge, passes the maximum and stabilizes; iii) homocharge reaches the maximum and then changes insignificantly. Experience shows that the dielectric with a low dielectric permeability features this or that case depending on the polarizing field strength. Thus, variation of the electret charge is described mainly by the dependence I, if the polarizing field strength $E_p < 5$ kV/cm. In most cases a homocharge is formed if $E_p > 10$ kV/cm (3). In between the two meanings a change of the charge sign is probable (2).

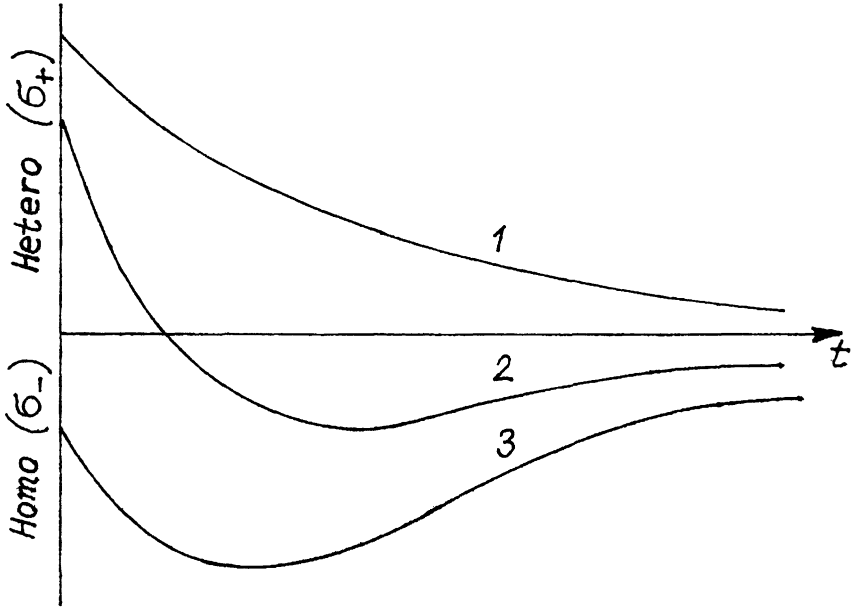

Fig. 1.5. Kinetics of heterocharge and homocharge variation upon dielectric polarization.

Surface density of the electret charge is measured by different methods. Most spread among them is the *compensation or induction* method. According to this method, voltage transmitted to electrodes is measured to compensate the electric field induced in the electret--movable oscillating electrode clearance [19]. The charge surface density is determined by the formula:

$$\sigma_{ef} = \varepsilon\varepsilon_0 U_e/L \qquad (1.17)$$

where U_e is the electret potential difference equal to compensating voltage; L - the electret thickness.

As the phenomenological theory of electrets demonstrates [4], the efficient surface density of charges, measured by the induction method, is composed of homocharge σ_p and heterocharge P:

$$\sigma_{ef}(t) = \sigma_p(t) - P(t) \qquad (1.18)$$

Both polarization and homocharge are varying exponentially with time. If we determine $\sigma_{ef}(t)$ under different temperatures, then having the dependence $\lg\sigma$ on I/T, charge relaxation time τ can be found. Relaxation time at operation or storage temperatures (about 20 °C) is estimated by extrapolation of dependence $lg\tau = f(I/T)$.

Since isothermal investigations are labor-consuming, nonisothermal technique is often used to determine the kinetics of decay σ_{ef}. With this aim surface potential $U(t)$ at a monotonous temperature rise and the *thermally stimulated depolarization* (TSD) currents are measured. TSD method consists in recording discharge currents in time at a controlled heating. Judging by the current dependence on time the parameters of charge relaxation as well as hetero- and homo-charges are determined. The charge accumulated in the electret is characterized by the area between the current curve and time axis (Fig. 1.6a), while the charge surface density equals to the remanent polarization.

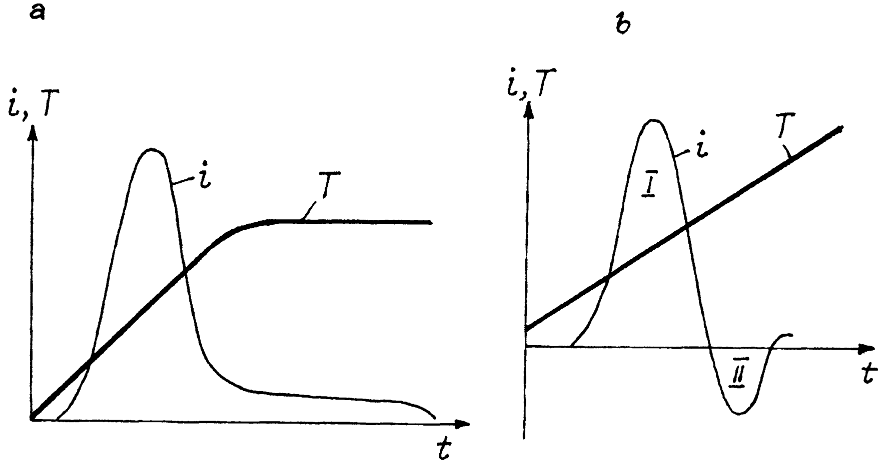

Fig. 1.6. Characteristic dependencies of TSD current (i) on time (t) at rising polarizing temperature (T) for ceramic electrets made of calcium titanate (a) and for polymethyl methacrylate (b).

The tests using TSD have shown that the charge surface density of carnauba wax electrets equaled to 10^{-7} C/cm^2. That of ceramic and metal-polymer electrets was even more (10^{-5} - 10^{-4} C/cm^2). At the same time, the changed by induction method charges are considerably less (10^{-9} - 10^{-8} C/cm^2) and are, as a rule, of a different sign. This can be attributed to a partial screening of polar charges by free charges, air electrons and ions, as well as by injected charges of the dielectric. All the mentioned charges are opposite by sign to polarization charge and correspond to the homocharge.

Heterocharge is observed when the polarized charge surpasses in magnitude the screening homocharge. The situation is vice versa for the homocharge. The electret charge transition via zero and its sign inversion are the result of the constant changes of homo- and heterocharges and difference in their relaxation times. Sometimes, homocharges are found at TSD. For example, for PMMA electrets two current maximums are reached (Fig. 1.6b). One of them (I) corresponds to the remanent polarization failure and the other (II) - to the homocharge break down.

An important parameter governing the electret quality is distribution of charges over the electret volume in direction perpendicular to its charged surface [5]. To define the distribution of both real and polarized charges such classical methods, including sectioning (sequential cutting of surface layers) and "detachable Faraday cylinder" were used. Sectioning technique was widely applied to study "thick" electrets and helped to gain further insight into the problem. Modern technique cuts layers (microtoms) up to 5 μm thick, being the sectioning resolution level.

The thin-film electrets utilize methods based on evaluation of the sample potential variation at its heat, ultrasonic or optical excitation. About twenty years ago, the use of pressure waves for nondestructive charge- or field-distribution measurements was suggested [20, 21]. Previous implementations of this idea were based on pressure-wave generation by means of a shock tube [21], a ruby laser [22], a high-voltage spark [23], and a Co_2 laser [24]. The direct experimental resolution of all these approaches is limited to a few tens of micrometers.

Recently, two complementary high-resolution methods (down to 1 m) for the direct and nondestructive scanning of polarization and charge distribution in the thickness dierction of thin films became available [25-29]. Both techniques are based on the idea of using pressure waves. A piezoelectrically generated pressure step (PPS) [26-28] leads to a uniform deformation of the sample volume behind the propagating step, whereas a laser-induced pressure puls (LIPP) [25, 29, 30] travels as a compression layer through the specimen [31]. The experimental arrangement of the PPS technique is schematically shown in Fig. 1.7.

Square pulses of 100-ns duration from a cable-discharge generator are used to drive a piezoelectric X-quartz plate. The resulting pair of alternating pressure steps ios coupled into the unmetallized sample and propagates through it. In propagating through the sample the pressure step moves space charges or deforms dipoles by which corresponding signal currents in the input of the wide band amplifier (500 MHz) are generated. The direct calibration of the measured signals with respect to excess charge distribution andpolarization is performed [32]. The signal is further amplified and displayed with a tektronix DSA 602 Digital Signal Analyzer with a band of 2 GHz. With this apparatus it is possible to detect spatial distribution in poled samples with densities less than 1 nC/cm^2 and spatial resolution of 1.5 nm [33].

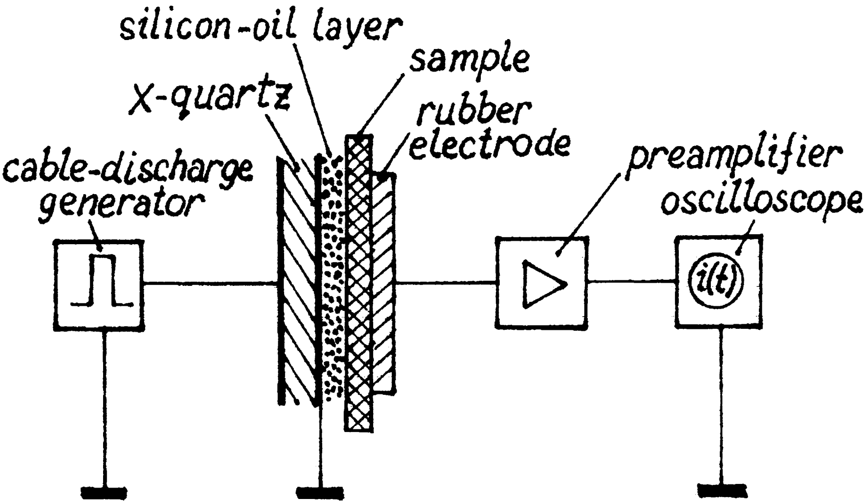

Fig. 1.7. Experimental set-up for the PPS method.

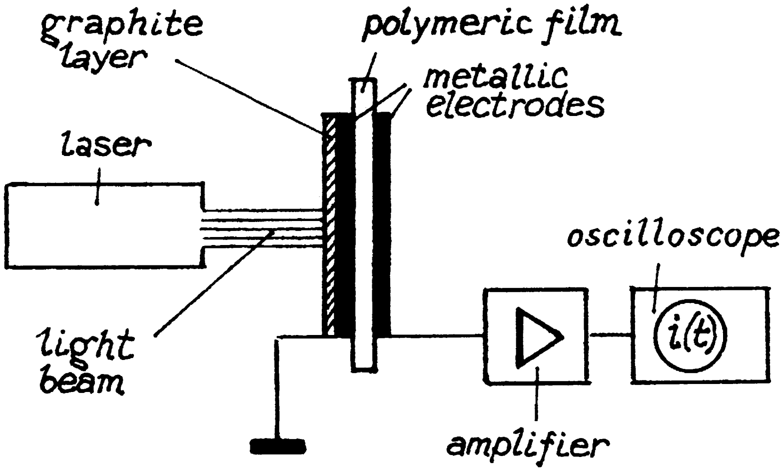

Figure 1.8. The experimental arrangement of the LIPP method.

The laser-induced pressure pulses arouse from interaction between laser radiation and the sample surface by means of thermal shock or radiation action. The method was streamlined by shortening the light pulse duration and improving the sensitive layer quality. The 70 ps light pulse is used for high-resolution measurements. The pulse interacts with a fine graphite layer on the sample surface and creates a pressure pulse above 500 ps. So, with sound velocity of about 2 km/s in polymers, the method resolution will be 1 μm.

1.2.3. Electret materials.

Electrets can be produced from different by their structure and properties dielectrics. First electrets were made of carnauba wax and its mixtures with rosin, beeswax, ethylcellulose and other components. The carnauba wax-based electrets display a long-living homocharge. It has been noted in a number of recent works [34] that the efficient surface charge density in such electrets has been preserved $(4.6\text{-}6.6)\times10^{-9}$ C/cm^2) for about 36 years practically unchanged.

In early fifties the electrets from polymers and inorganic dielectrics have received a great deal of attention. Some researchers attempted to classify dielectric materials by their electret properties, particularly, by the magnitude and stability of charge surface density (see Table 1.4).

Table 1.4. Dielectrics for electrets displaying good, medium or poor qualities

Good	Medium	Poor
Polyvinylacetate	Sulfur	Polyethylene
Polyamide resins	Polymethyl methacrilate	Polystyrene
Multicomponental organic compositions on wax and resin base	Palmitic acid	Polytetrafluoroethylene
	Saccharides Esters	Paraffin
		Stearic acid
Titanium derivatives	Phenolic derivatives Nylon	
Polyethyleneterephthalate	Ebonite	

However, data obtained by different authors did not agree and sometimes contradicted one another. PTFE can serve an example of the considered to be "poor" electrets. Yet, PTFE-based coronaelectrets made as thin films (11-25 μm) show a stable, high homocharge (up to 7.5 10^{-8} C/cm^2) [35].

At present it is assumed that the electret effect is peculiar to all dielectrics [12]. The electret state can be brought about by any type of "internal" relaxation polarization or by entrapped injected charge. Any dielectric has its natural and doped structural defects and the consequent relaxation processes. Relaxation times of these processes are sufficiently high at low temperatures and provide for the emergence of electret state in dielectrics.

To classify substances judging by their disposition to electret state is, apparently, impossible, the more so the different kinds of electrets of the same dielectric can show different properties. Today electrets are produced from different classes of materials, including natural waxes, resins, synthetic polymers, ceramics, monocrysltals of various substances. Table 1.5 lists the main and most studied dielectric materials with electret properties.

Table 1.5. Different classes of electret materials

Class of materials	Material
Natural wax, resin	Carnauba wax, rosin, beeswax, paraffin, schellak
Polymers	Polymethyl methacrylate, polyvinylchloride, polytetrafluoroethylene,polyethylene terefthalate, polystyrene, polyethylene, polypropylene, polycarbonate, polysulfone, polyamides, polyimides, polymethylsiloxane, polyvinylftoride, polytrifluorochloridethylene, polyvinylidine fluoride, epoxide resin.
Biopolymers	Proteins (polypeptide, callogen, hemoglobin, gelatin, trypsin, urease, ribonuclease); polynucleotides (DNA, RNA); polysaccharides (chitin, cellulose)
Low-melting dielectrics organic	Benzoic acid, citric acid, rosin
Ceramic dielectrics, glasses, metals	Titanates of alkali-earth metals ($MgTiO_3$, $CaTiO_3$, $ZnTiO_3$, etc), aluminum oxide $Al_2 O_3$, silicon dioxide SiO_2, pirex glass molten quartz, borosilicate glass, porcelain glass.
Monocrystals	Strontium titanate $SrTiO_3$, alkali halogen monocrystals, rutile, corundum, ice, quartz, calcite.

Owing to lately developed novel techniques, electret materials with unique properties (organic and inorganic) have been produced [36]. Of particular significance is the superb charge storage capability of silicon dioxide/silicon nitride double layers which was discovered only very recently [37]. Perfect electret properties display Teflon AF (amorphous copolymer of tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxole) supplied by Du Pont. Other types of Teflon (FEP, PTFE, PFA and since 1992 amorphous Teflon, type AF) are nonpolar polymers of high electrical resistance. Due to their excellent charge storage properties they are very important for electret applications, e.g., microphones [36].

1.2.4. Electret properties.

Among the main characteristics of electrets we can name the charge value, relaxation time (life of electret charge), charge sign inversion, presence of "internal" and "external" remanent polarization, coexistence of two charge types (hetero- and homo-), volume distribution of charges. Their parameters are conditioned by both technological regimes of electret production and external factors effecting the electret during storage and operation (see Fig. 1.9).

The intensity and duration of physical treatment are the most effective factors among *the technological conditions* which can change the electret charge type and magnitude. Some aspects of such an influence were discussed earlier. As it was noted before, homo- or heterocharges are formed depending on the polarizing electric field voltage, besides, the heterocharge can turn into homocharge. On voltage increase the electret charge grows and reaches, for e.g., for calcium or magnesium titanate 10-30 nC/cm^2 at $E_p = 10^4$-10^5 V/m.

The relation of electret charge versus time of polarization is in the simplest form (for orientation polarization of polar dielectrics) described by the formula:

$$\sigma(t) = \sigma_{max} (1-e^{-t/\tau}), \qquad (1.19)$$

where σ_{max} is the maximum heterocharge value for a given dielectric at E_p and T_p. With increasing t_p the charge augments exponentially followed by stabilizing.

Electrode nature exerts a definite effect on the MPE charge [38]. The occurrence of homocharge in MPE is supposed to depend on formation of metal-containing organic compounds in the metal-polymer contact and their further diffusion into the polymer bulk. The process is greatly influenced by the galvanic metal1-polymer-metal2 pair which functioning governs charge transfer in the polymer interlayer [39]. This mechanism explains the dependence between electret charge and metallic electrodes nature by the latter activity in contact reactions.

Each electret charge value and its life are also conditioned by the sample configuration and size. Though systematic investigations have not been undertaken in this direction, the main tendency can be traced: "thick" samples of a small diameter possess a minor heterocharge with dominating homocharge, but their life is shorter than the "thin" electrets have [12].

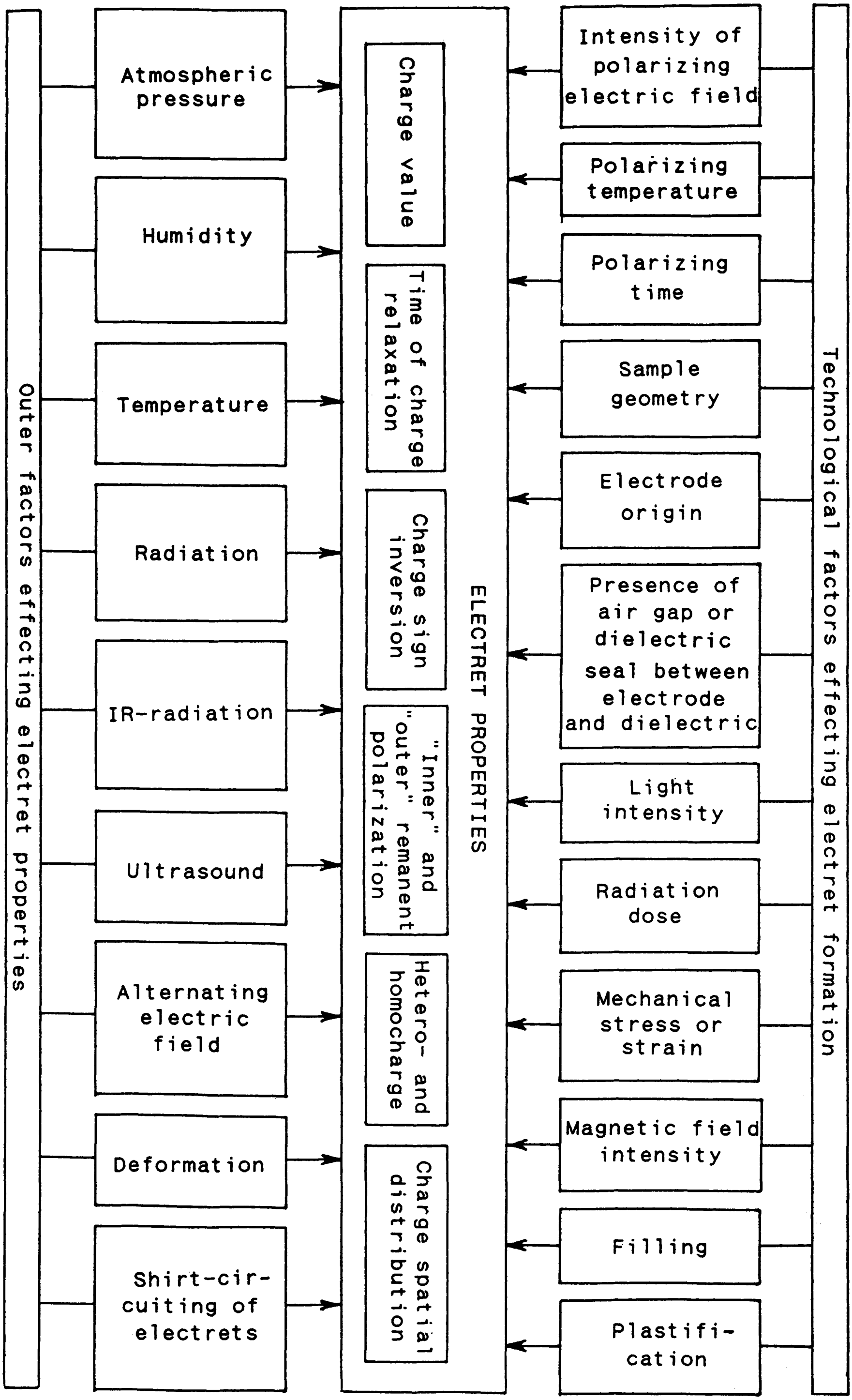

Fig. 1.9. Different factors effect on electret properties.

In the process of polarization air gap between the dielectric and electrode effects the heterocharge-homocharge ratio. Gross [40] has shown that the homocharge has been formed due to breakdown of the air gap between the electret and electrode. By placing a dielectric cushion in the electrode-dielectric clearance the homocharge value is reduced considerably and when the dielectric is polarized in vacuum the homocharge does not appear at all.

Irradiation of a dielectric causes, from the one hand, the formation of spatial charges and, from the other, facilitates discharge of the polarized dielectrics. With increasing radiation dose the charge grows up to the limiting for the studied sample values. If the dose exceeds the needed for reaching the limiting charge value, the established charge diminishes due to rise of dielectric conductance.

The influence of mechanical stresses and deformations on the electret state formation have been studied mainly on polymers [41, 42]. As it was mentioned above, mechanoelectrets display a mosaic distribution of charges over the surface. The increased rate of deformation leads to the charge growth. Similarly to compression, mechanical orientation at stretching and rolling favors the formation of orientation polarization and charge carrier injection from metallic rollers into the polymer film. This leads to further dipolar polarization.

The magnetic field (MF) strength and thermo-magnetic treatment duration define the value σ_{ef} of the polymer-based magnetoelectrets. This is conditioned by variations in both the dielectric permeability and magnetic receptivity of polymers in MF. In this connection a temperature interval has been established within which the PE melt is found in a relatively ordered (quasi-liquid-crystalline) state under MF action. MF threshold strength at polymer transfer to quasi-liquid-crystalline state is 80-120 kA/m [43]. As a result of structural elements orientation at a thermo-magnetic exposure the polymer becomes electrically polarized and thus, a magnetoelectret is formed. The value σ_{ef} of magnetoelectrets from structural polymers is 1.7-2.9 nC/cm^2. It is caused by disorientation of the emerging C-O groups and disordering of quasi-liquid-crystalline state. σ_{ef} dependence on polarization temperature is expressed by a curve with a maximum. σ_{ef} maximum values are observed at temperatures corresponding to the polymer quasi-liquid-crystalline ordered state.

Introduction of dielectric fillers and plasticizers into the polymer matrix effects MPE charge [44]. Each polymer-filler combination has its optimum concentration regions at which TSD is higher than that of the non-filled polymers.

The *external factors* influence much the electret characteristics. With decreasing pressure of environment the electret charge surface density lessens. On increasing relative humidity the electret charge decreases abruptly, but further fall of humidity is accompanied by a slower charge recovery.

Electrets are sensitive to temperature variations. This is because, from the one hand, the electret depolarizes and free charges breakdown at heating and, from the other hand, the dielectric conductivity rises sharply and assists neutralization of bound charges. In general, on temperature rise both charge value and the electret life decrease.

When electrets are irradiated an abrupt rise of .air conduction occurs and, as a consequence, a layer of charges is formed on the electret surface able to fully screen the electret charge. On the increase of radiation dose the electret charge decreases. Data have been obtained evidencing that failure of the electret state proceeds more intensely at exposure to ultrasound or alternating electric field, while IR-radiation speeds transfer from hetero- to homocharge.

Short-circuiting, i.e. electric connection of the electret poles helps to prolong its life. This means that the field inside the electret diminishes and hampers discharge due to inner conductivity.

A decrease in surface density of the electret charge can be observed during deformation. It can be caused by damage of structural traps and liberation of charge carriers. In polymers this process is also influenced by orientation of macromolecules and leads to considerable decrease of surface charge. A different behavior displays MPE during deformation. As far as metal diffusion in MPE effects deep layers [45] the generated during deformation charges neutralize not emerging on the sample surface and surface charge density does not practically change [46].

1.2.5. Thermally stimulated currents and metal-polymer electret formation.

A few years ago electric current generated in the metal 1-polymer-metal 2 systems (M1-P-M2) attracted attention of a number of scientists. In 1975 Japanese researchers published a paper [47] devoted to spontaneous thermal currents in PTFE sample placed between electrodes of unlike metals. Several papers on the subject were published later [48-52]. The emerging spontaneous currents are like thermally stimulated (they are by their essence) ones and are dependent on the disconnected circuit voltage between unlike electrodes. A supposition has been put forward that the voltage is of electrochemical nature [53]. Works [49, 50, 54] suggest an electrochemical model where electrode reactions at the metal-polymer interface are considered as the basis of arising voltage in the opened circuit. This galvanic effect can exert, as it will be shown below, a noticeable influence on the polymer surface and physico-mechanical properties.

The present authors have investigated thermally stimulated currents (TSC) generated in the M1-P-M2 systems. When the polymer interlayer installed between two short-circuited unlike electrodes is heated, electric current emerges in thecircuit. The current direction is determined by the combination of metals M1 and M2, i.e. by their relative disposition in electrochemical line (see Table 4.1). If to interchange electrodes M1 and M2, the current direction will change for the opposite. The fact proves that TSC is governed by rather electrode potential difference of metals M1 and M2, than by the presence of temperature gradient in the sample or anisotropy of the polymer materials:

Pairs of electrodes M1 and M2	Current value, μA	Electrode potential difference, V
Cu - Al	0.240	2.00
Pb - Al	0.155	1.53
Cu - Pb	0.085	0.40

Let's consider the role of *electrode processes* at the metal-polymer interface and their effect on current generation in M1-P-M2 systems. Vijh [49] has suggested an electrochemical model of voltage emergence in an open circuit. Its essence is in the following. M1-P-M2 system is treated as a battery (or galvanic element) which negative electrode reacts with environment moisture and forms metal oxide according to the formula:

$$xM + yH_2O \rightarrow M_xO_y + 2yH^+ + 2ye^-, \qquad (1.20)$$

So, the negative electrode acquires $M\text{-}M_XO_Y$ pair with its own characteristics of the electrode potential. The freed protons inject into the polymer and participate in conductivity.

In case the model is used in a system whose electrode does not oxidize in the studied temperature interval (in paper [49] gold is taken as a reference electrode), it can perfectly describe test data. For other cases it is offered [54] to consider metal oxidation using the scheme of (1.20) for both electrodes. Voltage in the open chain and, consequently, the generated current will be then conditioned by the difference of oxide electrode potentials ΔU_{ox} of metals $M1\text{-}M_XO_Y$ and $M2\text{-}M_XO_Y$.

Current maximum is observed for TSC temperature tendencies corresponding to different electrode pairs (Fig. 1.10) independently of electrode materials in the 433-443 K temperature interval. Current value for M1-P-M2 system exceeds by more than an order that of the system with identical electrodes.

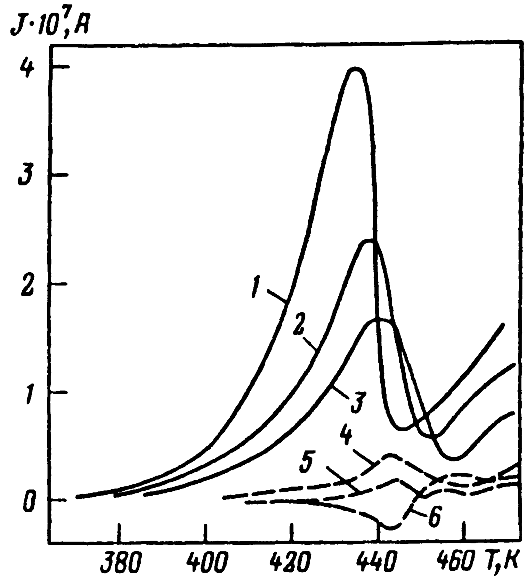

Fig. 1.10. Temperature dependence of TSC in PVB (polymer layer thickness 600 m) with electrodes from unlike and like metal pairs: Cu - Al (1), Cu - Zn (2), Cu - Pb (3), A; - A; (4), Cu - Cu (5), Pb - Pb (6).

When electrode metals are unlike, M-P-M system current is relatively weak and the open circuit voltage is governed mainly by the inner resistance of the polymer interlayer. Electrode processes at the metal-polymer interface would proceed to a certain degree with formation of products following the scheme (1.20). This is proved by low current values and their vague polarity for the system with like electrodes (Fig. 1.10, curves 4-6).

The maximum current J_{max} is determined, as it is shown in Fig. 1.10, by the electrode metal nature. A correlation is observed between J_{max} and electrode potential difference of the oxide metal pairs (Fig. 1.11, Table 1.6). It is seen from the figure that line 1 extrapolation to the ordinate yields a nonzero current value at $\Delta U_{ox} = 0$. The fact can serve a qualitative proof to the appearance of a negligible current in the M-P-M system with like electrodes.

There are believed to exist some other explanations of TSC emergence in M1-P-M2 systems. The authors of [51], for example, tried to prove that the open circuit voltage in the system with a polyvinyl alcohol interlayer depends on the difference of electrode work functions. This explanation is doubtful at least because there is always an oxide film on the metal surface experiencing interphase transformations at the metal-polymer interface. Table 1.6 shows work function to correlate neither with the current value in M1-P-M2 systems, nor with its direction (for e.g., for Pb-Al, Cu-Fe, Cu-Ni pairs work function difference disagrees with experimentally determined current direction).

Table 1.6. Electrode characteristics of M1-M2 pairs used in M1-P-M2 systems: ΔU is standard electrode potential difference of metals, ΔU_{OX} is electrode potential difference of oxide pair [49], $\Delta\varphi$ is metal work function difference

Electrode pairs	ΔU, V	ΔU_{ox}, V	$\Delta\varphi$, eV
Pt-Al	1.2-(-1.66) = 2.86		6.27-4.20 = 2.07
Ag-Al	0.8-(-1.66) = 2.46	1.18-(-1.35) = 2.53	4.45-4.20 = 0.25
Cu-Al	0.34-(-1.66 = 2.00	0.42-(-1.35) = 1.77	4.45-4.20 = 0.25
Pb-Al	-0.13-(-1.66) = 1.53	0.25-(-1.35) = 1.60	4.00-4.20 = -0.2
Au-Cu	1.53-0.34 = 1.16	-	5.20-4,45 = 0.75
Cu-Zn	0.34-(-0.76) = 1.10	0.42-(-0.42) = 0.84	4.45-4.00 = 0.45
Cu-Fe	0.34-(-0.44 = 0.78	-	4.45-4.77 = -0.32
Cu-Ni	0.34-(-0.25) = 0.59	-	4.45-4.75 = -0.3
Cu-Pb	0.34-(-0.13) = 0.47	0.42-0.25 = 0.17	4.45-4.00 = 0.45

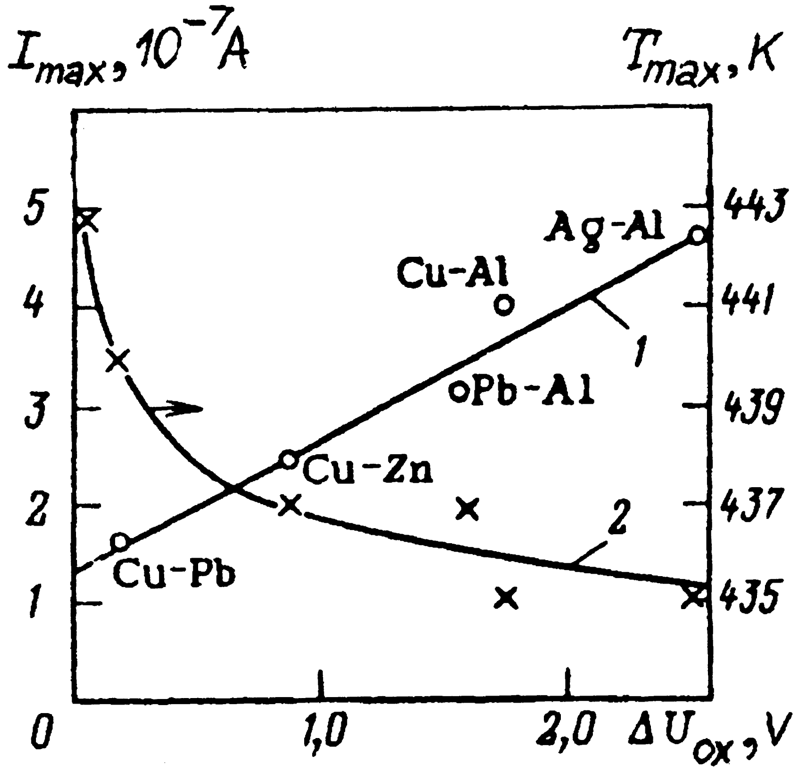

Fig. 1.11. Maximum current I_{max} dependence in PVB samples (1) and temperature maximum T_{max} (2) on electrode potential difference ΔU_{OX} of metal-oxide pairs M1 and M2.

TSC passage in M1-P-M2 systems leads to polymer electric polarization and occurrence of electret state in the polymer layer [38]. The new type of polarized state was called *metal-polymer electret* (MPE). The term was introduced due to the presence of metal in the polymer bulk and the dependence of polymer electret state on metallic inclusions in the polarized dielectric structure. Most close to the discussed type of electrets, from the point of view of formal definition (not by the mechanism), stand triboelectrets, i.e. electrets produced at friction or dielectric sample contacting a solid, while to produce MPE, the polymer contact with two bodies is necessary (unlike metals). The scheme of MPE formation is shown in Fig. 1.3b.

The determined by TSD value of polarizing charge volume reaches 10^{-4} C/cm^2 for MPE and exceeds by several orders that of the efficient surface charge density σ_{ef} measured by contactless induction method. The results of charge distribution investigations in MPE bulk show that the polarizing charge is mainly accumulated in the sample surface layers (Fig. 1.12, curve 1). It reaches 60-80 μm in amorphous PVB and 40-50 μm in crystallizing PPl and PA. It has been found out that polymer polarization in M1-P-M2 systems is accompanied by metal transfer from electrodes to the polymer (Fig. 1.12, curve 2). A negligible dissolution of electrodes is also observed in reference (nonpolarized) samples. Metal concentration, however, is 4-5 times lower in the polymer than in MPE. Probably, e.m.f. emerging at electrode shorting during thermal treatment accelerates metal diffusion into the polymer.

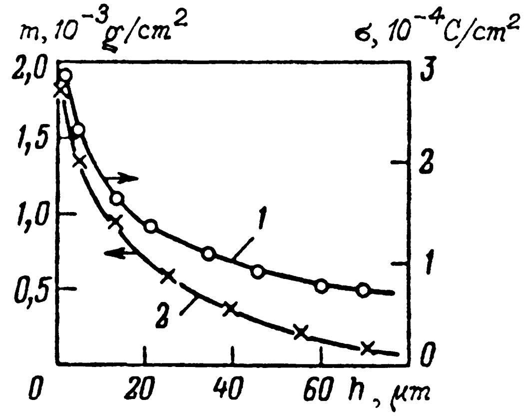

Fig. 1.12. TSD charge density σ(1) and copper content *m* (2) in polarized PVB samples depending on removed polymer layer thickness. Initial film thickness 300 μm; electrodes Cu – Al.

Metal diffusion into the polymer and volume charge formation are accompanied by rearrangement of the near-electrode layer structure. Thus, increase in "X-ray" crystallinity degree of polarized PPl samples, as compared to thermally treated nonpolarized ones, is 4% from the copper electrode side and 6% from the aluminium one side.

As a result of experimental data analysis a mechanism of MPE polarization is suggested which is a combination of electrochemical and space-charge polarizations [16, 54, 55]. The formation of metal-containing compounds proceeds in the near-electrode layers, particularly, carboxylic acid salts are formed, followed by their decomposition and metal particles separation. Electret charge arises from charge carriers entrapment by structural traps localized in defective zones of polymer structure and at the polymer-metal particle interface.

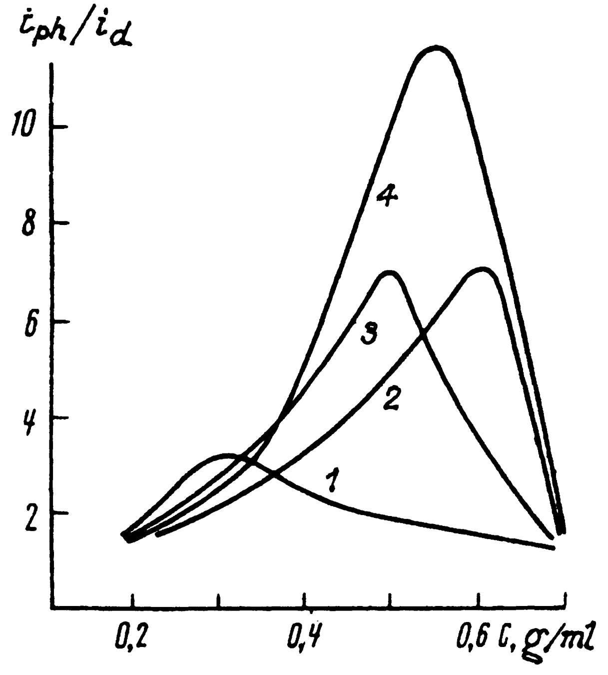

Fig. 1.13. Photocurrent (i_{ph}) ratio to dark current (i_d) depending on concentration (C) of PVB solution for different electrode pairs: Ni - Cu (1), Al - Cu (2), Ni - Pt (3), Al - Pt (4).

The suggested mechanism has been verified by the results of electret-thermal analysis [56] and experiments on UV-radiation effect upon charge transfer in M1-P-M2 systems [57]. To study structure of the polymer layer, being the polarized charge carrier, a PVB solution was used as a model medium. The solution viscosity was constantly growing due to solvent evaporation drawing the model nearer to solid state. It is seen from Fig. 1.13 that photocurrent i_{ph} value in a closed M1-P-M2 circuit depends on solution concentration and electrode metal nature (one of which is made as a grid). The curves configuration is, probably, governed by photoemission of electrons into the model medium, as well as by conditions of charge carrier transfer between electrodes. Electric conductivity of low concentration PVB solutions (C<0.2 g/ml) is known to be of ion origin under high carrier mobility. Photoemission from electrodes contributes little to the total conductivity, so, $i_{ph}/i_d \approx 1$. When PVB concentration rises, properties of a solid start to dominate in the model medium. At C>0.7 g/ml the dark current and photocurrent values are limited by the carrier mobility and $i_{ph}/i_d \approx 1$. Since solvent evaporation conditions were identical in all experiments, it can be supposed that the magnitude and position of maximums in Fig. 1.13 are due to the following factors: photoemission properties of electrode metals, their reactivity towards model medium, ability to initiate the formation of layers-carriers of polarized charge and contact potential difference or electrode potential difference of electrode metals.

MPE main properties and possible fields of their application are discussed in the corresponding chapters.

1.3. ELECTRIC FIELDS AS REFERRED TO MATERIALS TECHNOLOGY.

Electret effect in different technological processes, devices and systems can be divided into two directions. The first one is related to the spatial displacement of charges in dielectrics and functionalization of the generated internal electric field as an energy source in the devices, systems and units. These questions will be considered further.

The second direction stems from an expanded understanding of electret effect as an electro-activation process which results in variation of material structure, properties (not only of dielectrics) under the applied electric field or a beam of charged particles. This direction includes a wide group of electrical techniques used for engineering materials production and processing, as well as for modifying and finishing article surfaces to improve operation characteristics. It was historically adopted that electric techniques in engineering were mainly bounded to arc welding and electrothermal treatment. Then, were added electro-erosion treatment of metals, coating application using electric field, plasma arc welding, etc. At present the range of electric field use in materials technology and articles production is extremely versatile, it embraces the methods of mineral materials processing till accurate dimensional machining of ready parts.

The present chapter gives a brief description of the most typical groups of electric technologies of engineering materials. They cover metallurgy, ceramic and polymer articles production, composite processing and surface treatment.

1.3.1. Processing of mineral raw materials.

There is practically no technological process in modern industry which purifies, modifies or prepares raw materials without using electric field. Below examples are cited of the most applicable and efficient electric technologies for engineering materials processing and those where electric field helps to produce special-purpose materials with unusual and even unique properties.

Electroconcentration of minerals is a combination of operations on the initial processing of ores and other raw materials aimed at removal of barren rock and separation of dielectric components by the static electric field. Another type of electroconcentration distinguished by physicochemical properties of components and technological media used is *electroflotation*. This is a method of minerals concentration in a water medium by electric charging. The concentrates stuck to air bubbles suspended in the foam layer and are further separated in the static electric field.

The main process in preparation of composite components is *electroseparation*, when solid particles are separated from gas, bulk or powder materials into components by electric field. To reduce dust content in the air, different methods of dust electric settling are used during separation.

Hydroelectrometallurgy, i.e. industrial production of metals via water media electrolysis, is one of the most important fields of nonferrous metallurgy. The overwhelming majority of world copper, as well as zinc, nickel, cadmium, gold and silver; a great portion of lead, tin, cobalt, antimony and some other metals are produced by this method. The main procedures of hydroelectrometallurgy are electrolytic refining and electroextraction. Electrolytic refining is electrolysis using soluble anodes of a ferrous metal and deposition of a highly pure metal on the cathode. Electroextraction is a cathodic deposition of metals during electrolysis of solutions obtained by ore leaching. The above methods include the stages of ore processing, solution preparation and metal extraction by application of electric field.

Electrochemical synthesis is used to obtain organic compounds by cathodic reduction or anodic oxidation of the initial substances. Due to low productivity of electrolizers, as compared to reactors of catalytic reduction or oxidation, and high energy consumption the industrial electrosynthesis is rarely used. Nevertheless, the method is waste-free due to the absence of special reagents and, as a consequence, its competability rises.

Electrolysis of melted salts is an industrial electric technique for manufacturing and refining aluminium, magnesium, sodium, potassium and lead-sodium-potassium alloys, and others. The process is carried out in electrolizers from refractory metals because the electrolysis temperature by 10-30 K exceeds that of salt crystallization, being 875-1275 K. Depending on the electrolizer power, the current parameters are within 30-40 to 100-150 kA.

1.3.2. Electrotechnologies for material processing.

Engineering offers a variety of technological methods to process engineering materials by electric current, electrolysis or their combination with mechanical working. The combination of such technologies, including ultrasound, plasma or a charged particle beam action, is united under the term "electrophysical and electrochemical methods of processing" (Fig. 1.14). Their development and industrial application were a qualitatively new step in materials processing technique. Electric energy, according to the technique, becomes an operating unit instead of being a complementary means for imparting motion to a blank or a tool during machining. The merits of electrophysical and electrochemical methods of processing are in their high productivity and capacity to fulfill operations inaccessible for machining.

Electroerosion is based on the action of electric discharge pulse occurring between the tool and the blank. Depending on duration and pulse power the electric-spark and electropulse methods of electroerosion can be discriminated.

Electromachining (electric-spark) was elaborated by N.I. and B.R. Lazarenkos in 1943. Metal removal from the blank surface is caused by strong hydrodynamic forces generated in the spark discharge channel. The relatively short spark discharges are of a low power capacity, so their effect on the material is negligible.

Electropulse method was proposed by M.M. Pisarevsky in 1948 and is accomplished by arc discharge. High temperature in the arc discharge area (4 000-5 000 K) promotes increase in pulse duration and reduction of intervals, thus introducing considerable power into the zone of machining (tens of kWt). The samarium-cobalt powder produced by the method achieves high magnetic properties and perfect particle shape for compacting in magnetic field.

Electromechanical technique unites the methods which combine a simultaneous mechanical and electrical treatment of metals.

At *electrocontact treatment* the tool cuts a layer of material softened by electric current passing through the tool-blank contact. The method variants are electromechanical treatment used to harden and finish friction units and electroabrasive processing by an abrasive tool made of conducting materials. Electric current introduced into the zone of processing reduces markedly the tool wear.

Magnetopulse treatment is intended for plastic deformation of metals and alloys. During interaction with a blank the quickly varying magnetic field energy excited by a powerful capacitor discharge on inductor transforms into mechanical work.

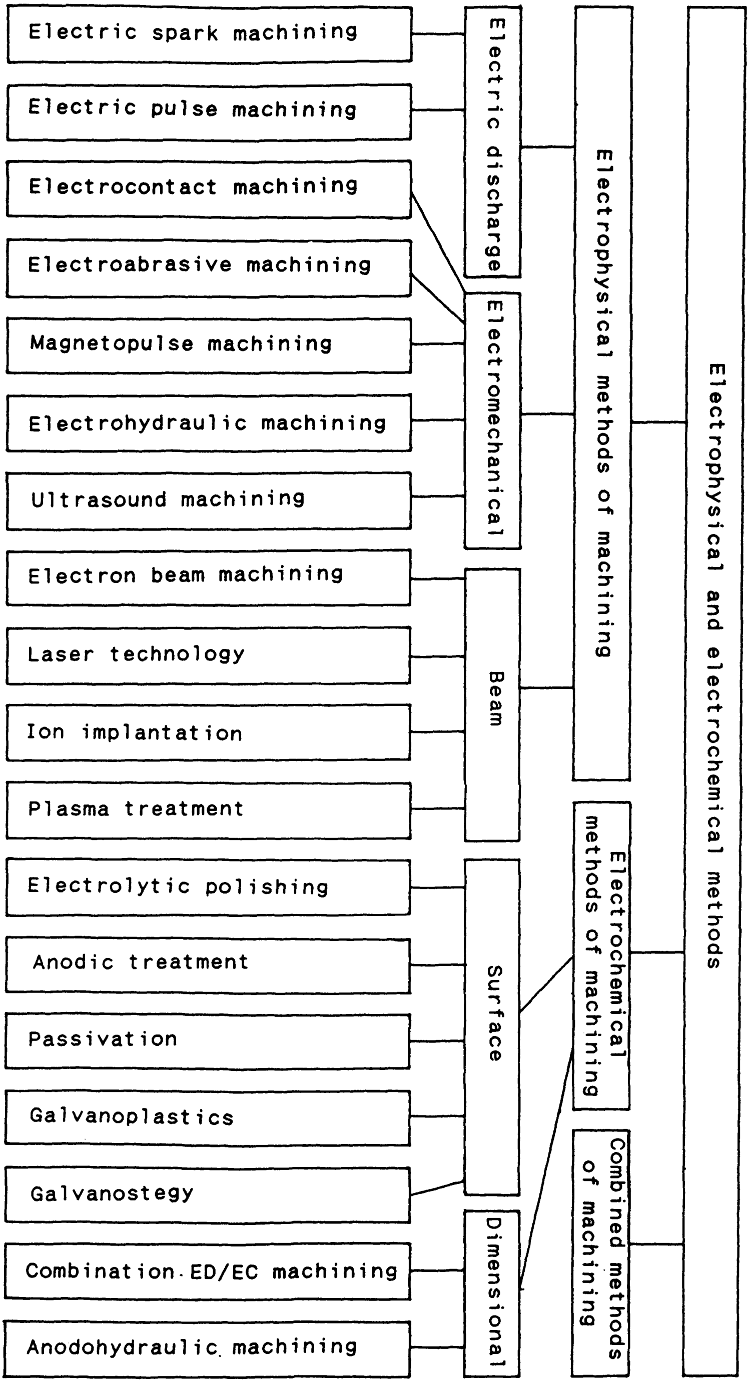

Fig. 1.14. Classification of the main electrophysical and electrohemical methods of material treatment.

Electrohydraulic treatment is based on the so-called electrohydraulic effect generated by the pulse electric discharge in a liquid dielectric.

Ultrasound treatment is used for welding, drilling, grinding, hard materials engraving, as well as for tinplating and soldering.

Radiation methods include treatment by flows of charged particles and light beams.

Electron-beam treatment is realized by a flow of electrons of up to 100 keV energy. High density of the electron beam energy (about 10^{13} Wt/m^3) provides for a high precision of microsamples processing with up to 5 μm holes.

Laser technique includes welding, drilling, cutting and other types of material processing by laser irradiation. The method helps to improve steel and cast iron microhardness and resistance to corrosion [58]. At laser exposure a hardened layer is formed on the part surface, while its core properties remain unchanged. Thus, wear resistance of aluminum and titanium-based materials can be enhanced and tribological characteristics of polymers improved.

The process of *ion implantation* (or ion alloying) involves the effect of charged particles of high kinetic energy (up to 200 keV). Extremely efficient turned to be implantation of light interstitial atoms (boron, carbon, nitrogen) which increases steels and alloys resistance to wear and fatigue. The implanted ions act to a considerable depth of the treated surface, being a rather important factor in prevention of wear and oxidation [59].

Plasma method is a combination of technological processes when materials are exposed to a low-temperature plasma generated either by the arc or high-frequency plasmatrons. The plasma treatment effect results from a high plasma temperature (ca. 10^4 K) and mechanical action of its particles bombarding the blank at a high velocity. Specific power transmitted to the material by the plasma arc reaches 10^5-10^6 and that by the plasma jet - 10^3-10^4 Wt/cm^2. The plasma heat flow can be disseminated to slightly heat the blank at coating deposition. Contemporary plasma techniques include welding and cutting of metals, precision processing of different material surfaces and application of wear-resistant coatings [60, 61].

Electrochemical methods using electric field in electrolyte are subdivided into surface and dimensional depending on technological means.

Surface methods are intended for regulation of surface properties by forming coatings or changing surface microrelief of the blank. The methods include *electrochemical polishing* patented in Russia in 1910 by Shpitalsky E.I. Its advantage, as compared to mechanical polishing, is no changes in the treated material structure. The essence of *anodizing* or electrochemical oxidation is in formation of a protective oxide film on the metal surface via electrolysis. What concerns *passivation*, the metal is treated electrochemically by a special substance - passivator. This results in increased resistance of the metal initial passive state and inhibited corrosion.

Electrochemical methods of surface treatment include electroplating which can be related to applied electrochemistry. It embraces the processes of electrolytic deposition of metals on conducting materials. It was Jacoby, who in 1838 reported on discovery and application of electroplating at a St.Petersburg's Academy of Sciences Session. The method comprises *galvanostegy*, which is the formation of metal coatings on article surfaces and *galvanoplastics* - the production of easily separating, sufficiently thick precise duplicates of various articles (so-called matrices).

The dimensional electrochemical methods are based on a high-rate solution of any conducting materials by electrolysis in a narrow clearance (0.1-0.5 mm) between the treated article and accessory electrode. Depending on the means of removing the products of electrolysis from the clearance there are the following types of dimensional electrochemical treatment.

Electromachining consists in a combined electrochemical and electroerosion action of current on the material in electrolytic medium. The method utilizes mechanical removal of products of the dissolved by anode metal. It was elaborated in 1943 by Gusev V.N. At *anodohydraulic treatment* the products of electrolysis are removed by a flow of electrolyte forced through the zone of exposure. The method was first applied in the USSR in late twenties to draw fragments of a broken tool out of a blank.

The *combined processing techniques* display advantages of both electrophysical and electrochemical methods. As, for example, the combination of electromachining and ultrasound method promotes, in a number of cases, a 20-times increase in productivity. When processing metals by electroerosion-ultrasound machine tools the two methods can be used either jointly or separately.

1.3.3. Coatings.

Application of coatings is an efficient means of modifying machine part surfaces. The method is highly applicable because it leaves the structure and properties of materials invariable through the bulk. Specifics of the methods aimed at forming coatings in electric field will be discussed by way of examples of polymer and metal coatings application.

Polymer coatings are applied using different methods depending on aggregate state of the polymer material, production technique of the formed article, operation conditions, etc. The great variety of existing methods gives grounds to extensive use of electric techniques.

Thin polymer coatings (10 μm thick) are precipitated mainly from a gaseous phase. The method of application under *electron exposure* includes the following stages. The sought article is placed into a working chamber evacuated to 10^{-4}-10^{-5} Pa and the initial substance vapors are let in (low-molecular hydrocarbons, silica compounds, etc.) at a pressure below 10^{-2} Pa. The coating is applied with exposure by a flow of electrons at an accelerating voltage of 200 - 1000 V and current density 0.2-3.5 A/m^2. The coatings formed by *glowing discharge* can undergo plasma-chemical reactions in the deposited layer by using higher partial pressures of the initial substances (1-10^{-2} Pa) and current density (1-10 A/m^2) [62].

Electrodeposition is used to apply thin coatings from polymer suspensions and solutions. Electrodeposition of polymer suspensions is an electrophoretic process involving separation of suspension into phases due to particle polarization in electric field and their aggregation by ion precipitation. Neither chemical nor structural variations of the polymer layer proceed during electrophoretic precipitation. Electrodeposition of solutions differs radically from electrophoretic precipitation of suspensions due to the presence of chemical transformations of the polymer material on the electrode and in the near-electrode space. In the constant field between the article and the accessory electrode, precipitation takes place of the film-former from solution. The process can be anodic (anaphoresis) or cathodic (cataphoresis).

Electric field is often used to reduce material losses and enhance quality of coatings applied from solutions or suspensions by *spraying*. Through aerosol particles of a polymer material the article accepts electric charges of different polarity. Most spread have become contact and ionic types of charging particles of liquid dielectrics. An indispensable condition of contact charging is corona discharge on the electrode with a voltage up to 120 kV. As a result, the field intensity near the electrode edge exceeds 10^3 kV/m and surface charge is transmitted by the contacting aerosol particles. Ionic charging takes place when the aerosol cloud is introduced into the ionized air zone between the electrodes having a heterogeneous electrostatic field of high voltage. During the cloud displacement along the force lines the charge is transmitted from gas ions to aerosol particles. The mechanism of electrification by polarization when molecules with dipoles orient along the force lines of the fieldis also possible.

Powder technology of polymer coatings has gained popularity in a number of industrial branches because of its ecological safeness and freedom from deficient solvents.

Application of electric fields at different stages of polymer powder coatings formation allows for a considerable enhancement of the polymer-substrate adhesive joint characteristics due to modifying action of the field on materials. In more detail the electric technique of polymer powder coatings is considered in section 4.2.3.

Plasma technology is in a number of cases most reliable and highly productive method of applying powder coatings based on thermostable and difficulty soluble polymers.

At the end of sixties a method of detonation spraying has been developed based on electrotechnology of gaseous mixture burst. The coatings are formed via explosion which mechanism includes chemical interaction of the coating and substrate detonation products, and mechanical action of the shock wave. Such coatings are highly wear resistant, feature perfect adhesive properties, negligible porosity and gas permeability.

Both the method and equipment for polymer coating application in electric field are based on employment of specific dielectric properties. In most cases they are used without any principal changes in machine when modifying surfaces of articles by different dielectric materials.

Electroplated coatings are, as a rule, 0.1-100 μm thick films applied by electrolytic deposition to protect articles from corrosion, mechanical wear, to dress or impart special physical or chemical properties to the surface.

The mechanism of coating formation consists in crystallization of metals from aqueous solutions of their salts under a constant electric field. Metal ions interact with electrons and recombine on the coated surface. The formed atoms join into elemental cells where monocrystals are formed. The formation of the crystalline nucleus is induced by electric field energy which consumption is alleviated with polarization growth. The reduction of metal ions concentration leads to polarization augment with further increase of the nucleus formation rate. As for cathodic passivation, it ceases crystallization. The passivation factors may be absorption of surfactants from electrolyte on the crystal edge, or chemical interaction between metal and electrolyte leading to oxide and sulfide films formation, etc. The kinetics of electric deposition is influenced by changes in electrolyte composition near the growing crystal edge or by electrolyte mixing and some other factors.

The quality of galvanic coatings depends on the degree of metal deposit graininess, its density, smoothness and evenness. Sometimes, a problem is put forward of depositing a mirror-like layer displaying less velocity of deposition and high anticorrosion properties. Energy consumption does not effect noticeably electroplating cost, that's why the requirements imposed on electrolyte conductivity are not decisive in choosing the material for metal deposition. Electroplating techniques of a complex electrolytic coating as well as those containing non-metal components (phosphorus, carbon) have been developed recently.

Metal spraying is a method of producing coatings on different materials by applying a jet of molten metal using compressed gas. One of the efficient methods for metallizing articles of any size is the *electric arc spraying*. It consists in melting a metal wire by the electric arc discharge, dispersion of the melt and its particles transport by compressed gas to the coated surface.

The coating composition and properties depend on the process parameters. Most important among them is temperature of the sprayed particles, which is much higher than the metal coat melting one at electric arc spraying. This provides for intensive interaction between the particles and the environment, so at a standard distance of spraying the particles are comprised of the overheated metal and oxide melt. The coating structure is, in its turn, conditioned by particles ionization in the arc discharge zone and abrupt cooling at collision with the substrate. This governs gas content in the particles corresponding to the liquid state.

A considerable porosity of the metallized coatings has defined their use as chiefly a primer for the following application of paint and varnish, polymer powder materials, putty, etc.

Metallized coatings on friction joints are produced by electrocontact technique, being a version of electromechanical treatment.

1.3.4. Polymer and ceramic materials.

Electric technologies for manufacturing composites on polymer and ceramic matrix base have the same physical grounds as those described above for materials treatment and blending. Nevertheless, electric field application to process composites has its peculiarities due to structure of multicomponental systems, their function and multistage technique of their mixing in one material.

The methods of **filled plastics** production, i.e. plastics with a powder or fibrous filler, involve electric technologies in a number of stages. For *metal-filled plastics* electric stimulation of metal and polymer particles interaction is used already at dry mixing of powder components due to frictional electrification of particles. A technology is known of metal-filled plastics production. It is based on mixing vibrogrist and electroerosion treatment of metal in the polymer or monomer medium. Plastics with a filler particle size below 0.25 μm are produced by electrolytic decomposition of metalloorganic compounds (carbonyls, formates) dispersed in monomers, olygomers, polymer solutions, melts or suspensions. A variant of the method includes metal particles precipitation via electrolysis, their tearing off from the rotating cathode and transport to the bath with a polymer solution. The articles showing anisotropy of electro- or heat conductivity are formed in electromagnetic field aimed at orienting filler particles and creation of conducting chains.

Gas-filled plastics constitute a dispersed solid-gas system. Foam polymer materials production techniques have been developed, which utilize electric field. The technique of foaming a cross-linked polyethylene in an alternating field of ultrahigh frequency [63] provides the reduction of energy consumption and cuts product losses during the polyethylene foam settling, etc.

A typical representative of the **layered materials** is *metaloplast*, being a sheet structural material produced as a metal strip with one- or two-sided polymer coating. The most spread technique of metaloplast production is application of polymer coatings using electric field. Metaloplast is formed by the metal sheet and polymer film winding with tension and reeling into a roll followed by passing electric current through the sheet. Pressure in the roll arises due to difference in the sheet and film expansion temperatures. To improve adhesion, the polymer film undergoes plasmachemical etching or corona discharge [64].

Ceramic layered materials are produced by different original methods reflecting the contemporary state of technology. Plasma spraying of powder ceramics (titanium, aluminum oxides, alkaline-earth metal carbonates, etc) is widely used in electronic engineering. Thus, for example, piezoelectric zinc oxide films used in acoustic instruments are formed by ion-plasma spraying in a constant or high-frequency alternating field. Glass substrates are also plasma-treated before magnesium-bismuth film application. To enhance adhesion of ceramic dielectrics to metals, charge carriers are thermally excited in the contact regions of dielectrics using electric field. When semiconducting sensors are produced, a glass interlayer is inserted in the silicon-Kovar adhesive joint. The layer treated in the constant electric field contributes to the joint strength. In order to save highly deficient metal solders when forming metal-glass ceramic junction, ultrasound metallization is used to intensify chemical interaction between solder components and non-crystalline phase of glass ceramics.

The industrial technology of **ceramic electrets** is now rapidly developing. The scientific basis of this field of materials science and the sphere of its application in engineering are standing on different stages of their development. Most widely used in radio-electronics materials displaying piezo- and pyroelectric effects are, in particular, segnetoelectrics [65]. The technology of ceramic segnetoelectrics was directed in the 50-70-es to utilization of predominantly their specific dielectric properties in capacitors production. Recently, the plasma-ion technique of oxide films formation has become widely applicable. Thus produced films show perfect piezoelectric characteristics. In optoelectronics the transparent ceramic segnetoelectrics with controlled optical properties are used. Among laser beam control systems (baffle, shutter) exhibiting high operation parameters stand out electro-optical devices, in which niobate-based ($LiNbO_3$, Ba_2 $NaNbO_{15}$, $KSrNb_5O_{15}$, etc.) electrets are used.

Textile materials compose a vast group of technological engineering materials. They are of diverse structure and their production technique frequently employs electron-ionic technology. Electrostatic spinning has been elaborated recently, where pulling, orientation and separation of fibers is performed by electric field. Chamois-like materials for polishing machine parts are produced by electroflocation. To improve physico-mechanical characteristic of wool, it is exposed to corona or glowing discharge and electric field is used for removing moisture from the moving threads, as well as fluff and dust from the working rooms, etc.

The present review points to the fact that the majority of widely spread electrotechniques for processing and manufacturing engineering materials utilize electric field as an auxiliary means. The group of methods where electric field transforms materials into a qualitatively new structure and critically varies properties is rather narrow. Electrets have not practically find their place in electrification technology of engineering materials.

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CHAPTER 2

TRADITIONAL FIELDS OF ELECTRET APPLICATION.

Electrets or electric analogues of magnets serve as permanent sources of electric field. Classical examples of electret application in engineering are based on their field action on objects, interaction with other physical fields or induction of alternating current in electret field. Designs, where a momentary current occurs during electret depolarization have gained a limited application.

The first applied engineering electrets utilized only their uncommon electric properties. Polarization effect on strength and other operation characteristics of electret materials were not considered, as a rule, for the time being. Nevertheless, such designs turned to be so efficient that have defined, to a certain degree, trends in some technological domains.

Electret microphones is a remarkable field of electret application. The first reference to such devices is dated back to the twenties. Of no lees importance for machine-building are electret gas filters. Contaminants in the filters are captured owing to polarized charge of the filtering material fibers. Electret systems have also gained popularity in the sphere of information recording. Practically all countries of the world produce miniature electric motors incorporating electrets. Each of the above designs can be a separate topic for a review or a book. So far, the present chapter discusses only the main aspects of electret materials formation and development in engineering.

2.1. TRANSDUCERS

Converters or transducers are the elements of automatic control and data processing systems. They are used to convert input signals into signals of the same or another physical nature, being more convenient for information processing, transmitting, recognition and recording. According to the input signal origin, electret transducers fall into mechanical, acoustic, electric, optical, heat and radiation transducers (Fig. 2.1).

2.1.1. Mechanical transducers.

Such transducers with electret elements are distinguished by a certain operation principle and design. The main units of a simplified

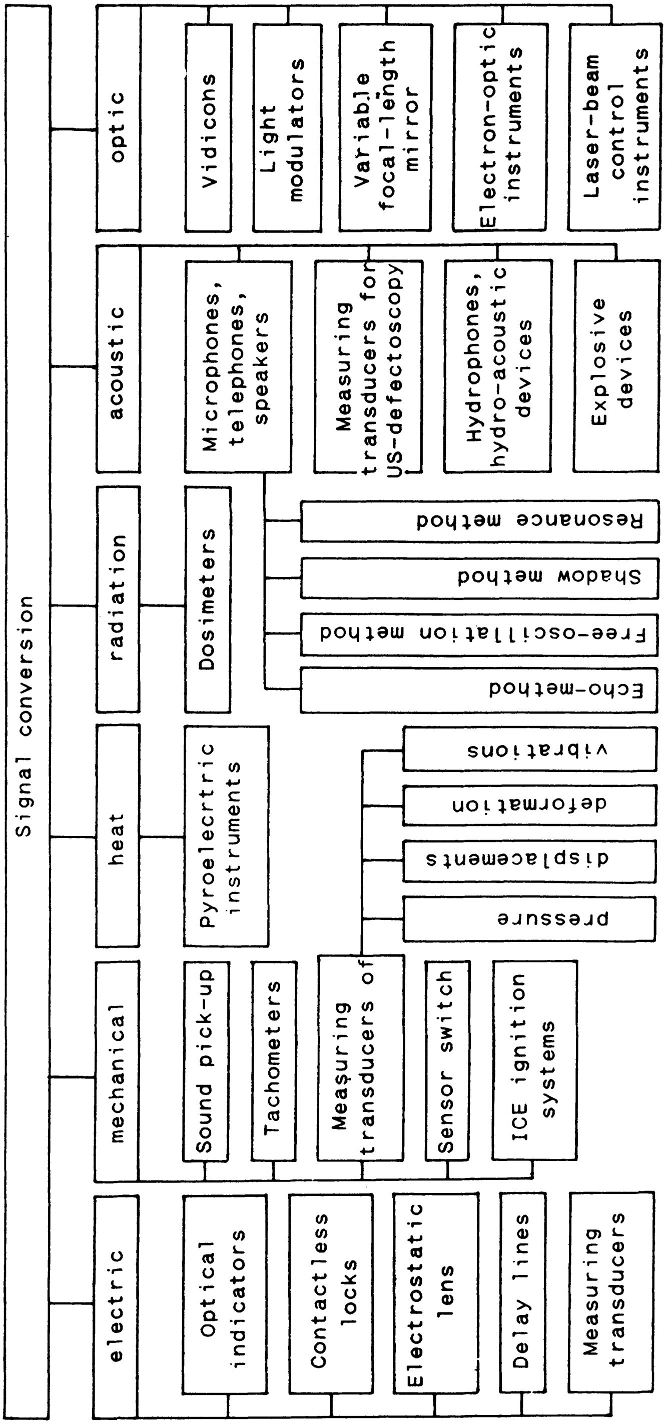

Figure 2.1. Classification of electret transducers.

mechanical transducer scheme are the plane parallel electrodes, between which an electret is placed. When the electret and electrode are approaching, a current passes in the circuit connecting the electrodes. A variant of the scheme presents one of the electrodes as a metallic coating on the electret.

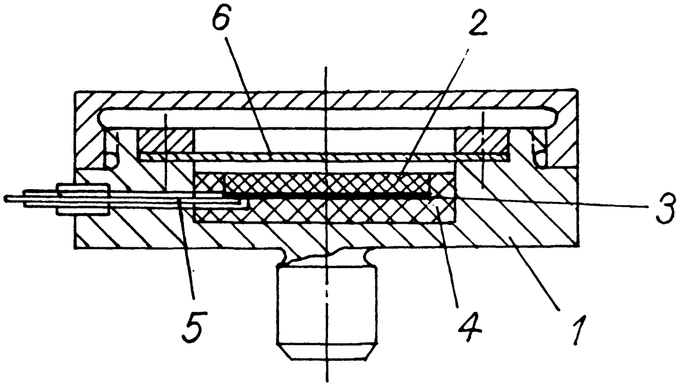

Figure 2.2. Measuring transducer of vibrations: 1 - body, 2 - electret, 3 - silver coating, 4 - dielectric seal, 5 - outer circuit wire, 6 - membrane.

Measuring transducers of mechanical signals embrace a vast group of electret transducers. They convert the measured value into a signal which parameters are easy to quantitatively estimate. A typical design of a vibration transducer [1] is presented in Fig. 2.2. An electret plate having a silver-plated surface is mounted in a casing with the help of a dielectric insert. Over it a metallic membrane is placed. The transducer is installed on the vibrating portion of machine so that it vibrates together with the machine. The membrane thus displaces relative to the casing and to rigidly fixed on it electret plate. Current generated in the external circuit has a frequency equal to that of the machine vibration. The described design is typical of all pressure transducers, as well as displacement and deformation ones, etc.

The electret element can contact both electrodes. As, for example, alarm systems have a specially designed transducer in the form of a coaxial cable with an insulating layer of polarized Teflon. As an electrode the central wire is employed and contacting the insulator metallic screen. If to deform the screen, a current occurs in the wire. The transducer sensibility is uniform along the cable length. The same principle is the basis of impact load transducers used to estimate the side skin deformation in American space stations upon collisions with meteorites.

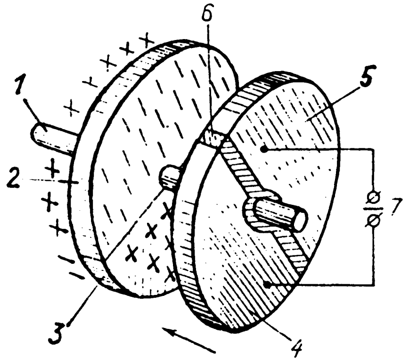

Figure 2.3. Measuring transducer of approach: 1 - shaft, 2 and 3 - electret semi-discs, 4 and 5 - metallic semi-discs, 6 - dielectric insert, 7 - outer power source.

Figure 2.3. demonstrates an original scheme of a transducer to record approach of conjugated with the shaft discs. One of them consisting of oppositely charged electret semi-discs is fixed rotary on the shaft. The other disc is the electrode displacing along the shaft without rotation. It is divided by the electret insert into two parts. When the latters are connected to the poles of a constant voltage, a torque tending to turn the electret disc emerges. The torque increases with the disc approach and the angle of rotation corresponds to the approach value.

Already first investigators of electret effect have discovered the dependence of electret charge value on the atmospheric pressure. The curve shape in Fig. 2.4. is governed by at least two factors: decrease of the air electric strength under atmospheric pressure drop and by removal of charge carriers from the electret surface in vacuum [1]. The principle of pressure meter operation is based on the described regularity.

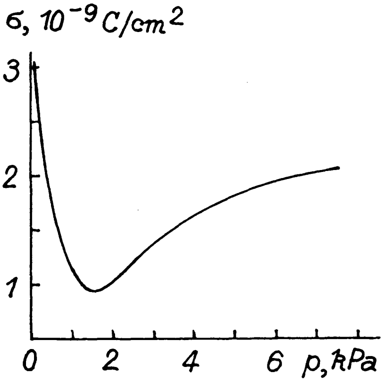

Figure 2.4. The dependence of carnauba wax electret charge on atmospheric pressure.

The relation between the field value and electret stress state served the base for measuring transducers of displacement and deformation. Their sensor is made of electret rubber. The transducer output signal depends on the sensor ability to generate electric field at deformation and to augment it with deformation increase. The electret rubber-based transducers were used to calibrate accelerometers in the 10 Hz - 10 kHz range [2]. Polymer binders of electret materials are usually filled with segnetoelectric ceramics. This enhances the elements piezoelectric coefficient and physico-mechanical characteristics.

The traditional field of mechanical transducers application is sound recording. *Sound adapter* converts mechanical oscillations of the stylus moving in the phonograph record grooves into electric voltage of sound frequencies. Two types of sound adapters are used in sound recording practice. The first one peculiarity is the presence of an acoustic transformer made as a closed air cavity. There, the stylus oscillations of a large amplitude are transformed into sound waves received by the electret microphone. The design advantages are compactness, high velocity of tracing the channel variation, linear character of frequency dependence in a wide range of output signals and insensitivity to magnetic fields. The second-type sound adapter has a holder carrying the stylus and two electrets. The electrets together with the holder units form a pair of electret transducers which input signals are the holder oscillations. This allows for reduction of crossed modulation and expansion of the output signal dynamic range [3].

Tachometer is an instrument used to measure rotation frequency of machine parts. Tachometer operation is based on charge induction on a stationary electrode in the electret field rotating simultaneously with the measured part (rotor). The rotation frequency value is consistent with the input voltage or the induced charge pulse frequency. In Fig. 2.5. diagrams of the electret tachometer are shown [1]. The electret can be fixed either on the cylindrical or face surface of the rotor. The mated with the electret fixed electrode is mounted on the machine body using an insulating liner and is connected through a terminal to a measuring instrument. The tachometer is simple in design and works without outer power source. It can be made as a separate instrument or built into the mechanism to be controlled. The tachometer electret unit looks like a 10 um thick light polymer film. It can be fixed on practically any rotating part not disturbing the machine operation.

Electret instruments can measure both angle and linear velocities of the moving objects. Works [1, 2] propose diagrams for measuring a bullet flight velocity. Electret transducers are placed on the controlled limits of the bullet flight. Signals generated close to transducers during the flight and the time interval between their emergence are recorded using electronic equipment.

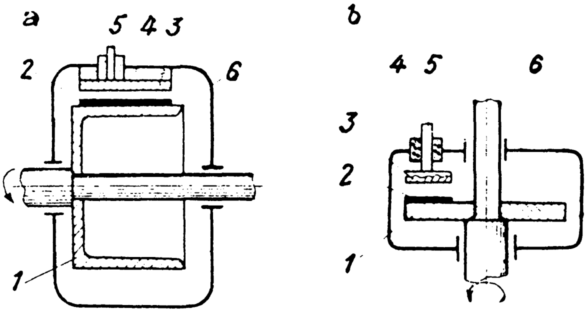

Figure 2.5. Tachometers (a) cylindrical, (b) face: 1 - rotor, 2 - electret, 3 - electrode, 4 - dielectric seal, 5 - terminal, 6 - body.

In recent years ceramic-polymer electret composites have been used [4] as acceleration sensors which have twice as much output voltage as that of ceramic transducers of a similar design. This was observed in a wide range of frequency and acceleration.

The devices for alphanumeric data input incorporate *sensor switches* (Fig. 2.6) responding to a touch. The main element of such a switch is an electret diaphragm. The diaphragm is a polyvinylidenefluoride film with a two-side metal coating displaying strong piezoelectric-electric properties. It is installed between foam-rubber pads, being simultaneously the insulator and mechanical proofing. The diaphragm deformation with a button evokes output signal in the switch circuit. Its amplitude is 10-100 V. To switch it a slight touch of the button is enough. Such switches endure about 15 million pressings and 2 million depressions reduce the output signal only by 10% [2]. Piezoelectric PVDF films are widely used in low pressure applications like keyboards [5] and tactile sensors [6-10].

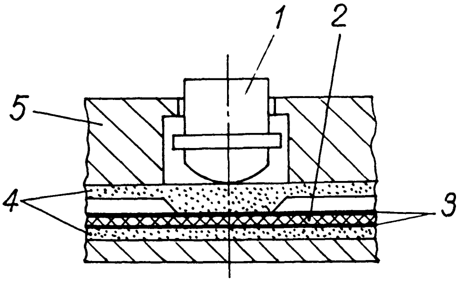

Figure 2.6. Sensor switch: 1 - button, 2 - PVDF film, 3 - metallic coating, 4 - foam rubber, 5 - body.

The main requirement to the *systems of ICE ignition* consists in accuracy of the fuel ignition moment depending on the cylinder pressure. Mechanical transducers for ignition systems on the multi-layer polymer piezoelectric-electrics base are characterized by a high energy yield (up to 10^{-2} mJ/cm^2) under momentary mechanical action (10^{-2} s) [11].

2.1.2. Acoustic transducers.

Such devices convert sound waves into signals of another nature. A typical acoustic transducer is a *microphone* which transforms sound oscillations into electric ones. Electret microphones are widely used today. There exist two principle schemes of such microphones. The first is identical with that of a vibration transducer (Fig. 2.2.) having a stationary electret and vibrating electrode-membrane. The microphone design differs from vibration transducer by a hole in the cap, through which sound waves effect the membrane. The other difference is in the electret element made as a perforated disc so, that the air gap between the electret and membrane communicates with the chamber under the electret.

The second scheme of the electret microphone is shown in Fig. 2.7. It has been designed upon elaboration of highly efficient film electrets on the base of polyethylene terephthalate, polymethyl methacrylate, polytetrafluoroethylene and other thermoplasts. The membrane of such a film has upper side metallized and its surface charge density is 10-20 nC/cm^2. It is installed over the stationary electrode with juts to provide for an optimum air gap (10-30 μm) between the membrane and electrode. The signal is received by the telephone. The electrode is made with ducts connecting the space above it and air chamber beneath, thus reducing the output signal resonance frequency and improving the microphone sensibility.

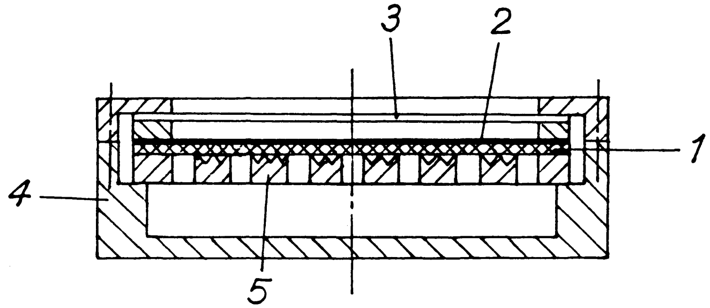

Figure 2.7. Electret microphone scheme with a polymer membrane [12]: 1 - electret polymer film, 2 - metallic coating, 3 - safety cloth, 4 - body, 5 - stationary electrode.

A great number of electret microphone designs have been developed since now with curvilinear membranes creating "acoustic effect". So, to lower vibration sensibility, a pair of membranes is mounted in the microphone. The membranes are bent along the cylinder generatrix and their bent-in surfaces face one another. The sensitive element of telephone microphones is made as a roll of the piled up charged in opposite directions electret films which metallized coats are consequently connected [13].

Any outer field fed to the membrane in a conventional condenser microphone is not necessary for the electret membranes. The output signal transducer is unnecessary too, so the preamplifier structure simplifies noticeably. As a result, mass and cost of a high-quality electret microphone is much less the condenser one. Its merits are also high sensibility, uniformity of frequency characteristics, design simplicity irrespective of magnetic field action and short-circuiting during water condensate formation.

The above described microphones have found application in household needs, instruments, information processing techniques. Electret microphones are also used for amateur and professional studio recording. They are constituents of noise gages and other sound level meters. They can be found in opticoacoustic spectroscopy for measuring air pollution, studying reaction kinetics in gases, examining optical absorption in solids, etc. Electret microphones enter tabular systems for coding input graphic information.

One of the promising fields of electret microphones use is the *directed electroacoustic* transducer. The principle of the directed microphone operation is based on sensibility of electret diaphragms to the gradient of sound pressure. The gradient microphone design provides for the microphone two-side action on the electret diaphragm. The microphone drawing near the sound source effectively suppresses signals from remote sources. They are used as sound-suppressing units in hearing aids and in airplane instrumentation for pilot communication.

Electret microphones with a toroidal characteristic of sound direction are a combination of acoustic transducers which input sound directions are mutually perpendicular. They look like two cylindrical hollow-space semi-bodies, with four sound wave tubes-receivers each, situated in the same plane normal to one another. An electret film element with a given distribution of polarized charges is installed in the two semi-bodies junction. Thus, the required microphone sensibility to signals and noise is attained. By varying the distance between the tubes inlets, the toroidal diagram of the signals direction might be deformed.

To convert low-frequency sound signals (up to 10^{-3} Hz) subsonic electret microphones have been developed. Expansion of the input signal band to the subsonic domain is reached by enlargement of the membrane area over 10 cm^2. This leads to the rise of the metallized membrane-electrode system capacity up to 2-3 nF.

Almost all of the commercially available electret microphones consist of nonsilicon materials, such as Teflon electrets either used as membranes or as layers on the backplate. In recent years, however, electret microphones made with micromachining methods on silicon wafers have been described and implemented. This started in 1983, when the excelent charge storage capabilities of surface-charged SiO_2 and the use of such layers in silicon microphones was first discussed [14]. Charge storage in SiO_2 was further investigated around 1990, also with respect to problems encountered with the charging of small areas [15-18]. It was also found that coating of the SiO_2 with Ta_2O_5 improves the charge storage [19]. More recently, the superior charge-storage capability of SiO_2/Si_3N_4 double layers was discussed [20].

The first silicon electret microphones consisted of a silicon backplate chip with a ~1 μm SiO_2 or 12 μm Teflon layer charged by a corona process [21-23]. A metallized Mylar film of 1.5 to 2.5 μm thickness was used as a membrane. With demensions of ~3×3 mm^2, the sensitivity of these hybrid silicon/polymer transducers was 4 to 20 mV/Pa over the audio frequency range with equivalent noise levels as low as 30 dB. Silicon microphones with ~2 μm SiO_2 membrane and a SiO_2 backplate electret also were discribed [23].

A resent development in the area of self-biased silicon capacitor microphones includes a transducer with a SiO_2/Si_3N_4 double layer electert membrane [24]. This transducer is shown in Figure 2.8. The membrane is corona charged before combining with a backplate chip. Advantages of this system are simple design and low stray capasitances.

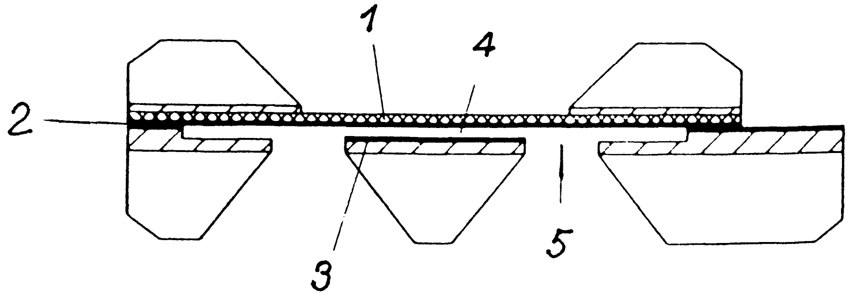

Figure 2.8. Silicon microphone with double-layer electret membrane [24]: 1 - aluminium (150 nm), 2 - Si, 3 - SiO_2/Si_3N_4 membrane (400 nm), 4 - SiO_2 (2 μm), 5 - boron-doped backplate.

Telephone is a low-power converter of sonic frequency electric signals into acoustic oscillations of the same frequency range. The electret telephone employs the principle of condenser microphones with external bias of electric signal. However, the bias in electret telephones, speakers and ultrasonic sources is performed by the intrinsic electret field. Such membrane disadvantage is nonlinear dependence of oscillation frequency on the electric signal frequency, which is eliminated using design and technological methods.

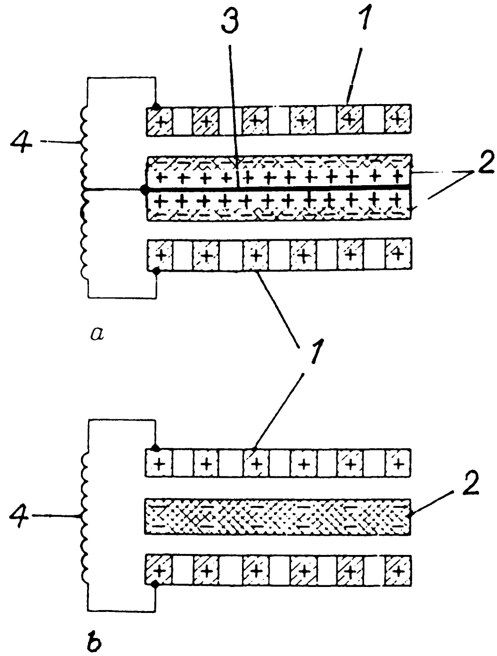

Figure 2.9. Telephone schemes with electret membranes: a) - from two metallized polymer films, b) - from monocharged polymer film. 1 - electrode, 2 - electret film, 3 - metallized coating, 4 - electric resistor.

Figure 2.9 shows electret telephone diagrams [3]. The membrane can be made (a) of two one-side metallized electret films put together with the sides inwards. It is symmetrically installed between a pair of metallic punched electrodes. When voltage is fed to the electrodes, the membrane is effected by a force proportional to voltage vector. The other telephone scheme (b) uses a membrane made of a monocharged electret film. The design advantage is availability of large clearances (about 1 mm) between the membrane and electrodes which are used without a noticeable weakening of the field in the clearance. Telephones of a considerable membrane deviation generate acoustic signals of wide amplitude.

Stereo head-phones utilize telephones of a simplified design. Its basis is a two-side metallized polymer piezoelectric film. Such a membrane is laid over a curvilinear (often spherical) polyurethane foam pad. When voltage is fed to the metallic coats, the membrane either elongates or shrinks and oscillates in axial direction. A sound signal is thus produced which acoustic focus depends on the membrane curvature. The polyurethane foam pad works as an absorber of the return sound wave.

According to the telephony standards, sound pressure on the ear should be about 90 dB for the optimum audibility. To provide the required level, the telephone is to receive an about 3 V input voltage. Conventional telephones have transformers with this aim. Electret telephones work without the transformers, though their operation range is limited to a small value of the generated sound pressure.

Electret *speakers* realize the ability of directed emitters to intensify the response with the rising frequency of the initial signal. Its maximum value is determined by the transducer resonance frequency. To improve frequency characteristics the electret speakers are furnished with a mouthpiece. The speakers based on the so-called slot effect have a linear characteristic of conversion. Their simplest design [25] represents a pair of oppositely charged flat condensers mounted on an electret bar transmitting oscillations to the membrane. In order to create a homogeneous sounding force in all directions of sound propagation, the speaker membrane is made as a cylinder which walls oscillate normally to generatrix. The cylinder cavity is filled with sound absorbing materials.

Hydrophones are devices intended for receiving sound and ultrasound oscillations in water and their conversion into electric signals. Most spread in underwater technology are two designs of electret hydrophones. One of them is to a great degree an analogue of a microphone (Fig. 2.7) with an electret membrane and obligatory gap between the membrane and stationary electrode. The clearance is a drawback leading to misalignment of impedances both in water and the hydrophone acoustic system. Besides, it bounds the hydrophone operation to only small depth and level of sound pressure.

A more reliable hydrophone structure is given in Fig. 2.10 [26]. The splice consisting of an inner electrode is separated from the electret films contacting a pair of outer screening electrodes by two dielectric seals and does not contain air gaps. Dielectric seals and electret films have different elasticity modules. This layered system is placed into a rubber or polyurethane capsule. Sound waves generate an electric signal in the splice which is removed using a coaxial cable. Such a transducer sensitivity is lower than that of hydrophones having air gap. Nevertheless, they are applicable in detecting sound waves of large amplitude in a wide range of submersion depth.

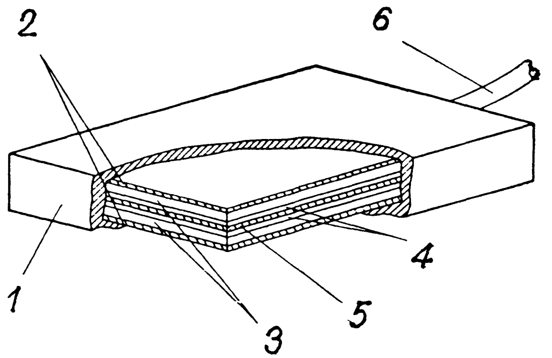

Figure 2.10. Electret hydrophone design [26]: 1 - case, 2 - screening electrode, 3 - electret film, 4 - dielectric seal, 5 - inner electrode, 6 - coaxial cable.

Because of its good matching to water, its mechanical flexibility and small demensions PVDF and its copolymers are extensitvely used for hydrophone probes [27-29]. The hydrophones are designed as membrane type [30-32] and as needle probes [33-35]. PVDF provides the possibility to measure shock waves in the range of 0.2 to 50 GPa [36, 37]. In such high pressure applications it has to be considered that the piezoelectric response is not linear with pressure but with volume compression [38].

An original variant of acoustic transducers is a piezoelectric film. The film is glued in a special way to the underwater body of a ship and 5-7 V and 10-20 kHz alternating voltage is transmitted through it. An ultrasound signal generated in such system eliminates the body overgrowing with algae and mollusks [2]. Already 1 % of the coated body shows noticeable efficiency.

Measuring *transducers for ultrasound defectoscopy* constitute a wide group of acoustic transducers. A number of electret instruments for nondestructive testing realize peizoelectric effect. They are intended to detect flaw (cracks, pores, voids, etc) by ultrasound defectoscopy, i.e. shadow, resonance, impedance, free oscillations and echo methods. Most critical defects are usually propagating in the near surface layers and along with mechanical loads experience the action of media, temperature variation, atmospheric moisture and other effects. Simplicity and technological efficiency is peculiar to capillary method of detecting surface defects. Electret instruments operation used for nondestructive control is based on ultrasound capillary effect, which essence is in ultrasound-induced enlargement of liquid capillary rise [39].

2.1.3. Electric transducers. Sensitive electret elements of electric transducers utilize variations in electric field intensity, capacity or some other characteristics under physical action (current passage, electric charge balance, magnetostriction, etc).

Optical indicators incorporating electrets are used in public lighting, illuminated call-outs, advertising displays, etc. Their main unit is a rotatable nontransparent electret film (Fig. 2.11). When voltage is fed to the mated electrodes, the rotating electret either opens or closes the light guide channel. The system disadvantage is in high voltage (500 V) in contrast to the negligibly low currents generated by the electret rotation [40].

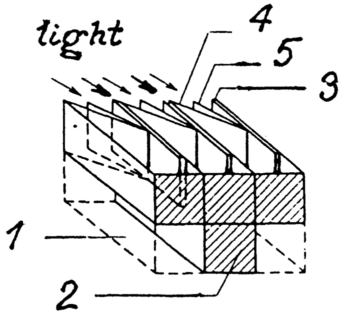

Figure 2.11. Optical display scheme [40]: 1 - body, 2 - dull wall, 3 - metal electrode, 4 - transparent electrode, 5 - electret.

Contactless locks are used to lock doors, windows, manholes, different devices in rooms, vessels, bodies and other closed volumes. A lock contains a mechanical closing device often with electromagnetic drive and a control system to it. The sensitive controlling unit is made as an electret transducer. When a special key is inserted into the lock, the transducer capacitance changes. As a result of the electret diaphragm displacement the transducer generates an electric signal with an amplitude of 10-100 V. The signal is fed to the lock drive controlling system and shifts the mechanical lock.

Elctrostatic lens is a device for generating a given configuration electrostatic field to focus a charged particles beam. The lens is mounted in electron-beam instruments which operation is based on the controlled flow of electrons concentrated in a narrow beam (electron beam). Electrostatic lens usually regulates the electron beam position and intensity directed to a target. When the latter interacts in elctron-beam instruments, the beam transforms into electric or light signals. Use of electrets in electrostatic lens has reduced considerably size and mass of electron-beam instruments, which is a leading trend in instrument-making, microelectronics, space technology and so on.

A Delay line is a device to reproduce the transmitting by it signals with a given delay interval. The 10^{-7}-10^{-2} s electric signal delay line is used in color TV systems, oscillographs, recording devices, computers, etc. The electret field helps to regulate the delay line band width and to simultaneously simplify the design structure and reliability.

There is a great variety by their structure and purpose *measuring transducers* of electric signals containing electrets.

Operation of humidity converter (hygrometer) does not essentially differ from the electret pressure meter which follows the relation $\sigma = f(p)$ (Fig. 2.4). The hygrometer structural difference is in nonhermetic chamber having an electret sensor and the electret-electrode clearance should be sufficiently wide for the instrument not to depend on atmospheric pressure.

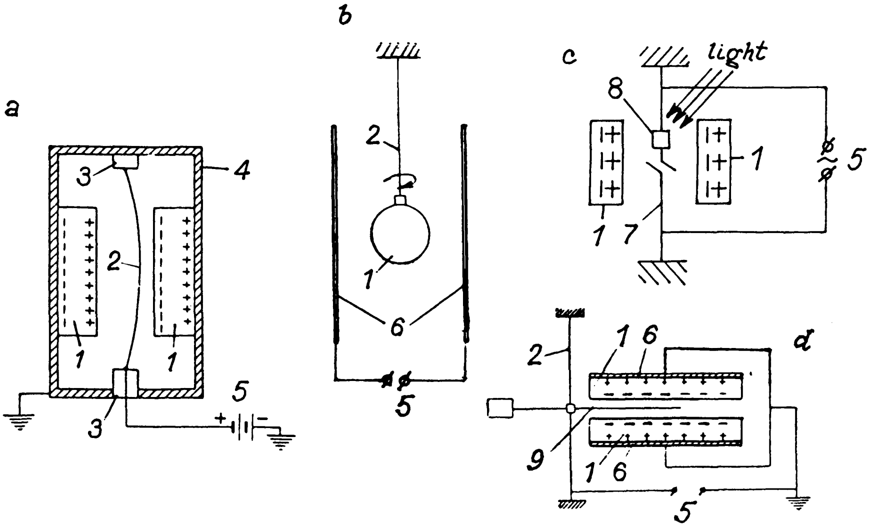

Figure 2.12. Schemes of (a) string and (b) disc electrometers, (c) vibration and (d) electrostatic voltmeters: 1 - electret, 2 - metallic filament, 3 - dielectric seal, 4 - case, 5 - terminal for measured source voltage, 6 - stationary electrode, 7 - rods, 8 - mirror, 9 - movable electrode

Figure 2.12 shows electret electric meters [1]. The string electromer (a) operation is based on the elastic metallic filament 2 deflection from equilibrium. The filament bears the measured voltage in electrets 1 field facing one another by oppositely charged sides. The filament is insulated from body 4 by dielectric seals 3. The deflection value is the larger the higher is the measured voltage.

In Fig. 2.12b an electromer scheme is shown which sensor is an electret disc 1 suspended on elastic filament 2. Electrodes 6 near the disc are fed from an electric source which voltage is to be measured. The disc tends to turn its positive side to face the negative electrode and vice versa. The turning angle is proportional to the measured voltage.

Vibration millivoltmeter (c) contains a vibrator as coaxially rigidly fixed thin elastic rods 8 which free ends are bent in opposite sides. The rods are placed between two electret plates 1 facing each other by oppositely charged sides. The rod bend plane is parallel to the plates. As soon as the measured alternating voltage is supplied to the rods, the sign-variable charges appear on the bent ends which interaction with the electret field makes the rods oscillate. The reflected from mounted on one of the electrodes mirror 8 light beam draws a light strip which width is proportional to the measured voltage.

Electrostatic voltmeter (d) consists of a thin metallic electrode 9 mounted rotary on metallic filament 2 between a pair of electret discs 1 facing the similarly charged sides. The discs contact the grounded electrodes 6. When electrode 9 accepts the positive potential it is drawn into the clearance between discs 1. With negative potential it is pulled out from the clearance.

A drawback of the instrument is the necessity to seal the chamber where electrodes are mounted.

2.1.4. Optical transducers. The field of optical transducers application in modern engineering ranges from photo-electronic devices to night-vision instruments.

Electron-optic transducers include vacuum photo-electronic instruments converting invisible images (in IR, UV and X-ray beams) into visible ones. They also help to improve image brightness. Their principle of operation is in conversion of optical or X-ray image into electronic one with its further transformation into visible using cathodoluminescence screen. Electrets in such instruments serve to control the electron beam when regulating image. Night-vision instruments constitute a wide group of electron-optic transducers. They are used to detect objects radiating IR beams for driving a car, night shooting, etc.

Laser-beam control instruments are optical shutters, deflectors, light modulators, etc. Niobate-based electret ceramics has been utilized in them for already several decades. Simple and reliable niobate-based electron-optical units have been developed recently able of regulating the transmitted light flow following a given program [41].

Vidicons, i.e. transmitting TV tubes with an electroconductive photoresistor target are used in commercial television setups. Under a light beam reflected from an object the target accumulates electric charge which distribution (potential relief) is consistent with the object image. The charge read-out from the target is performed by the electron beam controlled by the electret electrostatic field.

Light modulators are employed in controlling amplitude, frequency, phase and other characteristics of harmonic electromagnetic oscillations. Most of them are based on electro-optical Kerr effect, i.e. a double beam refraction in optically isotropic substances (liquids, gases) in electric field. Gases and liquids in the electret field acquire the properties of a uniaxial crystal which optical axis lies along the field.

Electrically polarized polymers possess uncommon optical properties useful in regulating resolving power of light guides and generation of secondary harmonics in a number of optical instruments. The polymer electret optical wave guides regulate the light wave parameters using the fact that the input signal refraction depends on the polymer polarization characteristics. The phenomenon was found out at the beginning of seventies but was not adopted in practise till the development of novel organic materials displaying perfect optical and mechanical properties.

Two methods are utilized in polymer optical wave guides to attain phase correlation between the main and harmonic frequencies of the optical signal. The first one consists in a selective polarization of the light guide leading to the corresponding modulation of refraction index. The second makes use of the optically transparent sandwich polarizing structures (for e.g., the polymer SiO_2-Si_3N_4) or polymer films with nonuniform polarization distribution across thickness [42]. Figure 2.13 shows the scheme of regulating the film optical properties by an electron beam polarizing the near electrode polymer layer. Equal refraction indexes are thus obtained for the main and harmonic frequencies of the optical signal passing through the film. This method is the basis for light guides, interferometers, wave guide couplers and diffraction switches production techniques.

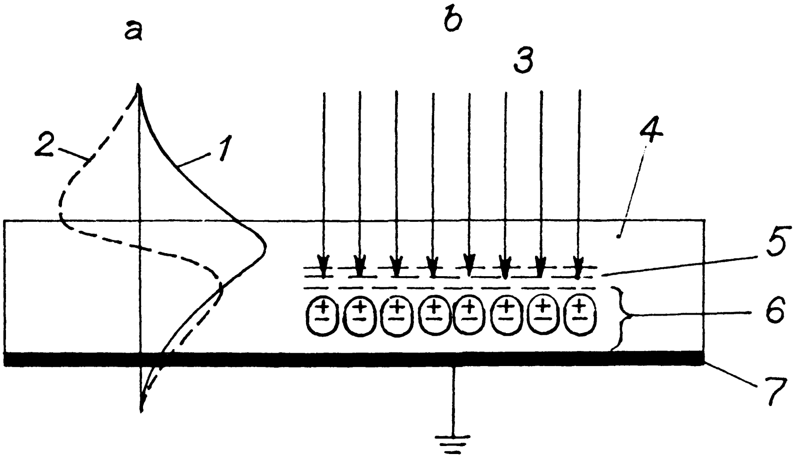

Figure 2.13. A wave-guide concept with 0 → 1 mode conversion (a) and diagram (b) of a polymer film polarizing by an electron beam [42]: 1 - main and 2 - secondary harmonics, 3 - monoenergetic electron beam, 4 - polymer film, 5 - deposited volume-charged layer, 6 - layer of oriented dipolar polarization, 7 - electrode.

Mirrors of a variable focal length are produced from electret films having a deposited metallic coating of high reflectivity. To displace the mirror reflecting surface, interaction between the electret film electrostatic field and the regulating field of the focal distance control system are used. This principle is employed in a large group of optical modulators.

2.1.5. Heat transducers. They operate using input signals supplied as heat radiation.

Pyroelectric instruments include a set of heat transducers converting heat signals into electric ones through materials displaying pyroelectric effect. Pyroelectric coefficients of polarized polymers (PVDF, PVF) are by almost an order less than those of ceramic pyroelectric. Nevertheless, polymer sensors appeared to be advantageous in a number of pyroelectric instruments due to their deformation and strength characteristics, low heat conductance and ability to form thin films. Pyroelectric current response is rather dependent on the rate of temperature variation than on its critical magnitudes. That's why pyroelectric instruments are especially sensitive to intermittent or modulating IR-radiation.

Pyroelectric detector (Fig. 2.14) incorporates a metallic heat absorber with attached PVDF film showing pyroelectric properties. The receiving electrode partially absorbing heat radiation is fixed on the film. The transducer heat relaxation time is determined by the pyroelectric film heat capacity and heat conductivity of the receiving electrode. Such detectors serve as damage sensing devices in heat supply lines and construction insulation.

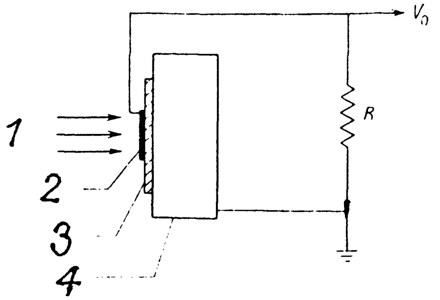

Figure 2.14. Pyroelectric detector [43]: 1 - IR-radiation, 2 - intake electrode, 3 - electret polymer film, 4 - heat absorber.

Most successful method for obtaining heat images has proved to be pyroelectric vidicon tube. Its pyroelectric plate back side is scanned by the electron beam as it is made in a conventional transmitting TV tube. The method was first suggested in [44]; the instrument general description and its application for receiving heat image were published in papers [45-47].

Figure 2.15 demonstrates a pyroelectric vidicon. IR-radiation of an object is focused on an electrode-target covered by a PVDF-based pyroelectric film. The latter forms a potential relief corresponding to IR-radiation intensity read-out by a scanning electron beam. Owing to a negligible heat distribution in PVDF the vidicons produce a better heat resolution as compared to ceramic-based electret instruments.

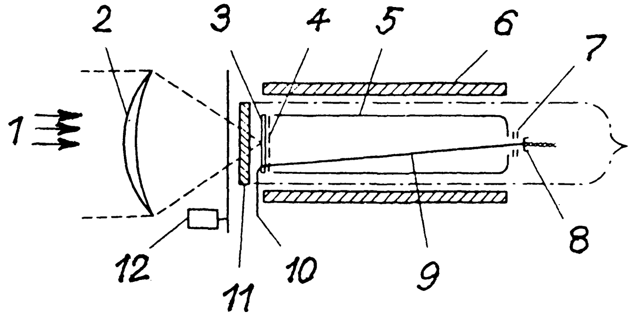

Figure 2.15. A pyroelectric vidicon diagram [48, 49]: 1 - IR-radiation from an object, 2 - germanium lens, 3 - target, 4 - grid, 5 - wall-anode, 6 - focusing and deflecting coil, 7 - control grid, 8 - cathode, 9 - electron beam, 10 - signal outlet, 11 - germanium window, 12 - interrupter.

2.1.6. Electret-based radiation transducers. They convert signals emitted by a flow of nuclear particles and γ-radiation into electric signals. Electret dosimeter is a typical example of such transducers. The above instruments serve to estimate nuclear radiation and associated values.

Electret dosimeter operation is based on charge accumulation phenomenon and emergence of induced conductance in dielectrics under nuclear irradiation. As sensing units of dosimeters, dielectrics forming spatial charges at irradiation are often used, or electrets produced before irradiation. Interaction energy of radiation fields and sensor is usually enough for the dosimeter to visualize readings. In other cases some outer source energy can be used for measurements.

A typical diagram of dosimeter [1] is shown in Fig. 2.16. Electret plate 1 is placed in a clearance between electrodes 2 and 3 fed from battery 4. Under nuclear irradiation air becomes ionized in the plate-electrodes clearance and the number of free electrons increases. The latters displace in the electric field direction, precipitate on plate 1 and create a layer screening the electret charge.

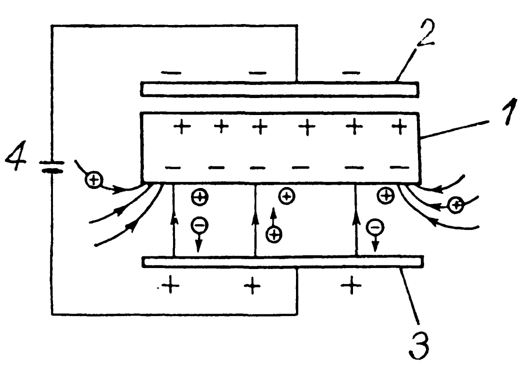

Figure 2.16. Electret dosimeter: 1 - electret, 2 and 3 - electrodes, 4 - battery.

When the PETF, PC or PTFE-based electrets are used, an almost linear relation is observed between the radiation dose logarithm and reduction of the plate surface charge density [2].

The instrument disadvantage is in spontaneous charge escape from the outer accessible surface of electrodes. This is eliminated in a dosimeter made as an ionizing chamber with a dielectric sensor and an electret field source inside. Charge carriers formed in the air under irradiation deposit in the electret field on the sensor surface. The sensor acquires a charge which surface density reaches 10 mC/m^2. To improve the dosimeter sensitivity, its ionizing chamber is filled with argon having a less ionizing energy as compared to air.

Dosimeters analogous to those shown in Fig. 2.16 record readings by using the movable electrode displacement caused by interaction between electret and electrode fields. The interaction force is balanced by a constant outer force, i.e. magnetic attraction, spring elasticity, etc. When the displacing electrode reaches the corresponding to limiting radiation dose position, an acoustic signal is generated. To visualize the dosimeter readings an electromer is frequently used connected to the ionizing chamber. Personal dosimeters of the type employ corona- or radio-electrets made of Teflon.

Electret dosimeters, first discribed about 40 years ago, were initially designed to measure γ-radiation. More recently, however, public concern about the health hazards of α-radiation by environmental radon prompted the development of electret-bazed radon dosimeters wich, over the past years, have come into wide use on a commercial basis for indoor and environmental measurment [50-51].

Other electret ionization chambers for measuring verious kinds of radiation have also been built: electret dosimeters for detection of radon in water [52], for X-ray monitoring [53, 54], for photon detection [55], etc.

To measure neutron radiation, secondary protons ionization is used emitted by hydrogen-containing materials of the ionizing chamber walls, for e.g., PE. In order to rise emission of the high-energy particles the walls are coated with a special substance, which can be $Li_2B_4O_7$ layer [56].

X-ray and γ-radiation dosimeters apply Compton's effect. Irradiation of electrodes made of certain materials provides for the formation of Comptonian electrons. They inject into the polymer film between the pair of electrodes of unlike metals leading to the polymer electric polarization. To determine the radiation dose the film (usually of PE) undergoes TSD. In this case, a special equipment is necessary and the measurement duration prolongs.

Increase of γ-radiation dose was shown [11] to rise TSD activation energy in polymer films preliminary polarized in contact with metal electrodes. Based on this phenomenon the simple method of dosimetry helps to determine 0.5 to 160 Mrad dosage. PVB, PVC or PP films are brought into contact with short-circuited electrodes of unlike metals and are heated to a temperature close to the polymer melting one. The polarized samples appear to be ready for work as dosimeters. Upon irradiation they are subjected to partial TSD and activation energy W of TSD is estimated on the initial portion of the current-temperature dependence. The absorbed dose is determined by the formula $D = A(\Delta W)^n$, where ΔW is the difference of irradiated and nonirradiated films activation energies; A and n are coefficients dependent on the film material. Due to such a procedure depolarizing time can be reduced and measurement simplified.

2.2. Energy Sources.

Operation of electret energy sources is based in most cases on alternating current induction in the constant electret field or on the electret and electrode fields interaction. Rarely energy is used liberated during electret depolarization or under impact loading of piezoelectric.

There is a lot of *electric motor* designs incorporating electrets. Most typical principle of their operation consists in the electret drawing into the clearance between electrodes in case their charge is opposite to those on the plate sides and its pulling out if charges are unipolar.

The simplest electrostatic motor contains a dielectric rotor, part of which is constantly corona-charged (U = 2 kV). It has not been practically applied due to its high operation voltage and strong susceptibility to atmospheric effects.

An electret motor design (slot-motor) is shown in Fig. 2.17. Each pair of stationary electrodes 1 and 2 is divided by a dielectric insert into two parts. In the clearance between electrodes an electret rotor 5 made up of oppositely polarized semidiscs is mounted on axle 4. The electrodes are fed by a constant voltage from sources 6 and 7 so, that opposite parts of electrodes have opposite polarity. The value of the torque effecting the rotor is directly proportional to the electret charge, electrode voltage and depends on the motor geometrical parameters. Most efficient are the motors below 1 Wt [57].

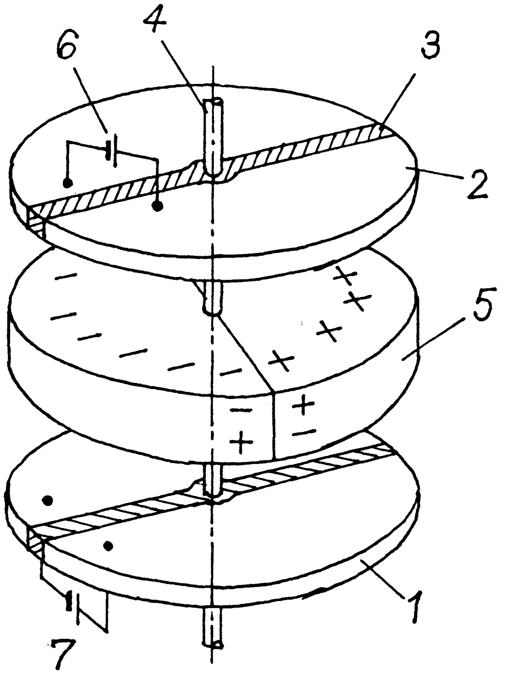

Figure 2.17. Electret motor [57]: 1 and 2 - electrodes, 3 - dielectric insert, 4 - axle, 5 - rotor, 6 and 7 - constant voltage sources.

Electret electric motor designs differ in the electret rotor and electrode shape as well as in the requirement to change voltage polarity supplied to electrodes depending on rotor position. In monograph [1] descriptions are given of electric motors actuated by high-voltage sources (up to 1 kWt) and synchronous engines fed from triphase alternating voltage. Other studies discuss new implementations of electret motors [58, 59] or review the forces in such motors [60].

AC generators with electrets show low power(about 10^{-6} Wt). A typical generator includes a one-side metal coated polymer film (the electret) and a conjugated with it metal electrode. The film oscillations are induced by an outer energy source. The generator design variant is a combination of a bulky electret unit and a light movable electrode displacing relative to the electret.

High-voltage generators incorporate a flat electret element placed between the grounded and stationary electrodes. When the movable electrode-electret contact is broken, the electrode-induced charges run over to the capacitor. The movable electrode is grounded when in contact with the electret and is disconnected before the contact breakage. By repeating the operation the capacitor can be charged to a voltage equal to potential difference of the electret element surfaces. Book [1] cites examples of generators based on vibrating, reciprocate or rotating motions. Generators utilizing polymer electret films are adopted in space apparatuses due to their small mass, design simplicity and reliable operation in vacuum. Electrostatic generators using PMMA electrets reach 220 μWt power at a 1600 rpm rotation frequency [2].

Instantaneous sources of constant current can be formed during electret depolarizing. Depending on the electret material and its production technique an up to 10^{-4} C/cm^2 charge is generated at depolarization and the outer circuit current can reach 10^{-5} A. This energy is sufficient to, for e.g., transmit a radiosignal. Such sources battery is able to generate a considerable power.

Polymer piezoelectric is used as instantaneous electric source since it is advantageous over ceramic one due to its low density, elasticity, easy manufacturing, use as thin films. Sandwich piezoelectric elements can produce high energy efficiency per unit area, especially necessary for ignition systems, explosive devices, etc.

2.3. Filters.

The development of electret filters has been stimulated by intention to reduce pressure differential in filters capturing submicron contaminants in the purified media. The electret filter operation consists in entrapment of charged particles drawn to the electret element of the filter by Coulomb forces and neutral dielectric particles which obtain directed dipolar charge in about 10 kV/cm electret field.

There are two main types of electret filters with either structural electret or fibrous electret unit. The former is used in water sprayers for dust settling [1]. Water powder is sprayed by the electret unit of nozzles, the drops acquire a charge by contacting the electret unit and effectively absorb the charged dust particles.

Electret air filters are in wide use today in applications where low air-flow resistance is essential [61]. Examples are respirators, vacoom cleaners, desk-top cleaners against tobacco smoke, and larger-scale air cleaning devices [62] with some never uses in such applications as recirculating systems. A related recent development is a passive sampler consisting of a film electert which attracts dust particles for later analysis

[63, 64]. In most of the filters, polypropylene is used for the electret films. Blending of PP with polycarbonate does not improve the charge stability and filtration characteristics [65].

Electret fibrous filters are widely used in engineering. Their design priority belongs to I.V. Petryanov [66]. He has developed filtering materials of FP type which include a layer of thin polymer fibers on a fabric substrate or an unwoven base of bonded thicker polymer fibers. At present a great number of electret filtering materials has been elaborated [67]. Their advantage is in low pressure differential during filtering, which is 4-20 times lower than that of analogous nonelectret filters under similar conditions of filtering fineness and degree of purification.

Electret fibrous materials are produced by charging fibers in corona discharge or by electron irradiation. Highly productive method of electret fibers production consists in corona discharging of preliminary extended polypropylene film followed by spliting it to separate fibers. Double-side charging with the both sign corona discharges helps to increase the film velocity during this operation up to 100 m/min. The film rupture is practically excluded and charge losses due to breakdown are reduced.

Electret fibrous materials are commonly used as constituents of combined filters involving the preliminary and fine purifying stages of aerosols decontamination. The first stage is made of standard polymer fibers aimed at capturing coarse contaminants and relieving the fine-purification stage. The second stage contains an electret filtering material providing for entrapment of submicron particles. These permit to attain high purifying degree of strongly contaminated aerosols (up to 5 mg/m^3 contamination) with preserving the filter electret long service life [66].

Fibrous electret filters efficiency is largely dependent on the filtering gas temperature and humidity. Figure 2.18 illustrates the electret charge stability on polypropylene fibers. Fast discharge of electret filters is due to accumulation of conducting dust. The deposited particles screen the electret element surface charge leading to the filter electric field weakening. The efficiency of electret filters impairs much under high filtration rates (above 20 m/s).

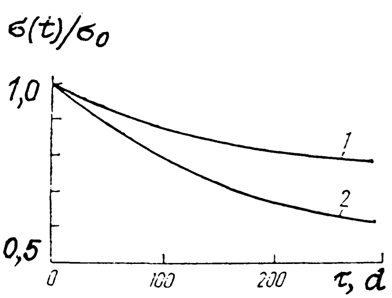

Figure 2.18. Electret charge variation in polypropylene film depending on time and storage conditions: σ_0 and $\sigma(t)$ - surface charge densities, initial and at moment t. 1 - at T = 20 °C and humidity κ = 70 %, 2 - T = 45 °C, κ = 100 %. Film thickness is 25 μm.

2.4. Information Recording.

The main fields of electret application in information recording are xerophotography and memory devices using symbols. In both cases the principle of recording is the creation of a given charge distribution or electric conductivity on a dielectric data storage.

Electrophotography is a combination of photographic methods to obtain image by converting the visual one into a relief of electrostatic potential in a semiconducting layer followed by visualization of the relief [68-70]. According to Schafert [68] xerophotographic methods are divided into xerography, photography according to the mechanism of photoconductance and photodielectric photography.

Xerography produces images by using plates of high-ohmic photoconducting material, for e.g., metallic plates coated with amorphous selenium or zinc oxide. The latters are characterized by a high dark resistance (10^{14} - 10^{16} Ohm·cm) and photosensitivity. The plate is first charged (sensitized) to attain an even charge distribution in the coating. The charging is performed by a corona discharge in darkness. Positive charges settle on the selenium coating and negative on that from zinc oxide.

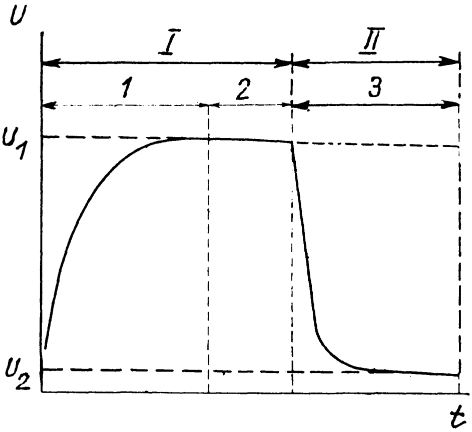

Figure 2.19. The effect of time (*t*) and illumination on electric potential (U) distribution on the plate at image xerography: I - in darkness, II - when illuminated, 1 - charging, 2 - dark discharge, 3 - lighted discharge. U_1 and U_2 - sensing and remanent potentials [68, p. 61].

It is seen from Fig. 2.19 that the plate potential approaches the so-called sensing potential value during charging, since the coating dark resistance drops with charge growth. Surface charge undergoes decay which rate increases with the rising intensity of light and depends on the light wave-length. When an image is projected on the charged plate, the charge decay corresponds to illumination of the surface portions. As a result, latent electrostatic image is formed, which visualization is reached using colored particles of a dry powder; optical, electrostatic or electron microprobes, potential relief conversion into thickness relief, etc.

Most often the image is developed using a pigment powder. When the powder is applied onto the plate the particles concentrate mainly on the charged surface parts. To improve the image quality a mixture of coarse and fine (cascade) powders is used and its distribution is regulated by a grounded electrode placed at a small clearance above the plate.

The developed image transfer to the paper is usually made electrostatically. A sheet of paper is laid on the plate and subjected to corona discharge of polarity similar to the plate charging one. The deposited on the paper discharges attract powder particles and remain on the sheet upon its removal from the plate. To fix the image the powder particles are melted and dissolved using vapors and liquids.

Of a significant practical use are two modifications of xerography, i.e. xeroradiography, which is the production of xerographic images in X-rays [71] (applied in medicine) and electrofax, which is a xerography-based method of facsimile communication (phototelegraph) combining image production, development and fixing on a special photoconducting paper in one process [72].

Photography based on photoconductivity principle joins methods utilizing rise of semiconductors electric conductivity under the light action or any other type of irradiation.

When projecting an optical image on a special plate, a conductivity (not charge) relief emerges in the latter corresponding to the image. It is preserved for a prolonged time if stored in darkness. This latent image can be developed in several ways. According to the first one the plate is corona discharged. The deposited charges decompose more intensely on the portions of higher conductivity. A charge relief is thus produced which can be developed xerographically. The other method used in engineering employs the plate with the latent image as one of the electrodes. Metal is electrostatically deposited on the electrode and its amount is the larger the higher is the corresponding surface portion conductivity.

Photodielectric photography is based on usage of photodiodes displaying semiconducting properties of unidirectional conductivity emerging under optical irradiation. The process scheme is shown in Fig. 2.20. Image carrying light flux permeates through a glass plate with attached to it by a transparent conducting glue photodiode. A conducting relief is created on it corresponding to the optical image. The photodiode has a clearance over a metallic plate with a dielectric coating. When a voltage of sufficient magnitude is generated between the plate and conducting glue, electric discharges appear in the clearance. Their intensity is higher in the more conductive portions of photodiode. The deposited on the dielectric coating charge is developed using one of the above described methods.

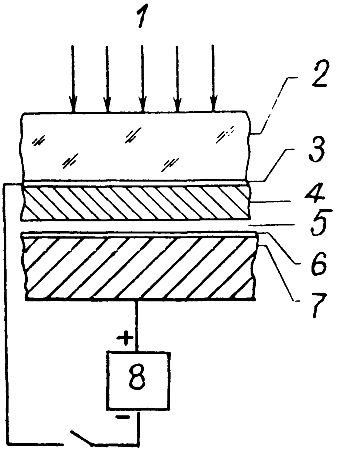

Figure 2.20. Photodielectric photography diagram [73]: 1 - light flux, 2 - glass plate, 3 - glue layer, 4 - photodiode, 5 - clearance, 6 - dielectric coat, 7 - metallic plate, 8 - constant voltage source.

Storage devices record, store and output information in a coded form. Alphanumeric units and facsimile are commonly recorded on paper or synthetic tapes. Among memory devices based on electrography (electrolytic and magnetic) most spread are those utilizing charge accumulation and retaining.

Videograph is a storage based on forming charge relief by electron beam. It looks like an electron-beam tube which screen has a great number of fused-in isolated thin wires. Their faces fill in the whole screen plane thus forming an electroconducting matrix. Latent image is produced by the electron beam sweeping across the screen creating a charge relief on the matrix wires. The latter contacts a dielectric coated paper tape. The charges transfer from the matrix on the tape dielectric coating and image is developed by using, for e.g., powder method.

Videographs have been elaborated to produce latent image on Teflon films by electron beam [74]. To read-out information, secondary electron emission induced by the scanning beam is used.

A principle diagram of *electrocharging devices* for electrostatic information recording are demonstrated in Fig. 2.21. A paper tape which sides have a metallized and dielectric coatings is transmitted through a clearance between the conducting substrate and recording head. The head is made as a point wire netting electrode fed from a pulse generator. When a certain combination of wires is excited a required discharge relief is obtained on the line. The relief development is performed by xerography.

A version of such device helps to record information using electrostatic charging of a polymer tape [75]. Information is read-out by the capacity probe method eliminating record erasion.

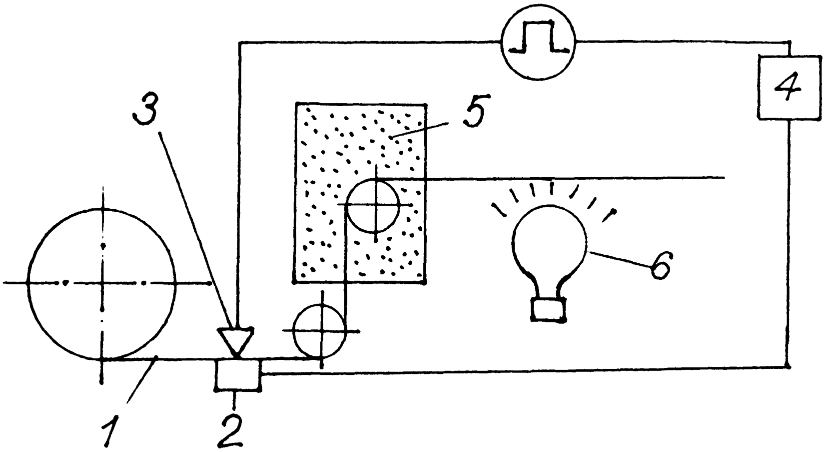

Figure 2.21. Scheme of electrostatic information recording using an electric discharge device: 1 - tape, 2 - conductive substrate, 3 - recording head, 4 - pulse generator, 5 - pigment powder, 6 - image fixative-heater [68, p. 204].

The scope of the present book does not allow to consider in detail one more interesting class of polarized materials - *ferroelectric polymers*. They have already found widespead application ranging from solid-state technology to biomedical engineering. Reader interested in this information could find it in book [76]. It contains examples of application of ferroelectric polymers in the field of electronic, photonic, and biomedical technology. Details of a wide variety of devices such as actuators, biomedical transducers, converters, hydrophones and arrays, detectors, diagnostic imaging, electro-optic, noninvasive cardiopulmonary sensors, optical data storage, photopyroelectric detection, vidicon tubes, robotics, sensors, transmitters, ultrasonic resonators and transducers, and underwater acoustic hydrophones are presented in this book. Piesoelectric polymers have also been used in the field of nonlinear optics for future optical communication and signal-processing technologies [77, 78]. The comprehensive, detailed describtion of ferroelectric polymers and their based technologies presented in the mentiond works benefit from the knowlege of tailor-made organic materials.

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CHAPTER 3

THE PRINCIPLES OF ENGINEERING ELECTRET MATERIALS DEVELOPMENT

Engineering material is a generalized definition of materials intended for manufacturing parts of machines and mechanisms. The development of engineering materials creates the basis for designing more efficient techniques, stimulates productivity, as well as energy- and material-saving in industry. The best engineering materials, which are, as a rule, bearing elements of machines, are imparting at the same time antifrictional and nonpermeable properties to joints, retard crevice corrosion, etc. Elaboration of such materials is an intricate scientific and technical problem. The materials science experience proves electret effect to be one of the promising ways of solving the problem.

Electret state of engineering materials was insufficiently investigated in the past decades. A few studies in the field were usually a know-how of production companies. Monopoly on the technique gave a considerable advantage to its designers in conditions of competition. Scientifically grounded application of the electret effect in manufacturing and utilization of engineering materials permits to most efficiently solve many problems the designers face. The problem essence is shown schematically in Fig. 3.1. The principles of engineering electret materials (EEM) development are being considered here through the analysis of electret effect profit in machine-building from the viewpoint of scientific concepts which treat industrial applications of electrets.

The problems solved by analyzing the electret state of engineering material components could be divided into technological and operational.

3.1. TECHNOLOGICAL DECISIONS.

The majority of EEM are composite materials which manufacturing process has been developed predominantly for polymer composites. Due to the fact, many of the below presented examples belong to this class of materials.

The dispersed solid particles distribution in the composite material bulk could be easily controlled by electric fields interaction effect on dispersed particles and other material components.

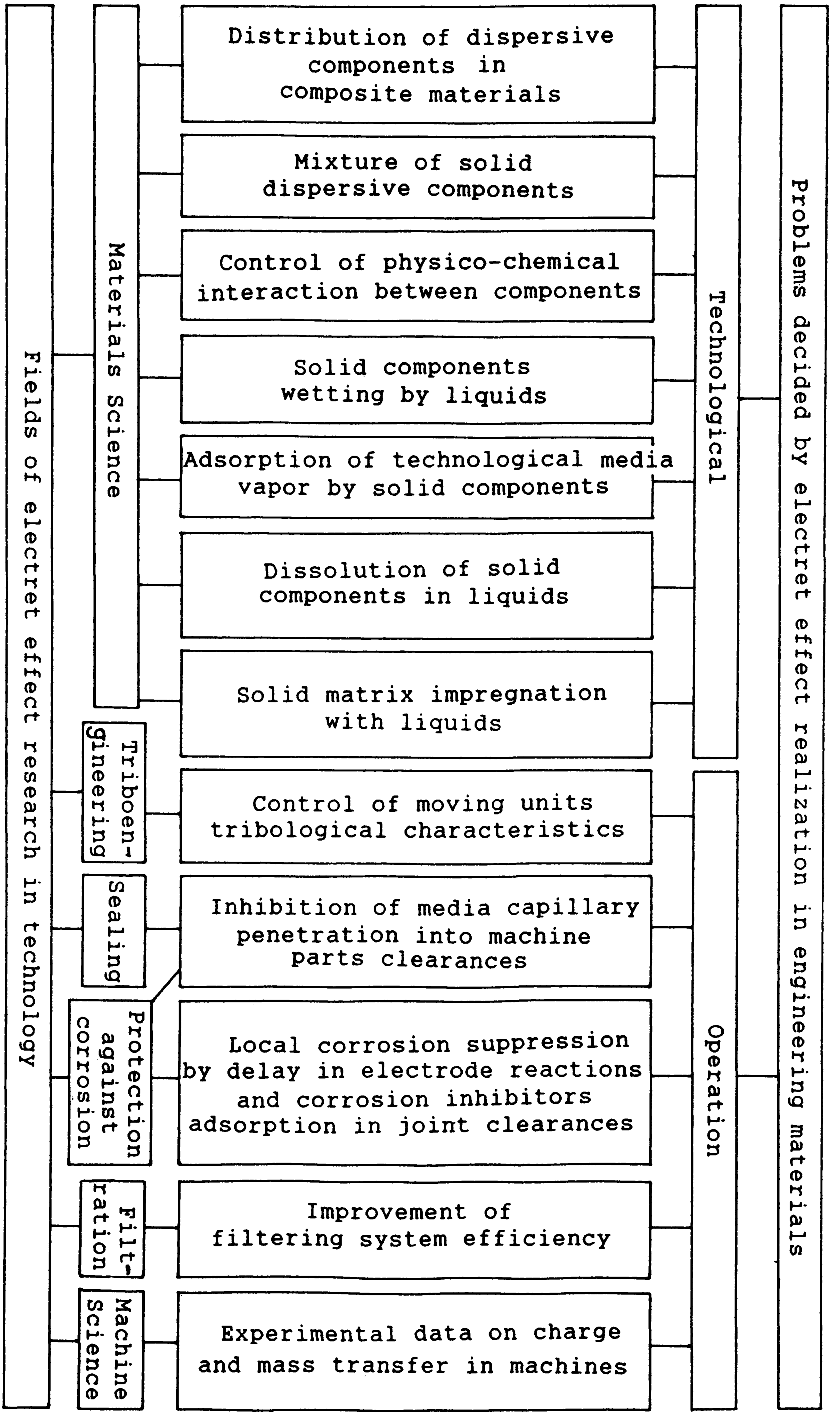

Fig. 3.1. Electret effect utilization in engineering materials.

Information is listed in Table 3.1 about corona discharge action on the fluidized polymer powder deposition. It is obvious, that the field voltage increase results in reduction of the electrically deposited layer integral charge, in nonmonotonous variation of its thickness, deposition rate and other parameters [1].

Interaction between electric fields of composite components allows for mass transfer control during articles production. This is realized in the process of the polymer powder binder electrical deposition on the reinforcing elements of composite materials (gauze, fabric, foil, etc.) during prepreg fabrication [2, p. 211]. Prepregs are semi-products of polymer composites used in large-sized articles production. Using high-voltage and grounded electrodes (Fig. 3.2) a two-side deposition is carried out of similarly charged particles (a) on conducting fillers and those oppositely charged (b) on dielectric ones. On fine materials (less than 0.5 mm) the polymer binder particles are deposited from one side (c).

Electret state of components is utilized in a number of branches to solve versatile technological problems in governing componential distribution in composites. An original technique has been developed in the textile materials science aimed at production of napped materials. A fleeced nap is electrostatically charged and supplied into inhomogeneous field on a vibrating disc. The hairs are attracted by their ends to disposed vertically disc. Under the action of inhomogeneous field they displace position from the disc center to its periphery along spiral trajectories. The longer and thicker is the hair, the larger is the trajectory and the faster the motion. The hairs with greater dielectric permeability obtain higher velocity. Thus, separation of hairs is performed by the criteria of electrical and optical properties using different batches of nap sticking to the substrate according to an assigned pattern.

Table 3.1. Characteristics of fluorplastic-3 powderlayer deposited onto grounded metallic plateas related to a constant-intensity electric field fed to particles

Parameters	Outer field intensity, kV/m				
	75	150	250	350	500
Specific charge, 10^{-4} C/kg	4.2	2.7	2.2	1.6	1.3
Limiting layer thickness, μm	115	305	460	825	515
Degree of thickness evenness (scatter across thickness), %	9	8	9	4	13
Maximum rate of deposition, 10^{-2} kg/ ($m^2 \cdot s$)	0.7	1.7	2.5	2.2	0.7

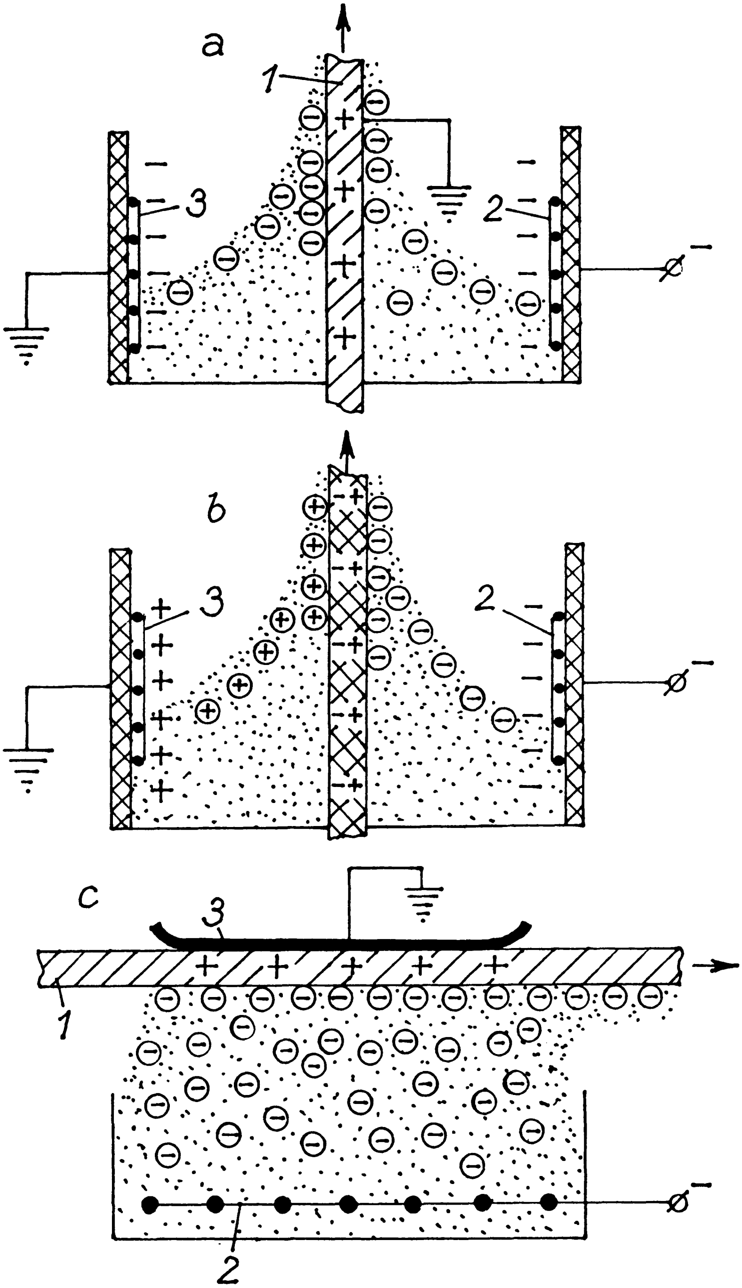

Fig. 3.2. Scheme of powder polymer binder electrical deposition on flat reinforcing fillers. a, b - bilateral deposition, c - on one filler side. 1 - filler, 2, 3 - elements of electrod system.

When emery paper is produced abrasive particles glued to a base are of irregular angular configuration. One of their angles is more acute. When the particles are conventionally deposited on the base by screening or spraying, the fact is not taken into consideration. Dielectric abrasive particles are oriented and glued in such a way that their acute angles are directed upwards by electric fields.

One more example is ruberoid - a roll roofing and waterproofing material. It is produced by saturating cardboard made of wooden or textile fibers with oil bitumen with subsequent protective sprinkling with asbestos, talc, etc. The fibrous raw material is fed from the hopper to conveyer belt and is caught under electrodes with passing pulse current. The fibers light fraction formed at electrical treatment is transported by the air flow to the interelectrode space of the forming device. The fibers charged by corona electrodes stick to conveyer belt energized by another pole of DC source. One layer of the fibers lie down lengthwise and the other crosswise to the belt. This is achieved by two pairs of accessory electrodes. One pair creates the field which force lines are directed along and another - across the belt. So, the fibers are oriented in two directions. The cardboard is formed and simultaneously saturated with bitumen using electric pulverizer. The blank is compacted by rollers and is sprinkled. The ready ruberoid is reeled into rolls and is cut.

Mixing of dispersed solid composite components is monitored using the method of particles electrization accompanied by their charge value control. This problem is complicated by inhomogeneity of components density and dispersion, their different electric properties, etc. Nevertheless, convergence of components into stable composite agglomerates can be realizede by nontraditional technological methods of electrical mixing. The peculiarities of agglomerate formation could be attributed to the component donor-acceptor properties when they are in contact interaction during fluidizing [1].

Practically inertialess electric mixers were designed in the 80-s. The mixer batchers can instantaneously feed components of hundredth gram fractions into the mixture flow, while the mixer productivity is up to 10 kg/h.

Physico-chemical interaction between composite components can be regulated by electrization. This is demonstrated, first of all, by change in the binder structure at the boundary with the filler. An increase in the polymer glassification temperature (T_g) has been recorded in the metal-polymer adhesive junction in response to a higher charge of electrically deposited layer. T_g dependence on the fibrous filler (glass, organic fibers) content in the binder differs markedly for adhesive bonds formed from electrically charged or not charged polymer particles.

Table 3.2 illustrates increase of carbon fiber adhesion to polymer binders in case of electrically charged polymer particles application onto the fibers in electric field. Adhesion has been estimated by the fiber shear force relative polymer matrix. Adhesion enhancement results from gain in orientation, polarization and rheological processes in the adhesive contact zone under the action of electric field [3].

Table 3.2. Adhesive strength of a carbon fiber and thermoplastic junction.

Thermoplastic	Forming regime			Adhesive strength, MPa
	T, °C	τ, min	electric field	
Polycarbonate	275	15	no	59.4
			yes	78.4
HDPE	200	15	no	14.3
			yes	21.0
Pentaplast	225	15	no	24.6
			yes	29.2

Liquid spreading and wetting of solid components of composite materials depend on the latter charge state. Below (ch. 4.1.3) data are given proving that pentaplast polarization and growth of electret charge are accompanied by reduction of the liquid spreading velocity over the electret film surface and, consequently, by increase of the equilibrium edge angle of wetting. This phenomenon can be used to improve protecting capacity of polymer coatings in electrolytes.

Adsorption of technological media vapors (solvents, plasticizers, stabilizers, etc.) by solid components is used in a number of techniques for achieving composite materials.

Hereinbelow (par. 4.3), the effect of polymer films electret state is described on kinetics of corrosion inhibitors sorption. This serves a prerequisite for working out electrical methods of a regulated merging solid and vapor components of composite materials. Regretfully, this perspective direction in materials science is not studied sufficiently.

Solubility of solid components in technological liquids is not a stable parameter. Already in the 60-s the electric field between ion crystal and polar liquid was found out to effect the velocity of the crystal solution [4]. Later, the representation was adapted for solution of electrets [5]. The present authors have justified the probability of controlling technological parameters connected with engineering polymers solubility [6].

Polymer films were treated with corona discharge (U = 15 kV) in order to form a bipolar symmetric charge controlled by contactless compensation method. The films were further immersed into solvents and the samples swelling $S = (m_{sw} - m_{dr})/m_0$ and the quantity of dissolved polymer, $D = (m_0 - m_{dr})/m_0$ were recorded, where m_0, m_{sw}, and m_{dr} are, correspondingly, mass of the original, swelled and dried samples.

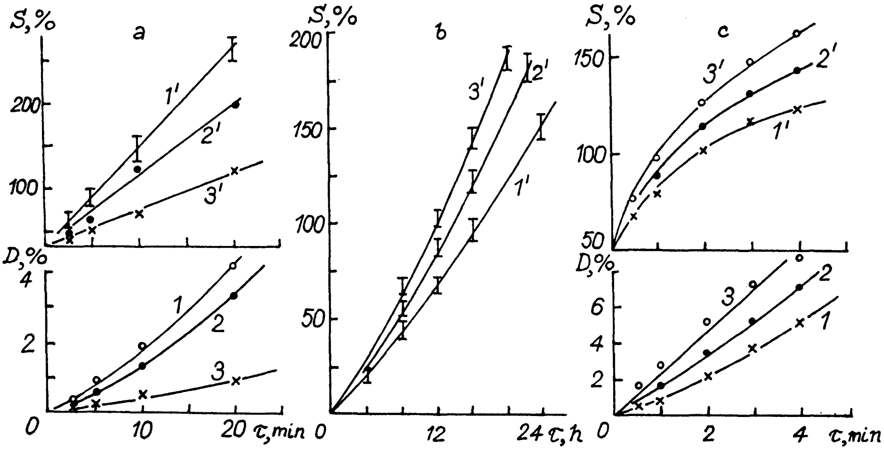

Fig. 3.3. Kinetics of swelling (S, 1'-3') and dissolving (D, 1-3) polymer films in low-molecular liquids under various regimes of electric polarization. a - PVB in ethyl alcohol, b - PVC in dioxane, c - PA in HCOOH. Time of film treatment with corona discharge: 1, 1' - 0; 2, 2' - 2 min.; 3, 3' - 20 min.

Figure 3.3 shows kinetic dependences of the parameters for samples with different electret charges. The parameters analysis has disclosed that the regularities of polar ion crystals dissolution [5] are true for noncrystalline PVB and weakly crystallizing PVC. The PVB dielectric permeability is $\varepsilon_s = 3.3$, while for its solvent $\varepsilon_l = 25.1$, i.e. $\varepsilon_s < \varepsilon_l$. Retardation of polarized solids dissolution is characteristic for such relation of dielectric permeability. This regularity is shown in Fig. 3.3, a. The curves are going downwards with increasing polarized charge. With film treatment time $\tau = 2$ min. (curves 2 and 2') the mean value of the effective charge surface density is $\sigma = \pm\ 10^{-8}$ C/cm^2, at $\tau = 20$ min (curves 3 and 3') $\sigma = \pm\ 2.4\cdot10^{-8}$ C/cm^2. Variation of samples mass at swelling correlates with the polymer mass growth in its alcohol solution. Variation of quantitative characteristics of swelling under polarization are by one and a half - two orders of magnitude higher than those for dissolution.

Dielectric permeability of weakly crystallizing PVC is $\varepsilon_s = 3.24$, that of its solvent (1.4 dioxane) $\varepsilon_l = 2.2$, i.e. $\varepsilon_s > \varepsilon_l$. Such relation of dielectric constants determines acceleration of the polarized substance dissolution. Figure 3.3 does not present diagrams of changes in solution concentration for the PVC-dioxane system. Mass m_{dr} of the swelled and afterwards dried PVC specimen appeared to be larger than that of the original m_0. That's why it became impossible to estimate polymer content in solution by variation of specimen mass. This can be attributed to phase separation of the system components during swelling, as well as to gel formation hampering complete removal of dioxane from PVC matrix at drying. Nevertheless, layout of curves in Fig. 3.3, b gives a real picture of correlation between PVC kinetics of dissolution in dioxane and regularities discussed in [5].

Figure 3.3, c shows kinetic curves of PA swelling and dissolution in formic acid. When dielectric permeability values of highly crystalline PA are $\varepsilon_s = 4.3$ and HCOOH $\varepsilon_l = 57.9$, then $\varepsilon_s < \varepsilon_l$ condition is preserved, under which polarization should promote retardation of solid dielectric dissolving. As far as PA solubility in HCOOH is considerably higher than that of PVB in alcohol, it is anticipated that the retardation effect on polarized PA dissolving is to be lower than on PVB. Position of curves in Fig. 3.3c demonstrates, however, that PA dissolving in HCOOH accelerates due to electrically induced polarization. This unexpected result is provoked by some new factors. PA is known to chemically interact with formic acid. Electrical polarization of specimens is, probably, an intensifying factor of chemical reactions between the polymer and solvent, which accelerates, in its turn, diffusion stages of PA solution. Thus, the general law typical of polar solids dissolving is complicated under polymer and solvent reaction by polarization effect on chemical reactions kinetics.

From the above procedure it follows, that the rate of solid organic polymers solution in low-molecular liquids depends on polarization charge of the dissolving specimen and the ratio between dielectric permeability of both polymer and liquid. In case dissolving is accompanied by chemical interaction of components, kinetics of the process is influenced by polarization, which can lead to diffusion acceleration of polymer solution. Electric polarization effect on polymer swelling is of great importance for technological modification and processing of composite materials.

Impregnation of composite matrix with liquid binders is one of the most low-productive processes. Intensification of the process represents an urgent problem to be solved in materials science.

Beginning from the end of the last century investigations in the field have shown that practically all liquids respond somehow to electric field action. It was found out that polar liquids viscosity at first grows with voltage boost proportionally to square voltage and then approaches some stationary value. Limiting viscosity magnitude when it becomes independent of voltage is called saturation viscosity. Its value depends on liquid conductivity [7].

In a number of cases saturation is accomplished with the help of suspension binders. The presence of electrical charges on particles in suspension imposes additional energy limitations on particle distribution and hydrodynamic parameters of suspensions. Such suspensions do not obey Einstein's law and their viscosity increments under shear flow by a value named electrostatic constituent of viscosity. The phenomenon of viscosity rise is called electroviscous effect [8, 9]. Three electroviscous effects can be discriminated. The first proceeds in diluted suspensions where interaction between double electric layers of neighboring particles is absent. The second electroviscous effect occurs in concentrated suspensions where overlapping of double layers takes place. The third one is characteristic of polyelectrolytes solutions and is stipulated by variation of macromolecules shape.

The above data evidences that impregnation of composite material matrix with liquid binders could be controlled by a directed change of its components charge state. Still, acceleration of saturation could not be reached by a simple field application, it needs a special treatment and witty technological decisions. So, it is not surprising that there is not any description of matrix impregnation technique in handbooks on composite materials. This perspective direction in composite technology requires further investigation.

3.2. OPERATION PROBLEMS.

Use of engineering electret materials for technical articles permits to take a new view in questions of improving serviceability of machines and equipment.

Monitoring of frictional characteristics in movable joints is an important tribological problem aimed at energy-, labor- and material saving.

One of actual directions in its solution consists in preventing lubricant removal from spaces between microasperities on the friction surface areas under maximum contact stresses. Magnetic lubricating systems and induction sealing can serve as an example of most efficient application of magnetic and electromagnetic fields in this problem [10-12]. In the first case magnetic field entraps in friction joint clearances solid lubricants possessing magnetic properties or magnetic liquids. In the second case ponderomotive force of electromagnetic field concentrates the liquid metal layer (mercury, gallium, bismuth, etc.) in the shaft-bearing clearance in the zone of the most field intensity and the layer is not removed from the clearance.

A similar result can be obtained when electret materials are used in friction joints. The mechanism of monitoring lubricant adhesion to friction pair walls with the help of electret field consists in the following. Lubricating fluids are dielectrics in their majority and are subjected to electrization during friction [13, 14]. In case the clearance walls are oppositely charged, the lubricant adhesion increases owing to electrostatic attraction (Fig. 3.4). The polarizing charge is induced onto a dual electric layer of the lubricating interlayer contacting the electret even in the absence of triboelectrization. The contemporary physico-mathematical models of wetting and spreading take into account the phenomenon and its dependence on solid body charge [15].

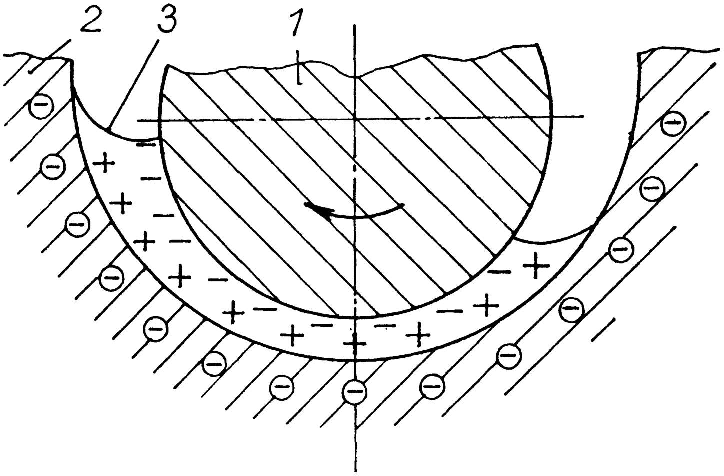

Fig. 3.4. Electrostatic interaction between dielectric lubricant and electret support of friction pair. 1 - shaft; 2 - bearing; 3 - lubricant interlayer.

Forecast study shows that electrets are useful in triboengineering to realize electroviscous-rheological effect, i.e. fast reversible rise of effective viscosity in non-aqueous dispersed systems under strong electric fields. The essence of such original structures as clutches, brakes and other frictional units is in regulation of slippage between two conjugated parts (driving and driven, moving and stationary) aimed at automatic velocity control. A prerequisite of such systems is electroviscous-rheological suspension placed in the friction pair clearance. It is composed of nonpolar liquid (petrolatum, vegetable oil, transformer oil, aromatic hydrocarbons, amines and etc.) and a solid dispersed phase with a fairly high dielectric permeability (silica of different modifications, metal oxides, aluminosilicates, etc.). Usually, powders of less than 1 um particle size are used with this aim. Electroviscous-rheological suspensions also include activators adsorbing on the solid particles surface (glycerin, diethyleneglycol, amines, etc.) and stabilizers which are surfactants of ion and nonion types. Depending on the value of charge on the EEM friction parts lubricated with electroviscous-rheological suspension, its internal friction can increase up to a seemed solidification. Frictional joint structures are based on this principle to control loads in electric engines of nonstationary regime, to provide a fixed velocity of winding and unwinding thread, band, cloth, etc. from spools, bobbins, reels (see 5.3.2).

Hampering of liquid capillaric penetration into clearances in machine joints is one of urgent problems in assurance of article tightness. Electret sealing components could be a technologically simple means of controlling capillaric leakage. Surface tension σ at the electrode-electrolyte boundary depends not only on the contacting media nature, but on the properties of originating double electric layer as well. The equation of electric capillarity takes this regularity into account:

$$\sigma = \sigma_0 - 0.5C\varphi^2 \tag{4.1}$$

where, φ - electrode potential, σ_0 - surface tension at $\varphi = 0$, C - capacity of the dual electric layer. EEM surface charge density is to a great degree determining value σ. Chapter 6 is devoted to electret application in sealings.

Crevice corrosion inhibition with the help of electret engineering materials is based on the following concepts.

Electrode potential (difference between galvanic electrode and electrolyte electric potentials) is the basic characteristic of the double electric layer at the electrode-electrolyte interface, which determines kinetics of electrochemical processes in the clearance, where electrode serves as a wall. Under the action of the electret field the conductivity electrons shift in the electrode, i.e. electric polarization of the electrode takes place (Fig. 3.5). This leads to variation in the dual electric layer, which results in electrochemical polarization. The clearance size is not large in machine parts, as a rule. It correlates with microasperity height of the contact surface. That's why attenuation of electret field in the joint clearance is negligible. Thus, polarization of the conjugated with electret electrode can considerably change electrochemical reactions in the clearance.

Expediency of EEM application as a means of crevice corrosion inhibition proceeds from the possibility to intensify corrosion inhibitors

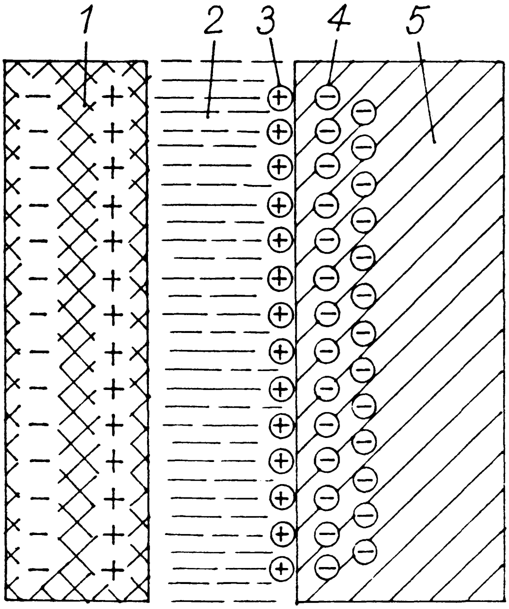

Fig. 3.5. Scheme of electric polarization in the electret field. 1 - electret; 2 - electrolyte; 3 - particles of double electric layer; 4 - conductivity electrons, 5 - electrode.

adsorption on the charged surface. By regulating the electret charge it is possible to produce inhibitors concentration on the clearance-facing surface sufficient for crevice corrosion suppression.

Efficiency of filtration systems has been raised by using EEM for more than 30 years.

The principle of a simplest filter operation is presented schematically in Fig. 3.6. A gas containing charged contaminant particles is carried through the clearance between the electret and electrode. The latter is closed to the second electrode located close to the oppositely charged electret surface [16]. The contaminant particles are to precipitate depending on their charge sign onto the electret or electrode. Upon a certain gas portion passage, the electret element, as well as electrode requires cleaning from the stuck particles which screen electret field. Chapter 2.3 cites some more examples of EEM application in filtration systems.

To optimize operation of machines it is necessary to obtain information on the processes of charge transfer, mass- and heat exchange. A unique property of EEM is, in this respect, the fact that the materials can fulfill simultaneously the functions of carrying and transferring mechanical loads and that of sensitive elements of measuring transformers. Chapter 2.1 is devoted to this subject and lists examples of electret field use as additional functional property of engineering materials.

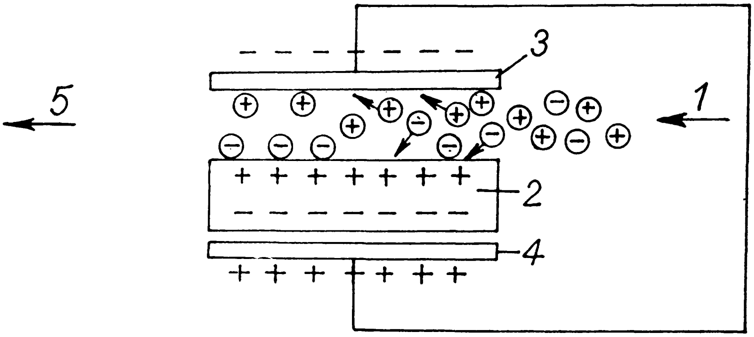

Fig. 3.6. Diagram of electret filter operation. 1 - contaminated gas flow; 2 - electret; 3, 4 - electrodes; 5 - flow of purified gas.

3.3. THE PROBLEMS OF EEM DEVELOPMENT.

EEM have been used in engineering for only about ten years. The principles of their development constitute a new paragraph in materials science. The requirement of preserving polarizing charge for the period the material satisfies strength criteria often comes into contradiction with common requirements to composite materials:

- special electric polarization methods violate in some cases optimum, from precision viewpoint, structural state of material and make it costlier;
- introduction of electrically treated components into the binder could impair technological conditions of composite production;
- the presence of electrical charge in structural materials often disturbs machine parts interaction and affects serviceability of neighboring joints and parts;
- electret field can affect auxiliary characteristics of engineering materials serviceability, e.g., as a result of electrostatic attraction of foreign particles (dust, abrasives, etc.), adsorption accumulation of separate environmental and working media components occurs;
- natural depolarization accelerates relaxation processes in EEM which also negatively effects articles serviceability.

In a number of cases electret state of engineering materials is not a scheduled but a random result of uncommon technological processes. It emerges, for example, when laminated plastics are produced by using a charged polymer powder as a binder [2]. Electret charge obtained by such composite materials is a side result of the technique and is not used during articles operation. A similar situation takes place when polymer components are activated in electric field, i.e. when modifying filler surface in plasma of glowing discharge in vacuum and gas mixtures, when processing rubber blends by rollers in the field of pulse electromagnetic discharge, etc. Electret effect is an unwanted consequence of production techniques and operation conditions of a number of polymer materials which speeds their ageing.

One of the few examples of the electret and electrization effect purposeful application as EEM components is the textile materials science. The technology of electrical spinning, artificial teasing, regulation of thread and fibre electrifiableness is widely used in EEM textile elements production.

A conclusion has been made from the above procedure, that the problems solved by the new materials science domain are rather complicated, involving many sciences and formulating a new nontraditional knowledge. It can be foreseen that the spheres of EEM materials science potentialities are much broader than those studied and approved, but to predict all fields of EEM application is at present a rather difficult or simply impossible task.

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CHAPTER 4

ELECTRETS IN ANTICORROSION TECHNIQUES.

The efficiency of hardware protection against corrosion depends on the presence of rustproof materials in their composition. Their major anticorrosion characteristics important for anticrrosion techniques are the following:

- low diffusion coefficient, ability to produce a barrier against corrosive medium penetration to the most rust-prone metal parts;
- electric conduction effecting the current level of electrochemical corrosion;
- ability to passivate or electrochemically protect rust-prone metal parts;
- adhesive or deformation and strength characteristics of rustproof materials used as coatings.

Most corrosion-resistant among engineering materials are polymers and ceramics. Electric polarization of ceramics is the basis for regulating all the above mentioned properties in a wide range. Polymers and ceramics are, as a rule, contacting metals in machines. Any contact, from anticorrosion technique viewpoint, is a potential source of corrosion. The given chapter quotes data evidencing that local corrosion of metals can be suppressed in the metal-dielectric systems by generating electret charge in dielectrics. There is also information on other corrosion characteristics of electret materials.

4.1. ELECTRET CHARGE EFFECT ON CORROSION.

4.1.1. Corrosion thermodynamics and electrochemistry.

The notion "metal corrosion" is disputable since an unambiguous determination subduing contradictions has not been drawn up till the present day. Corrosion is traditionally considered as metal damage resulted from chemical (electrochemical) interaction with environment. This definition was valid in the State Standard system of the former USSR. International Standards Organization has a somewhat wider definition: "Physico-chemical interaction between metal and environment which affects both metal and environment with often impairment of metal functional characteristics".

It is accepted to classify corrosion by the following main criteria: the proceeding processes behavior, conditions and character of corrosion-induced damage. Judging by the corrosion mechanism it is subdivided into chemical and electrochemical corrosion.

Chemical corrosion occurs in nonelectrolytes and dry gases. It obeys the laws of chemical kinetics of heterogeneous processes. Chemical corrosion is characterized by metal interaction with corroding medium when metal oxidation and reduction of the corrosion medium oxidizer proceed simultaneously. As compared to chemical corrosion, *electrochemical* one takes place in electrolyte solutions and in humid gases. It is characterized by a parallel proceeding processes of oxidation and reduction. Such a corrosion is accompanied by a directed transfer of electrons in metal and ions in electrolyte which generates electric current.

Depending on conditions of corrosion we discriminate gas, liquid, atmospheric, nonliquid, biological, radiochemical, hydrogen, electric, mechanical or tribocorrosion. According to the character of damage corrosion falls into non-equal (selective), uniform, pitting, point, thread-line, crevice, contact and intercrystalline corrosion. The first two types belong to the general corrosion and the rest to the local one.

Corrosion emerges due to thermodynamic instability of metals, that's why most of them exist in nature in an oxidized state. Corrosion behavior can be determined by Gibbs's energy variation (isobar-isothermal potential). A rough estimate of different metals thermodynamic instability in electrolyte solutions can be made using the *standard metal electrode potential.* Table 4.1 arranges the known in technology metals in ascending order of the standard electrode potential U_0 [1, 2]. Negative values correspond to more reactive metals.

A more detailed data on thermodynamic stability of metals in different media and conditions can be obtained based on Pourbaix diagram (Fig. 4.1). Such diagrams have been compiled for the majority of metals [3]. They visualize the conditions (potential domains and pH) when metals are either thermodynamically stable (immunity) or react and form ions, oxides or complex compounds.

Metal corrosion stability is governed in practise by not only thermodynamic stability, but by kinematics as well, i.e. by the actual established corrosion rate. According to the electrochemical theory, metal damage by corrosion is based on *anodic and cathodic processes* characteristic of galvanic element operation. Both processes are connected by the fact that the number of electrons liberated during metal ionizing should correlate with that interacting with depolarizer.

Table 4.1. Standard electrode potentials U_0 of metals at T = 25 °C [1, 2].

Electrode reaction	U_0, V	Electrode reaction	U_0, V
Li + *e*	-3.045	Mn + 3*e*	-0.283
K + *e*	-2.925	Co + 2*e*	-0.277
Ca + 2*e*	-2.87	Ni + 2*e*	-0.250
Na + *e*	-2.714	Mo + 3*e*	-0.20
Mg + 2*e*	-2.37	Ge + 4*e*	-0.15
Be + 2*e*	-1.85	Sn + 2*e*	-0.136
U + 3*e*	-1.80	Pb + 2*e*	-0.126
Al + 3*e*	-1.66	W + 3*e*	-0.11
Ti + 2*e*	-1.63	Bi + 3*e*	+0.226
Zr + 4*e*	-1.53	Sb + 3*e*	+0.24
Ti + 3*e*	-1.21	Re + 3*e*	+0.30
V + 2*e*	-1.18	As + 3*e*	+0.30
Mn + 2*e*	-1.18	Cu + 2*e*	+0.337
Nb + 3*e*	-1.10	Cu + *e*	+0.521
Zn + 2*e*	-0.763	Hg + *e*	+0.789
Cr + 3*e*	-0.74	Ag + *e*	+0.799
Ga + 3*e*	-0.53	Rh + 3*e*	+0.80
Fe + 2*e*	-0.44	Pd + 2*e*	+0.987
Cd + 2*e*	-0.403	Ir + 3*e*	+1.000
In + 3*e*	-0.342	Pt + 2*e*	+1.19
Tl + 3*e*	-0.36	Au + 3*e*	+1.50

*Electrode reactions $Me^{n+} + ne = Me$ are briefly noted as Me + n*e*.

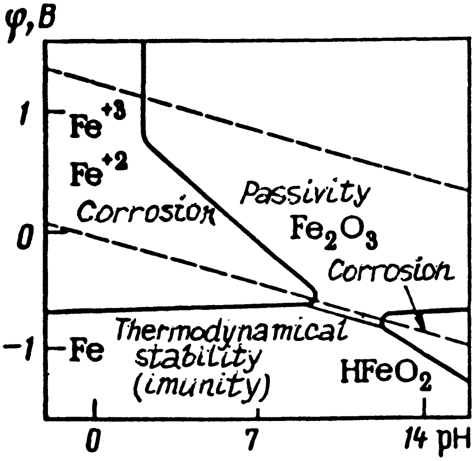

Fig. 4.1. A simplified Pourbaix diagram for iron at T = 25 °C [3].

Many of electrochemical reactions are known to run at a relatively low rate, so to maintain a certain value current in the circuit, it is necessary to impart an excess energy to the electrode in order to shift its potential from equilibrium. Such a shift of the electrode potential at current passage is called *polarization*. At anodic polarization the potential shifts to the positive and at cathodic - to the negative side.

Polarization might emerge due to different reasons. Retardation of anodic reaction occurs most often because of discrepancy in velocities of the anodic reaction and electron removal in the outer circuit or due to the insufficiently fast removal of the migrated to solution metal ions. The cause of cathodic polarization is untimely assimilation of the running-over electrons or low velocity of oxygen feed to the cathode. Anodic polarization can take place due to passive films formed on the metal surface as a result of oxygen adsorption from air.

Passivity is a state of metal or alloy of elevated resistance to corrosion (in conditions of being quite reactive from thermodynamic viewpoint). The state is produced by the dominating suppression of anodic process of metal solution [4]. It is characterized by an abrupt reduction of corrosion rate and a considerable shift of metal potential to the positive side (for iron it is -0.2...+1.0 V, for chromium -0.4...+0.9 V).

The analysis of corrosion systems commonly utilizes the corresponding diagrams where the anodic or cathodic reaction kinetics is reflected graphically. The curves of potential variations visualizing current passage or current density dependence on potential are called *polarization curves*. Most convenient configuration of corrosion diagrams was suggested by Evans [5]. Negative values of potential are laid upwards on such diagrams, while the anodic and cathodic current values are laid on the abscissa despite their opposite direction (Fig. 4.2). The anodic and cathodic curves cross-point corresponds on abscissa to the maximum density of corrosion current.

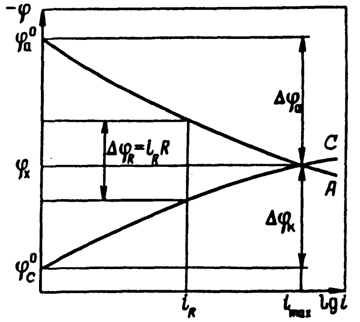

Fig. 4.2. Evans corrosion diagram: A and C are anodic and cathodic curves; φ_a^0 and φ_c^0 - initial (equilibrium) potentials of anodic and cathodic reactions; $\Delta\varphi_a$ and $\Delta\varphi_k$ are anodic and cathodic polarizations; i_{max} is the maximum corrosion current density; φ_x - stationary potential value; $\Delta\varphi_R$ - ohmic retardation of corrosion.

4.1.2. Polymer effect on metal polarization kinetics in electrolyte solutions.

As it was mentioned above, one of the factors determining the polymer-based systems protecting efficiency is barrier action of polymer elements insulating metals from environment. When polymer insulation is broken its influence on metal corrosion in electrolyte solution ceases. Nevertheless, a factor should be taken into account that under the action of different operation phenomena polymers can produce products changing corrosion kinetics in the metal-polymer contact.

Model experiments helped to investigate polymer powder and film effect on steel corrosion rate in electrolyte water solution and the latter physico-chemical properties. Powders were chosen with a high specific surface values allowing to simulate conditions when considerable changes in physico-chemical parameters of electrolytes were recorded at a relatively short time intervals. The experiment methodology is as follows. The initial values of the studied parameters were recorded (electrode polarization potential, corrosion rate, redox potential). Then the measurements were repeated upon each cycle of dispersed polymer (m = 200 mg) hanging on electrolyte surface and powder removal.

The rate of steel plates (steel 3) corrosion is shown to be much dependent on the recurrence of polymer powder substitution on the solution surface (Fig. 4.3 a). Also, the solution redox potential variation takes place in similar conditions (Fig. 4.3 b). The comparison of results obtained shows good agreement between values which correlated variation is unambiguously governed by the polymer origin.

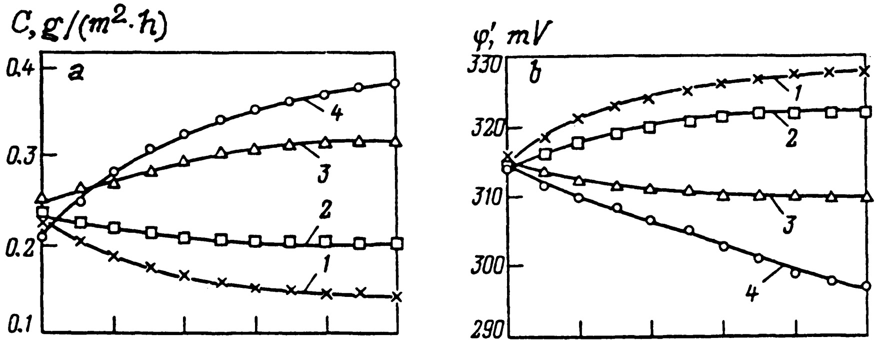

Fig. 4.3. Corrosion rate C of steel plates (a) and redox potentials φ' (b) versus recurrence of polymer powders change on NaCl solution (10^{-4} mole/l) surface. Powder dispersity is 160-200 μm: 1 - PPl; 2 - PE, 3 -teflon; 4 - PVB.

Application of polymer powder or film on the solution surface evokes the redox potential gradient in the solution bulk. Most prominent potential reduction with time is recorded at a minimum electrode distance from the powder surface layer. With increasing depth the potential variation becomes negligible and is not recorded at about 60 mm depth (Fig. 4.4).

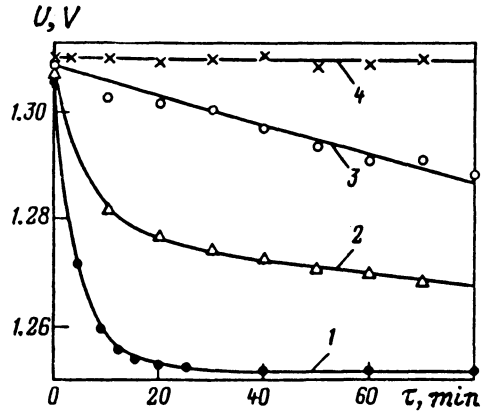

Fig. 4.4. Potential U of platinum electrode in NaCl solution with PVB powder on surface versus time τ and depth of electrode immersion (mm): 1 - 15, 2 - 30, 3 - 45, 4 - 60. Polarization current density is +0.1 mA/cm^2.

From the viewpoint of electrode process kinetics the results can be attributed to local variations of depolarizer concentration near the upper electrode (as compared to the bulk) due to polymer powders placed on the solution surface. This is proved by the data on the electrode potential variation at a different depth. Such a variation can be a result of the depolarizer adsorption on the polymer particles. It has been also established that PE, PVB and PPl powders do not practically change their polarizing kinetics in distilled water, their influence, however, becomes perceptible in diluted electrolyte solutions (10^{-4} mole/l). In more strong solutions (0.1 mole/l and above) the polarizing intensity varies negligibly when powders are placed on the electrolyte surface. This also serves in favor of adsorption mechanism of polymers effect on metal polarization in electrolyte solutions.

The above data demonstrate that the polymers specific effect on polarizing kinetics of contacting metals should be taken into account in metal-polymer joints design and in forecasting their performance.

4.1.3. Polymer electret permeability.

Let us digress from the electrochemical aspect of corrosion processes in the metal-polymer contact (see paragraph 4.2. on the polymer coating example) and dwell at length on barrier properties of the polymer electret materials.

There are three stages of hostile medium penetration through the protective polymer barrier: 1) liquid spread and polymer surface wetting; 2) sorption (adsorption and absorption) on the polymer surface; 3) diffusion through the polymer bulk. It is possible to regulate the three processes by way of polymer transfer into electret state and changing polymer electret charge.

Liquid sorption by polymer electrets is described in paragraph 4.3. In this chapter we shall consider in more detail the first and third stages of liquid penetration through polymer electrets.

The effect of polymer electret charge on *liquid wetting and spreading* is treated in work [6]. Experiments were carried out with reference (nonpolarized) and electret (thermo- and corona-electrets) films from pentaplast. Tested liquids were diethylene glycol (DEG) and glycerin displaying rather high viscosity allowing studying kinetics of spreading during relatively long time intervals. This helped to visualize experimental results and to enhance their reliability.

The obtained data shows that polarization of films and increase of electret charge provides for decreased initial spread velocity (Table 4.2) and reduced actual area of the drop-film contact (Fig. 4.5).

Table 4.2. Initial velocity v of DEG spreading over PPl film surface as a function of surface charge density σ.

Sample	σ, C/m^2	v, 10^{-4} mm/s
Reference	0	2.8
Thermoelectret	$4.96 \cdot 10^{-6}$	1.4
	$2.78 \cdot 10^{-5}$	0.6
Corona-electret	$3.60 \cdot 10^{-5}$	0.4

The electret charge effect on liquid spreading can be explained as follows. The spread motive force effects the liquid local microvolumes and is directed to the solid-liquid interface. It increases with improving capacity of solid for sorption and assists rise of spread velocity. Sorption intensity in electret films is lower than in reference ones [7], so far DEG spreading over them is slower too. Apparently, the polarizing charge creates an energy barrier and the spread motive force is spent to overcome it. Consequently, the electret film wetting is lower than the reference one with other things being equal. Figure 4.6 is the proof to the above stated.

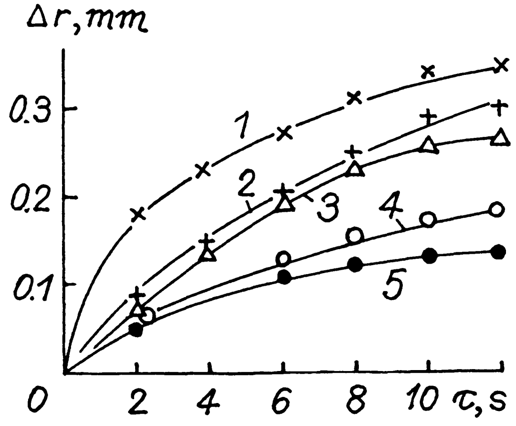

Fig. 4.5. Growth of DEG drop radius Δr spreading over PPl film as a function of time τ from the moment of drop placing on the film and the film charge density σ (C/m^2):
1 - 0; 2 - 1.16·10^{-5}; 3 - 2.78·10^{-5}; 4 - 3.6·10^{-5}; 5 - 5.8·10^{-5}. Δr = r-r$_0$, where r and r$_0$ are radius values in moments τ and 0.

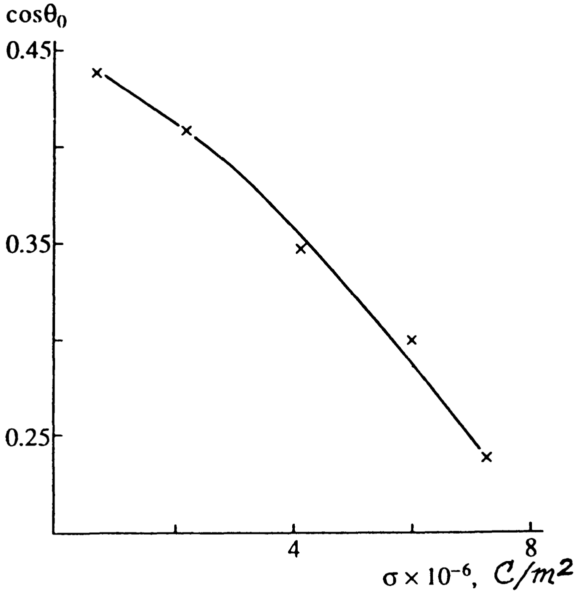

Fig. 4.6. The dependence of an equilibrium edge angle cosine of glycerine drop on surface charge density of the pentaplast film.

Diffusion permeability of polymer electret materials has been studied by Yu. Voronezhtsev. Charge effect of PVB and PPl-based electrets on electrolyte diffusion into the polymer coating on a metal substrate has been investigated as exposed to 0.1 n HCl solution. Experimental results are presented in Table 4.3.

Table 4.3. Amount of liquid Q diffused into PVB coating and diffusion coefficient D at a different polarized charge density σ.

σ, 10^{-5} C/cm^2	0	0.05	0.18	0.98	2.0	2.94	3.51	4.80
Q, 10^{-7} kg/cm^2	1.51	1.48	1.38	1.02	0.76	0.57	0.44	0.29
D, 10^{-11} m^2/s	1.20	1.15	1.05	0.62	0.31	0.16	0.11	0.05

Based on the results an analytical dependence has been derived for the amount of diffused into the coating liquid versus polarized charge value. If to suppose that C_0 concentration at the polymer-medium interface is constant throughout diffusion running, then the quantity of sorption by a moment t equals:

$$Q = \frac{2C_0}{\pi} \cdot \sqrt{Dt} \cdot exp\,(-\alpha\sigma)\,, \tag{4.1}$$

where D is diffusion coefficient for nonpolarized polymer; σ is polarizing charge surface density determined by TSD. Parameter α reflects the degree of diffusion permeability dependence on polarizing charge surface density σ and is defined experimentally for each coating-medium combination. According to data from Table 4.3, parameter α equals $0.34 \cdot 10^5$. Equation (4.1) describes satisfactorily diffusion processes in coatings, where $\sigma > 5 \cdot 10^{-7}$ C/cm^2. The reduction of diffusion permeability in polymer materials due to electric polarization is limited because the charge density of $\sigma > 5 \cdot 10^{-5}$ C/cm^2 is unattainable for them. This happens because polarization products block the electrodes [8]. Nevertheless, even at lower σ values a 3-5 times reduction of diffused liquid is observed.

4.2. POLYMER COATINGS.

4.2.1. Electrochemical interaction in metal-coating systems.

Adsorption of low-molecular liquid on the polymer surface and its diffusion into the bulk finally leads to the polymer swelling and its dissolving. These processes result in variation of molecular interaction in the polymer and effect its physico-mechanical, electric and other properties.

Electrochemical interaction of components should be taken into account in metal-polymer (for e.g., as polymer coatings on metals) adhesive joints operation. This interaction arises from the presence of sites having different electrode potential values [9]. It mainly effects two factors determining polymer coatings reliability and protecting efficiency. The first factor is permeability of hostile media initiating corrosion and metal damage in the metal-polymer contact. The second one effects physico-mechanical properties and adhesive strength of polymer coatings.

The "polymer coating - metal substrate" system is a convenient model for studying crevice corrosion at the metal-dielectric interface when the coating peels off in an aggressive liquid. The methodology of studying resistance to peeling consists in recording the coating peeling parameters round an artificially created point defect (puncture) reaching the substrate [10].

The polymer coating peeling under the action of aggressive media is accompanied by the electrode potential shift from the substrate to the negative domain (the so-called "unrefining"). Change of the substrate potential when the coating peels off is an evidence of inhibited oxygen cathodic reaction under the coating or acceleration of metal ionization. Both anodic and cathodic reactions were controlled by maintaining the required level of substrate potential.

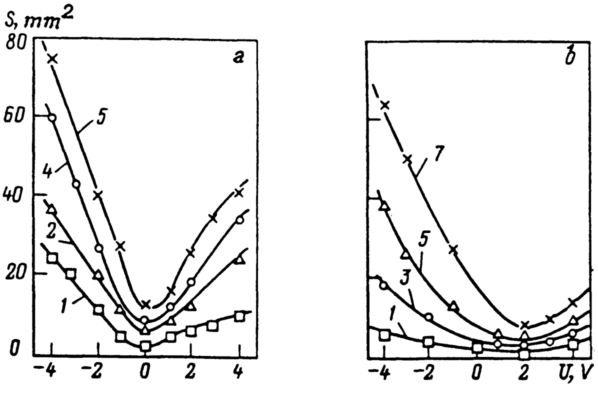

Fig. 4.7. Area S of polyethylene coatings lamination from graphite (a) and steel (b) substrates in a 5% solution of H_2SO_4 as a function of potential U supplied to the substrate and endurance time in electrolyte (numbers on curves is endurance time in hours).

Figure 4.7 presents diagrams visualizing that kinetics of polymer coatings peeling is to a great degree determined by the transferred to the substrate potential value and sign. Difference between graphite and steel position of minimums on the curves proves that peeling is conditioned by redox reactions on the substrate surface which promote oxide films formation or failure. Thus, by varying the substrate electrode potential, the protective capacity of polymer coatings in electrolytes can be regulated.

However, such a method of enhancing metal-polymer adhesive joint anrticorrosion properties calls for an outer power source, being uneconomical in some cases. It is logical to assume that the substrate electrode potential could be shifted by varying the polymer coating charge state. If a coating is formed so that the negatively charged surface contacts the metallic substrate, then the substrate "unrefining" reduces considerably. The described charge distribution is performed using *electret coatings* [11].

The polarizing charge effect on polymer coatings and their protective efficiency was estimated using the following parameters: the area of coating peeling in conducting liquids, variation of substrate electrode potential, strength of the coating-substrate adhesive joint.

Table 4.4. Area of coating lamination *S* and change of electrode potential ΔU of substrate as a function of time.

Coating group	Coating material	S (cm^2) per time *t* (days)					ΔU, V in 5 days
		1	2	3	4	5	
A	PPI	0.25	0.74	2.03	2.76	3.97	0.24
	PVB	3.03	6.24	10.32	--	--	--
B	PPI	0	0.01	0.02	0.02	0.04	0
	PVB	0.01	0.02	0.04	0.07	0.08	0.02
C	PPL	0	0.01	0.02	0.02	0.03	0
	PVB	0.01	0.02	0.05	0.07	0.08	0.02

Table 4.4 cites test results of punched coatings behavior in a strong NaCl solution. Group A coatings were formed following a classical vibro-vortical method. Group B coatings were melted in electric field of E = 20 kV/cm intensity. The upper electrode was connected to the positive pole of a high-voltage source and the substrate was grounded. To melt the C group coatings a closed to a steel substrate copper foil was placed on the polymer layer. Upon cooling the foil was peeled off. Electret coatings (group B)

whose negatively charged surface contacts the metallic substrate peels off slower, while their substrate "unrefining" is less than the nonelectret ones (A) show. Analogous results were obtained for coatings based on metal-polymer electrets (C) formed without any outer electric sources.

Similar investigation results were obtained for adhesive joints strength which proved positive effect of the coating electret state on its protective efficiency. Figure 4.8 visualizes that PVB-Al adhesive joint strength determined by the peeling method upon enduring in electrolyte is higher for the coatings formed in electric field so, that the space charge field is directed from the coating to the substrate. The period of endurance in a 5% H_2SO_4 solution when the strength limit reduces twofold is about 8 hours for nonpolarized coatings and about 75 hours for the electret ones. Thus, electret polymer coatings can considerably enhance corrosion resistance of metal articles in hostile liquid media.

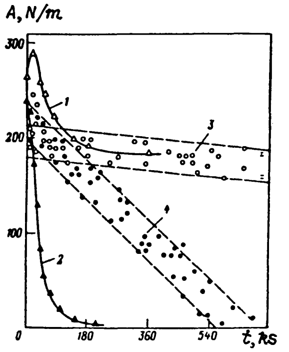

Fig. 4.8. Strength of PVB-Al adhesive joint versus time of exposition in air (1, 3) and in 5% solution of H_2SO_4 (2, 4). Electric field intensity during coating formation: 0 (1, 2) and 20 kV/cm (3, 4).

Another method of improving adhesion and protective ability of polymer coatings is *filling* with *electret or electrochemically active fillers*.

There exists a thermoplast-based composite coating material with about 13 mass % of ground epoxy resin. The powder of the set epoxy resin is subjected before mixing with a thermoplastic binder to electric polarization of up to a 100 nC/cm^2 electret charge value. The prepared composition is electrostatically sprayed on the metallic substrate and melted at a temperature below the binder melting one. Thus produced coatings show higher adhesion to metal than reference ones (by 30-50%). For e.g. under a PVB-based coating, the steel substrate corrosion rate in a 0.1 n solution of NaCl reduces from 0.76 $g/(m^2h)$ for the reference and up to 0.29 $g/(m^2h)$ for the electret coatings.

The effect of polymers and metals electrochemical interaction on protective efficiency of polymer coatings has been studied elsewhere [12]. It has been shown earlier [11] that local electric fields emerging in polymers contacting short-circuited electrodes of unlike metals with a polymer insert in between exerts a considerable influence on the metal-polymer joint properties. Passage of current in the metal1-polymer-metal2 system leads to metal-polymer electret formation (see ch. 1.2.5) and provides for improving its adhesive strength 1.5-2 times. Optical and spectrometric investigations [11] proved the adhesive strength growth to result from contact reaction products diffusion into the polymer interlayer under the action of the field generated by the standard electrode potential difference of metallic facings. This means that the mechanism of adhesion rise is of electrochemical character.

To explain the mechanism of electrochemical interaction between polymers and metals a model of composite material is suggested which includes a thermoplastic polymer binder and fine-dispersed particles of various metals with different magnitude of standard electrochemical potentials [12]. Fuming oxides (FO) of non-ferrous metals being products of zinc and lead extraction, including zinc, lead, magnesium and copper oxides were used as a filler. In Fig. 4.9 characteristics of filled with FO thermoplast-based coatings are listed. The optimum filler content depends on the binder origin and constitutes 10-40 mass %.

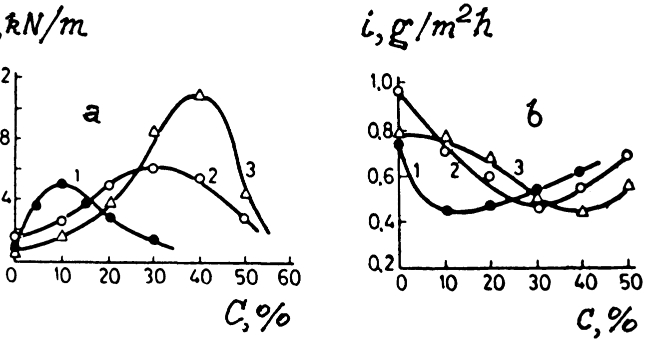

Fig. 4.9. Polymer coating strength of adhesive joint with Al substrate (a) and corrosion rate of steel samples under coating (b) as a function of FO content and binder type:
1 - PE, 2 - PVB, 3 - PPl.

Figure 4.10 illustrates the possible mechanism of imparting improved adhesion and protective ability to polymer composite coatings. In the process of thermal treatment the coating experiences a partial FO reduction to the metal. Lowered polymer film ohmic resistance and X-ray analysis results are the evidence to this (Fig. 4.11). They show that with increasing time of the coating thermal treatment the intensity of peaks governing oxide crystalline structure reduces, while the intensity of peaks corresponding to pure metal increases.

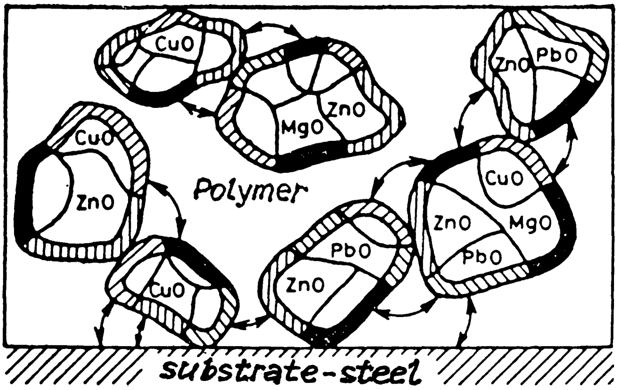

Fig. 4.10. Diagram of metal1-polymer-metal2 microcircuit functioning in a composite polymer coating.

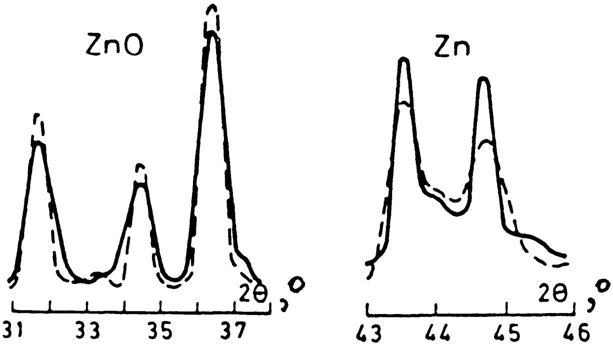

Fig. 4.11. X-ray spectra of a composite material (PE + 30% of FO) upon thermal treatment during 0.3 ks (dotted line) and 180 ks (full line). (CuK_α radiation, wavelength $\lambda = 1.542$ Å.)

As it is known, when the conducting filler content reaches some value in a composite material, the formation of conducting bridges is possible and the particles contact is not obligatory for the current to pass. Metal1-polymer-metal2 microcircuits are originated both between the particles in the bulk and between a separate particle and the coated metal substrate surface. So, during thermal treatment of a coating electrochemical interaction of components occurs in the composite leading to increasing adhesive strength and protecting capacity of the coatings.

4.2.2. Discrete coatings.

The effect of electrochemical processes on adhesive strength and porosity of coatings in metal-coating systems has been studied by way of example of discrete polymer coatings on metals. Discrete polymer coatings (DPC) are a combination of local sites of polymer material adhered to the article surface. DPC elements are characterized by a similar or close by configuration microrelief and regular disposition on the substrate surface. DPC are used as decorative, antifrictional, electroinsulating coatings or the base for engineering composite materials.

Paper [13] establishes a dependence of TSC in a discrete polymer layer between electrodes of unlike metals versus coating porosity and adhesion to metal. DPC were formed on Mg and Al substrates from epoxy powders of P-EP-177 and P-EP-91 grades on the base of 2.2'-bis(n-oxydiphenyl)propane with epichlorohydrin (relative molecular mass 1400-2500, epoxy group content 2.5-5%). Each coating site represents a spherical segment 0.8-1 mm high and about 1.5 mm in diameter. The coatings were brought into contact with replaceable electrodes (aluminum, copper, steel) and thermally treated. TSC was simultaneously recorded. Adhesive strength A was characterized by a mean shear force of 10 coating sites and was calculated using the formula:

$$A = \frac{P}{S(1-\eta)} \tag{4.2}$$

where P is shear force; S is the area covered by the coating sites; η is adhesive contact porosity determined by SEM after the coating peeling off from the substrate or the electrode.

It is seen from Fig. 4.12 that with increased standard electrode potential difference, the maximum TSC values grow too (curve 1). Porosity in the coating contact with the substrate (aluminium) and electrode (curves 4 and 2) also increases, while the coating adhesion to the substrate reduces substantially. From the one hand, the data prove the existing idea on

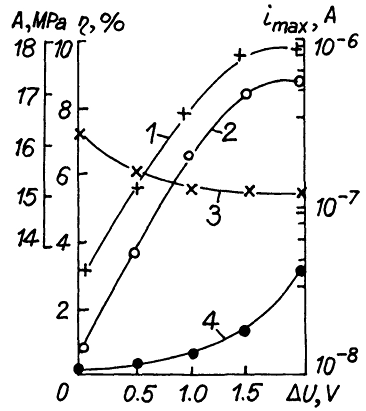

Fig. 4.12. The dependence of adhesive strength A (3), maximum TSC i_{max} (1), porosity η in contact with substrate (4) and electrode (2) on electrode potential difference ΔU of the substrate and electrode for P-EP-91.

porosity-adhesion dependence, i.e. when polymer powder coatings are formed, their adhesive strength reduces with the widening pore volume near the metal surface. From the other hand, thermoplast polarization between two unlike metals results in enhanced adhesion of the polymer-metal joints. Two competing processes run during polarization, i.e. the formation of space charge in the coating layers contacting metal and accumulation of low-molecular products of electrochemical reactions in these zones. Under certain conditions the products favor pores formation. Just this phenomenon is observed in coatings from epoxy powders. Growth of porosity in the zone of electrode contact can be promoted by emanation of volatiles (epilchlorohydrin, toluol, phenol, etc) due to reduced recombination ability of ions generated in the polymer bulk during thermal treatment in contact with metals and because of increased intensity of reduction reactions on the electrode.

4.2.3. Electric technologies for coating formation.

The described methods aimed at increasing adhesive strength and protective capacity of coatings are based on electric polarization of materials during solidification of the polymer layer. This is the last stage of coating formation technology which is preceded by the stage of powder layer application on the coated article. All without exception methods of coating application from powder materials are characterized by intensive electrization of particles. Electrization exerts a considerable effect on formation regimes, the formed coating structure and properties.

Powder technology of coating application is widely applicable in engineering due to its efficiency and ecological safety as it does not use costly and highly toxic solvents. This is still more important as the ecological questions are in the center of public consideration these days. Most economical and productive are electrostatic methods of coating application, i.e., the methods where electrization displaces powder particles in electric field to the charged (or grounded) article and deposits them on the surface.

Electrostatic techniques utilize traditional methods of forming a gas-powder suspension and its spraying in combination with different processes of powder electrization. There are two main types of charging particles in polymer powder materials:

- contact electrization, where powder particles acquire a charge upon contacting the charged electrode, or at friction (triboelectrization);
- ion absorption electrization, i.e., under the action of a strong heterogeneous electrostatic field when air ionizes and transfers charge to the polymer particles.

The force of electrostatic attraction keeping the polymer particles on the substrate is determined by several factors. They are the particle charge value and sign, the substrate surface properties, the deposited layer thickness and electrostatic field intensity in the polymer particles-substrate contact. Most important factor is, evidently, the particle charge obtained through electrization.

At present most researchers treat electrization from the viewpoint of the double electric layer theory put forward by Helmholtz in 1879 [14]. A convincing proof to the theory are data cited in Loeb's monograph [15], which is devoted to the process of charge separation in the double electric field leading to electrostatic electrization. When spraying different powders with less than 30 μm particles Loeb observed a practically symmetric (bipolar) charging. For coating application powders having larger particles are commonly used. The present authors have obtained data evidencing that when polymer powders with 50-300 μm particle size are sprayed, an asymmetrical unipolar charging proceeds and charging asymmetry grows with increasing particle size.

The principle of particle electrization by friction against the transporting duct walls of a sprayer is attractive due to simplicity and minimum unproductive losses of powders. Electrostatic methods are subdivided into jet and chamber ones by the type of apparatus used to deposit the charged powder on articles. Also systems are known based on a combination of principles.

A set of devices has been developed recently for polymer powder coating application (Fig. 4.13). Their unit of tribocharge generation is made as a vortex tube. Their operation is based on two effects: "cold" and "hot" air flow separation in a scroll (vortex effect) and triboelectrization of polymer particles in the helical gas flow.

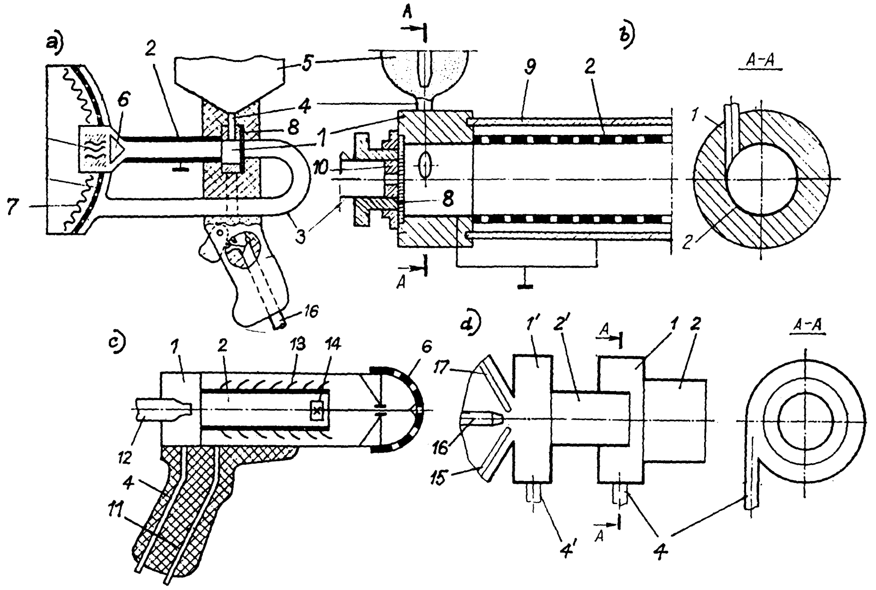

Fig. 4.13. A device for coating deposition: a) spray-gun with a unit for coating melting [16]; b) for coating spraying on inner surface of pipes [17]; c) for multicomponent coatings [18]; d) for metal-polymer coatings [19]: 1, 1' - vortex tube scroll; 2, 2' - "hot" socket; 3 - "cold" socket; 4, 4', 11, 12, 16 - ducts; 5 - powder hopper; 6 - sprayer nozzle; 7 - heater; 8 - filtrating insert; 9 - coated pipe; 10 - diaphragm; 13 - electrodes; 14 - blade wheel; 15, 17 - wires.

The gas-powder mixture is fed with a compressed gas flow through ducts 4 into scroll 1 of the vortex tube where a strong circular flow is formed. Cooled by the vortex effect the near-axis air layers are removed through tube 3, while the heated peripheral layers of the powder mixture flow off tube 2. An intense powder triboelectrization and heating proceeds when it runs down tube 2. By nozzle 6 the powder is directed to the covered article (Fig. 4.13 a, c) and melted by heater 7. The removed by tube 3 cooled flow can be used to cool heater 7. Filtration insert 8 hampers powder particles carrying away by the cold flow.

A modification of the device for *applying coatings on the inner surface of pipes* (Fig. 4.13 b) has "hot" tube 2 perforated and concentrically placed in the coated pipe 9. Under the action of centrifugal and electrostatic forces charged powder particles pass through holes and deposit on tube 9 inner surface. By varying diaphragm 10 flow section the particle charging regimes, rate of their deposition and the deposited layer thickness can be regulated.

To deposit *multicomponent coatings* the device (Fig. 4.13 c) can contain additional ducts 11, 12 to supply powder mixture components. Powder fed through duct 4 and scroll 1 moves spirally in "hot" tube 2. The powder and tube 2 acquire tribocharges of opposite signs. Induced on electrodes 13 charge is transferred to supplied through duct 11 powder. Socket 12 becomes rarefied and the third component is thus sucked to the scroll cavity. The components are mixed due to electrostatic forces and rotation of pulverizer 6 connected to blade wheel 14.

A coaxial connection of two vortex tubes together with metallic pulverizer is used in the device for applying *metal-polymer coatings* (Fig. 4.13 d).

An electric arc is generated between two wires 15 and 17 and the melted metal is sprayed by compressed air supplied from nozzle duct 16. Gas flow from socket 4' adds helical motion to metallized particles moving along socket 2'. In vortex tube 1 the flow interacts with the gas-powder mixture fed from the socket through the second vortex tube and moving along its outlet socket 2 also helically. When the two flows of different velocities and spiral parameters superimpose, an intense mixing of components takes place. Mixing parameters, mixture velocity and pressure in the socket 2 outlet can be varied in a wide range by regulating the first and second vortex tubes output.

The fact that the powder dielectric particles obtain tribocharge during their motion in the helical gas flow is the peculiarity of the mentioned devices. This allows for controlling particles velocity, the processes of their interaction with frictionally electrized walls of the device and powder components mixing by varying spiral parameters using heterogeneous electrostatic field generated by triboelectrization.

4.3. POLYMER FILMS.

Films are materials which present a continuous thin layer of a substance. They are characterized by a uniform surface (as compared to dispersed systems) and have a greater than conventional solids surface area to volume ratio. Polymer film thickness does not exceed 0.25 mm. Analogous but thicker materials are commonly called sheets. Technological simplicity of film formation is a specific property of polymers. It is a result of a considerable length of macromolecules and permolecular structure orientation during polymer samples drawing. The latter suggests the formation of electret charge in the polymer films following the mechanism of dipolar polarization at drawing.

Performances of anticorrosion polymer films are diverse. To realize them, different polymer, mineral and metal components (fillers, reinforcement, coating, foil, etc) serving as barrier and protective elements are mixed in the films, as well as corrosion inhibitors and other substances which thermodynamic compatibility can be different. The components bonding varies from stable and strong (between the film layers, polymer binders and fillers or reinforcement) to breaking under operation conditions (bonds between corrosion inhibitor and its layer-carrier).

Such hard to attain and partly contradicting requirements cause the necessity of different technological methods to combine the components in the film. Problems arising at formation of anticorrosion films can be solved using electric polarization. It provides for adhesion between layers and reduction of the layer permittivity. The method also improves the quality of polygraphic printing on films, the film saturation with corrosion inhibitors, reduces the protected elements wetting by using films for hydroinsulation and etc. Some aspects of the problems solution are considered below.

Sorption and permittivity are important properties of anticorrosion polymer films which are not an absolutely tight barrier against water, oxygen, electrolytes and other corrosive media. Corrosion rate of metal samples is defined primarily by diffusion characteristics of packing.

Sorption characteristics of polymer films were examined by thermostating them in organic solvent vapors, for e.g., that of diethylene glycol (DEG) and coal benzene [7]. To create the electret charge the film was thermally treated during 3 h under T = 393 K in contact with a shirt-circuited facing of aluminium and copper foils. TSD charge density was 10^{-5}- 10^{-6} C/cm^2. The experimental results are given in Fig. 4.14. It is seen that DEG sorption by electret films is much less than that by the reference ones. The difference grows with temperature rise providing acceleration of conformation transformations of macromolecules (T = 232 K corresponding to PVB glass-transition temperature). Similar results were obtained for benzene (Table 4.5).

Table 4.5. Sorption of benzene vapors (m, 10^{-5} kg) by PVB films at T = 50 °C.

Time of exposition, min	m, for samples	
	reference	electret
75	0.55	0
107	1.10	0
122	1.30	0.01
180	1.50	0.05
232	1.66	0.14
258	1.73	0.24

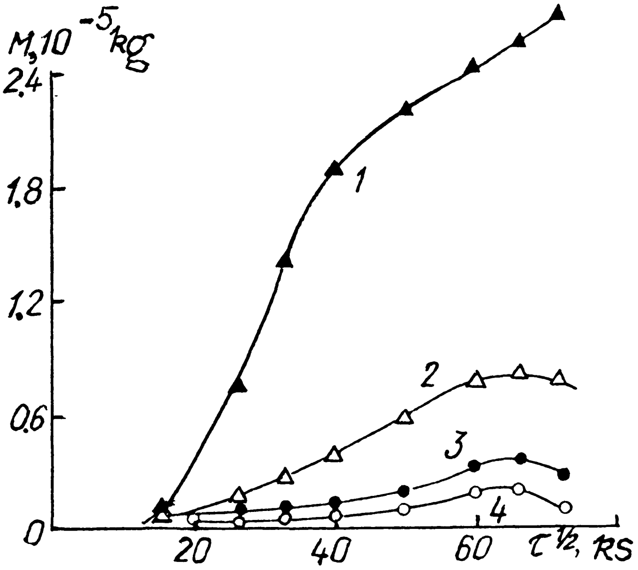

Fig. 4.14. Sorption of DEG vapors by nonpolarized (1, 3) and electret (2, 4) PVB films. Temperature: K: 1, 2 - 323; 3, 4 - 303.

The mechanism of DEG sorption by electret films can be presented as follows. DEG polar molecules are attracted in the film electrostatic field to its surface and form a layer of oriented dipoles hampering further sorption. Upon the layer formation an equilibrium concentration of DEG is set.

The effect of film electric polarization on nonpolar benzene sorption (benzene dipolar moment equals zero) is conditioned by the following factors. Firstly, an ordered distribution of permolecular structures evidencing to their orientation has been found in electret films at microscopic analysis in transmitted polarized light. Secondly, electron microscopy helped to visualize that metal ions injected into the polymer matrix during film polarizing fill vacancies in the matrix noncrystalline areas where sorption mainly proceeds. And finally, nonpolar molecules of benzene can acquire an induced moment in the electret field and interact with the film following similar with DEG mechanism. The rate of benzene sorption is higher than DEG has, since benzene is a stronger solvent of PVB.

As a result of solvent sorption the reference (nonelectret) films acquire a specific relief characteristic of plasticized polymer articles. Electret films do not have such a texture.

To approximate the dependencies in Fig. 4.14 the equation was used

$$M_t/M_\infty = 1 - \frac{8}{\pi^2}\exp(D\pi^2 t/h^2) \qquad (4.3)$$

where M_t and M_∞ are mass of liquids sorbed by the film during time t and $t \to \infty$; D is diffusion coefficient, h - film thickness.

The calculated values of D (m^2/s) for nonpolarized PVB film is $2.2 \cdot 10^{-16}$ and for the reference - $3.2 \cdot 10^{-14}$. PA films thermostated in water has $D = 1.7 \cdot 10^{-14}$ for the electret and $4.8 \cdot 10^{-12}$ for the reference ones.

So, electric polarization reduces considerably sorption and diffusion of liquid and gaseous media in polymer films and can be used to improve anticorrosion properties at film formation.

Methods of anticorrosion films polarization most often utilize production techniques of thermoelectrets and corona-electrets. They are realized, as a rule, in the process of film formation.

In the first case the film with a temperature close to the polymer softening one is endured and cooled in electric field. Its intensity is $E < E_{br}$, where E_{br} is field intensity causing electric breakdown of the film. The field is usually applied when the film passes the interelectrode clearance. One of the electrodes is stationary and the other is made as a rotating roller. Electric machining intensity is regulated by varying the electrode voltage, clearance between them and velocity of the film pulling through the clearance.

When combined films are produced without gluing components, the layers are corona discharged under room temperature and pulled between two cylindrical electrodes. Then high voltage from tens to thousands kV and up to hundreds of kHz frequency is applied. Electric machining is accompanied by ozone formation which strongly oxidizes the film surface. The efficiency of treatment depends on composition of gaseous medium where discharge occurs. Thus, polypropylene film adhesion to the polyurethane layer rises 100 times after treatment in gaseous medium containing 5% of carbon oxide.

Other methods of polymer electret films production are: film formation from solution or a plasticized compound and its further curing by solvent evaporation in the constant electric field, ionizing irradiation in magnetic field, etc.

Space charge in polymer films can be generated without electric devices. Polymer film polarization between short-circuited electrodes of unlike metals favors combination of the film formation and polarized charge creation in it in one technological cycle. The method consists in the following [20]. The extruded polymer film is drawn in the viscous-flow state and is brought into contact with the forming parts. The latters are made of unlike metals and short-circuited. Upon cooling to a highly elastic state the film is disengaged.

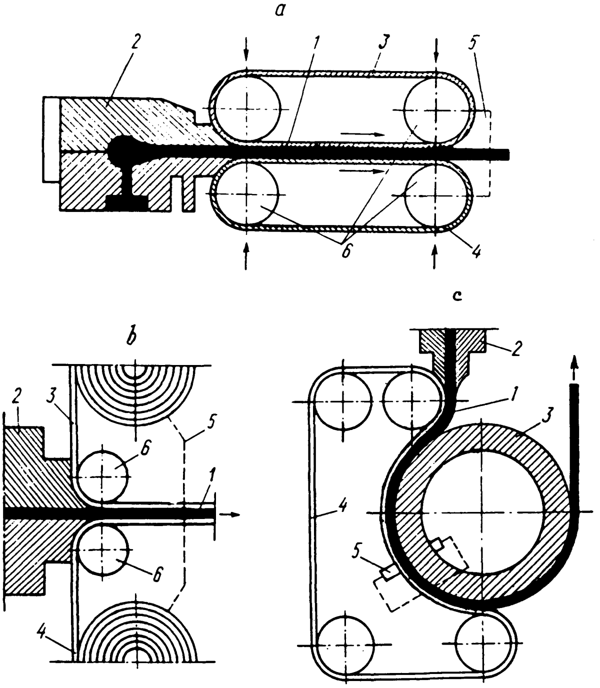

Fig. 4.15. Technological process flow chart for producing electret films and sheets.

Examples of the method are shown in Fig. 4.15. Polymer melt 1 flowing from extruder head 2 contacts two continuous bands 3 and 4 from unlike metals (a). The bands are closed to bridge 5 and are driven from rollers 6 which rotation velocity governs the film extension and cooling rate. Polymer melt can be extruded into the clearance between two foils rolled from the rolls 3 and 4 (b), or between a continuous band 4 and roller 3 covered by a metallic coating (c). The method can be applied to produce multilayered metal-polymer packaging films.

The procedure of film polarization using charged fillers is described in work [21]. Introduction of corona discharged PVB oxide powders into the films causes a maximum on the TSD current temperature dependence of the filled films (Fig. 4.16).

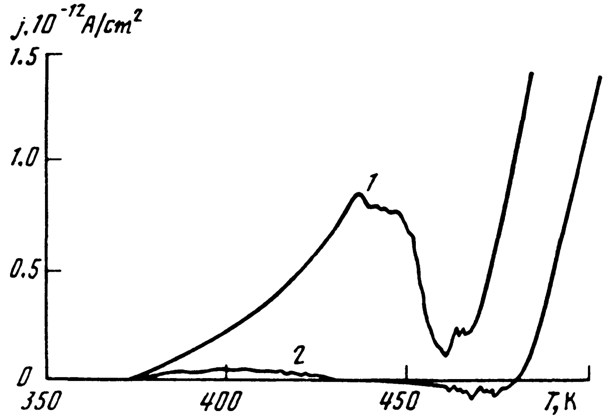

Fig. 4.16. TSD currents in PVB, filled with SiO_2 (up to 20 mass %) depending on temperature and filler charge: 1 - corona charged, 2 - initial.

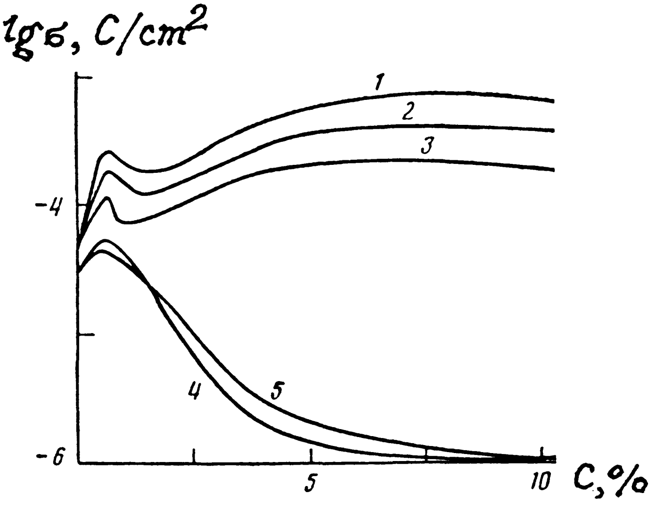

Fig. 4.17. TSD charge density in PVB samples depending on filler content: 1 - carbon cloth; 2, 3 - Cu and Al powders, 4 - basalt fiber, 5 - glass fiber.

Filling effects electric polarization of polymer films. PVB films were thermally treated under 393 K in contact with short-circuited copper and aluminum electrodes. Plots of such films TSD charge versus filling degree fall into two groups corresponding to conducting and dielectric fillers (Fig. 4.17). The conducting ones (curves 1-3) are characterized by a high charge density (up to 10^{-3} C/cm^2). Probably, the conducting filler particles serve during polarization as additional electrodes. Correspondingly, the amount of charge carriers transmitted from electrodes to the polymer matrix rises. The second group (4, 5) displays charge decrease with increasing dielectric filler content. The latters participate in the film electric conductivity at polarization. That's why with the rising filler content the polarizing current reduces and, consequently, TSD charge reduces too.

All the dependencies in Fig. 4.17 have a maximum corresponding to about 1 mass% of filler concentration. According to physical chemistry notions, small quantities of impurities evoke the formation of perfected permolecular structures in polymer binders. This, apparently, effects positively charge formation in electrets. Further filling increment results in disordering of permolecular structures accompanied with TSD charge reduction.

After the maximum at C = 1% further increase in conducting filler content (1-3) is accompanied as before by the charge growth. Then the charge decreases because of reduced quantity of the polarized polymer. The described process is most prominent when films are filled with dielectrics (4, 5).

Among polymer anticorrosion films most efficient are those containing corrosion inhibitors. They are produced by saturating the films during their formation with inhibitors in vapor [22] or liquid [23] phases. Electret state of the films effects much kinetic dependencies of inhibitor sorption by the polymer. The effect is intensified if corrosion inhibitor dispersions are additionally charged in the outer electric field.

Electric polarization effect on mechanical properties of polymer films consists in the following. Rearrangement of polymer permolecular structure which accompanies polarization leads, as a rule, to strength improvement and impairment of the film deformation characteristics. Thus, thermally electrized polycarbonate and PETF films show rise in breaking stress at tension by 15-60% and several times in time of mechanical stress relaxation. Analogous results were obtained for PA and polytrifluorochloroethylene-based films.

Exposure to electric fields under elevated temperatures can cause electric aging of polymers. It involves reduction of electric strength and volume electric resistance. The reason is destruction of macromolecules provoked or accelerated by electric field.

Treatment of polymer films in magnetic fields is frequently accompanied by strengthening. For example, polystyrene film breaking stress at tension increased from 6.4 to 14.2 MPa when heated in a constant magnetic field (H = 640 kA/m) to viscous-flow state and cooled to room temperature. Even more efficient is polymer film treatment in heterogeneous magnetic fields. Strengthening was found to rise with increasing crystalline phase in the polymer material.

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CHAPTER 5

ELECTRETS IN FRICTION JOINTS

Friction is usually accompanied by processes of electric origin, i.e. accumulation of static electricity in rubbing materials, electrode processes, current passage through the friction zone, etc. Electric charge storage results in friction materials polarization. Some processes assist friction and wear reduction in movable joints, others increase friction force and impair wear resistance.

The processes can, apparently, be controlled by using electret elements in friction joints. Attractive, from tribological viewpoint, is the fact that electret formation involves rearrangement of physico-chemical structure in materials. This helps to regulate their tribological characteristics by polarization methods. Polarizing charge effects wetting and spreading of liquids over the electret surface. This phenomenon allows for lubricant retaining in the friction zone, reduction of liquid capillary permeation into clearances between moving joints, etc. However, above methods of rising friction joint efficiency are rarely used in engineering.

The present chapter attempts to scientifically substantiate electret application in friction joints.

5.1. PHYSICO-CHEMICAL PROCESSES AT FRICTION.

When friction joint contains a metallic rubbing part and a conducting liquid lubricant, it can be treated as electrochemical system with the friction part serving as electrode and the lubricant layer as electrolyte. Such a system experiences electrode processes characterized by charge transfer through the electrode-electrolyte interface.

Below the main notions used in this chapter are defined.

Electrode processes involve the following consequently proceeding stages: reacting particles are brought on the electrode surface, enter the double electric layer; charge carriers pass through the interface (discharge-ionization) and reaction products are removed from the electrode. Reagent supply and reaction products removal are defined as mass transfer stages. The rate of electrode process is conditioned by the most slow, the so-called limiting stage.

This exerts a significant effect on each stage. Mass transfer in static conditions follows diffusion and convection mechanisms. They are supplemented during friction, or sometimes suppressed by frictional transfer.

Friction often violates continuity of protecting passivating layers on the electrode and causes freshly formed surface sites where discharge-ionization is by three orders higher than in static conditions. Electrochemical system initiates tribochemical reactions and new phases are formed due to, for e.g., electrode cold-working, mechanical destruction of the polymer counterbody or tribological polymerization of lubricants. These phenomena change kinetic parameters of electrode reactions and become most prominent at fretting-corrosion, i.e. corrosion damage of contacting metal parts executing minor recurrent displacements relative one another.

So, structure and properties of the electrode surface, electrolyte and double electric layer vary with time. As far as such electrochemical system is noneqilibrium, current appears in the circuit between electrode and electrolyte, and electrode potential shifts from its stationary state to a value ΔU. Current density i is the electrode process rate in the friction joint and dependence $\Delta U = f(i)$ is the tribosystem polarizing index. Bearing in mind regularities subduing polarizing index, one can regulate electrode processes and tribosystem wear.

Electrochemical processes in metal-polymer friction pairs occur even at dry friction. Friction causes frictional heating in polymers and mechanical destruction of macromolecules leading to charge carrier formation (organic ion-radicals) participating in electrode processes. That's why friction of metal-polymer pairs is always accompanied by electrochemical reactions [1].

Factors influencing electrode process kinetics in dielectric-metal pairs are shown in Fig. 5.1.

5.1.1. Liquid Friction.

Liquid friction can take place in both conducting and dielectric lubricating media.

Conducting liquid lubricants are electrolyte solutions (coolants, sealing liquids in movable seals of chemical equipment, lubricants for electric contacts, etc.), some brands of petroleum oils, metal or polymer melts. Friction in this case is accompanied by the following physico-chemical processes in the lubricating layer.

Frictional transfer in electrolyte results in increased area of electrode wetting by electrolyte as compared to static conditions. Shaft surface is, as a rule, fully wetted by electrolyte to a plain bearing length. This increases leakage area, as well as volume and output of electrode reactions. Electrolyte mixing intensifies mass exchange in the lubricant layer causing acceleration of discharge-ionizing stage and increasing yield of electrode process products.

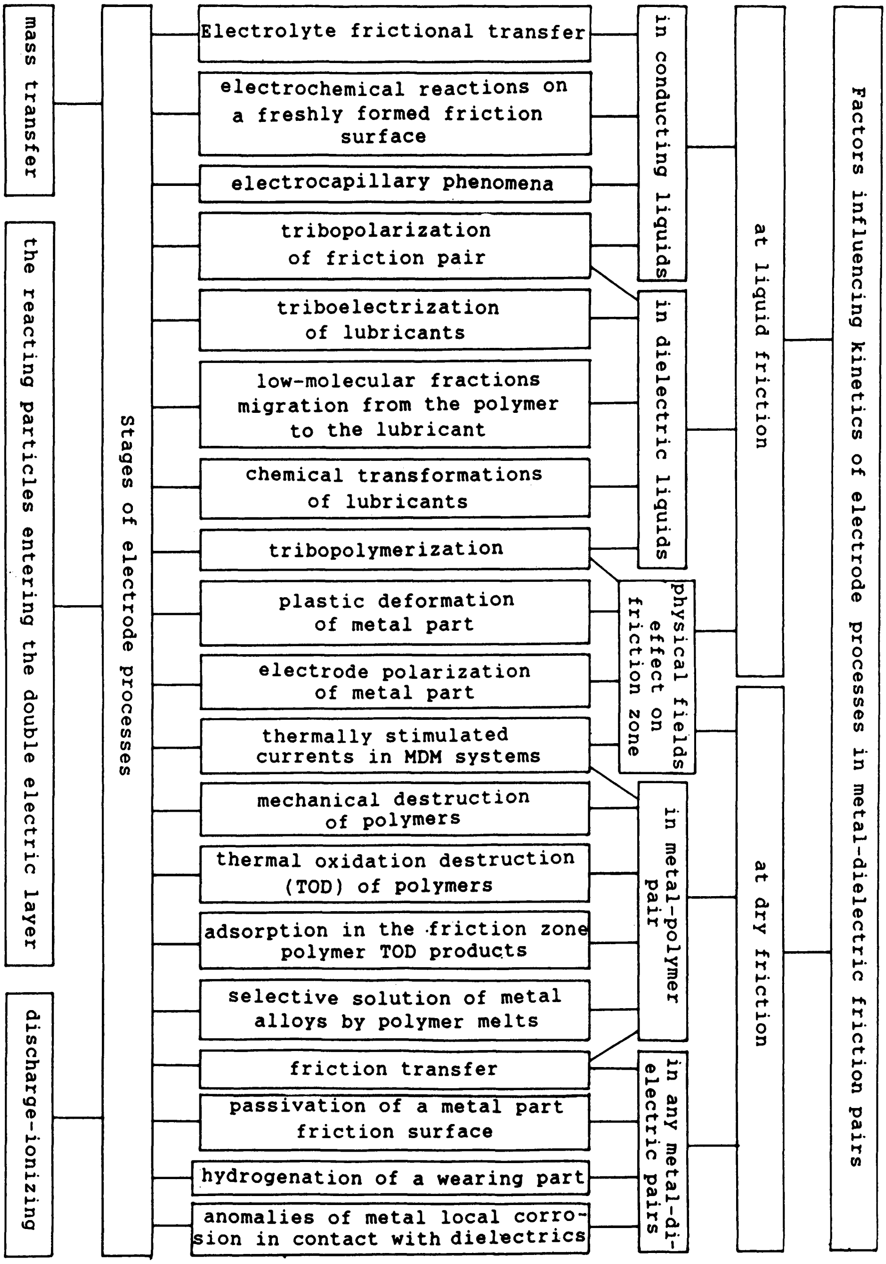

Fig. 5.1. Physico-chemical processes taking place at friction.

Freshly formed sites on the metal electrode friction surface are found in the points of electrode actual contacts with the counterbody. This is because of disturbed continuity of the electrode passivating layers due to elastic deformation and plastic displacement of metal. On the freshly formed (juvenile) surface the metal dissolves by 7-8 orders faster than on the electrode covered with an intact passivating film. When the film is damaged by a point indenter, a momentary current flash-up occurs which attenuates with time 10^{-4} to 1 s according to exponential law. So, the velocity of electrode anodic dissolution during friction can surpass in intensity its wearing due to fatigue failure at deformation.

Electrocapillary phenomena consist in variation of surface tension at the interface due to occurring there leap of electric potential. These phenomena constitute the base of a number of methods for controlling spread of liquid metals used as lubricants.

There exists a problem of sealing input joints of rotating shafts introduced into vessels with electrolyte. It is often solved by filling the shaft-bearing clearances with liquid metal. Using electric field, the potential difference can be changed at the liquid metal-electrolyte interface. This leads to variation of surface tension at the interface which reaches (10-100) mJ/m^2 and the spreading motive force [2]. Thus, liquid metal spreading over the shaft-bearing friction surface can be regulated, as well as the zone of metal part wetting by electrolyte which area depends on quantitative indices of electrode processes in the given tribosystem.

Tribopolarization of a friction pair parts effects much mass transfer kinetics in the lubricating layer and the pair tribological properties.

Triboelectricity, i.e. generation of electric charges at friction, takes place under all types of friction and any combinations of conjugated elements in both dry friction or lubricated with oils, water emulsions and other liquid lubricants. Triboelectricity in solids is attributed to charge carrier migration from one body to another. Triboelectricity in metals and semiconductors is generated by electron migration from a substance of a lower work function F to one having higher F in the metal-dielectric friction pairs, i.e. electrons transfer from metal to dielectric, while at two dielectrics friction - by electron and ion diffusion. Different frictional heating of two bodies might cause transfer of carriers from local heterogeneities of a more heated surface ("real" triboelectricity). Mechanical removal of debris from the friction surface of pyroelectrics or piezoelectrics can also evoke triboelectricity.

Charge carrier migration at friction provides for triboelectrization which, under certain heat conditions, transforms dielectric into electret. Electret state of a dielectric counterbody is produced in the process of the actual contact spots formation and failure at dielectric-metal friction. This assists charge carriers injection from the metal and their localization in entrapping centers on the counterbody friction surface. Triboelectrization current effects mass transfer when electrode processes run in the friction pair. Electret field determines to a great degree the kinetics of reacting particles entry in the double electric layer and discharge-ionization intensity. The electret state increases dielectric activity in tribo-chemical reactions.

Tribopolarization of the friction pair parts proceeds in both conducting and dielectric lubricants.

Dielectric liquid lubricants include petroleum oils and synthetic products (chlorinated and fluorinated hydrocarbons, silicon or organofluoric liquids, aromatic compounds, esters, polyisobutylenes). The following physico-chemical processes take place when the friction joint is lubricated with a dielectric liquid.

Triboelectrization of liquid lubricants arises from formation and failure of the double electric layer at the liquid-friction surface interface. In metal friction pairs triboelectricity arises from electrolytic separation of charges at the metal-liquid interface. Friction-induced electrization in both liquid and solid dielectrics is the result of double electric layers formed at two dielectrics interface of different dielectric permittivity ε. A substance with higher ε obtains a positive charge and that with lower - a negative (Kowen's law). Failure of double electric layers at the liquid-gas interface generates triboelectricity when liquids are sprayed. This is the base of some widely spread in triboengineering methods of lubricating.

The presence of uncompensated electric charge in the lubricant exerts a substantial effect on the rate of all stages of electrode processes in the friction joint, i.e. on friction surface wetting with liquid, supply of reacting particles and removal of reaction products, particles transfer through the interface, etc. Depending on electric potential distribution in friction joint units, lubricant electrization can speed up or hamper electrochemical processes occurring at friction.

Migration of low-molecular fractions from the frictional polymer material to the lubricating layer changes the lubricant corrosion activity.

First investigations of corrosion activity of substances separated from polymers were undertaken in 1972 [3]. It has been established recently, that low-molecular components migration is characteristic of all plastics (Table 5.1). It proceeds for a prolonged time but in low amounts. The main mass of separated substances include nonpolymerized monomers, initiators, catalysts, polymerization and polycondensation inhibitors, rubber accelerators, stabilizers, antistatics, plasticizers, fillers, solvents, pigments, plastics aging agents. Work [4] analyzes the existing methods of studying corrosion induced by polymer destruction products. This is just the reason of corrosion-mechanical character of metal-polymer pair wearing [1].

Table 5.1. Chemical substances migrating from polymers to liquids.

Polymer	Separated substances
High-density polyethylene	Aluminum, chromium, titanium salts; formaldehyde, methanol, chlorides, colors.
Polypropylene	Formaldehyde, chlorides, methanol, topanol, benzene, colors.
Polyvinyl chloride	Lead, zinc, cadmium, barium salts; tinorganic compounds, chlorides, vinyl chloride, phthalates, phosphates and other plasticizers, colors, blowing agent.
Polystyrene & styrene copolymers	Styrene, α -methylstyrene, acrylonitrile, methyl methacrylate, plasticizers, colors, ethylbenzene, cumene.
Polyamide	Caprolactam and its oligomers, amines, colors.
Fluoroplast	Fluor-containing compounds
Polyvinyl acetate, polyvinyl acetals	Vinyl acetate, acetaldehyde, paraldehyde, formaldehyde, ethanolamine, phthalates, phosphates, chlorinated diphenyl.
Polyesters	Ethylene glycol, dimethyl terephthalate, methanol
Epoxy resins	Epichlorohydrin, diphenylolpropane, amines anhydrides of dicarboxylic acids, acetone, toluene, ethylene glycol, phthalates.
Phenoplasts	Phenol, formaldehyde, methanol.

Migration of polymer components is, however, insufficiently studied. This is because of traditional concepts which consider polymers to be chemically inert materials and due to methodological problems in migration experimentation since its mechanisms are very intricate.

Chemical transformations in liquid lubricants are induced by frictional heating and contact loading under catalytic action of metals in the friction zone. In such conditions in the air lubricant oils oxidize and products are formed of acidic type which corrode metal parts. A conventional method to suppress the phenomenon is antioxidant additives.

Recent decades show an extensive use of anticorrosion additives to lubricants. They chemically interact with metals and modify their friction surface. The additives contain chemically active groups involving atoms of chlorine, sulfur, fluorine and nitrogen. Their action mechanism consists of three stages: 1) additive adsorption (chemisorption) on the friction surface; 2) chemical transformations (decomposition) in the friction contact; 3) chemical interaction between active products of additive transformation and metal on the friction surface [5]. Some active additives interact with metal on the freshly formed surfaces even at 20-30 °C. Such modification of metal friction surface reduces friction coefficient and the pair inclination to jamming. Friction surface passivation influences much electrochemical kinetics in the friction zone.

Tribopolymerization is a tribochemical transformation of lubricants leading to polymer film formation on the friction surface. The films are, as a rule, assisting antiseizure, wear-proofness and resistance to friction. Tribologically polymerizing additives are intensely expended in the initial period of friction on the films covering the whole contact area excluding actual contact spots. Further on, the additive is spent on restoring the tribological polymer film on the friction surface local sites [6].

Tribopolymer films isolate friction surface from contact with electrolyte and reduce the electrode processes area.

Tribopolymerization is more intensive under electric field action when films grow following the mechanism of tribochemical and electrochemical polymerization.

Physical field effect on the friction zone is a strong factor of electrochemical kinetics found in friction pairs. Below, the main consequences of its effect are considered observed in both liquid and dry friction.

Plastic deformation of a metal part at contact loading beyond yield point (cold working) changes the stress state and structure of the surface layer participating in friction.

Cold working reduces plasticity and impact viscosity but increases proportionality limit, yield point, fatigue strength and hardness of the metal. Simultaneously, the metal resistance to deformation of the opposite sign reduces (Baushinger's effect)

The mechanism of cold working is determined by the presence of different strength structural constituents in engineering metals. Structural variations are caused by interaction between dislocations and the emergence of new sliding systems of constituents. When surface layer is cold worked, defects can be formed, i.e. pores, vacancies, submicrocracks, etc.

Electrode polarization of a frictional metal part occurs during outer electric field passage through it. This results in deviation of the part electrode potential from equilibrium. Electrode polarization of the friction pair depends on the friction part material, electrode process behavior on the friction surface, lubricant composition and temperature and the dependence is the stronger, the higher is the current density.

Thermally stimulated currents (TSC) in the metal-dielectric-metal systems (MDM) evoke spontaneous electrode polarization of the friction joint metal parts. The mechanism of current generation in such systems has been described in ch. 1.2. It is also, to some extent, typical of some other types of dielectrics.

5.1.2. Friction without lubrication.

Dry friction imposes a number of limitations on electrode processes in metal-dielectric friction pairs.

Metal-polymer friction pairs show a specific behavior as electrode systems, which origin is described in chapter 1. Electrode processes in metal-polymer friction pairs are effected by the following factors.

Mechanodestruction of polymers implies frictional failure of macromolecules under shear stress. Macromolecular fragments are active radicals able to chemically interact with the freshly formed sites on the friction surface. The interaction is accompanied by charge and mass transfer proceeding similar to classical electrode processes having stages of reacting particles (radicals) supply (mechanical) to the metallic electrode friction surface, electron and ion exchange between the metal and radicals on the electrode surface and mechanical removal of reaction products from the friction surface. Mechanodestrcution of polymers serves to intensify the moving joints run-in, finishing, polishing, grinding, treating with ultrasound erosion, etc.

Thermooxidative destruction (TOD) of polymers is macromolecules failure under a simultaneous action of heat and oxygen. Both factors acting in the friction pair lead to the polymer counterbody TOD. TOD arises from the radical-chain oxidation resulting in formation of low-molecular radicals. Their concentration growth increases TSC density in short-circuited M1-P-M2 systems as shown in ch. 1.2. Thus, polymer TOD contributes much into electrode processes in the metal-polymer friction pairs.

Adsorption of polymer thermooxidation products in the friction zone is accompanied by chemical reactions between low-molecular radicals and metal on the freshly formed sites of the electrode friction surface, i.e. it is similar to chemisorption mechanism. This process is accompanied at friction by radical recombination and formation of the so-called frictional polymer different from the initial one by its chemical structure. As a result, a new phase is formed on the metal electrode surface inhibiting electrode reactions. Chemisorption on the electrodes from metal alloys proceeds selectively depending on the radical affinity to the alloy components. A considerable amount of heat is liberated at chemisorption (about 10 kJ/mol) accelerating, in a number of cases, chemisorption and effecting all stages of electrode process.

Selective dissolution of metal alloy components by polymer melts found out in the seventies [7] means that when the polymer melt contacts metal alloy, the metal solution occurs. The rates of the alloy components dissolving are different and correspond to metal position in the series of catalytic activity as related to polymer oxidation. This phenomenon is utilized to enhance adhesive strength of polymer coatings and to surface modify metal parts. Variation of chemical composition and crystalline structure of the electrode surface layer wearing against a polymer counterbody also exerts an effect on electrode processes in the friction pair.

Metal-dielectric friction pairs suffer the action of described below specific factors.

Frictional transfer is metal or its components transfer from one frictional surface to another. Transfer films of a dielectric material in metal-dielectric friction pairs insulate electrode surface from charge carriers. Macrotransfer is observed in fatigue separation of dielectric particles and their sticking to the metal counterbody. A particular case of macrotransfer is galling which can result in the friction pair seizure. The processes of synthesis of compounds formed from dielectric debris dominate on the electrode friction surface at selective transfer. The mechanism of frictional transfer is of electric origin [8].

Adsorption or chemical passivation of a metal part surface by the dielectric counterbody debris retards electrode processes in the friction pair. Wear debris of solid dielectrics involves substances of any phase. They are, as a rule, of high surface activity and are adsorbed by the electrode friction surface. Debris chemisorption takes place predominantly on the freshly formed sites of the friction surface. Electrode adsorption or chemical passivation hinders its dissolution, oxidation and interaction with passivators. Most important is passivation of the friction surface under oxygen action released at dielectric wearing or adsorbed from environment.

Hydrogenation or hydrogen adsorption by the metal part at friction is because of tribochemical decomposition processes occurring in either frictional material or environment and due to diffusion concentration of hydrogen initially found in the metal near-friction surface. In metals with exothermal adsorption of hydrogen (titanium) it saturates the electrode cold areas. Hydrogen is adsorbed in metal structural defects and, acting as a surfactant, enters crystalline lattice, thus reducing the strength of metal bonds. So far, the electrode stationary potential varies at hydrogenation.

Numerous surface cracks might merge in the process of hydrogen wearing and instantaneously turn the part surface layer into powder [9].

Anomalies of metal local corrosion in contact with dielectrics are induced by the formed concentration elements [10]. Iron, low-alloyed steels and aluminum corrode unusually in contact with dielectrics. An etched scar appears on the metal-dielectric boundary along the dielectric perimeter. This phenomenon, called the linear-selective dissolution, occurs not only in electrolytes but in humid atmosphere as well. It is caused by unequal adsorption of ions facilitating metal ionizing on the open electrode areas and those in the clearance. Etched scars are found on the rotating in plain bearings steel shaft in places corresponding to the bearing end faces.

All the mentioned factors effect the kinetics of electrode processes in metal-dielectric friction pairs but can be regulated by using electrets. Below, examples are enumerated showing highly efficient design and technological solutions of electret application in metal-polymer friction joints, lubricants, ceramics-based tribological materials.

5.2. METAL-POLYMER FRICTION JOINTS.

A metal-polymer joint (MPJ) involves into mutual operation metal and polymer parts. MPJ serviceability is conditioned by its design, properties of materials it is made of and operation conditions, including temperature, pressure, velocity of its parts mutual displacement, action of media, physical fields, irradiation, etc. MPJ operation leads to change in material structure due to wear out reducing the joint efficiency and life (see Fig. 5.2, full arrows on the scheme).

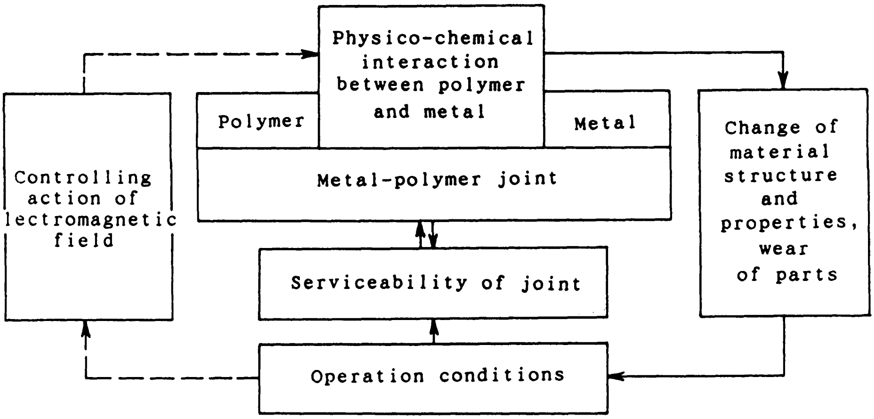

Fig. 5.2. The principle diagram for monitoring metal-polymer friction joint operation efficiency.

MPJ contains electrode metal elements and polymer materials displaying simultaneously electrolyte and dielectric properties able to polarize under electric field action.

The negative influence of operation conditions on MPJ performance can be reduced with the help of electric and magnetic fields. Electric polarization can modify polymer materials structure, improve strength, adhesion, resistance to corrosion, reduce permittivity [11]. In response to magnetic field the particles of magnetic solid filler or structural elements of the polymer begin to orient. This leads to structural modification and change in the polymer composite operation characteristics [12]. Application of electromagnetic field, as a whole, assists regulation of the contacting parts surface structure and, consequently, monitoring MPJ elements interaction.

The problem of enhancing MPJ serviceability can be efficiently solved only in case electromagnetic field is switched in response to varying conditions, i.e., when a closed feedback system which actuates electromagnetic field is used to control MPJ operation conditions. Figure 5.2 shows the system for the joint operation control using electromagnetic field (broken line). Such regulation can electrize or polarize the polymer, shift the metal electrode potential and the filler particles or the polymer structural elements orientation. This results in smearing, reduction of the sealing unit penetrability, etc. Feedback is initiated by operation conditions, i.e., their variation gives rise to regulation action of electromagnetic field.

5.2.1. Electrochemical processes at friction.

The processes specifying corrosive-mechanical character of metal wear take place when metals rub in pair with polymers. Corrosive-mechanical wearing is a complex process associated with mechanical action accompanied by electrochemical interaction between the material and environment. The role of corrosive and mechanical factors in corrosive-mechanical wear is estimated differently. Some authors consider the process to be purely corrosive, others treat it as a mechanical one and the rest think that both factors are equivalent. Such a discrepancy in opinions can be explained by the process intricacy and inexactness of the methods used.

In contrast to observed in electrochemistry processes, those at friction proceed in conditions of displacing and deforming discrete contacts of separate asperities. The presence of electrolyte as a gap film in the friction pair causes potential difference at the metal-solution interface. As a result, a short-circuited galvanic microcell is formed and a potentiality is created for redox reactions on its electrodes. Thus, a self-acting electrochemical mechanism is formed during friction pair operation, which controls its wear and depends on the galvanic cell electromotive force, potential difference at cell shorting, polarizing ability of electrochemical circuit, rate of electrochemical processes, etc.

Electrode potential magnitude measured in static conditions can differ much from that of metal at friction [13]. This is attributed, firstly, to mechanical removal of oxide films from the surface, secondly to formed at friction secondary structures shifting potential to positive or negative domain, and finally, to plastic deformation effecting potential shift and leading to formation of dislocated atoms in the metal crystalline lattice.

As far as the system electrode potential φ is the basic electric characteristic of the metal-electrolyte interface, it can exert a significant effect on metal friction and wear in electrolytes. Bowden and Yung [14] were the first to discover polarization effect on friction coefficient and metal surface damage which was further studied by many authors. The friction coefficient versus electrode potential dependence for platinum, nickel, cadmium, lead and copper is shown to have configuration of electrocapillary curve. Friction coefficient reduction with growing surface charge at polarization is due to increasing wedging action of the double electric layer between the rubbing surfaces.

It is known that the application of an electrochemical potential influences the tribological characteristics of lubricated contacts involving a metal counterface. Zhu et al. [15] pointed out the four main mechanisms proposed to explain this effect.

1. In 1875 Thomas Edison suggested that an electrochemical potential gave rise through electrolysis to the evolution of gases at the contact, friction being increased when oxygen was liberated and reduced when hydrogen was liberated [16].
2. The electrochemical potential affects the hardness of metal surfaces, and therefore their contact mechanics and wear resistance [17].
3. The electrochemical potential causes the formation of charged layers on the interacting surfaces. This can lead to low friction by Coulombic repulsion between charged layers on the counterfaces or as a result of the layers having a low shear strength [18].
4. The electrochemical potential influences the reduction and oxidation reactions which give rise to surface films, the characteristics of the surface are, therefore, modified by it [19, 20].

The first two of these mechanisms have been largely discounted because later research revealed that friction is modified even at electrochemical potentials at which no gas evolution occurs and there is no measurable change in the hardness of metals with electrochemical potential. It is now thought that electrode potential influences friction and wear through redox reactions at the surface and charge layer effects.

A great deal of work has been carried out on the effect of applied electrical potential on lubricatrd sliding metal-metal contacts, but relatively little research has been carried out on its effect on polymeric materials and dry contacts. Zaki and Dowson examined the effect of applied electrical potential on the friction of biomaterials with various liquids [21] and Savkoor and Ruyter examined its effect upon the friction of a carbon filled slider in both wet and dry conditions [22].

Two interrelated directions are discriminated when studying electrochemical processes at *metal friction*. The first is application of electrochemical parameters to obtain data on contact processes and the second - metal friction and wear monitoring by polarizing the frictional system [14, 23]. The first direction was extended in investigations where electrode potential was treated as an important frictional characteristic giving information on the state of the rubbing surface boundary layers. The second direction suggests interference into electrochemical process behavior on the frictional contact. It is rapidly developing at present, especially after discovery of selective transfer at metal friction [24] which nature is largely of electrochemical character.

Polymer materials add specialty to electrochemical processes proceeding in the friction zone of friction joints. Polymer components acquire surfactant properties when rubbing in metal-polymer pairs and alter considerably electrochemical behavior of metals.

In work [25] the present authors have investigated the relation between friction and kinetics of electrochemical processes taking place at metal-polymer pair polarization.

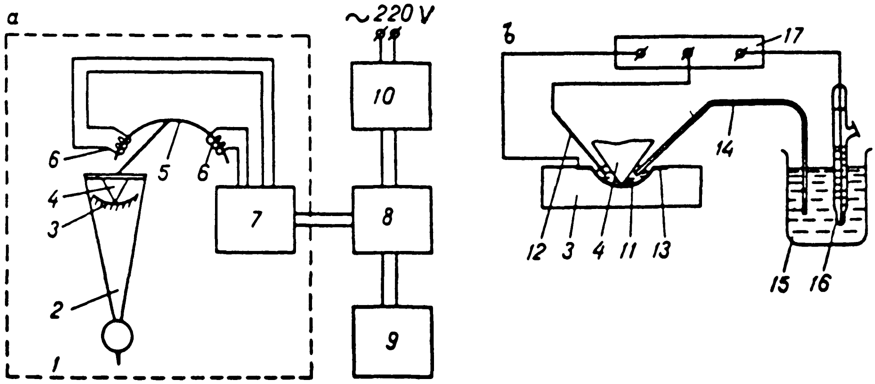

Fig. 5.3. A pendulum tribometer scheme (a) and an electrochemical cell to polarize friction zone (b).

A tribometer 1 used in the experiments (Fig. 5.3, a) consists of pendulum 2, support 3 and prism 4 where pendulum hangs. The pendulum mass was varied 50 through 250 g. The tribometer advantage is in the presence of only one friction pair tested. Support 3 is made as a vessel containing electrolyte with immersed friction surface of the prism. The pendulum has a constant initial amplitude. Oscillation attenuation is recorded as follows. A bow-shaped core 5 is alternately introduced into one or another coil of inductance gage 6 and a sinusoidal signal is generated at the pendulum outlet synchronous with pendulum oscillation. The signal is rectified using a rectifier block with generator 7, transmitted to amplifier 8 and recorded by potentiometer 9. The amplifying regime is maintained by stabilizer 10.

The friction pair was polarized following a three-electrode scheme (Fig. 5.3, b). Metal tray 13 mounted on dielectric support 3 served as a working electrode. Pendulum prism 4 rests on the bottom of the filled with electrolyte 11 tray. Platinum wire 12 was used as an auxiliary electrode. Chlorosilver error electrode 16 was placed into tank 15 communicating with the cell through electrolytic switch 14. Electrodes were closed on terminals 17 of potentiostat. Trays 13 were made of copper and aluminum; prisms 4 from PMMA, PTFE, PE and PA. Aqueous solutions of sodium chloride were used as electrolyte. Metallic trays were polarized in potentiostatic regimes under varying loading (pendulum mass), then polarizing current, amplitude and time of pendulum oscillations were recorded. After each experiment the tray bearing surface was cleaned and degreased.

The experimental loading was low so, that the prism-tray contact area can be considered constant. Under the given loading range the transition from dry friction to that in electrolyte was not always accompanied by increase in time of pendulum oscillation (Table 5.2). The growing resistance to prism motion at its sinking into electrolyte was, in a number of cases, a stronger factor than lubrication of the friction zone with electrolyte.

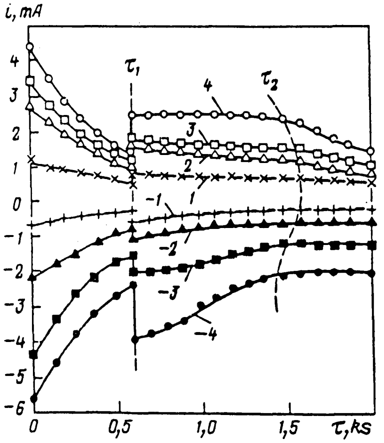

Fig. 5.4. Kinetics of polarization current variation for PA-steel friction pair. Numbers on the curves correspond to polarization voltage in volts. NaCl (10^{-4} mol/l) solution; load 0.3 MPa; τ_1 starting moment, τ_2 - moment of pendulum stop.

Figure 5.4 shows characteristic graphs of polarizing current variation at pendulum start and stop. Before start, the pendulum metal support was polarized. The given voltage was kept for 10 min. till the stable value of polarizing current was reached. When the pendulum was driven, the polarizing current leap was observed. It occurred due to discontinuity formed in the film of electrochemical reaction products on the tray surface during pendulum motion. The leap value reduced in the series Cu-Fe-Al, all other things being equal. This corresponds to mentioned metals position in the series of standard electrochemical potentials (see Table 4.1).

Table 5.2. Time of pendulum oscillation (ks) versus friction pair material, load and friction conditions.

Friction conditions	Load, MPa, on supports made of:			
	Aluminum 0.1 0.3 0.5	Steel 0.1 0.3 0.5	Copper 0.1 0.3 0.5	Prism material
Dry friction	0.84 1.80 2.10	0.90 1.56 1.68	0.90 1.86 1.68	PA
In solution without polarization	0.78 1.56 2.04	0.78 1.50 1.74	0.84 1.56 1.92	
Polarization potential, V				
		0.96 1.50 1.50	0.96 1.68 1.50	
	0.66 1.44 1.74	1.84 1.32 1.38	1.80 1.50 1.56	
	0.72 1.50 1.80	0.96 1.50 1.62	0.92 1.68 1.20	
	0.60 1.32 1.62			
Dry friction	1.02 2.04 1.98	1.05 1.26 2.04	1.08 1.68 2.82	PE
In solution without polarization	0.90 1.80 1.56	1.02 1.26 2.34	1.02 1.32 2.82	
Polarization Potential, V				

	0.78 1.68 1.50 0.78 1.68 1.80 0.66 1.68 1.44	0.78 1.44 2.22 0.96 1.68 2.34 0.66 1.62 2.16	0.84 1.80 2.10 0.66 1.26 2.34 0.66 1.26 2.52	
Dry friction In solution without polarization Polaization potential, V	0.93 1.74 1.62 0.93 1.74 1.50 0.78 1.62 1.44 0.72 1.44 1.20 0.66 1.32 1.14	0.72 1.50 1.32 0.66 1.38 1.38 0.60 1.08 1.32 0.62 1.32 1.56 0.60 1.44 1.14	0.84 1.56 1.68 0.90 1.80 1.92 0.90 1.68 2.10 0.78 1.32 1.98 0.78 1.68 1.86	PTFE

It is well known, that electrode potential of a frictional system effects adsorption, diffusion, oxidation and other processes contributing much into friction and wear of metals in conducting media. The potential optimum values depend intricately on the metal origin, composition of environment and loading parameters. Raise of loading within a given loading range under a constant polarizing voltage differently influences friction of a metal-polymer pair. Sometimes, increase in pendulum mass resulted in friction reduction (PE-Cu, PTFE-Cu, PA-Al, PE-steel pairs). In other cases it caused stabilization (anodic polarization of PA-steel pair) and some gain in friction (cathodic polarization of PTFE-steel, PE-Al, PTFE-Al and PA-Cu pairs). Further increase in loading up to 4 MPa leads, in all cases, to reduction of pendulum oscillation time to values below initial.

Within the investigated range of potentials, aluminum polarization in a neutral solution always leads to friction increase. Anodic polarization of copper and cathodic polarization of steel favors friction pair operation and reduces friction in majority of the cases studied. It is worthwhile mentioning, that the optimum value of the metal support polarizing potential corresponds to the longest duration of pendulum oscillation (i.e., minimum friction) and depends considerably on polymer material the prism is made of. Polymer materials investigated in a certain loading range differ negligibly what concerns their deformation and strength characteristics. It's highly improbable that differences in frictional and electrochemical characteristics of friction pairs are due to mechanical reasons, i.e., different degree of the film damage formed from electrochemical reaction products on the metal support surface by prisms with different deformation and strength parameters.

Probably, one of the factors determining variation of polarization current density at starting and the optimum value of polarizing potential is adsorption of potential-determining electrolyte ions on the forming at friction juvenile surface of the polymer prism and its debris [26]. In favor of the supposition evidence data of polymer effect on metal polarizing kinetics in electrolytes (see ch. 4.1.2).

It should be also mentioned, that specifics of metal-polymer pair friction is governed not only by the polymer origin, being a component which exerts a direct influence on kinetics of electrochemical processes at friction zone polarization by an outer voltage source. This is because metal-polymer parts and joints used in modern machines and equipment can be themselves the sources of friction zone polarization.

When heating a metal-polymer sample placed as a polymer interlayer between short-circuited electrodes of unlike metals, electric current is generated in the circuit closing electrodes, which augments with temperature rise (see ch. 1.2.5). Current direction is conditioned by the magnitude of the electrode metal potentials forming the electrode pair. During operation of a friction pair from unlike metals separated by a polymer layer, self-polarization of the friction zone can occur.

The source of friction zone polarization in work [27] was a metal-polymer sample made as copper and aluminum foil plates separated by a PVB film. The sample electrodes were closed in a prism and a pendulum tribometer support (see Fig. 5.5). The total electrode potential of both support and prism was measured depending on polarization current. Figure 5.5 shows that in the absence of polarization, the total electrode potential monotonously shifts to anodic domain (curve 3) and its bias occurs during pendulum oscillation. The sample heating to 360 ± 5 K leads to generation of 0.005 mA polarization current of this or that polarity (curves 2, 4) and the corresponding bias of the total electrode potential. Temperature rise up to 380 K spurs further growth of polarization current till 0.01 mA and greater bias of electrode potential (curves 1, 5). In cathodic polarization domain the highest velocity of potential bias to the negative side coincides with the period from actuation till pendulum stop, after which the potential stabilizes.

Almost negligible variation of electrode potential observed in the studied polarization range exerts a noticeable effect on the prism against support friction. The result obtained suggests that, for e.g., cathodic polarization of the friction pair closed in a steel support of aluminum electrode in the metal-polymer sample increases time of pendulum oscillation (friction reduction) as compared to anodic polarization, though the latter does not practically exert any influence on friction in the studied regime.

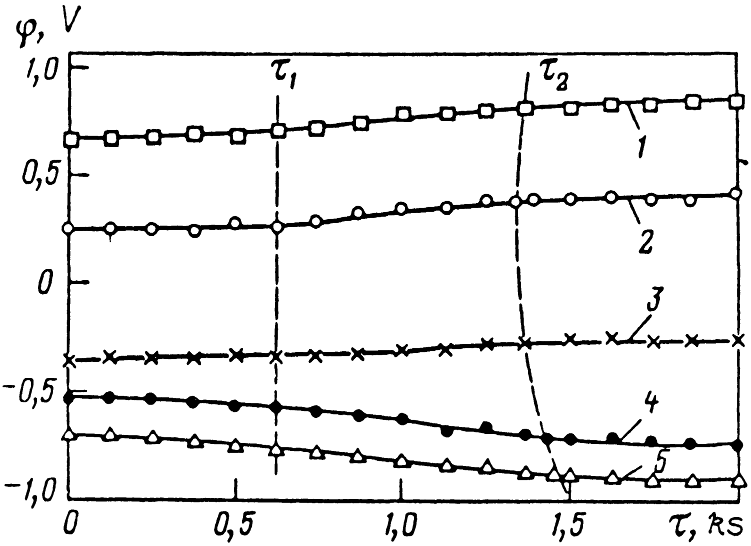

Fig. 5.5. Change of total electrode potential φ of pendulum support and prism in time τ depending on polarization current value (mA): 0.01 (1); 0.005 (2); 0 (3); -0.005 (4); -0.01 (5); τ_1 and τ_2 are moments of pendulum start and stop; P = 0.1 MPa; NaCl (0.1 mol/l) solution.

We wouldn't dwell in detail on the mechanism of electric current generation in polymer materials contacting short-circuited plates of unlike metals with a polymer layer in between (see ch. 1.2.5), but characterize only some regularities of the process. Current in the polymer layer augments with increasing difference of standard electrode potentials of metal plates in the metal-polymer sample. It also increases with temperature rise reaching about 0.1-1 mA/cm^2. Probably, such current generation can provide for a metal friction pair stable polarization. Polarization occurs when PA, PPl, PVC, polyolefines or other thermoplasts are used for the interlayer in the metal-polymer samples. Such polarization sources can emerge in seals containing polymer inserts, in friction joints, polymer-coated parts, reinforced polymer articles, etc. Such sources functioning exerts a substantial effect on friction and wear of metal parts in friction joints operating in aggressive media under electric contact with parts from other metals.

So, it can be concluded from the above procedure, that metal friction and wear can be controlled in metal-polymer friction pairs by maintaining a given optimum potential which value is to be found for each separate case.

5.2.2. Polymer tribopolarization.

Among complex phenomena running at polymer friction, electric processes are the least studied, though their effects are not the secondary ones. Although, available in this field experimental data are often contradicting. Let's consider some aspects of polymer electrization kinetics in the process of metal and dielectric frictional interaction.

It is known that when two solid surfaces are rubbed together, opposite surface potentials are generated on the mating surfaces. This phenomenon is called *tribocharging* or *triboelectrification.* Several mechanisms have been proposed to explain the tribocharging, such as the work function difference for metals [28], assymetric rubbing [29], charging by protons or hidroxide transfer [30], pyroelectricity and pyezoelectricity [31], and weating down of the neutralized surface layer to expose an intrinsk charged surface [32]. However, there is no unified theory that explains the tribocharging phenomenon. This suggests that tribocharging may occur as a result of the complex effects of these cause factors [33].

A number of works show that *electrization potential* of the polymer element in a metal-polymer friction pair rather quickly reaches saturation (in a few seconds). At the same time, some plastic-steel friction pairs (PMMA, PTFE, polyimide, epoxy resins) initially show change in electrization potential sign. The authors [34] attribute this to the possible moisture loss by the polymer surface layers.

Polymer electrization in contact with metals is strongly influenced by environmental humidity or the presence of a liquid lubricant film in the contact. Interesting results in measuring the potential sign and value during polymer friction against metal were obtained in work [35] when a lubricant containing polymer additives was introduced into the friction zone (Fig. 5.6). The authors explain the obtained dependences based on the Cornfeld theory treating uncompensated charge of the dielectric surface. When electrically negative fluoroplastic or polyethylene additives are present in the lubricant, they are adsorbed on the positive PA 6 leading to reduction of its positive potential. Polyizobutylene addition increases PA 6 positive potential. At pressure and corresponding temperature rise in the friction zone, desorption of the earlier adsorbed components can occur causing recovery of the initially positive PA 6 potential. Figure 5.6 shows that capron in all cases charges positively if $p > 2$ MPa for the Vaseline oil with any additive.

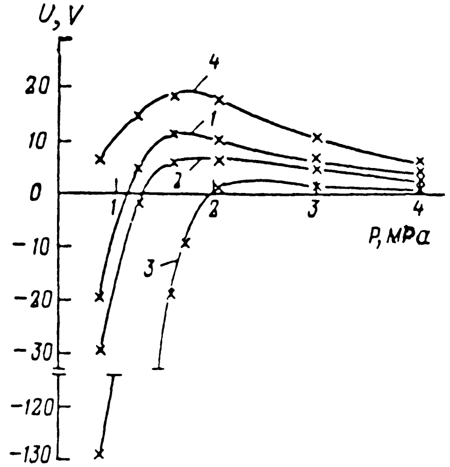

Fig. 5.6. Potential U of capron sample to steel counterbody relation versus pressure P when lubricated with Vaseline oil: 1 - without additives; 2-5 % of PE; 3-5 % of PTFE; 4-5 % of polyisobutylene [35].

It should, although, be noted that division of polymers into electrically positive or negative is not always justified as is marked by the authors in [36]. They conducted analysis of current diagrams for polar caproimide and nonpolar PE. It showed that in both cases, positive and negative values of polarization current were recorded depending on friction regimes. The predominantly positive polarity of the current in case with PA 6 can be explained as follows. PA 6 is known to be characterized by a high hydrophily, while water possesses donating properties. Donor addition leads to negative charging of both semi-conductor and dielectric, so loss of water will, evidently, result in positive charging. During PA 6 friction dehydration of the surface was observed by the authors [34, 36].

Numerous recent investigations prove that during frictional interaction with a solid counterbody, *triboelectret state* is generated in polymer materials due to intense electrophysical processes [37, 38]. The mechanism of its formation can be described by the following [37]: during electrization surface and space charge are formed in the polymer and its polarization occurs in this field. As a result, electret state emerges which parameters are conditioned by the injected charges and polarization.

Such a state has a multiple action on different polymer properties [39]. This allows for a supposition, that its formation can lead to change in kinetics and intensity of the whole physico-chemical complex of processes running in the friction zone and governing largely the polymer frictional characteristics. Since triboelectrization rate is closely connected with the value of the formed in the polymer space charge and orientation of macromolecular segments causing polarization depend much on the load-velocity regime and friction medium, so far the material triboelectret state parameters would be largely specified by friction conditions [40].

The main experimentally recorded characteristics of the polymer triboelectret state are the value of effective surface charge density (ESCD) and TSD current spectrum, which analysis helps to estimate homo- and heterocharge correlation in dielectrics, as well as activation energy of charge relaxation, relaxation time, etc.

The parameters of triboelectret state of polymer materials are strongly dependent on friction regime and polymer origin. In a general case, growth of friction power varies extremely ESCD value in polymer coatings when it passes the maximum, while tribocharge relaxation time, determined by kinetics of ESCD decay at prolonged exposition of samples, increases.

Table 5.3. HDPE and PTFCE-based tribolelectret characteristics under different friction velocities [40].

Polymer	Friction velocity m/s	Friction temp. K	ESCD 10^{-6} C/m^2	Temperature of TSD current peak maximum, K			Activation energy for TSD current peaks, eV		
				I	II	III	I	II	III
HDPE (ε = 2.3)	0.5	300	-30.7	351	-	408	1.47	-	-
	1.0	317	-39.4	353	400	413	1.65	-	-
	2.0	340	-47.6	358	400	415	1.96	-	-
PTFCE (ε = 2.7)	0.3	298	-17.7	315	391	425	-	1.59	2.64
	1.0	320	-38.7	-	394	435	-	1.86	2.91
	2.4	358	-58.6	-	393	451	-	1.51	2.72

TSD current spectra for both polar and nonpolar triboelectret polymer coatings show three peaks (Table 5.3) and the PE inverse peak II [40] is attributed to relaxation of remanent polarization due to accumulation and orientation of strongly polar groups in the polymer surface layer composed from PE thermooxidation and mechanical destruction products.

The analysis of the studied polymers TSD spectra yielded a conclusion that triboelectret state is to a great degree determined by the arising space charge which high-temperature relaxation is caused by either molecular mobility at the interface between amorphous and crystalline phases or on the crystallite surface (α_c-relaxation), or by a large-scale displacement of macromolecular chains during crystallite melting (α'-relaxation) and rising electric conductance of the polymer (Maxwell's relaxation) [40].

It is interesting to note that, when PE coating frictionally interacts with a dielectric counterbody, TSD spectra also show three peaks specifying different mechanisms of tribocharge relaxation [41]. In a general case, rate of electrization in the polymer-dielectric frictional contact is lower than in the polymer-metal one. Judging by the character and regularities of electrization, most close to the polymer-metal system stands nonpolar PEVB-polar PA 6 system. As for electret characteristics, most essential and reproducible one is the triboelectret state arising at different polarity polymer dielectrics friction [41].

The preliminary created in the polymer electret state exerts a considerable effect on the polymer material wear in pair with metal [42]. The rate of mass wear looks like a parabolic dependence versus both-sign ESCD value (Fig. 5.7).

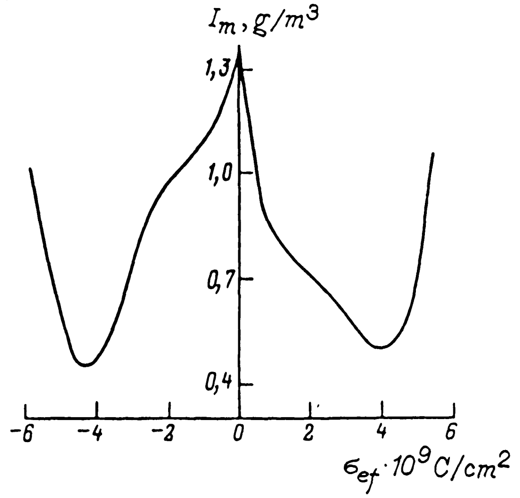

Fig. 5.7. Mass wear rate I_m versus ESCD sign and value for PE electret coatings. Friction regime: P = 0.5 MPa; v = 0.5 m/s [35].

Polymer impregnation with dispersed fillers in a relatively low concentration can cause gain in electrization, enlargement of remanent charge and variation of friction coefficient. Still more stronger effect on polymer electrization at friction against metal is exerted by the composite impregnation with an electret filler. Depending on direction of the field intensity vector formed by electret filler particles, the field formed during triboelectrization can be either attenuated or amplified, i.e., the principle of electret-triboelectrization superposition can be realized [43]. Thus, the parameters of frictional interaction can be monitored. As for e.g., introduction of electret filler (mechanically activated F-3 powder) causes friction force reduction.

5.2.3. Metal-polymer electret wear.

Electric fields can have an effect on friction properties. It has been shown with polymers [44] that the friction coefficient of polymer films of the modified polyethylene type varies linearly with the corresponding adhesion energy of the same polymers on an aluminium film substrate. The influence of a d.c. electric field on the adhesion properties of polymers is also known [45]: in the case of PETP films, it has been shown that the presence of an electric field improves wettability and the also adhesion to a gelatine layer, for example. The role of the electric field is then essentially to promote the orientation of the polar end groups at the polymer surface. If the unteractions are hindered by the presence of an electric field, the friction coefficient decreases because friction occurs fewer adhesive interactions and less polymer transfer [46].

Other authors [47] have studied the effect of electrical fields upon the wear of HDPE and PTFE at different humidity. It was shown that at high humidity electrical fields affect the wear behaviour of HDPE, the wear factor being reduced by a field in either direction. A 45 % reduction in the wear factor was observed when the steel counterface was charged negatively and 30 % reduction when it was charged positively. One of the first attempts to define the dependence of the wear rate at friction and the value of polymer electret charge has been undertaken for PE thermoelectret coatings [38] in conditions of the charge uniform distribution across thickness. During coating wearing, any variations in charge value or friction characteristics of the electret were not recorded.

A characteristic feature of MPE is uneven distribution of charge carriers across thickness (see Fig. 1.11) effecting the magnitude of frictional wear. MPE wear has been studied by the layer-by-layer removal of material in planes parallel to the friction surface [48].

PA and PPl with low friction coefficient and high resistance to attrition were used in experiments, as well as PVB, being a convenient model of antifrictional electret material. Polarization of the samples was carried out between aluminum and copper electrodes under T_p = 430 K during 5 h with electrodes closed in ampere meter. Reference samples (nonelectret) were produced in similar conditions with opened electrodes. Two groups of samples were examined. Polymer material of the first group was cut from the surface contacted copper foil during polarization and for the second group material from that contacted aluminum. Friction tests used the pin-on-disc geometry under 0.11 MPa load and 1.4 m/s velocity.

As it was already noted, polarized charge of metal-polymer electrets was mainly stored in the surface layer 20-60 μm thick (see Fig. 1.12) and the charge localized near the copper electrode was larger than that near the aluminum.

More intense variation of the wear rate (Fig. 5.8) at a sequential removal of the polymer layers is observed in the surface layers, where the main portion of the space charge is accumulated. Wear of the surface contacting aluminum during polarization is lower than that contacting copper (curves 1 and 2). Seemingly, the reduction of electret wear rate with increasing TSD charge density is the common tendency. It is violated only for the thin surface layers (15-20 μm) of the samples with high concentration of chemical structural defects. This is also typical of nonelectret samples (3) though to a much less degree.

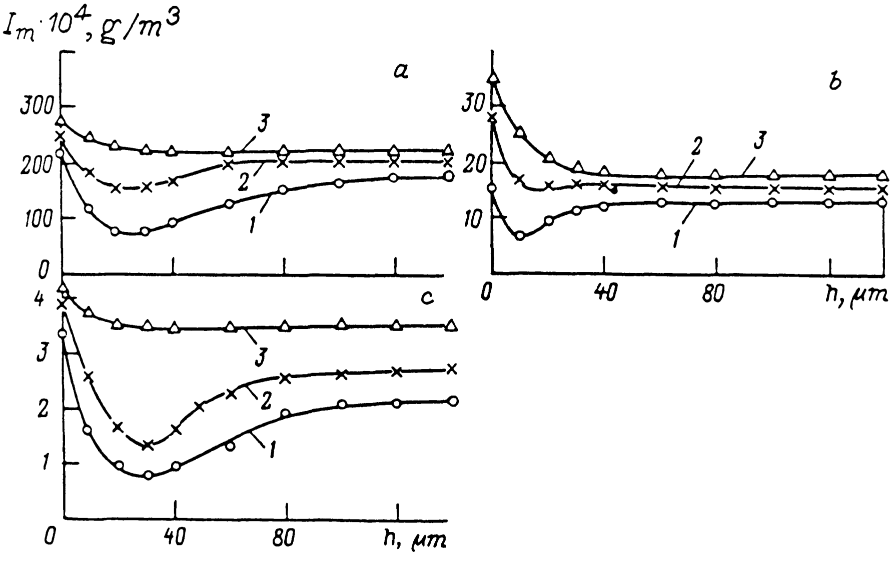

Fig. 5.8. Wear rate dependence on layer thickness removed from the sample contacted aluminum (1) and copper (2); 3 - nonpolarized sample. Sample materials: a - PVB, b - PPl, c - PA

Variation of metal-polymer electret properties is because space charge formation is accompanied by rearrangement of the near-electrode layer structure. As it has been noted in 1.2.5, the polarized PA samples show a 4-5% higher crystallinity as compared to reference ones. Analogous rise in crystallinity of PPl samples constitutes 4% from the copper electrode side and 6% from the aluminum one. Upon removal of 80-100 μm thick material layer, the polarized and nonpolarized samples do not show difference in degree of crystallinity. Apparently, the formation of space charge in the near-electrode regions hampers macromolecular packing during crystallization. So, the higher value of the charge localized near the copper electrode corresponds to a lower crystallinity degree.

The data cited suggest that metal-polymer electrets should be used to improve frictional properties of materials and rise durability of friction joints.

5.2.4. Wear monitoring (control over friction).

One of directions aimed at improving serviceability of machines is associated with material accommodation to operation conditions. Modern machine-building is in need of materials based on metal, polymer and ceramic matrices, which structure and properties can self-regulate in response to varying operation conditions [49]. Let us analyze the frames of improving metal-polymer friction joint serviceability by using electric fields.

The degree of material electrization and polarity of the forming charged layers exert the direct effect on dynamic equilibrium of the polymer decomposition and formation velocities (those of copolymers) which corresponds to the established in metal-polymer system friction regime. Actually, plastic sliding against metal is accompanied by disturbance of electronic density in all points of frictional contact. Charge transfer through the interface can occur in this or that direction. As a result, plastics charges either positively or negatively relative to the mated metal counterbody. The acquired by the dielectric surface several thousands volts potential spurs the formation of a strong electric field in the friction zone causing tearing and transfer of metal ions on electrically negative plastics, or vice versa, transfer of electrically positive products of polymer thermal destruction on metal surface, followed by the protective film formation.

Recent studies have shown that *ion implantation* and *plasma surface treatment* are effective techniques to significantly improve surface related properties such as hardness, wear and chemical resistance. The implantation process modifies the near-surface microstructure of the polymer by several processes such as cross-linking, considered to be mainly responsible for improved properties, chain scission and, to a lesser extent, the injection of ions as new chemical charged species. In several polymers, such as PC, PS, PES, significant improvements in tribologycal properties have been obtained using polymeric counterfaces [50-52]. The study [53] shows the existence of an optimum implantation condition for PEEK for best improvement in wear properties after Ar^+-ion implantation when tested using a hard steel counterface.

Friction and wear tests showed [54] that the nitrogen ion implantation significantly improved the wear property of PI, and with the implanted dose $5 \cdot 10^{16}$ ions·sm^{-2}, both friction and wear of the PI could be remarkably reduced.

Plasma treatment was shown as a useful surface modification technique for PEEK and based on PEEK composite materials [55]. After this treatment, the tribological properties of soecimens improved to a great extene. Their sliding friction coefficient and specific wear rate decreased markedly. Plasma treatment is simular to a quenching process, and thermal degradation occurs wich also an improvement in the tribological properties.

Preliminary electrization of the friction pair elements can be efficiently used to inhibit *hydrogenous wearing*. Hydrogenous wear is characteristic for metals in loaded friction joints working in contact with organic polymers. This type of wear occurs due to hydrogen accumulation in the surface layers of parts and their embrittlement, which is the loss of plasticity. The authors of [35] have fulfilled the analysis of electric field value and direction effect on intensity of steel hydrogenation and wear resistance. To create an electric field in the friction zone of a required direction and magnitude, it is necessary to insulate one of the metal-polymer system elements from the friction machine body and to supply from an outer source a certain value and polarity voltage to the conjugated parts. The results show that with the positive potential on the plastics the conjugated metal counterbody (Steel-45) wear is 2-3 times higher than with the negative.

Intense tribological hydrogenation at negative potential of the metal is because the surface, in this case, catalyzes dissociation of hydrogen molecules, since metal negative potential reduces activation barrier for the electron outlet captured by hydrogen molecule followed by negative ion H_2^- formation. The latter dissociation energy is considerably lower than the neutral hydrogen molecule has. Proceeding from the above investigations it is obvious that the negative triboelectric polarity of plastics is necessary to improve wear resistance of the metal-polymer joint by inhibiting hydrogenous wearing.

The prospects of increasing durability of machines by using electric techniques are closely related with the development of engineering materials and articles which functions are bearing and transfer of mechanical loads with simultaneous generation of electric field.

As it was mentioned above, electric polarization of polymers in contact with metals makes it possible to improve friction characteristics of parts at production, as well as to raise their operation serviceability. Below examples are given of technological and design solutions in used in practise.

A device to manufacture articles [56] provides for different levels of lubricant content in polymers not reducing its deformation and strength characteristics. One of the device forming parts surface incorporates dielectric and conducting units. The latters are closed in the second forming part made of unlike metal. The difference between the standard metal electrode potentials of the forming parts does not exceed 2-3 V.

A variant of the device is shown in Fig. 5.9. The mold to produce a thrust bearing from a thermosetting molding material involves punch 1 and matrix 2. The steel punch is fixed on the upper plate 9 of the press which has heating elements 8. The matrix is fixed through the insulating lining 4 on the lower plate and contains dielectric insert 3 with pusher 5 which calorized end forms the thrust bearing seat face. When the mold is closed, circuiting of chain 7 occurs and the process of polymer 6 moulding and thermal treatment is accompanied by TSC between pusher 5 and punch 1. The current value depends on electrode potential difference between steel and aluminum (ΔU = 1.22 V). Thus, the thrust bearing bottom is electrically polarized and acquires MPE properties. Upon further treatment in lubricant the thrust bearing bottom sorbs liquid to a less degree than its conical body. As a result, the bottom carrying axial load strengthens and acquires resistance to contact loading, while the body walls modified by the liquid lubricant display self-lubricity.

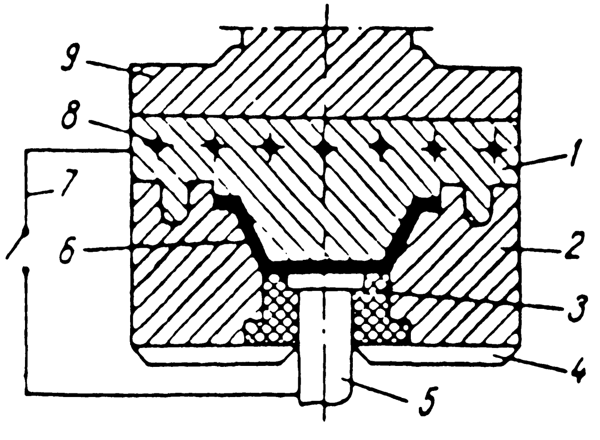

Fig. 5.9. A scheme of device for manufacturing articles form polymer materials.

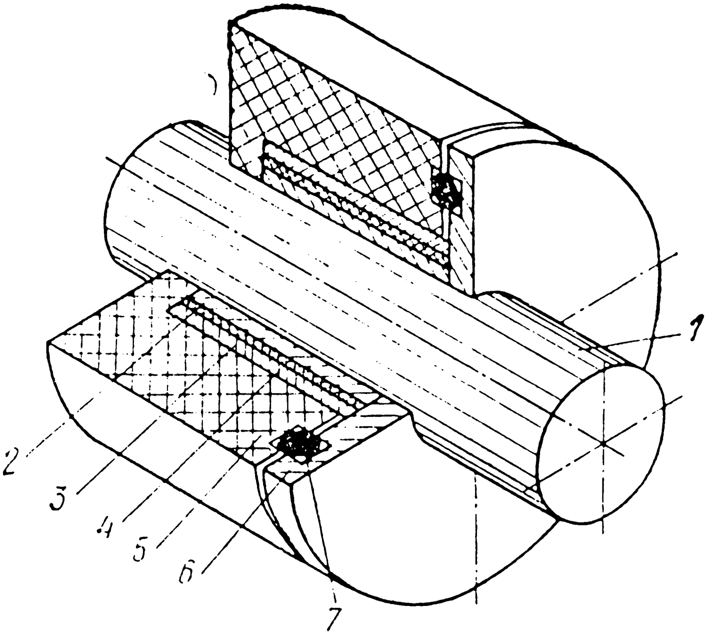

Fig. 5.10. Sliding support.

Sliding support [57] can serve an example of the polymer polarized state reducing corrosion-mechanical wear in friction joints.

A sliding friction joint consists of shaft 1 and mounted in shell 5 bush composed of three coaxial sleeves (Fig. 5.10). The middle sleeve 4 is from polymer material, sleeve 2 facing the shaft is from metal showing a higher positive value of electrode potential than the metal of outer sleeve 3. The sleeves are closed in a metal slid 6. The shell-slid junction has seal 7. When the friction joint is in operation, the metal-polymer sleeve frictional heating generates electric current in the polymer layer which direction is conditioned by position of metals the sleeves are made of in the electrode potential series (see ch. 1). Thus, the metal-polymer sleeve functions as an electric generator providing for the friction zone polarization. When the shaft contacts sleeve 2, its electrode potential shifts in positive direction. If the shaft is made of a metal or alloy able of passivating in conducting liquid present in the friction joint at anodic polarization, for e.g., steel, then even at a negligible shift the shaft electrode potential reaches the values corresponding to the steel passive state leading to reduction of corrosive-mechanical wear of the shaft.

Friction machine SMC-2 was used in the friction joint tests with parameters: bush area 2 cm^2; load p = 0.35 MPa, sliding velocity v = 2.4 m/s. The shaft is made of steel St.45 with diameter 40 mm, hardness HRC 40-45, roughness R_a = 0.8-1.0 μm. The outer sleeve material is aluminum, that of inner - copper and the polymer interlayer is of 200 μm PVB. A 0.1 n. NaCl solution was supplied to the friction zone and wear rate was estimated by the weight method. Test results are given in Table 5.4.

Table 5.4. Corrosion-mechanical wear of shaft.

Electric circuit of the bush	Wear value (10^{-6} g/m^2) at test time (h)				
	3	6	9	12	15
Closed	0.3	0.5	0.6	0.7	0.7
Opened	1.7	2.8	3.2	4.0	4.2

Notice that, at closing the bush circuit during potential shift, the shaft wear reduces 5-6 times as compared to bush which metallic sleeves are opened and no current passes through the polymer layer. For sliding supports which shaft is a more expensive and critical component, such wear reduction increases support life several times. Apart from protecting the shaft electrochemically without using outer source of polarization, such design advantage is in utilizing frictional heating to generate polarization current and its operation without seals hampering the conducting working liquid penetration into the friction zone.

5.3. LUBRICANTS.

The main designation of lubricants is the reduction of wear between rubbing parts in order to increase lifetime of machines and mechanisms. Aside from this, lubricants perform several other functions. They hamper harsh liquids, gases, vapors and abrasives (dust, contaminants. etc.) penetration onto friction surfaces. Practically all lubricants realize the protecting function. They inhibit corrosion of metallic surfaces of articles, machines, equipment when transported and at prolonged storage (*preserving and operation-preserving lubricants*). To seal clearances in mechanisms, as well as in pipeline and stop valve junctions, *sealing lubricants* are used. Sometimes, special requirements are imposed on a lubricant: to rise friction coefficient, perform the role of insulating or conducting materials, provide for friction joint operation in conditions of radiation, deep vacuum, etc. Such lubricants constitute a special group of *special-purpose lubricants*. Only 14 % of lubricants is spent on preservation and about 2 % on sealing. The rest lubricants are used to reduce friction and wear of rubbing parts as antifrictional substance [58].

Lubricants consist of a liquid base (dispersed medium) and a solid thickener (dispersed phase). To improve performances, additives of different functional purpose are introduced into lubricants (e.g., surfactants) and solid additions (fillers). Different lubricating oils and liquids serve as a lubricant liquid base, for e.g., petroleum and vegetable oils, organosilicon liquids, esters, fluor- and chlorocarbons, and others. To thicken the lubricant, salts of higher carboxylic acids (soap) are used, as well as highly dispersed inorganic (silicagel, graphite, asbestos), organic substances (polymers, pigments, polyurea, soot) and high-melting hydrocarbons (ceresine, paraffin, ozokerite, different natural and synthetic waxes).

Lubricated state of metal-polymer contacts in friction joints is observed in case a lubricant is introduced into the friction zone, also when metallic materials rub in lubricants containing additives of high-molecular compounds or when tribologically polymerizing lubricants are used. In all cases mentioned, running of complex physical and chemical processes is feasible in the zones of frictional interaction in the presence of boundary lubrication. We shall consider only separate aspects of this interaction specified by either presence of electric fields in conjunction or fillers in electret sate.

5.3.1. Polymer-containing lubricants.

Polymer used in lubricants are related to either additives or fillers depending on their chemical composition, properties and impregnation method.

When polymers are thermomechanically dispersed in the lubricant (it is, as a rule, the preliminary solution in dispersed medium before thickener introduction) they behave as additives. In this case, polymers participate in the process of lubricant structural formation which varies their performances. If a polymer is introduced as a highly dispersed powder under temperatures below its melting one, then it accomplishes the role of fillers not practically effecting the lubricant structure, but improving its performance. Concentration of additives in such lubricants varies in a wide range from 0.2 to 20 %.

Furthermore, the so-called solid or semisolid lubricating compositions are available based on high-molecular compounds, where polymer content reaches several tens mass percents.

The known solid lubricants based on low-molecular hydrocarbons (e.g., paraffin) and high-molecular binders contain antiwear and antiscuff additives, which can be lead and zinc oxides, molybdenum disulfide or some other costly components. Such lubricants are characterized by improved performances, but their processing is highly labor- and power-consuming and, consequently, expensive.

The present authors have developed a highly efficient *lubricant for friction joints* [59] based on paraffin and polyamide. It contains fuming-oxides (FO) of non-ferrous metals, being a product of slag sublimation after lead smelting.

The lubricant is produced by mechanical mixing of components followed by fusing under 220 °C. The lubricant friction coefficient f was estimated at shaft-partial insert dry friction under sliding velocity $v = 0.15$ m/s, load $p = 5$ MPa. Adhesion was characterized by the breaking stress value σ_b when separating the lubricant cylindrical sample, using normal tearing method, from a preheated to 180 °C steel plate upon its cooling to 20 °C. Corrosion rate i_g of steel samples protected by a lubricant film was measured in a 0.1 n. solution of Na_2SO_4 by the method of polarization resistance. Optimum FO content is 30-50 % (Table 5.5). Further increase of filling degree impairs the lubricant operation characteristics due to reduction of the binder plasticity, Increase in paraffin concentration above 12% results in friction coefficient rise and reduction of the lubricant adhesion.

The mechanism of FO effect on adhesion and anticorrosion properties of polymer compositions have been discussed in par. 4.2.1 (see Fig. 4.10). As for the lubricant tribological characteristics, the following can be proposed. The high antiscuff properties and low friction coefficient are owing to reducing from FO metals' catalytic effect on "frictional polymer" formation from mechanodestruction products of the lubricant organic components. The efficiency of frictional polymers has been repeatedly proved both in model experiments and in real friction joints.

Table 5.5. Lubricant performances.

Composition no.	Component content, mass %			f	σ_b, MPa	i_g, g/(m^2·h)
	paraffin	FO	polyamide			
1	12	30	58	0.03	0.06	1.35
2	10	40	50	0.03	0.07	1.25
3	8	50	42	0.03	0.06	1.30

5.3.2. Electrorheological suspensions used as lubricants.

Electrorheological (ER) effect is a fast reversible rise of efficient viscosity in nonaqueous dispersed systems under strong electric fields. This effect was first established by Winslow in the 40-s [60]. In monograph [61] different authors' data on ER effect were systematized and generalized.

Advantages of ER suspensions as special-purpose lubricants are in feasibility of their retaining and displacing in the friction zone by using electric fields. In this case, ER suspensions can be considered as an electric analogue of magnetic liquid and related to the class of "intellectual" materials [62].

ER suspensions consist of a nonpolar dispersed medium and a solid dispersed phase with high dielectric permittivity ε. Petroleum and vegetable oils, diethers, acids and kerosene can serve as a dispersed medium. Fine-dispersed powders of different modification silica, alumasilicates and metal oxides with below micron particle size are used as dispersed phase. To produce a suspension showing noticeable ER effect, an activator which is a substance adsorbing on solid particle surface, and a surfactant providing for stability of suspension properties with time are also necessary.

The efficient viscosity of suspension increases with the rising field intensity. It has been found out that ER effect [63, 64] is insignificant till a certain threshold of electric field intensity E_{th} (Fig. 5.11). Upon reaching E_{th}, the efficient viscosity increases approximately in parabolic dependence versus field intensity till saturation. The efficient viscosity value depends much on dispersed phase concentration and electric field frequency.

We shall not describe in detail all the feasible mechanisms of ER effect, but notice that, processes of particle aggregation and structurization in homogeneous electric fields lie in its basis. Thus, Winslow has established when studying moistened silicagel suspensions in kerosene with surfactant addition that, suspended in a low-viscous medium solid particles distribute under electric field action in direction of force lines and form fibers (particle chains) crosswise the interelectrode gap. Increase in efficient viscosity at shear was attributed to elastic extension of fibers, whereas at large concentrations it is jamming of closely lying particles [60].

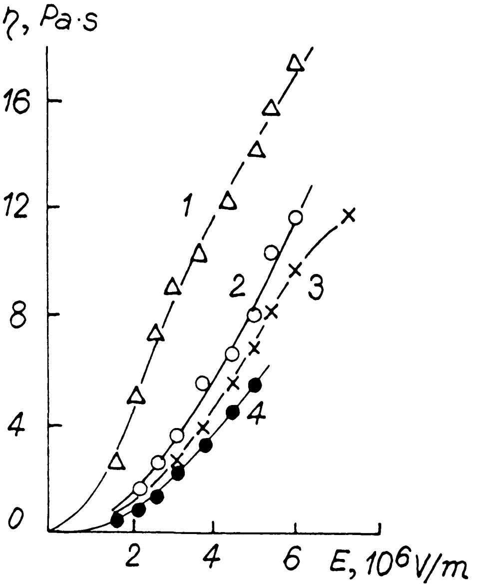

Fig. 5.11. Effect of the outer electric field intensity E on efficient viscosity η of suspension containing (mass%) kerosene - 89, polyisobutylene - 1, diatomite - 10, under shear velocities (c^{-1}): 1 - 38; 2 - 72.5; 3 - 107.1; 4 - 141.6 [64].

Orientation and interaction of dispersed phase particles in electric field is caused by particle polarization and field action on the induced dipolar moments. Particle polarization and orientation in the field of shear stresses results in change of ER suspension dielectric permittivity. This is the reason of ER sensibility to those dispersed system parameters, which govern polarization process.

Generalized data and theoretical substantiation of ER effect allows for the following conclusion. Peculiarities of dispersed system dielectric polarization are determined by the presence of the interface and processes running in the double electric and adsorptional layers. Migration and surface polarizations cause deviation in dispersed system dielectric permittivity from the values calculated based on the mixing law [65] and ER effect emergence. The particle dipolar moment in a constant electric field depends on phase conductance to medium dielectric permittivity ratio. The maximum dipolar moment obtains a particle of a conductor or dielectric surrounded by a conducting film in a nonconducting dispersed medium. Generation of a considerable ER effect is feasible in such systems [61].

Probable fields of ER application are immensely versatile. They involve [60, 61]:

- blocking and regulation of liquid motion pumped through a narrow channel;
- new clutch designs, those of brakes and frictional devices;
- clamping and fixing devices;
- setups to smoothly regulate load at material winding and unwinding from reels, bobbins;
- mixers, pumps, separators, purifiers;
- electric generators, transducers, electrokinetic balances.

In addition to the above list which can be extended considerably, hereafter some examples of ER suspensions use as a lubricant are enumerated.

Figure 5.12 presents a scheme of a simplest clutch. In the absence of field in the clearance between rotor 1 and coupling 4 a thin ER liquid layer plays the role of the lubricant and driving shaft 6 is immobile during rotor rotation. When a potential is supplied on the rotor, a strong electric field is generated in the clearance between the rotor and coupling. As a result, the lubricant film viscosity increases thus rising its resistance to shear, the rotating rotor engages on the coupling and transmits torque to the driving shaft.

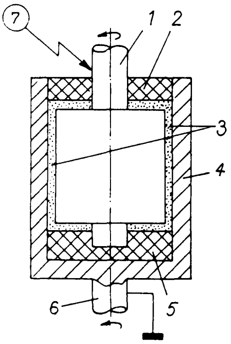

Fig. 5.12. A clutch scheme containing ER liquid: 1 - rotor; 2, 5 - insulators; 3 - ER liquid; 4 - coupling; 6 - driving shaft

A similar principle is utilized in a device for automatic gauging of clutch slippage depending on operation conditions and load variation (Fig. 5.13). A single-phase electric motor 1 is connected with load 4 through disc clutch 3. Even (inner) discs are connected with the motor shaft, odd ones (outer) with the loading shaft. Clearances between discs are filled with an ER liquid. Conductor 2 connects outer coupling discs with the motor supply circuit. The inner discs are connected by conductor 5 with supply circuit through transformer 6. If the loading current of electric motor is too high, then an elevated voltage is induced in the coil. So, voltage in the coupling circuit drops and ER liquid viscosity reduces, thus increasing slippage between discs. As a result, load on the motor falls. Such a scheme is good for any electric drive with either direct or alternating current. The devices described can be additionally equipped with a connecting pipe to renew liquids, as well as by cooling jacket and liquid circulation fitting [66].

Fig. 5.14 shows the scheme of a relay device [67]. Driving shaft 3 supports cup 4. Driven disc 10 of shaft 9 is insulated from the cup by a layer of ER liquid 11. Relay blade 8 secured on shaft 9 between a pair of contacts 5 and 6 is constantly attracted by spring 7 to contact 6. The direction of cup 4 rotation is such, that makes the blade to deflect from contact 6 to contact 5. The latter can control any chain elements. Electric field between cup 4 and disc 10 is generated by source 1. The circuit is closed and opened at required moments by any commutative device 2 [67].

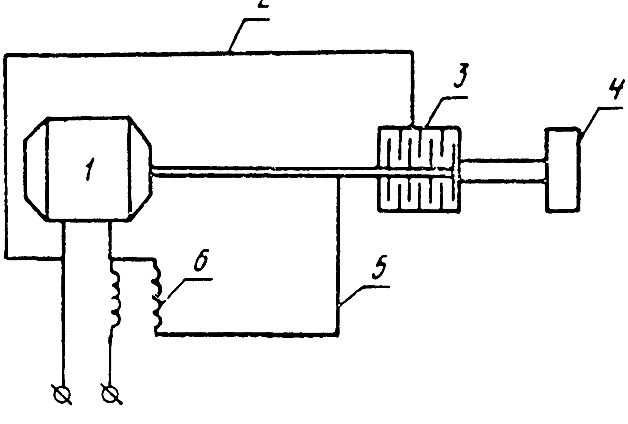

Fig. 5.13. A scheme of device to control disc clutch slippage: 1 - electric motor; 2, 5 - conductors; 3 - disc clutch; 4 - load; 6 - transformer [66].

5.3.3. Liquid-crystalline lubricants.

Despite the fact that liquid crystals (LC) were discovered at the end of XIX century, investigation of their tribological properties have been started quite recently [68]. The diversity of LC properties and vague representations on what concerns the liquid-crystalline state origin were the obstruction in attempts to characterize LC and wear problems interrelation. Nevertheless, a large number of publications has appeared in this time period in which unique lubricating properties of both separate LC substances and those containing their oils or lubricants have been reported. Furthermore, data are cited on low friction and practically wear-free operation of natural tribological joints due to the liquid-crystalline state of their lubricant. The sphere of LC tribological properties and their practical application is reviewed and generalized in works [69, 70].

Due to a certain "cigar-like" structure of LC molecules they occupy an intermediate position between liquids and crystals. French physicist Friedel suggested the term "mesomorphous state" as a synonym to that of "liquid-crystalline state" by deriving it from a Greek word "mezos", which means intermediate [71]. By the method of LC substance formation, they fall into two groups: thermotropic (formed at heating) and lyotropic (formed in solutions). The basis of LC structural classification is the order of molecular arrangement. Friedel has divided LC into smectic (Greek "*smegma*" - soap) and nematic (Greek "*nema*" - filament). Nematic LC he divided, in their turn, into proper nematic and cholesteric [71].

Smectic LC molecules are located so, that their long axes are parallel each other and mass centers of molecules are disposed in one plane. As for nematic LC molecules, they are oriented parallel one another, while their mass centers are chaotically scattered as compared to smectic ones. Cholesterines are characterized by molecular layers in which peculiar for nematics molecular distribution is observed. Though, at transition from one layer to another, the direction of dominating orientation of the long molecular axes shifts by a an angle. This shift is accumulated with the consequently passed layers so, that in general the molecule ends describe a spiral.

The original molecular structure of LC conditions some of its specific properties, i.e., anisotropy of dielectric and magnetic susceptibility, capability of molecular orientation in electric and magnetic fields, anisotropy of viscosity.

The effect of varying nematics orientation under electric field was first observed by Friderix [72]. It was shown that there exists a limiting thickness value of the layer found between the supporting surfaces (for e.g., between a convex and flat glasses). Below this value, reorientation of molecules under a given field intensity is not observed. Threshold character of Friderix's transition is governed by a rather strong bonding between LC molecules and supporting surfaces. It begins only in case the electric field intensity is sufficient for a nematic to overcome its bonding forces with supporting surfaces.

The orienting force of electric field is complicated by LC electroconductivity. LC is anisotropic and may cause substance displacement and redistribution of electric fields. This is the reason of a series of new effects characterizing the liquid-crystalline state (piezo- and pyroelectricity, electrohydrodynamic instability, etc.).

The capacity of LC molecules to orient in electric field allows for treating LC state as the *liquid analogue of a substance electret state*. The importance of such approach results from comparison with phenomena occurring in living nature, in particular, when studying the probable friction mechanisms in men's and animals' articular.

From the one hand, the mechanism of low friction in articular based on LC state of articulation lubricant incorporating cholesterine [68, 73] can be considered a known fact. From the other hand, the presence of a quasi-stable bioelectric field in biological objects is an unambiguous evidence of a nonequilibrium component included into the natural electric polarization of living tissues. This is equivalent to the presence of electret state, i.e. bioelectret effect [74]. In our view, just superposition of the two factors (LC state of synovial liquid and quasi-stable electric field conditioned by electret state of living tissues) can explain the *abnormally low friction* in men's articular. Further studies in these phenomena would be helpful to extend our understanding of physico-chemical origin of life, to develop novel medicinal drugs, methods to cure arthroso-arthritis and medicinal articles to correct articular pathology.

Use of LC substances in friction joints of machines and mechanisms has been considered problematic till recently. This was, probably, because the majority of LC is in the solid state at room temperature, which hampers its use as a lubricant. Besides, high cost made its wide application in engineering doubtful and hindered tribological investigations. Nevertheless, accumulated in the recent years data on lubricity of some LC and their lubricants containing LC additives removed the afore existing contradictions.

As compared to other phase states, higher lubricity of LC substances in the mesomorphous phase is observed in both homogeneous and heterogeneous friction pairs from metals, polymers and glasses. High efficiency of cholesteric LC lubricating layers is supported by investigation results of metal surface wear rates. Thus, when lubricated by a liquid crystal in the mesomorphous phase, wear rate is $1.3\cdot10^{-11}$, while when lubricated by oleic acid forming a smectite-like structure on the friction surface, it is $2.2\cdot10^{-10}$ [75].

Almost all authors studying antifrictional properties of LC-doped oils recorded the reduction of friction coefficient and wear. Separate cases showed the 5 time reduction of friction coefficient and more than 20 times wear reduction when cholesteric LC were used. It has also been established that [75] LC addition into lubricants widens loading range of friction pairs from unlike metals.

LC contribution into friction processes is not well understood. Though, it is known that low friction is realized only with attaining certain roughness parameters on friction surfaces. Surface microrelief depends on lubricant composition and LC additive content. Work [76] shows that when LC additives are used, the formation of a less order microroughness is observed on the friction surface as compared to cases with other lubricants. It means that LC additive protects rubbing surfaces against wear and provides for a lower friction coefficient.

The above peculiarities condition LC application as a lubricant in heavy-loaded friction joints. LC can also be used as an additive to a fuel mixture aimed at intensifying technological run-in of ICE friction parts. LC additives to motor oils reduce wear rate of engine parts, mechanical losses on friction and fuel consumption in urban vehicles. LC additives to coolants improve surface finish for all types of metal machining.

The mentioned examples of LC use in friction joints do not fully characterize their tribological potentialities, but show the prospects of this tribological direction and expediency of its development.

5.4. CERAMICS.

Ceramics are defined as solid materials having as their essential component inorganic nonmetallic substances. They include not only materials such as pottery, porcelains, refractories, cements, abrasives and glass, but also nonmetallic magnetic materials, ferroelectrics, and a variety of other products synthesized recently. Ceramics play a major role in engineering and tribological applications because of their unique and varied properties, abundance in the earth's crust and a relatively low cost. The renewed interest in ceramics is rooted in recent advances made in materials science, which have led to introduction of new ceramic materials with unique properties [77].

Selection of ceramics for tribological purposes is based on their high compressive strength, fatigue resistance, corrosion resistance, low density, high contact toughness and perfect dielectric properties. Ceramics disadvantages are brittleness, high cost of powder production and power-intensive techniques for processing ceramics into articles. They are widely used in ball points, precise bearings, blades for cutting tools, articular endoprosthesis, parts for rocket engines, etc. Five important classes of advanced structural ceramics are used in engineering based on alumina (Al_2O_3 - corundum), zirconium (ZrO_2), silicon nitride (Si_3N_4) sialons (solid solutions of Si, Al, O, N in b-crystals of Si_3N_4) and silicon carbide (SiC) [10].

The main tribological problem limiting ceramics application consists in their high friction coefficient ($f > 0.4$). The admissible in practise friction coefficient ($f < 0.1$) is realized mainly in friction joints working at liquid lubrication. Nevertheless, ceramics shows advantages in conditions (vacuum, high temperatures, inaccessible for lubrication friction joints, etc) where the lubricants turn to be inefficient. So, the problem of ceramics solid lubrication is rather actual. It can be solved by applying solid lubricant film on the friction surface or by creation of novel composites based on ceramic matrix containing lubricating components.

Let us consider the development and operation problems of materials able to transfer electric charges.

5.4.1. Solid lubricant films.

Such films may be applied on ceramics by ion-beam technique based on directed flow of ions. It is commonly used for ionic etching, i.e. removal of impurities and contaminants from solid surfaces. Ion plating of thin solid films on metals is another example of the technique application. Plasma is easily on electrically conductive substrates and the depositing species are accelerated to subsrtrate surfaces with sufficient energy to establish a strong bonding. Not electrically conductive ceramics are unfit for ion plating since they tend to accumulate positive charge and repel depositing particles of the same polarity. The problem is solved by the methods of ion beam mixing and ion beam-assisted deposition [10].

Ion beam mixing (IBM) is used to fix the previously deposited on ceramics solid lubricant by a directed high-energy ion flux (from hundreds keV to several million eV). Such energy ions penetrate through the thin lubricant film further into the ceramic substrate (depth of penetration is about 1 μm at 1 MeV). When passing through the film, the ions collide with the lubricant atoms and drive some of them into the substrate. Bombarding with high-energy ions creates many vacancies and interstitials in the coating and substrate near-surface layer, thus promoting interdiffusion of film and substrate atoms (Fig. 5.15). The originally sharp coating-substrate interface becomes broadened and adhesion of the film improves dramatically. Ion bombarding initiates chemical reactions at the interface and can further increase adhesion.

Use of IBM to bond Ti and Ni coatings on Si_3N_4 ceramics promoted *f* = 0.06 - 0.09 at 800 °C during sliding on TiC counterbody [78]. Using Ar^+ ion beam NB coatings were formed on SiC substrate. While sliding against a diamond pin, no wear was recorded and the friction coefficient of ceramic was about 0.04 [79]. Ion-beam mixed MoS_2 film sputtering on sapphire showed the increased by 2-3 orders lifetime of the lubricant layer during friction in argon in dry or humid air [80].

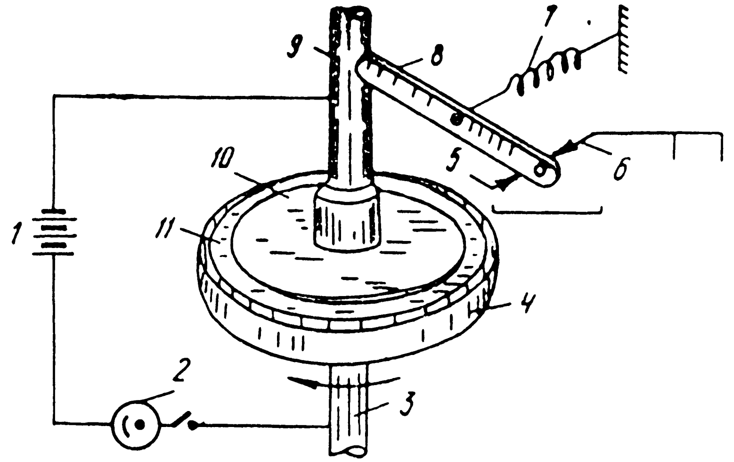

Fig. 5.14. A relay scheme: 1 - voltage source; 2 - commutating device; 3, 9 - shafts; 4 - cup; 5, 6 - a pair of contacts; 7 - spring; 8 - relay blade; 10 - disc; 11 - ER liquid [67].

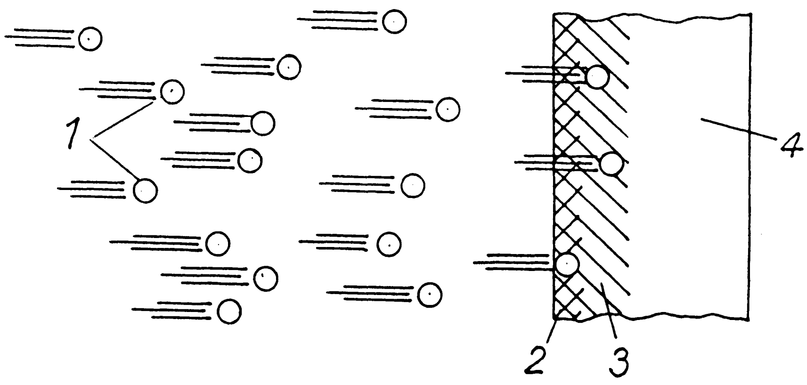

Fig. 5.15. Process diagram of ion-beam mixing (IBM). 1 - high-energy ions; 2 - preliminary deposited layer; 3 - zone of ion-beam mixing; 4 - substrate.

Ion beam-assisted deposition (IBAD) is an alternative to IBM method eliminating the latter drawbacks. During IBAD the solid lubricant film is deposited on the ceramic substrate surface using vacuum evaporation. The growing film is bombarded by 50 eV to 10 keV energy ions. Bombarding starts before and terminates upon the film formation. Energy of ion collision with the film and substrate atoms is much lower at IBAD than at IBM. So, the depth of ion penetration is from a monolayer thickness to several nm. Energy of ions is, however, sufficient for the substrate surface to be cleaned from contaminants before the film deposition and for adhesive joint to be formed due to the substrate and film atoms interdiffusion in point defects arisen from ion attack. The process scheme is presented in Fig. 5.16.

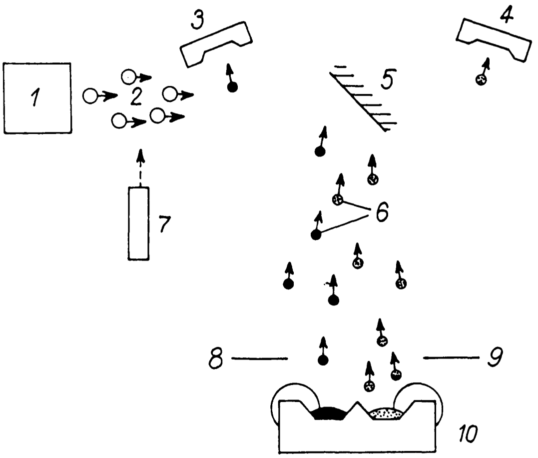

Fig. 5.16. A scheme of ion-beam-assisted deposition (IBAD). 1 - source of ions; 2 - ions; 3 and 4 - atoms A and B velocity meters; 5 - sample; 6 - evaporated atoms; 7 - calorimeter; 8 and 9 - atoms A and B shields; 10 - electron-beam source of evaporation.

The formation of interphase transition layer with the film and substrate atoms gradient is considered to be a determining factor in improving adhesion of lubricating coatings. Ionic cleaning of the substrate surface from contaminants preceding film formation, is of no less importance. A dependence exists between adhesion (A) of solid lubricants to ceramics and wear rate (W), i.e., the less W corresponds to higher A [10]. It is shown in work [81] that wear rate of Al_2O_3, Si_3N_4 and ZrO_2 reduces by 1-3 orders with Ag IBAD-produced films. Such lubricant films do not show any signs of damage after 110 recurrent tests under p = 10 N, sliding velocity $v = 0.05$ m/s and relative humidity 20 %.

IBM and IBAD-produced coating or/and substrate acquire polarized charges. The homocharge surface density on oxide ceramics is 10^{-6}-10^{-4} C/m^2. It is localized in the coating and/or in the substrate surface layer. Its lifetime reaches several decades and reduces with temperature rise.

It is known that [81], interaction of surface charges on parts being in frictional contact creates a resultant moment which increases friction force. At the same time, wear reduction has been recorded [10] with increasing solid lubricant adhesion, which is the higher, the larger is electrostatic component of adhesion. Thus, IBM or IBAD-induced polarized charges in ceramics increase friction but reduce wear.

5.4.2. Composites based on ceramic matrix.

Such composites with solid lubricant containing matrix are an alternative to covered by solid coatings ceramic friction parts. The latter service life is limited by their wear rate. This limitation can be eliminated by composites providing for a constant lubricant supply to the friction zone. Some examples are considered below [10].

Tribological characteristics of pin-on-steel disc pair have been investigated. Si_3N_4 and SiO_2 pins had graphite inserts. This promoted reduction of friction coefficient from 0.45 to 0.17 and from 0.48 to 0.20, correspondingly, as compared to original ceramics. Graphite, ferric oxide and ceramic wear debris were recorded in their composition using X-ray analysis and electron microscopy. Debris in friction pair with Si_3N_4 contained silicates formed as a result of tribochemical reactions. Graphite in transfer films has a disordered structure with grain size of about 40 Å. This is its essential difference from the initial graphite, which particle size is on the average 100 um.

The results obtained initiated the development of composites with evenly distributed lubricant components. The samples were obtained by slip casting on ZrO_2 and graphite base. With graphite impregnation the sample friction coefficient against steel reduced 0.35 to 0.22. Using scanning electron microscope graphite smearing over friction surface and graphite-containing transfer film formation on the steel counterbody were observed. Low strength of such composites conditions their high wear rate. To eliminate the drawback, the ceramic matrix is reinforced with ceramic fibers and whiskers [10] or the participating in friction surface layer of the matrix is hardened, which is to be discussed below.

So, tribological characteristics of composites on ceramic matrix base are dependent on ceramics nature, as well as on solid lubricant and the counterbody material. The criterium for choosing components is the formation of transfer film on the friction surface. The film enrichment with solid lubricant component during matrix wearing reduces the friction surface damage.

Transfer film formation largely follows electrization mechanism. Since ceramics is mainly dielectric, so in friction pairs it takes part, triboelectricity is generated.The forces of electrostatic attraction and repulsion effect transfer film adhesion to ceramics, as well as friction force and some stages of electrode processes classified in Fig. 5.1. Differentiation of electrization contribution into these characteristics is the object of further investigations.

Active ceramic dielectrics are materials with properties regulated by outer energy source influence. Ceramic segneto-, piezo- and pyroelectrics are used in electronics as friction joints, being its functional units.

Barium titanate $BaTiO_3$ and crystalline quartz segnetoelectrics show piezoelectric properties. They are displayed in emerging opposite-polarity electric charges on opposite sides of polarized ceramic plate at its compressing. Thus, the mechanical work can be transformed into electric energy and vice versa. Both quartz and $BaTiO_3$ perform the function of wear-resistant piezo-sensitive material in friction joints used in information storage, sound recording and pickup devices. Widely applied in piezotechnology are segnetoelectric ceramics on the base of solid zirconate solutions, i.e., plumbous titanate $PbZrO_3$-$PbTiO_3$, $BaNbO_6$-$PbNb_2O_6$ and $NaNbO_3$-$KNbO_3$.

Service life of a number of friction joints is conditioned by the friction heating temperature. To record temperature in the friction joint, ceramic pyroelectrics are used which spontaneous polarization (and consequently, charge value) varies with temperature. All segnetoelectrics in monodomain state show pyroelectric properties, i.e., at similar spontaneous polarization of domains. To produce a heat gauge, ceramics is used based on barium-strontium niobate $Sr_xBa_{1-x}Nb_2O_6$, that of lithium $LiNbO_3$ and triglycin sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ of lithium tantalate $LiTaO_3$, etc. Introduction of lanthanum oxide into ceramics helps to approach Curie temperature of the sensitive to heat material to the room one and, consequently, to achieve a higher pyroelectric coefficient.

5.4.3. Strengthening of ceramic articles surface layer.

Strengthening of friction surfaces when all other methods of improving material strength are in vain is an urgent problem solved by triboengineering. It rests on the following concepts. Metal contact with inorganic glass melt is accompanied by charge and mass transfer through the material interface. Common character of anionic conductivity exhibited by substances in glassified state [82] is the stem of ceramic concentration polarization in contact with metals in electric field. Ceramic dielectrics polarize mainly following the mechanism of charge carrier injection from metal electrodes. Modification of ceramic physico-chemical structure near electrodes changes its surface layer mechanical properties.

Samples from sitals (inorganic glass-crystalline materials) based on $Li_2O \cdot Al_2O_3 \cdot SiO_2$ were formed by pressing and sintering. The samples were polarized at heating in contact with metal electrodes in a constant electric field. Reference samples were similarly heat treated, but not contacting electrodes.

Table 5.6 shows the strength values of the samples polarized in contact with electrodes of unlike metals. The least strength show the samples contacted the refractory practically not oxidizing under polarization temperature chromium and platinum. Analogous heat treatment of samples in contact with electrodes without field does not practically effect the sitals strength.

Table 5.6. The dependence of electrically polarized sital breaking stress (τ) at its symmetric bending versus electrode material.

Electrode material	Cr	Pt	Cu	Ti	Fe	Al	Ni
τ, MPa	58.7	63.4	72.5	76.8	85.2	85.5	86.1

Polarization regimes: temperature 973 K, field intensity 0.6 kV/cm, time 30 min.

Modification of inorganic glass surface layers by ion-exchange processing in salt melts is known to result in glass strengthening, whereas heterogeneous distribution of charges in the units of crystallizing material structure effects nucleation and glass strength. Change of the sample strength at polarization can be resented as follows: 1) by charge carrier injection from electrodes into the glass phase, heterogeneous distribution of polarized charge across sample thickness and its effect on sital crystallization; 2) by physico-chemical interaction between metal diffusive ions and sital oxides leading to crystalline phase nucleation.

Charge carriers injection from metal into sital and their nonuniform distribution in the samples was proved during TSD current measurements generated at thermal treatment of samples polarized between Pt electrodes. TSD current density reached 80 nA/cm^2 which corresponded to the polarized charge density of up to 10^{-3} C/cm^2. Current in the reference samples fluctuated about zero in the range of ± 3 nA/cm^2.

X-ray spectra analysis of polarized samples (CuK$_\alpha$-radiation) evidence that the sital crystalline structure underwent transformation in the near-electrode regions. Lines corresponding to α-Al_2O_3, hard alloys $Li_2O{\cdot}Al_2O_3$ and $Li_2O{\cdot}Al_2O_3{\cdot}SiO_2$ intensify. Simultaneously, the intensity of the main crystalline peak [83] reduces 2-2.5 times. A considerable content of metals diffused from electrodes into the sample surface layers has been

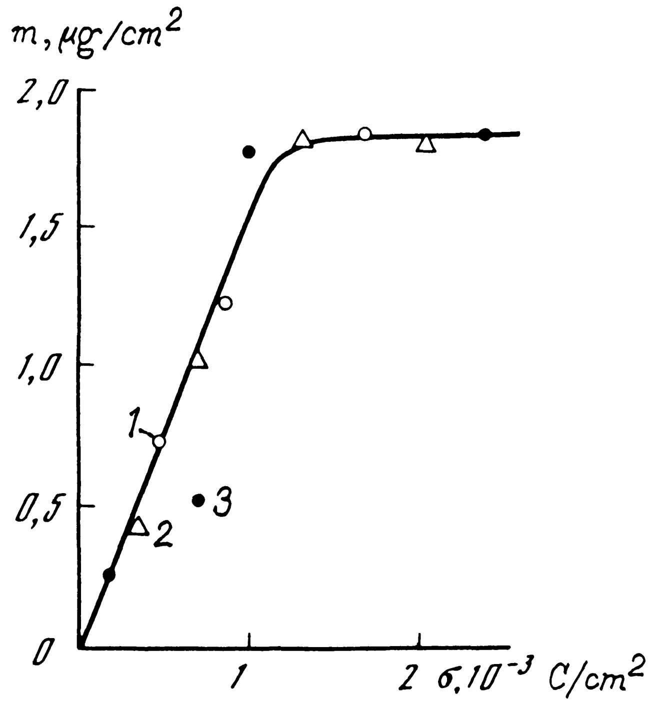

Fig. 5.17. Nickel mass (m) in sital samples as dependent on polarization charge density (σ). Field intensity , kV/cm^2: 1 - 0.6, 2 - 2.0, 3 - 4.0.

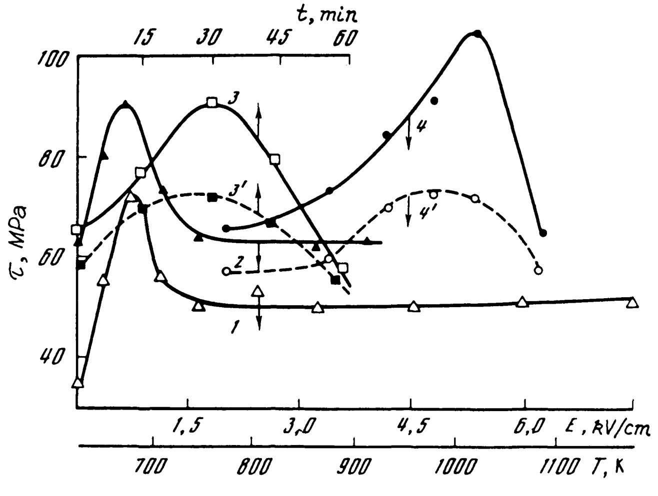

Fig. 5.18. The dependence of breaking tensile stress (τ) of sital samples on electric field intensity E (1, 2), temperature T (4, 4') and its time t (3, 3').

1 - $T = 870$ K, $t = 30$ min; 2 - $T = 970$ K, $t = 30$ min;

3 - $E = 0$, $T = 970$ K; 3' - $E = 0.6$ kV/cm, $T = 970$ K;

4 - $E = 0$, $t = 30$ min; 4' - $E = 0.6$ kV/cm, $t = 30$ min.

recorded photometrically. Fig. 5.17 presents data which relate Ni content and the sample polarization regimes.

X-ray analysis has recorded a new phase of nickel aluminate $NiAl_2O_4$ in the sample near-electrode layers connected nickel electrodes. Its amount grows with increasing polarization time. The phase formation leads to reduction of Li^+ bonding in the sital silicon-oxygen frame and may follow chemical reduction mechanism [84].

Rise in sital strength as a result of polarization is shown in Fig. 5.18. The dependences of breaking stress on temperature (cures 4 and 4') and its duration (3 and 3') reach the maximum. This is the proof to the formation of the greatest number of crystallization centers in sitals under optimum time - temperature regimes. The maximum for polarized samples is much higher as compared to reference ones. Evidently, the crystallization nuclei are additionally formed due to aggregation of diffused from electrodes into sital metal atoms and ions. One of strengthening mechanisms can be compression stress in the surface layer arising from the field-induced metal diffusion into sital crystalline lattice and close microcracks in the faulty surface layer.

Tribological characteristics of the sital-steel system are cited in Table 5.7. Notice that, there exists correlation between properties and sital sample strength (Table 5.6). This supports the opinion that metal inclusions effect sital mechanical properties not as strengthening or lubricating components, but as crystallization nucleation and flaw healing agents in the surface layer.

Table 5.7. Triboengineering characteristics of the polarized steel-sital friction pair as dependent on the polarizing electrode materials

Characteristics	Values of characteristics depending on electrode material						
	Cr	Pt	Cu	Ti	Fe	Al	Ni
Sital wear rate, 10^{11} m/m	186	173	97	102	48	14	1.2
Friction coefficient	0.53	0.49	0.49	0.48	0.39	0.38	0.35

Polarization regimes are described in Table 5.6. Face friction machine with dry sliding at 140 N load and 0.4 m/s sliding velocity.

The technique of strengthening ceramics by electric polarization has been used when manufacturing face seal rings [85]. The rings were formed from a mixture of forsterite ceramics ($2MgO{\cdot}SiO_2$) and glass ceramics ($LiO{\cdot}Al_2O_3{\cdot}SiO_2$) taken in 1:3 proportion by mass. When sintering the blank it was brought into contact with Ni electrodes between which electric field (E = 20-30 V/mm) was generated under 600-800 °C. The ultimate bending strength of the rings constituted 120-140 GPa, density - 2.5 g/cm^3, microhardness - 8-9 GPa. The rings worked in pair with carbon-graphite counterbody of face seals in centrifugal pumps. The liquids were cyclohexanol and acid organic products pumped under 25-40 °C, the shaft rotational speed was 3,000 r.p.m. The service life of seals with polarized rings is more than 10 thousand hours, while without, it is much less.

The considered data show feasibility of improving ceramic tribological characteristics using electric polarization in contact with metals.

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CHAPTER 6

ELECTRETS IN SEALING SYSTEMS.

Electric field action on sealing and separating media contained in seal's gaps forms the basis of hermetizing methods. Electric field influences both wetting and spreading of liquids and effects kinetics of liquid capillary flow in clearances between parts. So, it conditions diffusive permeation through films, coatings and vessel walls, governs processes of lubricant film transfer in the friction zone and contributes much to capturing contaminants by filtering materials. All the mentioned processes can be realized in engineering articles by using electrets. Below a review is given of physico-chemical mechanisms of electret field effect on media permeation through sealing elements of different structures and examples are discussed of electret application in sealing systems.

6.1. ELECTRET FIELD EFFECT ON MEDIUM PERMEATION.

Penetrability of solids, as related to liquid and gaseous media, is assisted by two different by nature and physical origin processes, i.e. diffusive and phase permeation of media.

6.1.1. Diffusive permeation.

Diffusive permeation of medium through solids is characterized by concentration gradient of diffusing in material substances which depends on temperature, pressure, physical field action, physical and chemical properties of both the material and medium. Diffusive permeation of media is mass transfer controlled by diffusion and sorption.

Diffusion is associated with the presence of vacant volume in the solid and can take on several mechanisms: jump of diffusing particles over the vacancies in the solid crystalline structure; particles migration between lattice points; simultaneous cyclic migration of some atoms or molecules of crystal lattice and a particle; metal exchange between neighboring atom or molecule and a particle. For the particle diffusion jump from one potential well to another, the presence of a "vacancy" near the diffusing particle is necessary and a sufficient amount of energy for it to overcome the energy barrier. Diffusion theory based on the mechanism of particle jump over the vacancies was put forward by Frenkel [1]. Time of the particle staying in the point next to the vacancy is

$$\tau = \tau_0 \exp(E/kT)$$

where $\tau_0 \approx 10^{-13}$ s is particle oscillation period, E is energy barrier height, k - gas constant, T is absolute temperature. So, diffusion coefficient will be

$$D = a^2/\tau_0 \exp(-W/kT),$$

where a is lattice constant, W is diffusion activation energy. If diffusion passes in an electret with a space charge, then

$$W = U + E + E_e, \qquad (6\text{-}1)$$

where U is energy of vacancy formation, E_e is energy acquired by the particle in the electret field. For polymer materials $U = \pi\sigma X^2$, where σ is the polymer surface energy, X - vacancy size. It is evident that σ is to a great extent defined by the polymer electret charge value. Depending on E_e sign, diffusion in the electret proceeds either slower or faster as compared to the nonpolarized dielectric.

Polarized charge effects, first of all, sorption of diffusing substance by the electret. This effect mechanism is associated with formation of the double electric layer. Figure 6.1 presents the diagram of electric potential distribution in electrolyte in the vicinity of electret surface. The double electric layer structure near the electret agrees with Stern's theory [2]. A dense ion layer is adsorbed on the electret surface, which polarity is opposite to the electret surface charge sign (Stern's layer). As a consequence, electric potential φ_0 on the electret surface reduces down to φ_δ. An opposite by sign ion layer retained by electrostatic forces adjoins the Stern's layer. Next to it, the so-called Guy layer with different-polarity diffusion-distributed ions is situated.

Sorption of organic solvent vapors by metal-polymer electrets was studied in work [3] using PVB samples made as 400 μm thick fine films. The films were heat-treated (T = 393 K, t = 3 h) in contact with short-circuited copper and aluminum electrodes. The determined by TSD method polarizing charge density on the samples was about 10^{-5} C/cm^2. The polarized and reference (heat-treated in contact with aluminum electrodes) samples were endured in diethylene glycol (DEG) or benzene vapors under T_1 = 303 K and T_2 = 323 K ($T_2 \sim T_g$ of PVB).

It is obvious from Fig. 6.2 that DEG sorption by electrets at T_2 (curve 2) is lower than by reference ones (1). When $T_1 < T_g$, differences in sorption are not so prominent (3 and 4). Analogous results were obtained when exposing the samples in benzene vapors (Table 6.1).

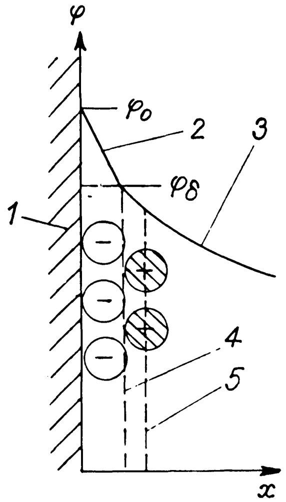

Fig. 6.1. Electric potential distribution near electret surface:
1 - electret, 2 - Stern's layer, 3 - diffusion layer, 4 and 5 - inner (IHP) and outer (OHP) Helmoltz's planes.

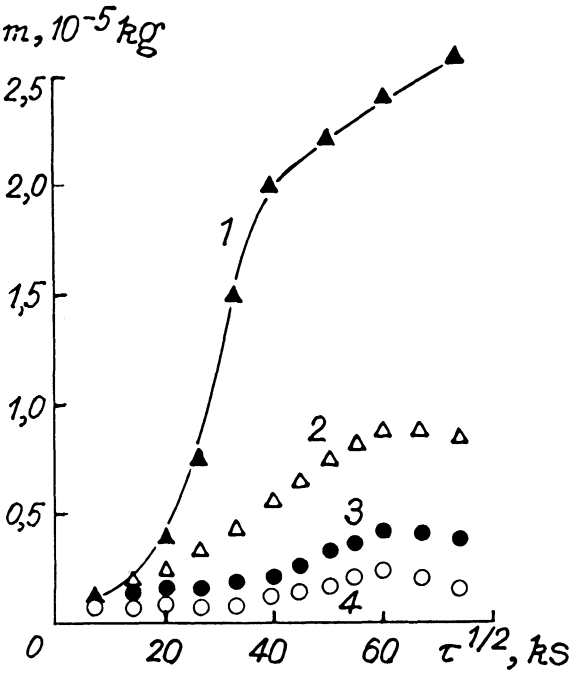

Fig. 6.2. Mass (m) of PVB samples versus time (t) of endurence in DEG vapors. Temperature, K: 1, 2 - 323, 3, 4 - 303. Samples: 1, 3 - reference, 2, 4 - electret ones.

It is known that at T < T_g the reduction of macromolecular segmental mobility bounds sorption due to lower velocity of conformation transformations. This limitation aligns differences in solvent vapor sorption by the electret and nonelectret films (curves 3 and 4 in Fig. 6.2). With the formed on the electret surface layer of oriented dipoles similar to that shown in Fig. 6.1, an equilibrium concentration of the solvent establishes in the sample. Ordering of the film permolecular structure in the process of electric polarization causes the reduction in both polar (DEG) and nonpolar (benzene dipolar moment equals to zero) solvents sorption. Apparently, nonpolar benzene molecules temporarily acquire dipolar moment in the electret field and interact with it by the mechanism described above. Difference in DEG and benzene diffusion is because DEG is a stronger PVB solvent.

Water absorption has been studied on PA film samples using the above mentioned method. Polarized and reference samples were thermostated in water under 375 K and periodically weighed. Water diffusion in reference samples proceeds more intensely in contrast to electret ones (Fig. 6.3). Their diffusion coefficients differ by more than two orders. For electrets it is $1.69 \cdot 10^{-14}$ and for reference - $4.75 \cdot 10^{-12}$ m^2/s.

The cited data point to the polarized charge considerable influence on both liquid and gaseous media sorption and diffusion in electrets.

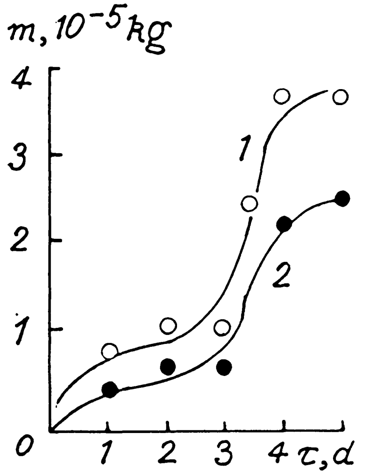

Fig. 6.3. Kinetics of water absorption by PA samples: 1 - reference, 2 - electret ones.

6.1.2. Phase permeation.

Permeation of media phase into solids is characterized by the penetrating substance transfer not as separate ions, atoms or molecules but as an amount which can form a phase, i.e. as a homogeneous by its chemical composition and physical properties aggregate of the penetrating substance atoms or molecules which is limited by the interface with the solid. Liquid phase permeation through solids is related to the field of capillary phenomena. The penetrating liquid phase in pores, microcracks or other microcavities of the solid can be formed following the capillary condensation mechanism of vapors.

Phase permeability is identified by abrupt acceleration of media transfer, for e.g., when the latter are forced into the solid vapors under excess pressure at solid deformation. Diffusion is considered to be a structural-sensitive process, whereas the transition from diffusion to phase transfer is an evidence of the jerky character of the solid microstructure variation. In polymer materials it comes about when microvoids are formed due to macromolecular breakage in noncrystalline sites of permolecular structure.

Table 6.1. Increase of mass (*m*) of PVB samples exposed to benzene vapors under 323 K as dependent on time (*t*)

t, 10^3 s	m, 10^{-2} g, for samples	
	reference	electret
4.5	0.55	0
6.4	1.10	0
7.3	1.30	0.01
10.07	1.50	0.05
13.9	1.66	0.14
15.2	1.73	0.24

Phase permeation of substances through electrets is accompanied by the polarized charge dissipation. Fig. 6.4 visualizes change in the PPl electret surface charge density at tension [4]. The charge formed in the high-intensity outer electric field (curve 1) varies when passing the minimum. The descending segment of curve 1 corresponds to elastic deformation of the film which is characterized by a proportionality portion on curve 2. Further charge increase is caused by the sample plastic deformation corresponding to dependence 2 deviation from the straight line. Under such mechanical stresses macromolecules break off and microcracks form in the sample, thus assisting its phase permeation. This is accompanied by emission and electron capturing by the polymer structural traps leading to increased surface charge density [5]. Released polarized charge carriers are absorbed in conditions of phase flow by the penetrating substance particles. This may result in ionization which, no doubt, will decelerate permeation.

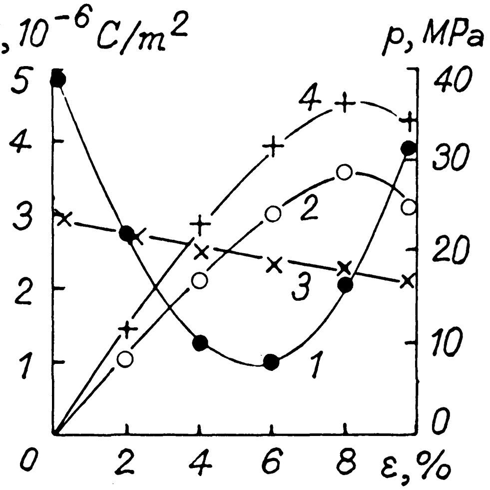

Fig. 6.4. The dependence of surface charge density σ (1, 3) and tensile stress ρ (2, 4) on PPl film relative deformation ε. 1, 2 - films polarized in outer electric field; 3, 4 - thermally treated in contact with short-circuited Cu and Al plates.

The polarized charge of metal-polymer electrets changes but slightly at deformation. Negligible reduction of surface charge density (curve 3) within the whole deformation range till the sample breakage (curve 4) can be attributed to its increasing area due to extension. Polarized charge of metal-polymer samples is induced by carrier injection from electrodes and is localized in the surface layers. Polarization is accompanied by metal transfer from electrodes to the polymer. Metal aggregations are concentrated mainly in voids and structural flaw of the sample surface layer that provides for its strengthening [6]. The zone with the most probable microfracture is located between surface layers of the samples. Charge carriers formed in this zone by structural elements microfracture do not emerge on the surface, so far the polarized charge density does not practically change.

Electret charge formation is accompanied, in a number of cases, by orientation of the dielectric structural elements in the polarizing field. This effects the dielectric strength and diffusion characteristics, i.e., parameters defining its phase penetrability.

Phase penetrability assumes feasible aggregation of polar molecules belonging to the penetrating liquid. Electret charge may either assist the formation of aggregates by inducing dipolar moment in molecules or destroy aggregates in case cohesive bonds between molecules in an aggregate are weaker than electrostatic forces of attraction between a molecule and micropore surface. Phase permeation assists diffusion of substances having volume, linear or chain molecules. The stepwise translational motion of such molecules over microvoids in a solid is hindered by electrostatic interaction of pore walls in the electret field.

Despite the conceptual plainness of how the polarization charge effects medium transfer in electrets, the methods estimating electret permeability are unsuitable for engineering practice. The known methods for forecasting serviceability of polymer materials used to ensure article tightness does not take into account the availability in materials. This field of physico-chemical mechanics of dielectrics is found at the interface between several scientific areas and its progress can be attained by joint efforts of different specialists in physics, liquid and gas mechanics, materials science and technology.

6.2. ELECTRET SEALS.

Electret units of seals are a compact and technologically simple means of regulating sealing parameters. Their high efficiency in contact seals can be explained by the following. Firstly, deformation and strength characteristics of sealants can be regulated by electric polarization methods. Secondly, the polarized charge influences liquid spreading over the electret and, consequently, the value of capillary leak. Thirdly, the promising prospects are opened for applying electrorheological effect in seals that can spur the development of principally new hermetizing means.

6.2.1. Deformation model.

A sealant deformation model for contact seals looks like a solid with deformation gradient and strength characteristics corresponding to increasing elasticity modulus and reducing deformation directed from the contact surface with counterbody. The model development is urgent because not a single engineering material can on a par successfully fill gaps between contacting parts, equalize pressure difference in sealing media and withstand other factors emerging during operation. Usually, different materials are combined in a sealant so that its deformation characteristics depend on the distance to contact plane.

The simplest model of a sealant is a three-layer element displaying the properties of, correspondingly, a liquid, visco-elastic medium and a solid. Using the notions on three deformation constituents of visco-elastic media, such model deformation can be described by the rheological equation of state

$$\varepsilon(t) = \varepsilon_1+\varepsilon_2+\varepsilon_3$$

where $\varepsilon_1 = pt/\eta$ is the Newtonian liquid deformation, p - stress, t - time, η - viscosity; $\varepsilon_2 = pJ\varphi(t)$ is decelerated elastic deformation, $J = 1/G$ is compliance, G - modulus of elasticity at shear, $\varphi(t)$ is decelerated elasticity function; $\varepsilon_3 = p/E$ - Hook's elastic deformation, E - Young's modulus.

The parameters of the model presented as a solid with a layer of elastic medium (h) and that of a liquid (H) contact with a rough counterface are shown in Fig. 6.5. When compressed at a constant stress σ the system deforms in three stages which correspond to model elements. The analysis of factors influencing the system gap value proves that in case the parameters h and H are commensurable with the counterbody microroughness height H_{max}, the gap can be fully filled with the sealant, i.e., absolute tightness of the system can be reached. In contrast to elastic or plastic sealants, this model is more efficient in energy parameters as far as absolute tightness is attained at a less p value.

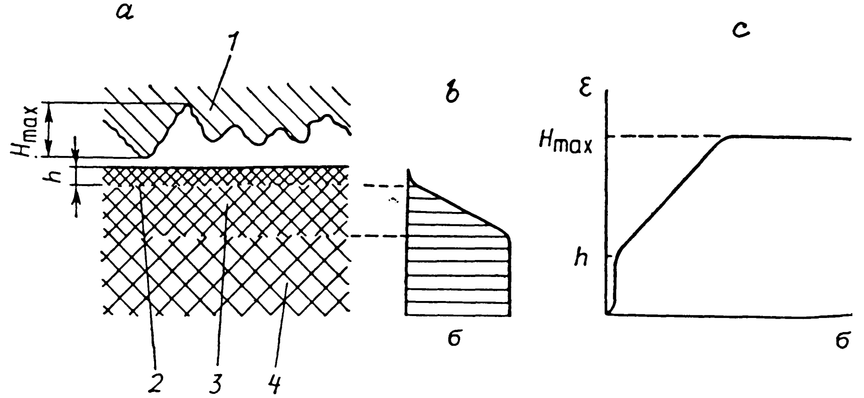

Fig. 6.5. Structure (a), pressure distribution curve (b) and deformation scheme (c) of a three-layered seal model by a constant voltage. 1 - counterbody, 2-4 - seal sections displaying liquid properties, elastic medium and absolutely solid body, correspondingly.

The model with electrets exhibits the following peculiarities. Electric polarization of dielectric materials is always accompanied by rearrangement of their physico-chemical structure and, consequently, change in deformation and strength characteristics. This is a means to approximate the sealant to an ideal model. The materials based on a polymer matrix with a pore system filled with a liquid have been developed recently to realize the model [7]. Nonuniform pore distribution in the material creates the gradient of deformation and strength characteristics which may be additionally regulated by the polymer matrix electric polarization. The degree of polarization and, consequently, that of the matrix deformation can also be regulated by using liquids with different dielectric properties.

The matrix may be filled with an electrorheological liquid. In this case, the liquid viscosity gradient will depend on the polarized charge distribution in the matrix. Such sealant structure as well as schemes of polarized charge distribution in it and electrorheological liquid viscosity are presented in Fig. 6.6. The polarized charge is formed in the polymer matrix so that its field intensity gradient across the pore layer thickness is $E_1 < E_2$. Accordingly, viscosity of electrorheological liquid filling the pores is also distributed unevenly, $\eta_1 < \eta_2$. The described sealant shows increased viscous-deformation characteristics directed from the contact surface deep into the matrix.

Electret charge in a multilayered sealant interacts with a separating or hermetizing media and can be formed in any possessing dielectric properties layer.

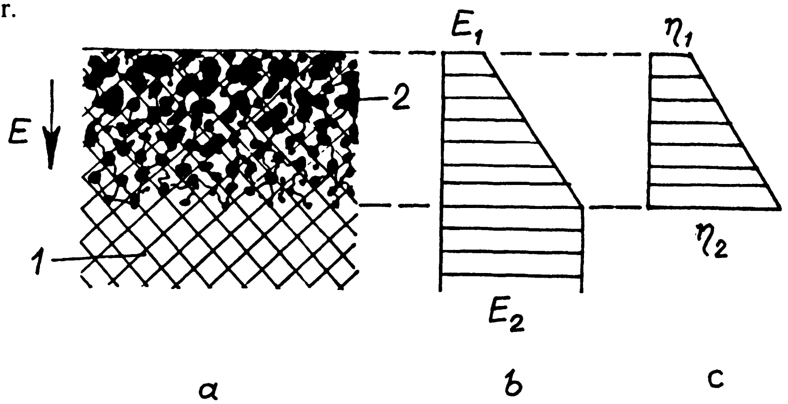

Fig. 6.6. Structure of a polymer seal containing an electrorheological liquid (a) and schemes of polarizing charge field intensity distribution in it (b) and liquid viscosity (c). 1 - polymer matrix, 2 - pores filled with electrorheological liquid.

6.2.2. Wetting and spreading.

Liquid wetting and spreading largely determining leakage through seals can be controlled using *electro-capillary phenomena*, i.e., change of surface tension at the solid-liquid interface due to electric potential difference at the interface. The mechanism of such phenomena was first studied by A.N. Frumkin on the metal electrode-electrolyte systems. Equation (3.1) of electro-capillarity describes surface tension at the electrode-electrolyte interface.

In the previous chapter 4.1.3. study results are quoted of liquid spreading over electret surfaces. Film polarization and electret charge increase provide for lowered liquid spread initial velocity (see Table 4.2) and reduced actual contact spot area between the film and drop.

Under all other conditions being equal, the electret film wetting is smaller than that of nonpolarized. This is experimentally supported by data in

Tables 6.2 and Fig. 6.7. The dependence in Fig. 6.7 is satisfactorily described by equation:

$$\cos \Theta = \cos \Theta_0 - 1.4 \cdot 10^4 \sigma - 2 \cdot 10^{-9} \sigma,$$

where Θ and Θ_0 are equilibrium edge wetting angles by glycerine for, correspondingly, electret and nonpolarized films; σ - surface charge density of the film.

Table 6.2. Variation of edge wetting angles Θ of PPl films by liquids versus time *t*.

t, 10^3 s	Cos Θ for liquids on films with different σ (10^{-6} C/m^2)				
	DEG		Glycerin		
	$\sigma = 0$	4.17	0	5.04	$\sigma = 7.24$
0.5	0.699	0.533	0.380	0.211	0.096
1.0	0.702	0.548	0.398	0.243	0.113
2.0	0.704	0.562	0.415	0.275	0.130
3.0	0.705	0.571	0.425	0.294	0.139
4.0	0.706	0.577	0.432	0.307	0.146
4.5	0.706	0.579	0.435	0.313	0.149

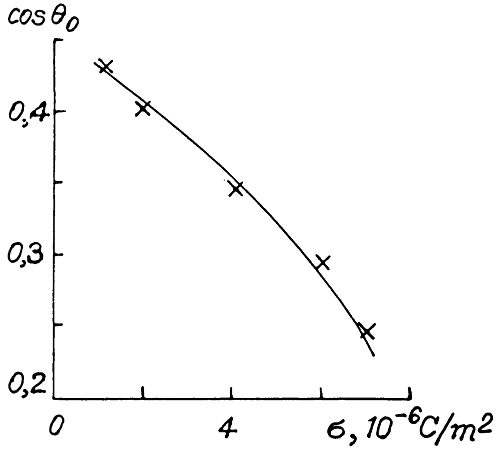

Fig. 6.7. The dependence of an equilibrium edge angle cosine of glycerin drop on surface charge density of the pentaplast film

To describe experimental data a model has been used according to which drop spreading starts from formation of a circular wedge-like in its cross-section liquid layer with a low hydrodynamic resistance. If to neglect the effect of gravity force, being much less than the surface tension forces, then the drop shape can be approximated by a spherical segment having a circular V-shaped collar (Fig. 6.8). In case the drop volume and the liquid viscosity are constant during spreading and diffusion or chemical interaction between the liquid and film do not take place, so change of the drop radius R relative time t can be expressed by equation [8]:

$$dt = \frac{\eta}{\Delta W}\left(\frac{\mathrm{R}\Theta}{\sin\Theta}\right)^2 \frac{ctg\Theta}{\xi} r' dr' \qquad (6\text{-}2)$$

where η is liquid viscosity, $\Delta W = W_{12}$ [cos Θ - cos Θ (t)] is the reduction of free surface energy of the film-drop system at wetting, W_{12} - surface energy at the liquid-air interface, Θ and Θ (t) - equilibrium and dynamic edge angles, ξ - wedge-like liquid layer thickness on the drop edge; $r' = r(t)/R$ - dimensionless current radius of the drop foot radius at a moment t.

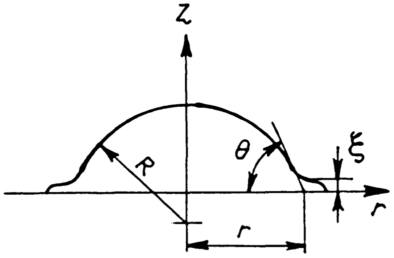

Fig. 6.8. Scheme of a viscous liquid spreading over a solid.

By integrating Eq. (6-2) using a numerical method of computing, the dependences have been obtained of increasing with time drop foot radius LΔR at different polarized charge densities of the film. The comparison of the calculated curves with experimental results (see Fig. 4.5) showes that the used model adequately describes the viscous liquid drop spreading over the polymer electret surface at the initial period.

6.2.3. Examples of designs.

Figure 6.9 shows the scheme of a setup to investigate capillary liquid flow in contact gaps between steel sample 7 and polymer electret coating 6 on substrate 4. The liquid flows over into the studied connector from a glass tube 1 and its level in the tube lowers by a value Δh. Capillary pressure of the liquid penetrated into the studied joint and that of liquid column of height Δh in tube 1 are equal. Proceeding from the above, the equation has been derived [7]:

$$\Delta h = \frac{2}{dS\rho g} \cdot \frac{W - \sigma_{12}}{\cos\Theta},$$

where S is tube 1 cross-section area, ρ - liquid density, g - free fall acceleration, W - work to be spent to separate liquid from the coating, σ_{12} - surface tension at liquid-gas interface, Θ - equilibrium edge wetting angle.

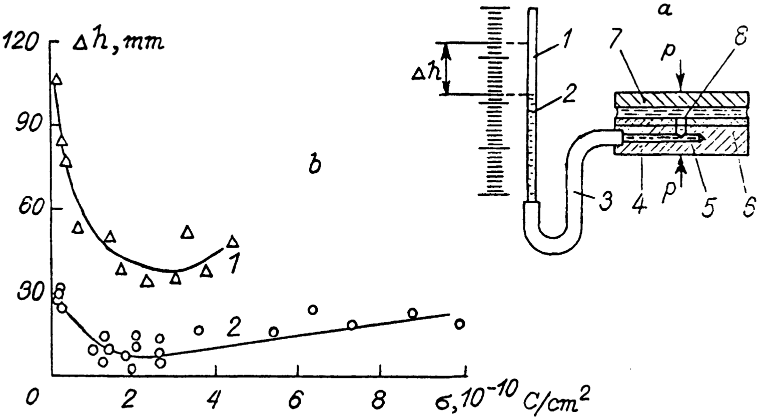

Fig. 6.9. Diagram (a) of a varying liquid capillary permeation into gap between solids and the dependence (b) of liquid level variation Δh in a capillary upon surface charge density σ of samples. a: 1 - glass tube, 2 - water, 3 - connector, 4 - substrate, 5 - duct, 6 - coating, 7 - sample, 8 - puncture in coating; b: 1 - PMMA, 2 - PTFCE.

Nonmonotonous character of curves 1 and 2 in Fig. 6.9 is the result of W and cos Θ reduction velocities superimposed at electret charge increase. The reduction of W dominates on the initial descending portion of the curves. Simultaneously, physical adsorption of liquid molecules increases leading to formation of the double electric layer on the electret surface. When the layer is fully formed, W values stabilize. This corresponds to the minimum of $\Delta h = f(\sigma)$ relation. The ascending portion of the curves is the result of cos Θ reduction at a constant W. The location of curves 1 and 2 corresponds to difference in parameters of polar PMMA and hydrophobic PTFCE wetting by water.

Electrorheological liquids are used in seals as a separating medium for gases.

Figure 6.6. shows the scheme of a contact seal sealant containing electrorheological liquid. Such a seal element can realize the advantages of

both liquid and solid hermetizing materials providing for durable operation under the varying hermetizing media pressure from vacuum to positive one.

Figure 6.10 gives an example of a noncontact helical seal design to seal hermetically the rotating shaft entry into the closed volume. The shaft has a certain profile threading. The body and shaft are insulated and connected to terminals from a constant electric voltage source. The clearance between the body and helical part of the shaft is filled with an electrorheological liquid which is influenced by friction forces at shaft rotation. They create a predominantly laminar liquid flow which head balances pressure difference in the seal. Viscosity and head of electrorheological liquid flow can be regulated by varying voltage between the body and shaft.

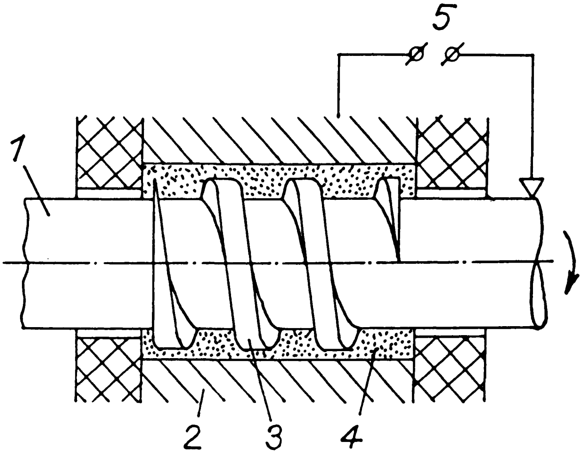

Fig. 6.10. Shaft sealing: 1 - shaft, 2 - body, 3 - helical thread, 4 - electrorheological liquid, 5 - terminals of constant voltage source.

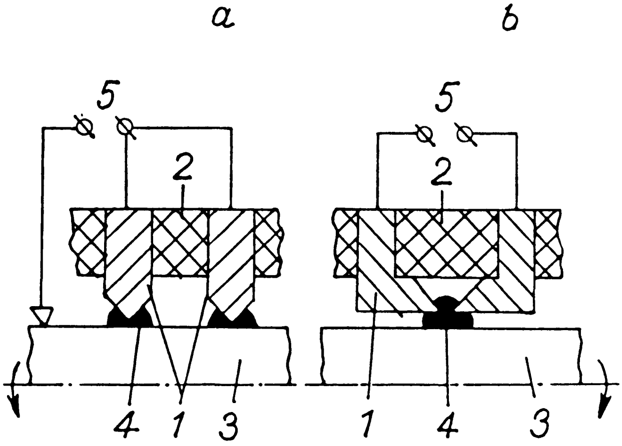

Fig. 6.11. Electro-liquid sealing of the shaft: 1 - electrodes, 2 - body, 3 - shaft, 4 - electrorheological liquid, 5 - terminals of constant voltage source.

The schemes of the rotating shaft seals are shown in Fig. 6.11. A pair of sharp circular electrodes are hermetically sealed in the body. The shaft is fixed in the bearings (not shown) to eliminate its contact with electrodes. Cirdular layers of electrorheological liquid cover the gaps between electrodes and the shaft, thus forming sealing steps. Constant electric voltage is fed to the electrode and shaft (a) or to the pair of electrodes (b). As a result, viscosity of electrorheological liquid increases, due to which one stage can withstand pressure difference up to 30 kPa. Under high differences the seal "breakdown" occurs. When pressure difference reduces, the seal tightness recovers, since there are no liquid losses at "breakdown".

Use of electrorheological liquids in stuffing, slot and dynamic seals, check valves, etc. imparts unique properties to such structures.

In immovable or operating with stops contact seals *obliteration* can take place which is the reduction (healing) of duct flow section in the process of liquid passing. Its main cause is physical absorption of media or additive molecules contained in liquids. Electrostatic interaction between electret and medium molecules with dipolar moment can hamper or speed up obliteration. It has been found out that negative charge on inner surfaces of artificial vascular, mitral valve walls and heart systems prevents blood clot formation, hinders blood coagulation [9].

6.3. HERMETIC COATINGS.

Hermetic sealing of machine part junctions by polymer coatings is widely used in machine-building. Polymer coatings are applied as an individual sealing element or serve as a means to improve contact seal tightness [7]. The present chapter cites examples of applying hermetizing electret coatings on contact surfaces of conjugated parts.

6.3.1. Tightness and toughness.

Hermetizing capacity of polymer coatings and contact toughness of involved junctions is determined by deformability and adhesive interaction of conjugated elements, as well as by gap size and distribution across the contact geometrical area. Shear stresses emerging during mounting contribute to redistribution of polymer material in microgaps, thus improving considerably the joint tightness and toughness.

As experiments have shown, growth of the actual contact area at loading by removing stresses proceeds due to increasing amount of contact spots. The initial loading is characterized by fast approach of the surfaces accompanied by increasing toughness of the joint. With the growing quantity of contacting microasperities the approach decelerates, while toughness approximates its constant value depending mainly on physico-mechanical properties of the polymer layer. This goes together with exponential growth of tightness.

Sealing of joints using coatings from commonly formed powder polymers (for e.g., electrostatically formed) displaying a considerable waviness has a number of peculiarities. Normal compression stresses do not result in the joint sealing till they reach close to maximum toughness typical of joints containing polymer layers (j = 250-300 MPa/mm). At the same time, tangent shear stresses facilitate much the joint gap filling with polymer material. This helps to successfully use polymer coatings to seal hermetically thread joints in various fields of engineering showing high degree of tightness (80 MPa - water, 50 MPa - air) and toughness.

However, toughness of joints containing polymer layers is determined by not only steric limitations of deformation transfer in the layer-supporting part contact, but by adhesive interaction of the joint elements too. The effect of adhesive bonds is most prominent at about 20-80 um coating thickness that provides for the maximum joint toughness. So far, it is important to develop production methods for sealing coatings which improve joint toughness and show high hermetic capacity. This aim is attained by creating the gradient of mechanical properties reinforcing across thickness in direction from the coating to the substrate.

In work toughness as well as tightness of joints containing a thermoplastic sealing layer have been studied as dependent on the layer physico-mechanical properties, gradient of spatial-mechanical properties across layer thickness and electrochemical interaction between the layer components and joint elements.

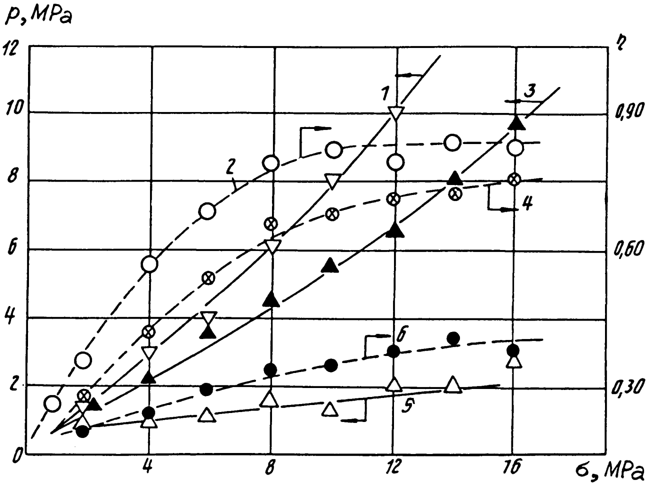

Fig. 6.12. The dependence of maximum permissible water pressure (p, 1, 3, 5) and actual contact spot (η, 2, 4, 6) on normal compressive stress (σ) in the joint between glass prism and a steel sample with PE-based coating: 1, 2 - thermally treated in mineral oil; 3, 4 - containing nonferrous metal oxides; 5, 6 - nonmodified.

Figure 6.12 shows the dependences of ultimate water pressure (P_{max}, 1, 3, 5) and actual contact area (η, 2, 4, 6) in a joint between glass prism and steel sample with a hermetical coating upon compression stress (σ). Ultimate pressure was defined as a limiting pressure of water forced into the joint center without leakage. Graphs 5 and 6 correspond to samples with a 70-80 μm thick polyethylene coating applied electrostatically, followed by melting. Curves 3 and 4 correspond to the coatings filled with non-ferrous metal oxides [10] and calibrated to roughness (microasperity height) R_a = 0.4-0.8 μm. Coatings described by graphs 1 and 2 were thermally treated in mineral oil instead of calibration.

As it has already been mentioned in ch. 4.2, coatings containing electrochemically active fillers (non-ferrous metal oxides) display electret properties and elevated adhesion. That's why they are more tight and tough (curves 3, 4) as compared to nonfilled coatings (curves 5, 6).

Still higher properties show coatings thermally treated in mineral oil or any other liquid-phase plasticizer. As a result of the melted and still hot coatings endurance in the liquid phase, diffusive permeation of the mineral oil into PE occurs leading to gradient formation of colloidal oil solution concentration in PE. When the coating is cooled, the colloidal solution transforms into a gel characterized by the presence of polymer matrix with distributed in its pores dispersed liquid. So, a system is formed possessing the gradient of pore distribution in the coating and conditioning the gradient of deformation and strength characteristics across the coating thickness. The adjoining metal substrate polymer layer does not experience liquid phase action and so, the coating-substrate adhesive joint stays intact.

Coatings with a system of pores narrowing in direction to the substrate show a higher hermetic properties, i.e., under similar compression stresses a larger actual contact area is revealed for them and a higher p (curves 1, 2). Such structure of the coating satisfies best of all the demands to the mentioned above ideal hermetic sealing.

Polymer materials as hermetic coatings and interlayers impose additional requirements. Aside from providing the needed toughness for the joint, the hermetizing coatings must be resistant to hermetizing agents. In a number of cases the agents are aggressive and the coatings must prevent for a prolonged time metal joints from corrosion (for e.g., flange and coupling joints).

As it has been mentioned in ch. 4.2, an elevated protective capacity show coatings containing non-ferrous metal oxides [10] or electret fillers [11] in their composition. Due to electrochemical interaction between the coating components and those with the substrate, such coatings exhibit elevated adhesion and inhibit corrosion in contact with metals. A similar protective ability display coatings having a pore system in the surface layer in case the solution of corrosion inhibitor in plasticizer is used as a dispersion medium.

6.3.2. Hermetizing methods.

The known methods of threaded metal joint hermetical sealing include application of a polymer material onto the thread surface and the joint screwing followed by the sealing layer solidification. High tightness and stability of such joints is owing to polymer composites with specific fillers in their composition. Often it is necessary to seal joints of unlike metals. As for e.g., drill pipes and tool joints are made of different steel qualities. In this case, high adhesion and hermetizing capacity should be attained by transforming the polymer layer into electret state.

A method has been proposed to produce a threaded joint between steel parts [12] by making an electric contact between the conjugated parts through a certain optimum resistance. The positive result is reached because of electric polarization of the polymer layer during its thermal treatment between unlike metals (see ch. 1.2.5). As experiments showed, electrode potential difference of different quality steels relative to PE melt reached 0.4 V and polarization current density $1.8 \cdot 10^{-4}$ A/m^2.

The highest polarized charge density is achieved at an optimum correlation between the outer circuit resistance, that of the polymer layer and time of heat treatment. Examination of the mentioned factors effect on the polymer-steel adhesive joint strength has shown the following: PE adhesion to steel increases by 40-50 % when outer resistance R = (0.005-0.04)R_0 (where R_0 is the polymer layer resistance) and endurance time equals 10-20 min under PE melting temperature. Thus, the hermetic electret coating is obtained without a substantial change in thread joint sealing technique. The advantage is also utilization of heat generated during the preheated part cooling and attainment of increased strength and tightness of the joint practically without additional energy, material and labor consumption.

Aside from their main purpose to hermetically seal joints, polymer sealing coatings and layers can bear an additional function of *contact pressure monitoring*. Sealing effect in immovable joints is known to be reached when the so-called minimum contact pressure of conjugated parts is created by filling all the seal microasperities and flaw. The continuous contact pressure control helps to avoid depressurization leading sometimes to dangerous and even catastrophic aftereffects (depressurization of poisonous, fire- and explosion-hazardous and corrosion-active media).

Pressure monitoring is commonly exercised by tensometers or some other sensitive units which electric resistance is varying under pressure action. Modern methods for measuring electric conductance of dielectrics involve high-voltage outer electric sources implying a special equipment and protective means. This hampers sensitive element production from thermoplastic polymers, being widely applied in sealing technique as layings or other sealing elements. The effect used for TSC generation in M1-P-M2 systems (see ch. 1.2.5) made it possible to estimate the polymer layer conductivity in terms of the measured current values with account for electrode potential difference (ΔU) and polymer layer thickness [24, 25].

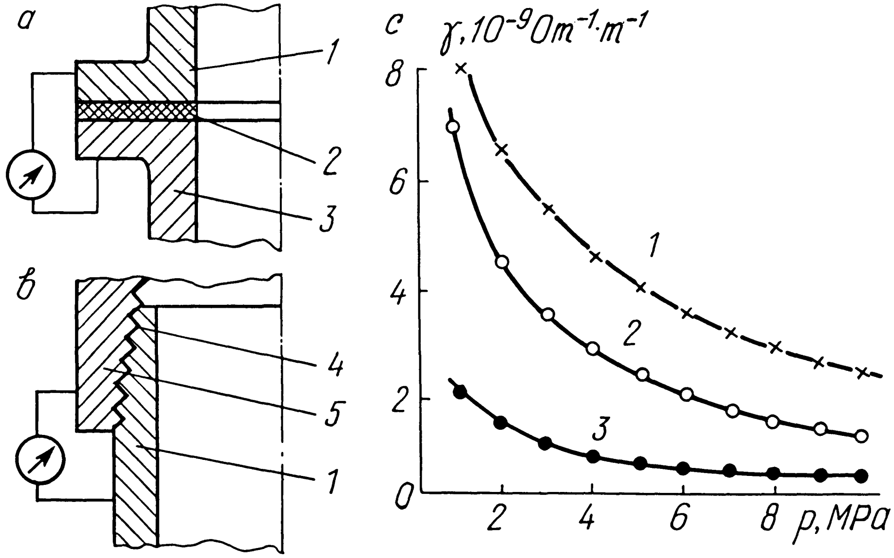

Fig. 6.13. Tensometer [15]: *a* and *b* are examples of design modifications (1 and 3 - nozzles, 2 - laying, 4 - coating, 5 - coupling); *c* - dependence of PVB coating conductivity on compressive stress under temperatures (K): 1 - 355, 2 - 335, 3 - 305.

As is shown in Fig. 6.13c, PVB electric conductivity depends on the applied to the system outer load and temperature at which measurements are conducted. Analogous data were obtained for a number of other thermoplasts (capron, PE, pentaplast). In case the varying factor in stationary conditions is the compressive force on the polymer layer, then a counter problem can be solved, i.e., the compression stress value can be determined by the change in conductivity. This principle is utilized in tensometer design [15] consisting of a polymer sensitive element and contacting electrodes of unlike metals. Several tensometer modifications are available (fig. 6.13) incorporating a polymer laying (a, flange joint) and a coating (b, threaded joint), as well as parts bearing the load (1 and 3) included into the studied joints. Calibration curves (c) help to determine contact pressure values corresponding to the joint polymer element conductivity under a stationary heat regime of operation.

Notice that, the tensometer sensitive element and electrode functions are performed by the parts of the joint to be sealed, i.e., by sealing layings (or coatings) and the joint metal parts. Often, no changes in the seal design are needed for such mating. Pressure can be remotely controlled and even automated.

6.3.3. Industrial applications.

Electret coatings from polymer materials have undergone production tests for sealing threaded joints of oil pipes. Rigid requirements to such joint tightness are due to risk of the running into the borehole string depressurization. Because of the increasing depth of boreholes and the corresponding growth of stratum pressure, the problem of ensuring pipe joint tightness becomes still more urgent.

Stand tests of casing pipe joints sealed by FO-filled PE coatings [10] were carried out in the State Design and Research Institute of Oil Industry (Kiev, Ukraine) and Russian Research Institute of Gas Industry (Moscow, Russia). Two 600 mm long stub tubes from 146 mm in diameter and 11 mm thick casing pipes screwed into a sleeve were used as test samples. Test results are shown in Table 6.3.

Table 6.3. Tightness of casing pipe joints.

Group of steel strength	Number of tested samples	Pressure, MPa		Test duration	Test results
		Standard	Actual		
Hydraulic tests					
D	16	25	60-65	1 h	Joints are hermetic
K	2	60	80	17 h	-"-
K	8	60	70	6 days	-"-
Air tests					
D	4	-	52	22 days	One sample leaks gas at 61 cycle

It is obvious, that the coatings guarantee the joint tightness under pressures surpassing much the State Standard requirements. Tightness under 60-80 MPa pressure, which is close to the pipe material yield point, is the evidence of the casing string full-strength.

On the base of stand tests a batch of casing pipes with a FO-filled PE coating has been prepared to be run in a borehole. The string of casing was run into the borehole, pressure tested and is operating successfully till now. To adopt the suggested technique in industry, a semiautomatic setup has been designed and manufactured to coat threaded parts of pipes.

The experience in *drilling string* operation shows that the threaded joint of both the pipe and tool joint is the weakest point of the string. Washout, local corrosion and corrosion-fatigue fracture are most probable in these places. In order to increase the joint durability, a method has been proposed to seal casing strings by polymer layings bonded adhesively with conjugated parts. Owing to different quality of steels used for pipes and tool joints, the polymer layings acquire a polarized charge when the junctions are screwed together. The suggested sealing technique enters well the process of the tool joint "hot" roll on and increases almost 2 times the joint durability as compared to batch produced ones. This technique is utilized commercially at Belarussian and Ukrainian ciland geological enterprises. Boreholes which utilize the mentioned method have raised tool joint life 2-3 times.

6.4. FILTERING MATERIALS.

This subject is discussed in this chapter because filters are specific hermetic systems in which filtering element captures dispersed components (solid particles, liquid drops) of heterogeneous media by forcing it through a continuous phase (gas or liquid).

Filters protect clearances of part junctions and working cavities of machines from abrasives, contaminants and other foreign particles. They help to most efficiently realize the resource imparted to machine designs, to rise their serviceability and reliability. Being used in engineering for more than 50 years, electret filter designs are constantly perfected.

6.4.1. Melt-blowing technique.

A great variety of electret filtering materials (FM) is produced using melt-blowing technique. It consists in spraying the extruded polymer melt by a flow of compressed gas. The technique was created in the 50-s in USA to produce microfiber adsorbent catching radioactive particles in the upper atmospheric layers which evidence about nuclear weapon tests [16]. With the emergence of other means for detecting nuclear tests, interest to it went down. Nevertheless, these works were renewed in Exxon Research which modified and patented the production technique for melt-blown articles [17] and started its commercialization. Beginning from 70-s an original direction of this technique is being developed in CIS.

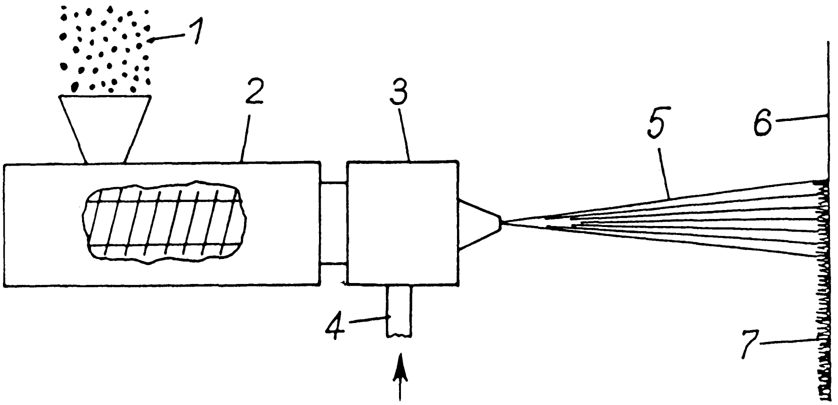

Fig. 6.14. Flow diagram of manufacturing fibrous polymer materials by melt-blowing: 1 - polymer granules, 2 - worm extruder, 3 - spraying head, 4 - compressed gas connection, 5 - gas-polymer flow, 6 - forming substrate, 7 - FM sheet.

Flow diagram of the melt-blowing technique for FM production is shown in Fig. 6.14. Polymer granules 1 are processed using worm extruder 2. Polymer melt is squeezed as fibers through heated to 610-625 K die of extrusion head 3. The latter has a device to spray the melt in the viscous-flow state by compressed air. Air fed into the head through nozzle 4 flows near the die holes and catches up fibers, disperses them and extends. Air-polymer flow 5 is supplied onto the moving forming substrate 6. Porous mass 7 deposited on the substrate consists from spherical in cross-section fibers mechanically bonded or fused in contact points. The mass may be calendered between heated rolls. Different variants of fiber laying on the substrate and FM catching have been suggested by using original auxiliary setups.

Melt-blowing technique is in its essence the electret technology, since the produced by it polymer fibrous materials acquire space charge and preserve electric polarization for a long period. This is proved by the following facts.

HDPE-based samples were produced on a device which scheme is presented in Fig. 6.14. Fiber diameter was 20-30 μm and sample porosity ~ 50 %. TSC currents of the samples were recorded at a 5 K/min heating rate immediately upon production and in the process of storage under 45-60 % relative humidity and T = 20 ± 2 °C. The efficient surface charge density σ_{ef} of the samples was measured by a noncontact compensation method. Garlick-Gibson's method was used to estimate activation energy W of charge carrier release, trapping section σ and life time τ of charge carriers, as well as charge attempt-to-escape frequency ν from the trapping centers.

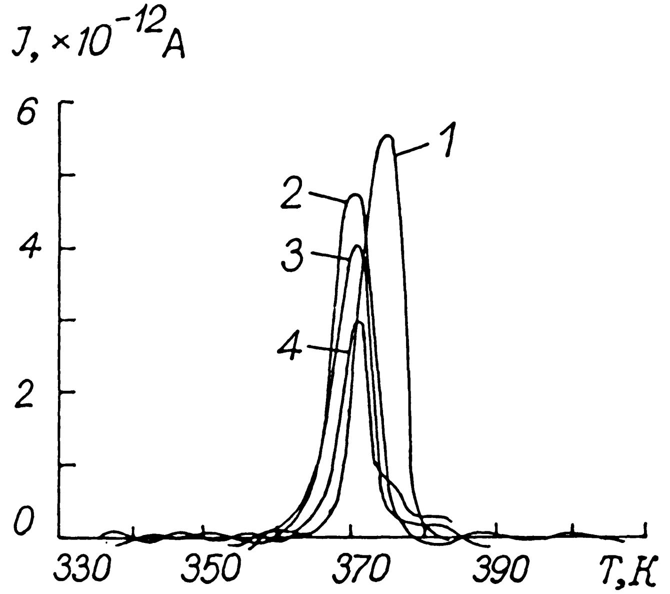

Fig. 6.15. TSC spectrum of HDPE-based fibrous materials taken after different periods upon sample production: 1 - in a day, 2-4 - upon 30, 60 and 160 days.

A characteristic TSC peak was observed for all thermally depolarized samples (Fig. 6.15) which did not appear at repeated depolarization. It corresponds to negative charge relaxation and has a maximum at 375 ± 5 K. Upon 160 days of storage in a humid atmosphere the peak intensity reduced by 40 % for all samples. The presence of only one peak in TSC spectrum suggests a supposition that space charge in HDPE samples is formed by carriers entrapped by localized states of a similar bedding depth in the forbidden zone [18].

The main parameters characterizing the processes of charge carrier trapping and recombination are given in Table 6.4. Their analysis brings to the following conclusion.

The positive polarizing charge formed in the samples has σ_{ef} = 0.39÷0.43 nC/cm^2, W = 0.83-0.85 eV. It is sufficiently strong which is supported by negligible changes in σ_{ef}, W and $\tau = (2.5 - 4.7)\cdot 10^{-5}$ s at sample storage. Rise of σ_{ef} is probably due to the negative charge relaxation which escape frequency increases, while relaxation time τ reduces during tests.

Electret effect is identified by three interrelated criteria [9]: i) the presence of a space electric charge in the sample, ii) prolonged preservation of charge in time, iii) generation of TSC spectrum in the sample-electrodes chain at heating. The results obtained confirm the existence of the above features in the studied samples and thus evidence that the melt-blowing technique provides for emergence of electret state in nonpolar and weakly polarized HDPE without any electric field application.

Table 6.4. Characteristics of a fibrous material charge state in time

Time from sample formation to test, days	σ_{ef}, nC/cm^2	W, eV	τ, 10^5 s	σ, 10^{-20} m^2	ν, 10^{10} s^{-1}
1	+0.39	0.84	4.7	1.9	0.8
30	+0.41	0.83	2.5	3.7	1.5
60	+0.43	0.85	3.1	5.7	2.3
160	+0.42	0.84	3.4	4.5	1.8

Depending on space localization of charge carriers in solid polymers, trapping centers fall into [19]: a) Coulomb centers of attraction, b) neutral centers, c) Coulomb centers of repulsion. Trapping levels change from 10^{-15} for centers of attraction to 10^{-25} m^2 for those of repulsion. The centers of strong trapping are characterized by attempt-to-escape of the carriers $\nu \sim 10^8$-10^9 s^{-1}. For centers with weak trapping $\nu \sim 10^{13}$-10^{14} s^{-1}. The comparison of data presented in Table 6.4 shows that charge carriers in the studied samples localize in neutral centers of strong trapping.

The cited data help to explain the mechanism of electret charge formation in fibrous material. When melt-blown HDPE is subjected to intensive heat and mechanical actions leading to mechanical and thermooxidative destruction of macromolecules. These processes increase the number of their own charge carriers in HDPE conducting zone. Free carriers appear at melt dispersion and oriented fibers crystallization, also due to contact electrization accompanying melt friction against spraying head and fiber motion in air flow, and fiber impacts on the forming substrate.

Peaks were identified in IR-spectra of the samples (Fig. 6.16) corresponding to vinylidene, vinyl and transvinyl groups formation. During interaction with charge carriers these groups having easily polarizing double bonds behave as neutral trapping centers. Trapping mechanism is, probably, analogous to formation of a small-radius polaron [18]. High stability of electret charge in time can be explained by carrier localization in neutral centers. Such centers do not experience Poole-Frenkel's effect which consists in reduction of potential barrier owing to the strong inner field of the electret hampering carrier release from trapping centers.

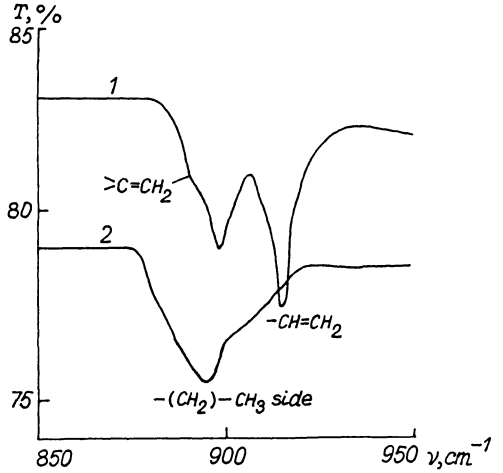

Fig. 6.16. IR-spectra of HDPE film passage: 1 - sintered from a fibrous materials, 2 - from initial polymer.

From the above procedure it is seen that melt-blowing technique provides for generation of electret charge in FM. Spontaneous electrization of fibers is caused by specifics of melt-blowing technological process. The formation of charge carriers in the polymer results from dispersion and contact electrization of the melt and crystallization of strongly oriented fibers. Process implementation close to limits of the polymer thermooxidative destruction spurs the formation of nonsaturated bonds functioning as neutral trapping centers.

6.4.2. Modifications of melt-blowing technology.

In the recent years melt-blowing technique was enriched with electric and magnetic fields application, processes of melt modification in gaseous, liquid and solid phases [20]. Below, some types of technique for its implementation are described.

Despite spontaneous electrization of fibers, the technique is implemented, in a number of cases, using outer electric fields. Fiber deposition on the forming substrate and the fibrous mass cooling is conducted in a high-voltage electric or corona-discharge field [21]. Coaxially to the rotating drum on which FM is formed and at a 10 mm gap to it a wire-gauze high-voltage electrode with an insulating fluoroplastic coating is placed. A negative 5-50 kV potential is created on the electrode and the drum is grounded.

A spraying head is proposed [22] transforming FM into electret state during melt extrusion through the die. In such a design (Fig. 6.17) the press-fitted into the steel body die consists of a copper 5 and aluminum 6 parts separated by a dielectric laying 7. The press-fitted into the body die provides for electric contact between these parts. The die hole axes are found in the laying cross-section contour and the hole diameter surpasses the laying thickness: $d > h$.

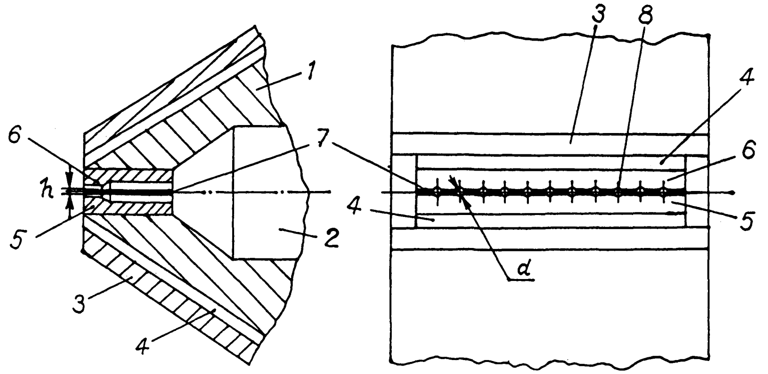

Fig. 6.17. Extrusion spraying head [22]: 1 - body, 2 - cavity, 3 - cover plates, 4 - gap, 5 and 6 are copper and aluminum parts of die, 7 - dielectric layings, 8 - die holes.

When forcing the polymer melt through hole 8, current occurs in the body 1-part 5-melt-part 6-body 1 closed circuit generated by potential differences of copper and aluminum from which parts 5 and 6 are made of. The polarized charge efficient density acquired by FM under such treatment is about 10^{-10}-10^{-7} C/cm^2.

Electret state of polymer fibers can be utilized to solve technological problems of FM formation. Flow sheet of filtering elements production and main units of device for its implementation are shown in Fig. 6.18 [23]. Die 2 of spraying head is insulated by dielectric laying 6 from extruder 1 and is connected to the negative pole of high-voltage source U_1. Plate electrodes 9 are closed on the negative terminal of potential source U_2.

Fibers during squeezing obtain the negative homocharge. Electromagnetic field of the charged fiber flow interacts with the constant electric field of electrodes. Under optimum disposition and potentials of electrode 9, the effect of "electrostatic lens" can be realized and a situation reached when width h of the polymer-gas mixture flow would not exceed the forming mandrel diameter d.

The flow passage through aerosol cloud 11 with a dropping-dispersed phase is accompanied by charge transfer and heat exchange between fibers and liquid drops. In case liquid is the conducting one, the fiber surface charge neutralizes. Charge relaxation rate depends on aerosol density, cloud size, flow velocity and charge state. Depending on polarity of dielectric drop charge in aerosol, either repulsion or adsorption of drops on fibers dominates during the flow and cloud interaction. In this case, charge on fibers do not disappear but is screened by the dielectric liquid drops.

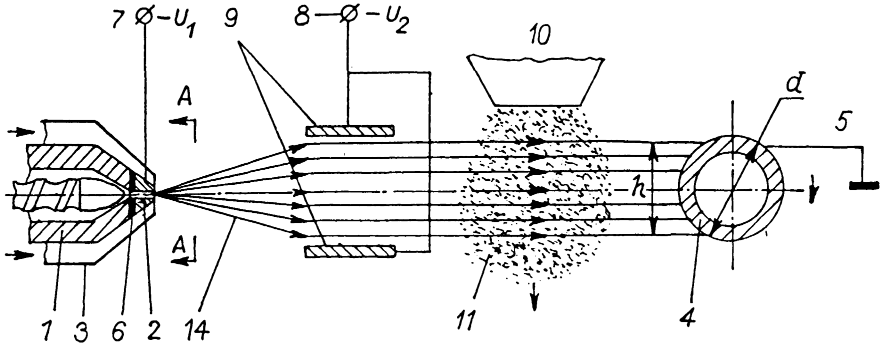

Fig. 6.18. Flow diagram of FM production by "electrostatic lens" [23]. 1 - extruder, 2 - die, 3 - body, 4 - mandrel, 5 - grounding contour, 6 - dielectric laying, 7 and 8 - negative terminals of high-voltage sources, 9 - electrodes, 10 - aerosol generator, 11 - aerosol cloud.

When the fibrous mass is deposited on mandrel 4, electrostatic repulsion of unipolar fibers aids the reduction of FM density. Mandrel grounding leads to fiber surface charge draining and to a more dense packing. Electrostatic attraction of charged fibers to the grounded mandrel reduces loss of flying past the mandrel fibers.

A method has been developed [24] for FM modification by solid particles introduction into the sprayed gas flow. If to subject the modifier powder to corona- or gas-discharge in a fluidizing apparatus, FM polarized charge would increase considerably. Particles contact the melt and adhere to fibers, powder charge partially passes into the polymer. Charge state of FM components can be regulated by spraying the melt using a gas-powder mixture with a modifier vapor addition. The latters can be glues, bactericides, deodorants, aromatizers, etc.

Modification of spraying gas by aerosols [25] and vapors of substances able of sublimation [26] helps to solve a number of technological and operation problems. Liquid-drop phase of aerosols, being polymer solvent, assists the fiber surface layer plactification and transformation into gel state. This facilitates introduction of such substances into FM which physico-chemically and biologically interact with media pollutants and assist FM regeneration. Such problems are solved by forming an adsorptionally active to contaminants layer of desublimated modifier on FM fiber surface.

The widened feasibility of technological action on melt-blown FM by substances in any phase necessitates precautionary measures. Some fiber modifying agents (solvents, filers, coatings, etc.) in contact with polymer melt in oxidizing medium can initiate ignition, explosion, poisoning of atmosphere and other effects impairing operation conditions. A device has been developed for safe melt-blowing production [27]. It provides for tightness of the volume in which spraying proceeds, use of not simply a compressed gas but aerosol and creation of a closed circuit for aerosol circulation.

To solve new problems in FM modification, an original equipment and technological attachments are needed. Multiple-slot spraying head designs have been developed able to regulate trajectory and efficiency of fiber electrostatic interaction at its way from die to the forming substrate. This is attained by optimizing the direction of die holes and adding a special configuration to ducts through which the sprayed gas flows are passing [28]. Using a head without movable parts, mutual cohesion between fibers can be regulated and, as a consequence, FM structure and strength. With this aim, pulsating gas flows are supplied into the ducts for polymer melt spraying [29]. The traditional arrangement of die holes along horizontal line is changed [30]. Lines, being hermetic centers of die holes, start from symmetry center of the spraying head body face. Here the ducts are connected with aerosol generator. Such die body can be made rotatable about symmetry center.

The reduction of the modifying agent losses is solved by using a head [31] which brings into contact at the forming substrate three flat parallel moving gas-dispersed flows, i.e., the gas-powder one with a modifier and two (disposed above and below the first one) flows carrying polymer melt fibers. The design is shown in Fig. 6.19. The polymer melt flows around torpedo 5, is divided by holes 7 and 7' into two parts and is forced through die holes 8 and 8' as fibers. Melt fibers are dispersed, extended and carried to the forming substrate by a joint dynamic action of gas flows from ducts 14, 14' and the gas-powder mixture flow from duct 12. The melt and solid particles are simultaneously brought into contact that leads to particle adherence to polymer fibers. Thus, favorable conditions are created to immobilize solid particles on the fiber surface, which reduces technological losses of the modifier. With the help of such a head, adsorptional FM can be formed consisting of polymer fibers and solid absorbents, i.e. activated carbon, zeolites, complexing agents with metal ions (crown-esters, heterocyclic compounds), etc.

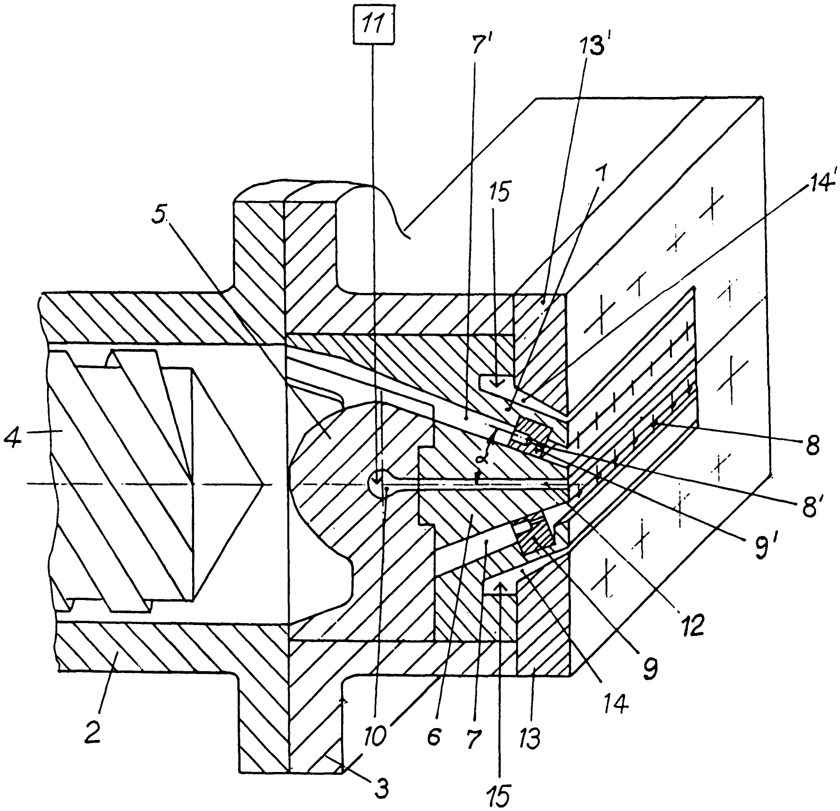

Fig. 6.19. Extrusion head [31]: 1 - body, 2 - extruder cylinder, 3 - jacket, 4 - screw, 5 - torpedo, 6 - plate, 7 and 7' are ducts for melt, 8 and 8' - holes, 9 and 9' - dies, 10 - chamber, 11 - gas-powder mixture generator, 12 - slot, 13 - cover plates, 14 and 14' - clearances for gas, 15 - main line of compressed gas.

New means of monitoring melt-blowing technique and FM structure are used for processing polymers filled with magneto-solid particles. Figure 6.20 shows the scheme for magnetic FM production [32]. The sprayed polymer flow is subjected to magnetic field (MF) B_1 action directed opposite to the flow. As a result of such a momentary action, magnetic particles succeed to achieve orientation with their axes of slight magnetization predominantly along fibers. This orientation is realized in FM structure as follows. A constant MF B_2 is created on substrate 5. The fibers deposit on the substrate and orient along its force lines. If fibers are sprayed from a single-nozzle head or that with a small quantity of die holes, then application of the rotating electromagnetic field B_3 adds spiral trajectory to the flow. In this case fibers stratify on the substrate in spiral strips, which makes it possible to regulate FM texture. By varying fields B_2 and B_3 intensity, FM strength can be enhanced, density and porosity can be regulated.

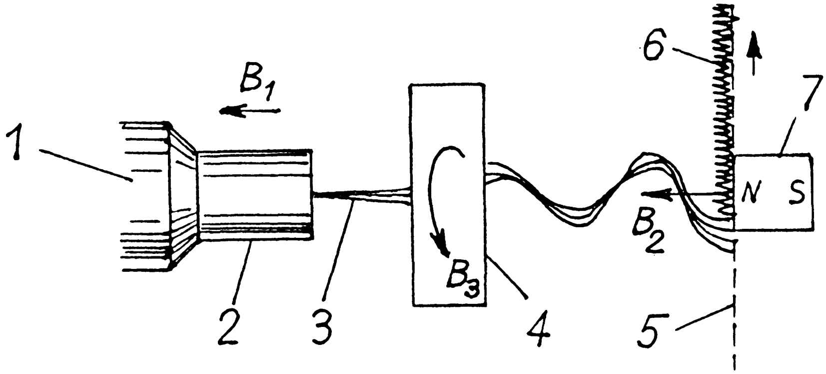

Fig. 6.20. Flow diagram of magnetic FM production [32]: 1 - spraying head, 2 - electric magnet, 3 - fiber flow, 4 - rotating MP generator, 5 - forming substrate, 6 - FM sheet, 7 - permanent magnet.

Such a method can be realized by mixing two flows: gas-polymer flow formed at magnetics-filled melt spraying and gas-powder one carrying coarse (up to 200 μm) magnetics fraction [33].

Thus obtained FM is the source of constant electric and magnetic fields. This helps to solve technological problems arising from magneto-solid filler particles aggregation due to electromagnetic field action on the melt. A certain correlation of constant and alternating electromagnetic fields with optimum parameters [34] causes intensive breakage of aggregates. Particles separated from aggregates are wetted by the melt which prevents their sticking together.

6.4.3. Electret materials and articles.

As it has been shown in ch. 6.4.1, all melt-blown materials display spontaneous electrization. Below, data are cited on FM, which polarizing characteristics are intensified by physical field actions or supplemented by new functional properties.

Electret FM are melt-blown materials subjected to additional electric polarization from an outer source.

Electret FM are efficiently used to purify gases from submicron solid particles and liquid drops in individual respirators, dust collectors, air conditioning lines, industrial gas purifying systems, etc. [16, 17, 20]. They are characterized by high efficiency, negligible pressure drop at filtration and considerable mud-capacity. The conventional mechanisms of contaminant capturing in electret FM are supplemented with electric force actions, i.e, those Coulomb's and induction. That's why they capture particles which size is much less fiber thickness and polymer matrix pore diameter. The efficiency of aerosol particles electrostatic deposition on electret FM several times surpasses that of traditional means of deposition and practically fully defines FM capacity.

Optimum polarization regimes of HDPE-based FM in corona-discharge are: field intensity 0.25-0.30 MV/m, treatment time 10 min, temperature 340-350 K. With rising temperature the stability of electret charge increases, but the probability of its sign change increases too, i.e., the formation of homocharge. So, the optimum σ_{ef} values for FM polarized at T > 350 K and at room temperature are approximately equal. However, at elevated temperatures the charge is more stable.

Corona-discharged fibers in the process of melt-blown FM formation [21] allow for manufacturing filtering elements with even polarized charge distribution through the volume. When a ready element is electrized, the charge is concentrated in the layer constituting 5-10 % of the element wall thickness. Even distribution contributes into charge stability under environment action. Nevertheless, terms of polarized charge preservation in corona-discharged FM do not always meet technological requirements.

The main factors increasing charge stability in filtering elements are the efficient correlation of polymer components and optimization of FM structure. It was shown, that during electret state formation and transformations in polymer-polymer compositions, Maxwell-Wagner's polarization dominates. As shown in ch. 1, electrets of alike materials are characterized by predominantly space-charge and dipolar polarizations. So, under all other conditions being equal, the charge of composite polymer-polymer FM is larger and more stable than that of homogeneous FM. Maxwell-Wagner's polarization to a great degree conditions even dipolar polarization process in composite FM.

A filtering element design has been developed on this base to purify aerosols. It incorporates a mixture of synthetic fibers with a given fiber thickness distribution in filtration direction [35].

Melt-blown magnetic FM are magnetics-filled fibrous materials [36]. They are intended for removing metal debris from working liquids (fuel, lubricant, coolants, hydraulic liquids, etc.). Magnetic FM can also be used to separate ferry-magnetic contaminants from gaseous media in pneumatic lines and air-cooling systems. Filtration through FM results in liquid magnetization and change of a number of its characteristics, as for e.g., viscosity, wetting parameters, electric conductivity, etc.

When media are passing through magnetic filters, the conventional mechanisms of depth filtration (collision, inertia capturing, diffusion, etc.) are complemented with coagulation effect on even nonmagnetic contaminants. They are initiated by particle migration in the filtered medium under the action of FM gradient electric and magnetic fields. The kinetics of coagulation is governed by magnetic, magneto-electric and electrokinetic properties of particles, as well as by the filtered medium viscosity and electric conductivity.

The efficiency of magnetic FM depends on structural parameters of polymer matrix (density, porosity and fiber diameter) and degree of magnetization. Under other conditions being equal, the completeness of sifting (E) of carbonyl iron particles (mean size - 2 μm) from petroleum oil changes depending on FM magnetic induction (B_r):

B_r, mT	0	0.4	0.8	1.2	1.4
E, %	20	35	50	75	100

B_r depends on FM magnetic texture determined by magneto-solid filler origin, despersity, concentration and distribution in fibrous matrix, as well as by fiber packing direction and FM density [37].

Adsorptional FM contain immobilized on polymer fibrous matrix solid adsorbents:

- highly porous carbon and inorganic substances (active carbons, carbon fibers, zeolites, Aerosil and etc.);
- ion-exchanging polymer fibers based on polyacrylonitrile, polyvinyl alcohol, polyamide, etc.);
- complexing agents with metal ions (crown-ethers, hetercyclic compounds, ferrocyanides and others).

Adsorptional FM are intended for purifying industrial wastes with coexisting suspended solid contaminants, dissolved salts of heavy metals, organic toxic substances and surfactants under strongly varying sewage pH.

Deodorizing melt-blown FM materials also belong to this group. They contain porous adsorbents impregnated with aromatic and deodorizing compositions.

Structure of these two classes FM is characterized by the adsorbent particles adherence to polymer fibers (as compared to magnetic FM, where magnetic particles are encapsulated by the binder). So, sorption capacity of FM is proportional to the filler initial one and its concentration in the polymer matrix. Spontaneous polarization of fibers and presence of functional groups on their surface assist the adsorbent particles adhesion to fibers.

The efficiency of adsorptional FM can be proved by the following. HDPE-based fibrous material adsorbs model contaminant (methylene blue) from aqueous solutions of 20 mg/l concentration in 0.1 mg/l quantity. 10 % of active char-coal introduced into the polymer matrix results in by two orders increase of adsorption.

Polyolefine-based FM absorb well petroleum and their adsorption capacity reaches 10 g/g. In dynamic conditions the amount of petroleum products extracted from water mixtures is, with all other conditions being equal, inversely proportional to FM density and fiber diameter. Notice that, petroleum products are the stronger adsorbed, the higher is the efficient FM charge density.

X-ray and IR-spectroscopy have shown that metal ion catching from aqueous solutions containing tetrasols as complexing agents [38] proceeds irreversibly following the mechanism of stable coordinating compounds formation.

Bactericidal FM include fixed on fibers active carbon particles impregnated with substances causing bacteria destruction. They are used to purify and disinfect gases and liquids.

HDPE-based FM and char-coal particles impregnated with alcohol solution of coniferous extract have been tested. From Table 6.5. it is seen that, the materials show a prominent antibactericidal action towards coccal microflora (Sarcinae flava, Sf), gram-negative spore-free (Proteus vulgaris, Pv) and gram-positive spore bacteria (Basillus subtilus, Bs). The influence of bactericidal FM on growth dynamics of test bacteria population is detected by a considerable prolongation of the growth-adaptation phase. It is therefore the beginning of the next phase of microorganism logarithmic growth is not detected still after 24 h of incubation. Investigation of polarized charge effect on FM antibactericidal activity is an urgent problem of applied microbiology.

Table 6.5. Antibactericidal activity of FM

Time of incubation, h	Width (mm) of zones suppressing microorganism growth round FM samples in nutritious medium		
	Sf	Pv	Bs
24	13.7	5.3	12.2
72	6.4	4.1	6.6

FM as a microorganism carrier is used in aerobic boifilters to clean waste water and gas. Biological methods of purification are considered to be most simple, ecologically safe and economical.

Biofilter capacity and reliability are to a great degree determined by the properties of immobilized biomass carrier. Melt-blown polymer FM most ideally meet the requirements imposed on carriers. They are stable in form, light, strong and chemically resistive. They show advantages over common biomass carriers (porous carbon and ceramic materials), i.e., low hydro- and gasodynamic resistance, bioconversion of contaminants by way of oxygen and purified medium free excess to the biomass. The main merit of melt-blown FM is its ability to perfectly sorb microorganisms along with preserving their activity. This property can be attributed to the presence of spontaneous polarizing charge. Thus, sorptional capacity of PP-based FM relative to complex microorganisms (Bacillus cereus, Aeromonas sp., Pseudomonas sp.) is 7.6 mg/g. For claydite, coarse and fine-porous ceramics this value is much less: from 0.6 to 4.2 mg/g. This is because of polymers and biocultures compatibility and due to the melt-blown material intrinsic field effect on bacteria vital activity.

Biofilters with HDPE tubular carriers produced by melt-blowing technique [39] were tested at a chemical enterprise in purifying wastage containing a bunch of chlorides and organic contaminants (alcohols, ketones, ethers) with total concentration about 14 g/l. Wastage contamination was estimated by the index of oxygen chemical consumption (OCC), purification efficiency by separate substances using gravimetry, spectrophotometry and gas chromatography. Test results are shown in Table 6.6 [40].

Table 6.6. The efficiency of chemical wastage purification by biofilters with a melt-blown carrier

Wastage discharge, m^3/m^3 of carrier in 24 h	COD at outlet, g/l	Purification efficiency, %
0.15	0.4	97.2
0.25	1.2	91.5
0.50	2.0	85.8
0.60	2.5	82.1

*COD - chemical oxygen demand.

Biofilters were tested at cleaning recirculation waters at a nuclear power station contaminated by petroleum products which showed that time of switch over to the process stationary regime reduces from 30 to 14 days when claydite carriers were substituted for melt-blown ones [39]. This is caused by a high initial sorption of microbic associations on polymer fibers having spontaneous polarization.

So, we can conclude that, melt-blown FM increase the efficiency of biofilters which surpasses that of typical biomass carrier materials. They accelerate considerably time of biofilter outgoing on stationary cleaning regime, rise the process reliability when biomass is toxicologically effected, reduce aero- and hydrodynamic resistance of the filtering biolayer, alleviate mechanical and gravitation loads on bioreactor bearing units and are easy to regenerate. Prospects of improving the carrier performance are related to increasing the affinity of the melt-blown FM and microbic cell membrane chemical structure. This can be attained by FM electric polarization, by filling with magnetics or conducting particles, by selective adsorbent adhesion to fibers or by some other method [40].

Due to such qualitatively new properties of biofilters with melt-blown microorganism carriers, they can be referred to the novel generation of purification systems governing the prospects of engineering ecology.

Sintered polymer FM produced as continuous profile articles with semipermeable coatings made a revolution in filtering technique [41]. As a result:

- gas purification system design was considerably simplified due to feasibility of producing large-sized filters with minimum included reinforcing metallic elements;
- mud capacity of filtering elements increased because solid contaminants could not penetrate inside the filtering material but settle down on semipermeable coatings;
- filter regeneration was reduced to removal of solid particle coat from the filter outer surface by a water jet or by counterpressure;
- filter maintenance charges were cut down owing to increased operating life and easy regeneration of filtering elements;
- feasibility of reducing filter production net cost appeared which involved highly efficient plastics processing technique, including electrization and use of reconditioned polymer materials.

A sintered filtering element [42] is composed of cohesively bonded particles of ultrahighmolecular polyethylene (UHMPE). Another variant of such FM structure provides for UHMPE particle bonding by a low-melting LDPE or HDPE adhesive (Fig. 6.21). The process of filtering element formation from a powder mixture involves preliminary melting of the particle surface layer, avoiding their full melting and closed pore formation, and especially removal of gaseous inclusions from the melt [43]. A number of technological problems including powder components mixing, mixture compaction and a semipermeable fluoroplastic coating application can be solved in terms of particle charge state regulation.

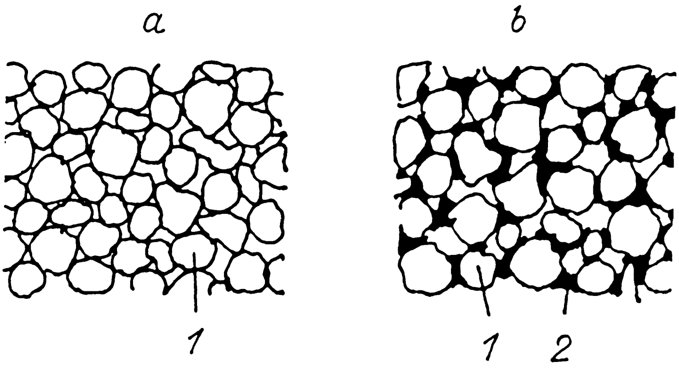

Fig. 6.21. Scheme of sintered FM porous structures: a - single-component, b - binder containing. 1 - solid particles, 2 - adhesive.

Gas filtration is accompanied by charge transfer in the contaminant particle-filtering element contact. Removal of electrostatic charge from the element lowers pressure difference at filtration by 10-15%. Along with this, charge state variation proceeds predominantly in the element polymer matrix and to a less degree in semipermeable fluoroplastic coating, which is the main cause of pressure difference. This opens new prospects in improving serviceability of filtering elements by monitoring electric polarization of both matrix and coating.

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CHAPTER 7

BIOLOGICAL AND MEDICAL APPLICATIONS OF ELECTRETS.

The discussed in previous chapters fields of electret application are mainly related to inanimate nature. Nevertheless, the universe character of the phenomenon of electric polarization of substances presumes that the electret effect significantly influences metabolism. This gives grounds to a highly efficient use of electrets in technologies connected with man influence on nature. Two aspects of man's activity draw special attention. The first of them arising from careless and incompetent intrusion into metabolic processes could lead to hazardous irreversible outcomes and violation of ecological equilibrium in nature. The second one presupposes naturalness of electret use in regulating vital activity of the objects of animate nature reacting to the signals by way of weak and superweak physical fields. Electric fields of this level are typical for electrets from majority of technical dielectrics.

The present chapter is devoted to electret application in two most important fields of human activity directly related to its action on nature, namely biotechnology and medicine.

7.1. ELECTRETS IN BIOTECHNOLOGY

Biotechnology is a complex of industrial methods utilizing living organisms and biological processes of commercial production. Bread-baking, viniculture, brewing, cheese-making and some other branches based on employing microorganisms have been known for centuries. The term «biotechnology» have come into vogue, however, only in the 20-s. Modern biotechnology has focused its attention on averting environmental contamination, protecting plants against diseases, pests and manufacturing biologically active substances (antibiotics, enzymes, hormonal preparations and etc.). Recent advances in genetic engineering, virology, bacteriology and other sciences have given a powerful impetus to biotechnology. The following section dwells upon its today's actual problems. The specifics of biotechnology as an instrument of knowledge is in the upgraded responsibility of its specialists for interference in nature. This imposes certain limitations on the use of electrets in biotechnology.

Below, two main aspects of electret effect application in biotechnology are considered. The first of them treats the existence of electric field intrinsic to all biological objects. Due to this fact the biotechnological processes are always accompanied by electric charge transfer and transformation. The second one consists in specifics of monitoring both biotechnological processes and structures of biotechnological equipment using weak electric fields which sources are electrets.

7.1.1. Contemporary trends in biotechnology.

Biotechnology onset dates back to the time when the man stood out from the animal world. Only in the 70-s biotechnology moved into the forefront of scientific and technical progress. Two circumstances promoted this event. From the one hand, this was rapid development of molecular biology and genetics leaning upon advances in physics and chemistry which made it possible to utilize the potential of living organisms in man's activities. From the other hand, there aroused a necessity in highly efficient technologies called to compensate the lack of food, energy, mineral resources, improve public health and environment. Biotechnology of the 70-90-s contributed much and will invest still more to the solution of global problems. This was a rare in history incident when application of investigation results in practice had rapidly transformed into the instrument of market policy. Biotechnology has gained the priority in national economy of practically all developed countries.

New actual trends in biotechnology have emerged in the abutment of traditional sciences and the latest advances in biology, including genetic engineering, namely:

- bioconservation of the solar energy;
- use of microorganisms to rise petroleum yield, leachability of nonferrous and rare-earth metals;
- elaboration of bacterial strains able to replace expensive inorganic catalyzers and change conditions of chemical compounds biosynthesis;
- bacterial stimulation of plant growth, variation of cereals genotype and their adaptation to ripening in severe conditions (without plowing, watering and fertilizers);
- directed biosynthesis of novel biologically active preparations, i.e., aminoacids, enzymes, vitamins, antibiotics, food additives and pharmaceuticals;
- screening, creation of databanks of cellular cultures and sea biooroganism genes, investigation of their function and elaboration technique of their cultivation;

- synthesis of hormones, regeneration of hard metals, development of superfine powders of magnetics, decomposition of hydrocarbons using sea bacteria;
- bioelectronics, i.e., material design for electronics using biotechnology methods.

Basically new methods have recently appeared in biotechnology. To indicate plants obtained by asexual reproduction, a biologist Webber from the USA Department of Agriculture suggested in 1903 a term «clon» (from Greek «klôn» - a shoot or a cutting for plant reproduction). The term has found use in describing DNA «reproduction», i.e., genes cloning in bacteria. *Cloning* means formation of an organism from a single cell by myotic fission and does not presume an accurate phenotypic or genotypical coincidence between the clon and the species it originated from [1].

An attentive consideration of new trends in biotechnology confirms this or that way their relation to charge transfer and charge state transformation of biotechnological objects. So, the biological method of metal extraction is based on the feature of the majority of microorganisms to carry negative charge. Their membrane and cell walls have a composition where the negatively charged ligands dominate. Due to this positive ions of metals are actively adsorbed from solutions. In this way Ca^{2+}, Mg^{2+}, Na^+ and other ions occur in the microorganism cells [2].

The process of photoreception (light perception by eye) is initiated by retina adsorption of photon. This leads to chemical reactions and generation of membrane electric potential [3]. It is registered by the brain as light perception.

Bioconservation of solar energy through hydrogen photoproduction started in the 60-s. Chloroplasts isolated from spinach in the presence of artificial electron donor and bacterial extract containing hydrogenase produce hydrogen in reactions with charge transfer [4]:

$$\underset{\substack{\text{donor}\\ H^+}}{\text{electron}} \xrightarrow{e^-} \text{photosystem 1} \xrightarrow{e^-} \underset{\text{carrier}}{\text{electron}} \xrightarrow{e^-} \text{hydrogenase} \longrightarrow H_2.$$

Based on the above method the technologies of hydrogen photosynthesis have been developed employing charge carrier separation using membrane. It has become adopted to achieve hydrogen using artificial electron donors (instead of water) and light adsorbing pigments (but not chloroplast membranes). Below we shall dwell at length on the general character of charge transfer phenomenon in biotechnological processes.

Contemporary problems in biotechnology stem, first of all, from its strong impact on economy like that the production of plastics made in its time. They are also conditioned by the place biotechnology occupies at the junction of sciences and in the hot spot of science integration with production. All those problems find response in governmental support of developments, specifics of the personnel policy and intensity of publishing investigation results in the field of biotechnology.

Biotechnology enjoys governmental support as one of the most significant directions of national economy in practically all developed countries. The governmental programs stimulate fast advancement of actual biotechnological directions. In a number of countries a trend has gained popularity of extending scientific investigations beyond the national boundaries. It aroused from aspiration to attain superiority in a certain biotechnological field as well as by the fact that fundamental investigations at the junction of sciences become still more expensive. Implementation of State programs gave birth to new relations between research institutions and industry. In the process of their establishment debates have spread on scientific problems in general and biotechnology in particular, and on science contacts with the world of business. They have reflected a vast spectrum of deductions from close cooperation to tough division of the spheres of activity [1]. Biotechnology have offered an excellent opportunity to find a compromise in the problem solution.

The system of training specialists for biotechnology able to work at the junction of sciences is a part of the general task of education. The specialists should show deep knowledge based on a new perception of the world open through understanding of new interrelations. The example of the problem solution in England is rather illustrative. First, the specialists of traditional professions were «requalified» into biologists at research laboratories or at industrial enterprises. An engineer-physicist became biophysicist, microbiologist became a technologist of biotechnological production. Such training did not fail since outstanding experts were responsible for it, including Nobel prize-winners who frequently combined teaching and managing in companies producing biotechnological products. After this, a Board of Directors have been organized at the British Council for Scientific and Engineering Investigations. The Board was engaged in establishing commercial ties between industry and Academic institutions of biotechnological orientation. He was also responsible for averting «brains leak», so hazardous for the advanced trend. The work was a success and guaranteed wide vistas for England in the field of biotechnology. At present several tens of educational centers of biotechnological direction are working at English Universities.

Analogous problems were to be solved in training specialists in the USA, Germany, Japan and other countries.

United efforts of scientists and manufacturers gave birth to problems connected with secret investigation results, struggle for priority, conflicts between specialists in fundamental and applied spheres. In a number of cases these relations were under the government control.

In the 80-s the German company “Hoecsht AG” and Massachusetts main hospital signed an Agreement on organizing a Department of molecular biology at the hospital. The partners found a compromise between the requirement of fuul freedom in activities of the hospital and aspiration of the company to make the quick profit from the capital they invested into investigations. The Agreement was criticized by Albert Gore, the member of The House of Representatives at that time. He suggested to study the contract articles to make sure that the company could not obtain exclusive rights on the use of investigation financed by the National Institute of Health. Gore’s activity did not arise sympathy in academic circles since international cooperation was a generally accepted norm at investigations.

Biotechnology like all other scientific spheres considers patenting as the best means of ensuring legitimacy in guaranteeing author’s rights. Patents are equally essential for companies investing money into biological industry and for proving the degree of importance of the work performed. Patent policy assists, however, secrecy as it is now with works conducted at the forefront of biotechnology.

In 1982 an Agreement was signed between «Monsanto» company and Washington University on joining efforts in studying peptides and proteins effecting the behavior of cells for medical applications. The company paid fundamental investigations pursued by the University. Each patent obtained in the course of the research was owned by the University but its commercial side was in Monsanto’s competence. Monsanto could obtain the right on the license only in case it financed the works fully. Publication of investigation results was under the company’s control. All the prepared papers passed expertise in Monsanto in order to estimate patentability of cited data. Such relations are characteristic of biotechnological research groups involved in competition which commercial and scientific interests are interlocked. The researchers occupying such a dual position between the pure science and commercial spheres encounter a contradiction. From the one side, they must as quickly as possible publish their achievements, from the other side, they must keep the secret and meet patent limitations. To avoid the risk of being overtaken, some scientists do not publish in scientific periodicals the results of the works subsidized by industry. An example of the trend was a many-years conceal of investigations in interferon - a protecting protein produced by cells as a reaction to virus infection. Debates on the problems of patenting biotechnological objects are on the table of discussion till now [5].

Just in biotechnology the problem of a scientist responsibility for the consequences of his work stays most brightly. The methods of genetic engineering differ from manipulations with usual microbes. The distribution of «constructed» strains can have serious aftereffects. Taking into account the above said some experts in biotechnology already in 1974 called up to self-limitation in genetic engineering experiments. This moratorium was, nevertheless, violated soon. In this connection, some recommendations were discussed in 1982 in Strasbourg at the Meeting of European Parliament concerning legitimacy of applying methods of genetic engineering to people. This was the first attempt at the international level to obtain legal defense against genetic manipulations. An important present-day factor that helps to draw up critical position and objective opinion on advantages and risk of biotechnological investigations is considered to be public information and highly qualified popularization of science and technology through mass media.

We have scrutinized the problems and tendencies in biotechnology since they are typical of all other fields of electret application at a highly efficient level. These fields lie, as a rule, at the junction of sciences, they are rapidly developing and give rise to problems like those treated earlier. The questions of training personnel, patenting, relations between specialists engaged in fundamental and applied research emerged and were solved analogous to those posed to specialists studying electret effect in microelectronics, medicine, filtration technique, triboengineering and etc.

7.1.2. Bioelectret effect.

Bioelectret effect is the ability of living tissues to exist in the state of nonequilibrium electric polarization owing to which tissues display electret properties.

The first scientific data on the existence of «animal electricity» were received in the 18th century when studying impact applied by some fishes with electric organs. Just to this time L. Galvani's investigations of bioelectric potentials can be related. The scientific dispute (1791-97) on the nature of «animal electricity» between Galvani and A. Volta resulted in discovering a new principle of electric current generation by a galvanic element. The first direct measurements of biopotentials using galvanometer were performed by C. Matteucci in 1837. The systematic study of bioelectret effect was started by E.H. Du Bois-Reymond in 1848. He showed that between the inner content of a cell and contacting the cell membrane outer liquid exists a stationary potential difference (*membrane potential*). At rest the latter value changes regularly at cell excitation. In 1868 J. Bernstein analyzed for the first time oscillations of potential generated at excitation spreading along the nerve fiber and lasting for thousand fractions of a second [6]. In 1883 a Russian biologist N.E. Vvedensky used the telephone to listen to discharges which accompany nerve pulses.

Further progress in studying bioelectret effect was connected with creation of electron-amplifying technique which successes should be attributed to the use of electrets. Study of biopotentials in separate fibers and cells has come into use owing to the method of microelectronic intracellular recording of potentials. Of great importance for analyzing mechanisms of biopotential regeneration was the use of gigantic nerve fibers of squids. Examination of those fibers permeability for Na^+ and K^+ ions depending on membrane potential made it possible for A.L. Hodgkin, A.F. Haxly and B. Katz (1947-52) to decipher ion mechanism of the action potential formation and to formulate the membrane theory of biopotentials [7, 8]. In ch. 7.2.3 data are given on applied in medicine diagnostic technique based on the study of man's organs biopotentials.

Simultaneously with investigations in electrogenesis of animal cells, studies of bioelectric potential of plants have been accomplished. In 1882 E.H. Du Bois-Reymond proved the common character of bioelectric phenomena in plants and animals. Initially, the researchers' attention was drawn to plants possessing growth movements. Then, J.Ch. Bose established in 1926 that biopotentials and electric responses to the irritant are peculiar to all plants. Designed by him sensitive self-recording galvanometers helped to obtain the plants recorder, that is, their specific responses to physical and chemical irritants. The classical object for investigating ion origin of biopotentials are large algae cells.

Now, the main regularities of bioelectrical potential variations are defined as a fundamental characteristic of living matter.

Rest potential (U_r) is the difference of potentials inherent for living cells in the state of physiological rest between cytoplasm and extracellular liquid. It appears due to unequal concentration of K^+, Na^+ and Cl^- ions on both sides of the cell membrane and its unequal permeability for the ions. For the majority of cells U_r is created by K^+ ions diffusion outside from cytoplasm. In skeleton muscle fibers the most important role in maintaining U_r is played by Cl^- ions diffusion from the outer medium into the cytoplasm. Electrical current passage through the cell membrane and instability of ion permeability of the membrane vary U_r.

Reduction of U_r is called *depolarization* in biotechnology. *Passive depolarization* arises at a weak electric current passage through the membrane (out of the cell) which does not vary ion permeability of the membrane. *Active depolarization* develops at its raised permeability to Na^+ ions or reduced permeability to K^+ ions. Prolonged depolarization of the membrane leads to inactivation of sodium channels and raised potassium permeability. This results in decrease or full disappearance of the cell excitation.

Increased U_r is called *hyperpolarization*. *Passive* hyperpolarization takes place when electric current passes through the membrane from the outer medium into the cell. *Active* hyperpolarization occurs at raised permeability of the membrane for K^+ and Cl^- ions. An example of active hyperpolarization is the inhibitory postsynaptic potential. This is local hyperpolarization of the membrane which hampers or makes it impossible to reach a critical level of cell depolarization. It proceeds at activation of ion channels by a physiologically active substance isolated from a nerve ending at its excitation by a nerve pulse. U_r plays an important role in keeping sodium channels of the cell membrane excited.

Action potential (U_a) is fast oscillation of membrane potential generated at excitation of nerve, muscle and plant cells. It appears when the irritator reaches some threshold value. Further increase of irritator intensity effects neither U_a amplitude nor its time. The reason of U_a appearance is the quickly reversible change of ion activity of the membrane related to acticvation of electrically excited ion channels. The rising phase U_a in the nerve and skeleton muscle fibers is connected with increased permeability of the membranes for Na^+ ions. The flow of Na^+ ions inside the cell along the open channels leads to fast overcharging of the cell membrane. At rest its inner side is charged negatively relative to the outer one, while at U_a peak it acquires the positive charge. Further inactivation of Na^+ channels and activation of K^+ ones results in U_a drop. Its restoration, however, up to the initial value is preceded by trace oscillations (depolarization or hyperpolarization of the membrane). U_a life is about 0.1-3.0 ms in the nerve and skeleton muscle fibers, and 10-100 ms in the cardiac muscle cells.

Refractivity is the reduction of cell excitability accompanying U_a initiation. At U_a peak the excitability disappears fully (absolute refractivity) due to the cell membrane Na^+ channels inactivation and K^+ activation. Upon U_a decrease the excitability rises for a few ms up to the initial value (relative refractivity). Refractivity is one of the factors determining the maximum rhythm of cell pulsation. Substances extending the period of relative refractivity (antiarrhythmics) reduce systole frequency and eliminate disturbance of cardiac rhythm.

Spontaneously emerging in living organisms electric potentials ensure their electret-like state. Living tissues of plants, cold-blooded and warm-blooded animals generate electric fields. Its intensity near the tissue surface is about 1-10 V/m. Oscillation of biofield intensity correlate with change in tissue metabolism [9]. Bioelectric effect gives grounds to consider in this book many of the processes taking place in animate nature.

7.1.3. Electric nature of biotechnological processes.

The cells of living microorganisms displaying bioelectric potential are like charged particles. Electric resistance of membranes separating the microbial cell contents from the outer medium is by many orders less than the cells of microorganisms with a powerful epithelial cover have. That's why the electric field of a microbial cell is always screened by ions of the outer medium and quickly attenuates with distance from the cell. The cell fields, however, propagate at a distance of about 10 Å even if concentrated electrolytes are present at screening. Microbial cells in the liquid or gas medium follow the Brownian motion. When in contact they interact by their electric fields. In usual conditions the frequency and intensity of these interactions do not exert a suppressing effect on microorganisms.

At dehydration, sedimentation, aggregation of the liquid or aerosol culture or at increased number of microbial population the distance between cells reduces. The frequency of approach and interaction acts of their electric fields increases. So, a *concentration electric stress* occurs. At strong dehydration the microbial population acquires a rather high surface charge. At a certain moisture content in the culture the charge might change its sign [10]. Thus, the microbial population displays electret features.

Heating of the bacterial suspension leads to increased intensity of Brownian motion and frequency of electric interaction acts between the cells. This is accompanied by varying ion permeability of membranes and bioelectric potentials of the cell. The analysis shows that any action exerted on the cells of living organisms evokes disturbance containing an electric component. This considers the mechanical effects, infection by phages, antigen interaction with immune system, ultraviolet and radioactive radiation and attacks of chemical agents. Electric disturbance serves for the cells as a signal about water deficiency, nutritious substances and other unfavorable changes in the environment.

A recurrent electric stress is the ecological norm for microorganisms. In response, they have developed in the process of evolution a population mechanism of adaptation to it. In work [10] a model of this mechanism combining the biochemical and electrical nature is suggested. The universal element of the population adaptation of microorganisms to different kinds of stresses is the electrical signal.

There exists an experimental proof to this model. It has been established that under the effect of constant electric field microorganisms excrete into the extracellular medium a regulating factor (EF-factor) which raises their resistance to unfavorable effects. Substances isolated by the cells in the process of electric treatment and those formed under the action of one cell field on another at culture concentration show the analogous type of biological activity. It is characteristic that EF-factor activation can be attained by both electric treatment of culture medium or by its heating. EF-factor does not show a strict specificity. This is the evidence of the universal mechanism of electrobiochemical regulation of microorganisms.

Respiration intensity, heat-generated products and other energy parameters of microbial cells reduce under the electric field action both, outer and inner, formed at concentration of cell suspension. This confirms that the level of metabolism in microorganisms falls. At electric treatment some intramolecular bonds break in the substances secreted by the cells into the culture medium. This was found out by chromatomass-spectrometry, optical spectrometry and NMR.

The concentration stress leads to raised intensity of electric action on the cells aroused from the population existence itself. Variation of bioelectric potentials influences physiological activity of the cells and causes electrostriction compression of the cell membranes. The reduction of membrane area is accompanied by impaired water filling of the cells which is supported independently by the methods of conductometry, spectronephelometry and elctron microscopy [10]This reply assists transformation of cells into the hypometabolic state.

The scheme of electrobiochemical adaptation of microorganisms to favorable factors at the population level can be presented as follows. Any stress (increase of numerical density of the population, heating, mechanical and chemical actions and etc.) is perceived by the microorganism as disturbance of bioelectric potentials, i.e., as an electric signal. When accepted, the cell excretes into the medium stress initiating substance. Its molecules contain weakly associated elements. Upon leaving the cytoplasm the molecules become open for energy effects which accompany the stress and dissociate forming elements with elevated biological activity. The latters effect membranes transforming them into the low-active state characterized by the raised resistance to environment. Correspondingly, bioelectric potentials of both separate cells and the population as a whole vary too. So, it is helpful to control technological processes accompanied by stress or impaired vitality of microorganisms by way of measuring redox potentials of cellular population [10].

Many facts found during technological processes serve in favor of this hypothesis.

The reduction of cell size under the outer electric field is accompanied by increasing ξ-potential of the cell suspension. It is thought to be [11] a physiologically justified reaction of cells directed to decrease frequency of their electric contacts. Moreover, the reduction of ξ-potential has been noted at cultivating bacteria in liquid culture media with cell population transition to the stationary phase. Here, the developed during evolution peculiarity of microorganisms is displayed to ease the mutually depressing influence of charged cells at increasing density of the population. This interpretation could not be called a contradictory. The reduction of ξ-potential in the process of the population growth is conditioned by variation of the membrane morphology. The increase in ξ-potential due to electric effect is an instantaneous response of the cells which is, probably, connected with their degradation. These regularities are of great importance for biotechnology. They show the way of increasing the limiting density of microorganism populations by not less than an order [258].

The electric nature of biotechnological processes is clearly seen in the interaction between cells and metal ions. In work [12] 17 algae cultures have been screened to define their ability of accumulating Au^{3+} ions from chloride solutions. A strong dependence has been established of Au concentration on energy metabolism of alga cells. A determining role in Au accumulation belongs to generators of the membrane potential. Increase of potential-forming K^{+} ion concentration is accompanied by depolarization of the membrane separating cytoplasm from the environment. The process correlates with Au accumulation. The greatest Au accumulation by the cells corresponds to the maximum of the membrane potential of chlorella. In the presence of adenosine triphosphate acid (ATP) the membrane potential forms through K^{+} and Na^{+} ions transfer against concentration gradient owing to the energy generated at ATP hydrolysis. These laws can be used at designing bisorbents on alga cell base.

The processes of charge transfer determine the ability of some microorganisms to resist Au^{+} and Cu^{2+} ions showing antimicrobial activity [13].

A number of the programs of drugs screening are based on analyzing channels in the membranes of microorganism cells. [14].

Electric origin of interaction of biotechnological objects is seen in the antigen-antibody reaction. *Antigens* are substances perceived by the organism as foreign bodies and cause a specific immune response. They are able to interact with their response products, i.e., with *antibodies*. Antigenic properties are intrinsic for macromolecular components of all living organisms. The reaction antigen-antibody is a specific binding of antigen to the corresponding antibody leading to formation of the immune complex. The reaction proceeds under the action of hydrophobic, hydrogenous, electrostatic bonds and Van der Waals forces. In Fig. 7.1 a scheme is shown of immune complexes formation. Electric origin of interactions at immune complex formation provides for the use of biophysical methods for determining the antibody-antigen affinity [16].

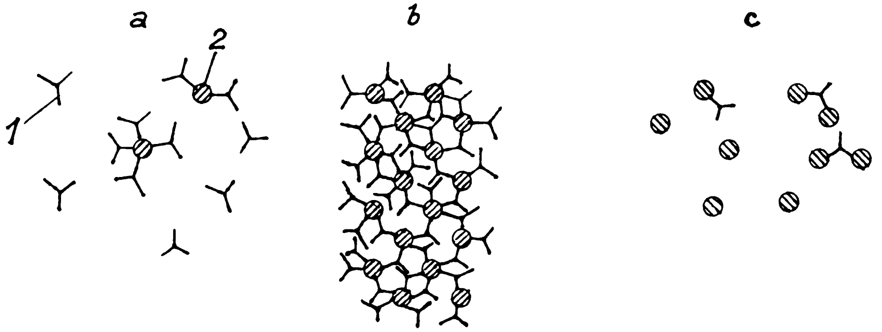

Fig. 7.1. Diagram of immune complex-forming: *a* - excess of antibodies, *b* - quantity of antigenes and antibodies is equivalent, *c* - excess of antigenes; 1 - antibody, 2 - antigene.

The above mentioned (7.1.1) systems of hydrogen biocatalysis were further developed using Ni-Fe hydrogenase. The mechanism of the process is based on formation of membrane potentials through proton and electron transfer [15].

In biotechnology Halobacterium halobium bacteria are used to accumulate sunlight. Its purple pigment bacteriorodopsin is found in the cell membrane. Under the sun radiation physical and chemical transformations take place in its molecule leading to proton migration through the membrane [17]. The pigment plays the role of the actuated by the light proton pump. Upon each photocycle lasting 10 ms the molecule is ready to be actuated by the light and to pump the next proton. As a result, the proton gradient is formed whose concentration is larger on the inner side of the membrane and is smaller outside. Based on the said, laboratory systems have been created able to generate electric current.

The mentioned data are a convincing proof to the fact that biotechnological processes have the electric origin and are accompanied by the bioelectret effect.

7.1.4. Bioelectronics.

The idea to use the materials of biological origin for designing electronic devices appeared at the beginning of 60-s. It wasn't realized since just at that time integrated circuits on silicon base were developed. Their production technique quickly advanced and prepared the elemental base for the contemporary computer equipment. It was found out in the 80-s that capabilities of silicon microelectronics were approaching its limits. This challenged the search for alternative ways of progress in the sphere.

There was an attempt to solve a number of problems in electronics by using biosystems. The researchers' optimism was heated by successes in electronics of organic materials and biotechnology. This road was attractive owing to perspective of overcoming physical boundaries and technological potentialities of silicon microelectronics as well as due to inexpensive and ecologically safe production.

Nevertheless, most attractive idea in bioelectronics has become the prospect of creating molecular electronic instruments which elements are individual molecules or groups of them. Substitution of semiconductors by organic molecules could make it possible to design miniature electronic devices having no analogues in modern technology. This faith proceeds from the fact that the density of elements in molecular schemes could be by five orders greater than the present integrated circuits have. Besides, molecular logical elements have already been elaborated with switching velocity by three orders higher as compared to traditional ones. It seems that the problems of molecular elements design and assembly into a single circuit can be solved by biotechnological means [18].

Below some examples are given of materials and methods application in biotechnology and electronics.

Langmure-Blodgett films are used in manufacturing insulating and passivating 2.5-50.0 nm thick coatings for semiconducting structures. The production layout is shown in Fig. 7.2. If to add an amphiphilous substance to the polar liquid, its molecules form a monolayer on the liquid surface. Polar «heads» of molecules would face the liquid, while nonpolar «tails» would be directed outside. When a plate is moved relative to such a system (by dipping or removing from the liquid) an oriented monomolecular layer of amphiphilous substance (Langmure-Blodgett film)is formed on it. The repeated process enables the formation of a multilayered film with given orientation of molecules in its layers and with a combination of layers consisting of differently oriented molecules. Orientation of molecules conditions their polarization due to which Langmure-Blodgett films bear the polarizing charge.

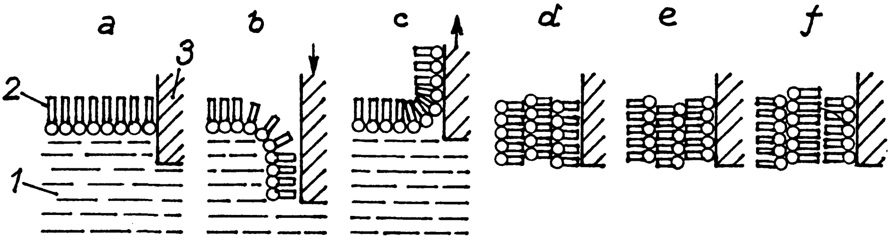

Fig. 7.2. Layout of Langmure-Blodgett films manufacturing(a, b, c) and structures of manylayered films of th3 types X(*d*), Z(*e*) and Y(*f*): 1 - liquid, 2 - a monolayer of the film-forming substance, 3 - plate.

This question is discussed in the chapter on biotechnology since the components of cell membranes (lipids, phospholipids, membrane proteins, etc) are perspective materials for Langmure-Blodgett films manufacturing [19].

Biosensors are intended for recording certain chemical substances and determination of their concentration in media. The fields of biosensors application are chemical industry, medicine and biotechnology.

Of particular interest for the founders of bioelectronics appeared to be sensors in which the function of sensing elements was fulfilled by enzymes [20]. Most spread are based on the field-effect-transistor (FET) sensors having metal-Si oxide-semiconductor structure. Enzymes are inserted into the FET lock. They react with a substance which emergence in the solution is to be recorded. As a result of the reaction, pH of the solution and the intensity of electric field in the lock change leading to variation of the signal in the FET outlet. Such a design makes it possible to unite several sensors in one microcircuit. As a result, a multisensor is obtained able to yield prompt information on the concentration of several components in the base solution.

Analogous sensors are used to measure concentration of blood sugar, protein and cholesterol in small samples of blood, lymph, urine and etc. In analytical biotechnology sensors are used sensitive to penicillin, glucose, urea and etc. [21]. Based on pH-sensible FET immune sensors have been developed to define interferon [22], formaldehyde, mercury ions and etc.

A vast group of biosensor designs constitute combinations of ion-selective electrode and enzymes [23]. In fig. 7.3 a scheme of such sensor is shown. Disposable cylindrical graphite electrode was made from a pencil lead. Polyethylene imine (PEI) from a methanolic solution was adsorbed into the electrode surface, onto which a glucose oxidase (GOD) - antibody conjugate was covalently immobilized. The PEI-graphite electrode was modified with an avidin-GOD conjugate for a competition assay using a biotin sensor.

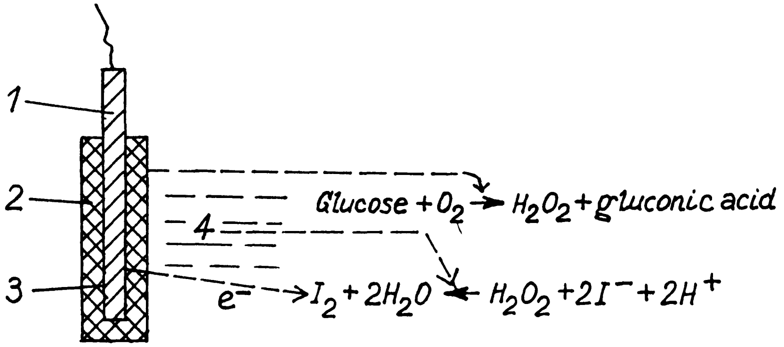

Fig. 7.3. Schematic illustration of the separate-free, amperometric enzyme-channeling immunoassay with immobilized antibody and glucose oxidase on the PEI-modified electrode surface: 1 - electrode, 2 - GOD, 3 - PEI film, 4 - peroxidase.

This system is dipped into the solution containing glucose, iodide ions and the appropriate analyzer, which in turn is bound to a peroxidase-labled antibody (biotin) conjugate. On the electrode surface the GOD catalyzes the oxidation of glucose to N_2O_2 and the iodine produced in the peroxide-catalyzed H_2O_2/iodine redox system is monitored amperometrically by the electrochemical reduction of iodine back to iodide.

Microdetermination method of heavy metal ions using apoenzyme-membrane sensors is proposed [24]. Apoenzyme (cofactor - free enzyme) is reactivating microassay for heavy metal ions with the use of immobilized metaloenzymes as recognition elements. Use of the apoenzyme membrane in the proposed methods enabled rapid assay for ions Cu^{2+}, Zn^{2+}, Co^{2+}.

A new concept of analyzing bioavailability of heavy metals was established. It is based on the creating microbial strains capable of sensing the environment by emitting light. These strains express a sensitive reporter-gene, firefly luciferase, connected to a promoter element responding specifically to various heavy metals. The biosensor developed responded to mercury, lead, arsenite, antimonite and cadmium. The lowest detectable concentrations are 1 fmol for mercury [25].

Photosensible biomaterials can be used as information carriers for PC memory devices, robot photoreceptors and analogue systems.

Most known among this class of materials is bacteriorhodopsin (Br), a membrane protein of halophilous bacteria *Halobacterium.* It enters the composition of the so-called purple membranes, where fulfills the function of a proton pump by transforming the light energy into the energy necessary for the halobacteria vitality. Br is characterized by a high velocity of the initial photoreception act ($\sim 10^{-12}$ s) and stable films can be obtained from it. Optical discs are made on their base in which photo-induced transitions are realized between the main Br form and its initial photoproduct under the temperature of liquid nitrogen [26]. Electrically induced variation of potential (up to 10 V)on oriented Br films enables transformation of optical information into electric signals and vice versa.

A perspective photosensitive material has turned to be *chromatophres*, cellular alga organs and membrane intarcellular structures containing pigments which assist photosynthesis.

Biosystems as analogues of electronic devices have been studied since the onset of electronic technique.

Electronic transport chains (ETC) have been found in metochondrion membranes (cellular structures generating electricity in the organism), chloroplasts of green plants and chromatophores of photosynthesizing bacteria [27]. A directed electron transfer along such chains is regulated by permolecular complexes consisting of ETC protein elements. The chain functioning is supported by *prosthetic groups* - nonprotein components of complex proteins, including some enzymes. Probably, the main mechanism of electron transfer in ETC is tunneling. Time of electron transfer between ETC elements is 10^{-12} to 10 s. This confirms the presence of ETC elements which fast-response corresponds to the requirements of electronic technique.

Quick-action of ETC elements is affected by distribution of biopotentials in proteins surrounding prosthetic groups [28]. In other words, electron state of the groups is dependent on the charge state of the surrounding proteins. The protein structure governs interdisposition of prosthetic groups.

Bioelectronics opens a new sphere of applying biotechnological materials and methods. This direction in biotechnology adjoins different sciences and develops through enriching with ideas and methods of physics of condensed media and molecular physics.

7.1.5. Electret materials in biotechnology.

Weak fields of electrets are used biotechnology as an optimum means of effecting microorganisms. Below, examples are cited and some aspects of electret use in membrane technique, adsorption systems and smart materials creation are treated.

Membrane technology of separation, purification and concentration of biological products shows a number of advantages. Filtration through the membrane is not accompanied by phase transitions, variation of pH and temperature of the products being filtered and does not necessitate reagents. Diversity of membrane processes (reversible osmosis, ultra- and microfiltration, dialysis, and etc.) provide for a wide spectrum of technological effects on bioproducts.

The following main trends of membrane usage have established [29].

A. Purification, desalination and concentration of protein solutions (milk processing, food ferments manufacturing using microorganisms and etc.).

B. Purification of products from accompanying or forming during their production impurities. Typical examples are: purification of dextranes, known as blood substitutes from toxic high-molecular fraction; antibiotics and aminoacids from proteins and pigments; drugs from lipopolysaccharides and so on. All these impurities show high adsorbtion activity.

C. Concentration of liquid products (instead of vacuum evaporation). At aminoacids and antibiotics production this operation is accomplished by introducing water-soluble polymers into the processed product. They contain functional groups selectively binding to the product ions and change their charge state.

D. Sterilization of liquids can become a dominating trend in membrane technology. The perspectives of streamlining its equipment are connected with utilization of physical fields as the sterilizing factor.

E. Fermentative processes employing membranes are the developing direction in biotechnology. Acceleration of chemical reactions under the action of enzymes arises from the lowered energy barrier through formation of complex compounds of the

> enzyme with the substrate. Such reactions proceeding during products filtration through the membrane are connected with the processes of charge carrier transfer and interaction.

So, the characteristic feature of all the enumerated trends is transformation of the filtrated product charge state. It is natural that difference of electric potentials establishes during filtration between the product components on both sides of the membrane. It is equally natural that filtration processes can be regulated by the intrinsic electric field of the membrane. Though this chance has not received much attention since now, the use of electret membranes intergrows into a promising biotechnological direction.

Electrical mechanism of bioparticle trapping realizes at filtration through the electret membranes of any biosuspensions, including electyroconducting liquid-based ones. Trapping proceeds in two stages. First, electric coagulation of particles takes place leading to dispersed phase separation from the liquid carrier. Then, electrophoretic migration of bioparticle aggregates carrying polarizing charge to the oppositely charged membrane elements is observed. Stability of its electret state guarantees that the particle aggregates would not break and be washed out from the membrane. Below examples are given of electret membrane and filtering elements use in biotechnology.

The completeness of bacteria and virus impurities removal from water (sterilization) is to a great degree determined by the filter-adsorbent permeability. The reduction, however, of the filtering element penetrability below a certain level doesn't practically improve the level of water purification but reduces much filtration efficiency. The efficiency of water sterilization by electret filters-adsorbents is by 2-3 orders higher as compared to traditional devices of ion exchange technology [30]. Electret filters realize simultaneously two mechanisms of bacteria capturing, i.e., screening and electrostatic ones. The bacteria commonly carrying the negative charge are practically fully captured by the electret filtering elements.

The method of electrophoresis is useful in separating biological objects. The matter is in the fact that heterogeneity of microorganisms by their genotype conditions heterogeneity of their biopotentials. Electrophoresis helps to isolate fractions from the population of microorganisms characterized by a narrow biopotential range. Both labor and time-consumption here are less in contrast to other methods. Installations for electrophoretic separation and concentration of cells [31] include connected by the source of constant field electrodes separated from the biosuspension by membranes. The installation design can be simplified if to use electret membranes as the field source.

Electret membranes are employed as an active part of immune sensors to directly measure the antigen-antibody interaction. Bioaffinity of electret polymer membranes with immobilized antibodies rises signal generation of immunochemical reaction [32]. An electret diaminobenzene membrane is used in immobilized enzyme reactors to insulate platinum electrode [3]. This results in the decreased response reaction of microorganisms and improved quality evaluation of food seasoning.

Electret charge of the membrane is in a number of cases unwanted. The dielectric membrane, however, always carries a weak polarizing charge even if it wasn't electrically polarized purposely. It can be formed as a result of charged particles capturing by the membrane in the process of preceding filtration operations. The charge value and, sometimes, its sign vary depending on the filtering medium pH. Electret charge intensifies adsorption of molecules (especially protein) on the membrane leading to impaired filtration efficiency and, often, product losses. In this connection, the commercial membrane installations usually undergo undivided cleaning and drying. The way to the problem decision is, in principle, in immobilizing enzymes on the membranes which assist the adsorbed products degradation [34].

Adsorption systems have found wide application in analytical investigations and commercial biotechnology. They are mainly used to immobilize microorganisms producing extracellular enzymes. Adsorption intensity predetermines the activity and stability of the system functioning. That's why the problem of adsorptional fixing of the cells on the carrier is actual in biotechnology. Use of electrets offers new opportunities for its solution. Immobilization of electrically charged cells on electret carriers intensifies adhesive interaction through electrostatic component of adhesion. Electric polarization of uncharged particles can occur in the electret field which then come into electrostatic interaction with the carrier.

The carrier for lysinamidase (LA), the enzyme catalyzing hydrolysis reactions of some polymers has been optimized [35]. The mechanism of LA adsorption on the porous polystyrene carrier shows a clearly electrostatic nature. The carrier surface charge was regulated by varying the buffer solution pH. Depending on the charge density LA kinetics of adsorption-desorption was varied.

The mechanism of gram-negative bacteria adsorption [36] is connected with electrostatic interaction of negatively charged cellular membrane and positively charged sorbent surface. In work [37] data are cited on sorption immobilization of yeast cells in cation-, anion-exchange and molecular adsorbents, porous glass, glass fiber, polyurethane foam and etc. A conclusion has been made that the polarizing charge sign on the adsorbent surface does not effect the quantity of adsorbed cells. This conclusion has been refined [38] at studying immobilization on vermiculite of nitrogen-fixing *Azospirillum brasilense* bacteria. For sorption not only the general surface charge of the adsorbent is of importance but the presence of polycharged exchange cations (Ca^{2+}, Mg^{2+}, Fe^{3-}) as well.

Pseudomonas alcaligenes bacteria (surfactant-alky-benzene sulfonate destructor) were immobilized on synthetic fibers. Isotherm analysis have shown that the cells block first of all active groups on the fiber surface. NH_2 groups have shown to be sorption centers than COOH [39]. So, more perspective adsorbents turned to be acetylated and aminizated PVC-fibers with elevated as compare to other investigated fibers concentration of active groups. In work [40] it is noted, that at enzyme immobilization (penicillin-linamidase, chymotrypsin) on PMMA, adsorption runs due to hydrogen links and elctrostatic interaction.

A promising trend in concentration of microbial biomass has become cell aggregation by polymer flocculants. Water-soluble cation and amphoteric polyelectrolytes are used with this aim. Cell flocculation is accompanied by recharging cellular surface which carryies negative charge. This is preceded by the reduction of ξ-potential of the cellular suspension. The efficiency of recharging is determined by the presence of positively charged ionogenic groups on macromolecules. This confirms the dominating contribution of electrostatic factor into the macromolecular adsorption on the cell surface [41]. Enzyme molecules form sorption complexes with ions which covalently join macromolecules. A specific pseudoelectret phase is formed separated then by filtration.

Processing of organic raw material in physical fields used in biotechnology attracts by its ecological safeness. The method can solve the problems of accelerating enzyme hydration of cellulose [42] and lignin [43], intensification of methane and hydrogen liberation from the biomass [44], and genetic transformation of cellular clones [45]. Presumably, a significant reason of such effects is the formation of electro-, magneto- and radioelectrets in the structure of biomass cell-adsorbents as well as electric polarization of DNA molecules.

Smart or intelligent materials are able to react to small changes in environment preset by the sample. Among the applied in biotechnology water-soluble polymers and hydrogels such materials can be the systems reversibly responding on pH, temperature, presence of certain substances in the medium and so on. This systems are used to isolate and clean biologically active drugs, immobilize biocatalyzers, in biosensors, for modeling regulation processes in the living cell connected with phase transitions in membranes, etc [46]. In biotechnology smart materials often utilize the electret effect.

Sensitive to changes in pH hydrogels respond on electric potential. So, a column (3 cm long) of partially hydrolyzed (20 % of amide groups) poluyacrylamide gel contracts 200 times in a 50 % acetone under the action of 1 V order potential [47]. In electric field hydrogel protons move to the cathode, while negatively charged acrylic groups of macromolecules migrate to the anode. Mechanical stress occurs in the gel (max - near the anode, min - near the cathde). This leads to a reversible collapse of the gel. In the absence of electric field the gel swells again.

Penetrability of membrane made of such materials depends on degree of gel swelling. In Fig. 7.4 schemes of increasing penetrability of the membrane with stable geometrical dimensions (isometric regime), and reduction of freely fixed membrane (isotonic regime) are given. In both cases removal of the field or washing of the membrane by a weak alkaline solution leads to dissociation of the polymer complex and rehabilitation of the initial penetrability.

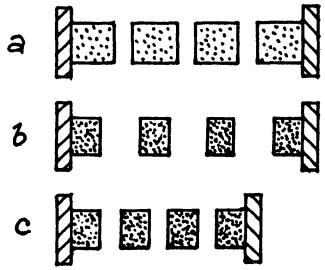

Fig. 7.4. Scheme of varying PMMA membrane permeability at interaction with polyoxiethylene: a - initial state, b and c - in isometric and isotonic regimes.

Capability of smart polymers of forming a separate phase in water solution at a negligible variation of conditions (e.g., at field application) is used at protein isolation and purification. The scheme of the process called *affinity precipitation* is given in [46].

Technical and economic aspects of electret application in biotechnology impose a discrepancy between the development of the science and economic conservatism of biotechnological industry. Most progressive biotechnological materials are marked by a considerable and, in many cases, radical transformation of industrial and consumer's spheres. The priority of using electret effect in biotechnology is conditioned by limiting raw material resources, fast recoupment and ecological purity of electret biotechnological systems.

7.2. APPLICATION OF ELECTRETS IN MEDICINE.

For almost a century a number of complex medical problems including diagnostics of diseases, regulated feeding of drugs, endoprosthesis biocompatibility, healing of operative wounds and etc. stay to be of utmost urgency. Experience in medicine and medical equipment shows that scientifically grounded use of electrets could contribute to each problem solution. Along with examples of highly efficient use of electret effect in diagnostics and curing a number of electret applications are described which have not been yet widely recognized but their potentiality is rather strong. Such solutions predetermine the nearest future of medicine. They are difficult to put into practice since the problem exists in between the adjacent sciences and should draw attention of experts from various domains of knowledge, first of all physics, biochemistry and medicine. The main problem of electret use in medicine consists in training specialists able to work at the junction of sciences.

7.2.1. Endoprostheses.

Endoprosthesis is a mechanical device designed to serve instead of damaged human organs or parts of body. It is implanted inside a man or animal's organism with the help of surgery.

There exists a concept of electret application in endoprostheses. All living beings are known to manifest a bioelectret effect. A sound organism distributes electret potentials in muscles, cartilage, ligaments and bones, but the distribution changes when the organism is ill [48]. In this connection it is worthwhile curing aftereffects of surgical intervention by forming an electret charge in the endoprosthesis that would distribute biopotentials in the operative zone like in a sound organism. Use of dielectric materials in endoprostheses ensures such an opportunity.

Electret endoprostheses are at present most efficiently used in traumatology and orthopedics.

A. *Electric stimulation* as a means of accelerating bone growth, rehabilitation and curing came into being upon discovering endogenous electric signals in bone tissue. They appear without application of any outer electric voltage or mechanical loading. Bioelectret potentials measured in vivo on long tubular bones using electrodes isolated one from another and contacting the bone are of the mV order. Bone tissue is more electrically positive as compared to bone marrow [49]. Close to fracture or bone tumor a considerable negative potential is formed [50]. When the bone bends, its compressed surface is charged negatively, while the stretched one positively [51]. A piezoelectric and electrokinetic mechanisms of biopotential generation in bones are supposed to exist. Bone feature to exhibit piezoelectric effect was experimentally proved in the 50-s [52]. Electrokinetic difference of potentials is directed along the flow of a liquid containing ions (blood, synovial liquid) in bone tissue, cartilage or connective tissue capillary [53].

Electric stimulation of bones has been for more than 20 years used for treating fracture, osteoporosis and infantine short extremity. Usually, electrodes contacting skin are applied or introduced into the patient surgically and the sore limb is placed in the induction coil [54]. Stimulation effects attained by these methods have been patented [55]. Electrochemical effects emerging at implanting endoprosthesis of unlike metals have been recorded. The experiments on white rats confirmed the dependence of osteogenic reparation on the electrode potential difference of metals the implants contacting the bone are made of [56].

Electret field effect on damaged bone and cartilage tissue compensation have been studied elsewhere [57]. Tantalum (Ta) oxide and polytetrafluoroethylene-(PTFE) based electrets were formed as coatings on highly pure tantalum implants. 0.15-0.45 μm thick coatings from Ta oxide were obtained by way of electrolytic anodizing. They possessed a stable electret state and physiological inertness. Polymer coatings on implants were sprayed from PTFE water suspension followed by drying and melting. The multilayer coatings were 30-40 μm thick. The coatings were electrized through corona discharge or an auxiliary liquid electrode.

The samples endured in a physiological solution showed a lowered electret potential which recovered partially upon its removal from the solution (Fig. 7.5). The potential recovery is, probably, due to the screening liquid desorption and the injected charge redistribution, i.e., liberation of carriers from traps and their drift in the electret field. The studied electret electrostatic fields stimulated physiological processes even after a prolonged exposure in a liquid conducting medium. This result corroborates with experiments on cellular culture, animals and clinical studies.

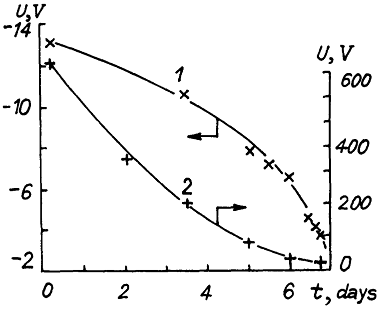

Fig. 7.5. The dependence of the maximum potential values of the electret restored upon sample withdrawal from a 5 % NaCl solution versus endurance time in the solution. The materials of electret coating: 1 - Ta oxide, 2 - PTFE.

Fibroblasts growth in a pure cellular culture has been investigated. In check experiments the fibroblasts were grown in a common Karel flask. During the study PTFE electret films were placed on the flask bottom. Calculation of fibroblast colonies using microscope not violating sterility have shown that there were more colonies in the flasks with electrets than in reference ones. On the second and third week of the experiment the fibroblasts oriented along the field force lines. An optimum for fibroblasts electric charge density has been traced. At a certain distance form the electrets the size of the cells was less while their density the maximum. This can be a proof to the cell regeneration capability.

The negatively charged electret side contacting the rabbit cartilage tissue raised its mineralization. The positively charged side did not practically effect the cartilage and bone tissue density. Ta rods were implanted into the rabbit radii subjected to transversal osteotomy. The rods with electret coatings stimulated a faster callus formation, mineralization and rearrangement as compared to reference ones.

The results agree well with experiments on bone osteosynthesis with 48 dogs. PTFE electret films were inserted into the region of tibia osteotomy and it was observed that atrophy of bone fragments under the electret fixative decelerated, osteocompensation activated, time of callus consolidation and rearrangement shortened and mechanical strength of bones recovered much faster.

The experiments with electret-coated fixatives have been conducted since 1981 for curing open, closed and gunshot wounds, pseudoarthrosis of tubular bones and some joint diseases [57]. They have shown that the mean time for rehabilitation and functional recovery reduces 1.5-2 times, number of misalignments sharply decreases. Electrets are especially effective for treating complex fracture and false joints.

The mechanism of electret field effect on the process of osteoreparation can be presented as follows. In the conducting and screening organism medium the field propagates to a small distance and excites mainly the nearest to the electret cells. Activation of remote cells in the field active zone is done through express transfer of excitation. Such an activation could spread to a considerable distance thus stimulating osteoreparation.

Electret implants have been patented. Osteoreparation stimulator [58] is made of a polymer film polarized so that on its working side the negative charge is localized. The film idle surface is coated by a metal physiologically compatible with the human organism (Au, Ag, Al, etc.). The coating is intended to prolong the electret life in specific conditions of the implant operation. The electret potential has a maximum in the stimulator middle point and falls down to its edge with 0.1÷100 V/mm gradient. Such stimulators are convenient in curing fractures by fixing the film on the skin or bone fragments. Stimulators of required shape and size can be cut during operation from the ready blank.

The element for osteosynthesis [212] looks like a perforated metallic plate with a dielectric coating. The coating is fit with the electret charge. The maximum electret potential corresponds to the plate mass center and decreases to its edge with 0.1-3.0 V/mm gradient.

In work [60] endoprostheses from carbon reinforced plastics with pizoelectric generators are proposed. Their signal is used to control mechanical stresses in the endoprosthesis-bone contact. The stress value conditions the time of callus formation. The generated charge can accelerate osteosynthesis. Such a system can be a base for intellectual prostheses responsive to the bone state.

B. *Biocompatibility* is capability of a material to cause a corresponding reaction of the organism-«host» under specific applications [61].

Biocompatibility of endoprosthesis presents an urgent problem which involves medicine, biology, materials science, materials technology, solid physics, surface engineering and etc. This field of knowledge has gained much more benefit from mistakes than from success. A significant conclusion has been made that there are practically only a few reasons of endoprosthesis refusal and the most important among them is insufficient biocompatibility [62].

Biocompatibility is a wider notion than nontoxicity. Experience in endoprostheses has given o lot of examples showing that biocompatibility is to a great degree conditioned by the charged state of the implant surface layer. Herein below some of them are listed [63]:

- cell cultures grow perfectly on of corona- or plasma-discharged polystyrene surface and poorly on the non-treated one;
- in the initial reaction between the implant and muscular tissue white cells react on the surface layer state by liberating chemical signal bands (cytocines) which control the operative wound healing;
- two of the used in endoprostheses materials, namely hydroxyapatite and bioglass show a unique biocompatibility with tissue integration into the implant. They have a carcass structure formed by O^{2-} and OH^- «bridges» carrying an uncompensated charge;
- best biological reactions are characteristic of materials (biologically active polymers, natural materials with immobilized by biomolecules surface, biologically degrading materials) with high radical concentration in the surface layer.

Plasma treatment of PTFE vascular endoprosthesis surface accompanied by surface charge generation is often in endoprosthetics use [64]. Accelerated growth and improved adhesion of epithelium to such implants have been recorded. Charging of inner surface of synthetic circulatory vessels by a negative charge [65] has become a classical example of highly efficient electret use in regulating endoprosthesis-blood compatibility.

Tyrosine which is polycarbonate derivative is applicable in fixative endoprosthesis for minor bones of the hand and wrist. It have shown perfect test results for biocompatibility producing remarkably similar to hydroxyapatite reactions promoting osteosynthesis. Thus, polycarbonate rods were implanted into a hollow bone of a dog. Observation which lasted for 48 weeks have shown their strong bonding with the bone. Histological analysis have proved bone spicules to penetrate into cracks and slots propagating on the rod surface [66]. Such a reaction of polycarbonate-derivative tyrosine differ basically from other orthopedic polymers.

Most probable cause of the phenomenon is the presence of non-amide links in their structure involved into the amino acid chain by linking individual amino acids or dipeptides through functional groups on amino acidic side chains (Fig. 7.6). Implants from these polymers carry a spontaneous surface charge restoring at macromolecular decomposition.

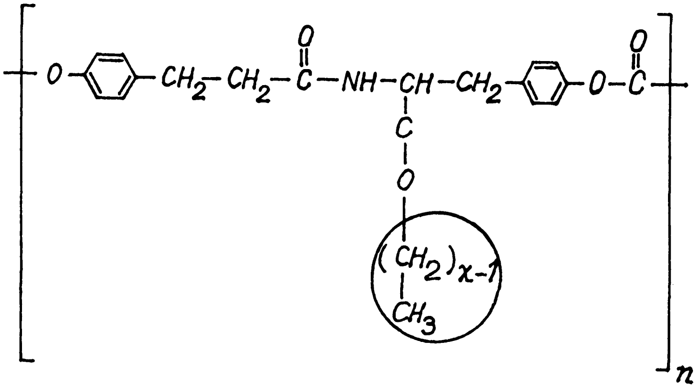

Fig. 7.6. Chemical structure of tyrosine-derivating polycarbonates consisiting of desaminotyrosyl-tyrosine alkylate ethers.

Physico-chemical methods of modifying implant surface have proved to be promising means of enhancing biocompatibility [67]. Polymer brushes [68] densely packed on a solid surface and attached to it by a polymer chain end change considerably biocompatibility. For example, a surface coated with polyethylene glycol do not accept protein adsorption and demonstrate high compatibility with blood [69].

Figure 7.7 shows the schemes of surface modification using polymer brushes. Surface potential ζ can significantly vary depending on the nature of functional groups on the brush free ends. Polysilamine-based brushes are sensitive to variations in environment. By regulating pH (from 2 to 10) or temperature (20÷40 °C) it is possible to change surface properties through making it positively charged and hydrophilic or negatively charged and hydrophobic [70].

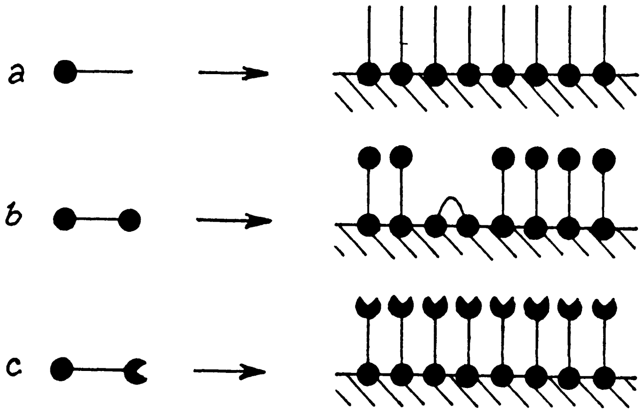

Fig. 7.7. Diagram of solid surface modification by: a - semitelechelic, b - homotelechelic, c - heterochelechelic oligomers;
1, 2 - functional end groups: 1 - hydroxyl, silanol, thiol, 2 - amines.

New methods of regulating surface properties have emerged in optico-electronic industry. They are attractive due to improved biocompatibility. Polymer electrostatic thin-film sets belong to them. The production technique of thin-film formations carrying this or that sign surface charge expands the Langmure-Blodgett method with minimum expences [71].

C. *Triboengineering characteristics* determine to a great degree serviceability and life of joint endoprostheses.

One of the most widely spread and cheap types of human endoprostheses is a movably conjugated joint of a polymer unit and metal or ceramic counterbody. In the recent years a tendency has outlined of transition to a more wear resistant endoprosthesis with metal-metal friction pairs. The problem of their biocompatibility has been solved through application of rust-proof alloys. Their design resembles machine friction joints and are insufficiently adjusted for operation in human organism. It looks advantageous to provide biocompatibility of endoprostheses by using materials approaching by their structure and properties cartilage and bone tissue. Among modern technical materials polymers most fully meet these criteria. Nevertheless, they are insufficiently wear resistant, for e.g., wear of UHMWPE cup in metal-polymer endoprosthesis of hip joint is in the average in vivo 0.2 mm/year and its durability does not exceeds 10 years [62].

Though a human joint consists of considerably less strong materials in contrast to polymers and metals, it surpasses metal-polymer endoprostheses in wear resistance. Most evident distinction between endoprosthesis and joint is in fundamentally different mechanisms of their lubrication. The key role in joint lubrication is played by the cartilage which bears the function of antifrictional material and porous reservoir for synovial liquid. There isn't any analogous elements in traditional endoprosthesis designs. That's why the main reason of endoprosthesis refusal is in fatigue wearing of polymer parts. Wearing mechanism in vivo has its specific features. In the surface layers (up to 40 μm thickness) of polymer parts cracks propagate parallel to friction surface. Their generation results in particles spalling from the friction surface. This causes a suddenly high wear rate of polymer parts in vivo which is by more than two orders of magnitude larger than at simulation tests [72].

In work [73] it was proposed to form a microporous layer on the friction surface of polymer parts of endoprostheses. The layer is created by transforming ~ 1 mm thick polymer layer into the gel state. The latter has a structure of a porous polymer matrix containing liquid in its pores (Fig. 7.8). The parameters of the layer porous system was estimated using computer analysis analogous to that suggested for debris analysis in joints [74]. The probability has been proved of forming UHMWPE gels which are actually full analogues of cartilage by the parameters of their porous structure. Upon removal of dispersed technological liquid from the gel the compatible with synovial liquid preparations and drugs are introduced into the polymer matrix pores which accelerate healing of operative wound. In the process of endoprosthesis operation they are substituted by synovial liquid.

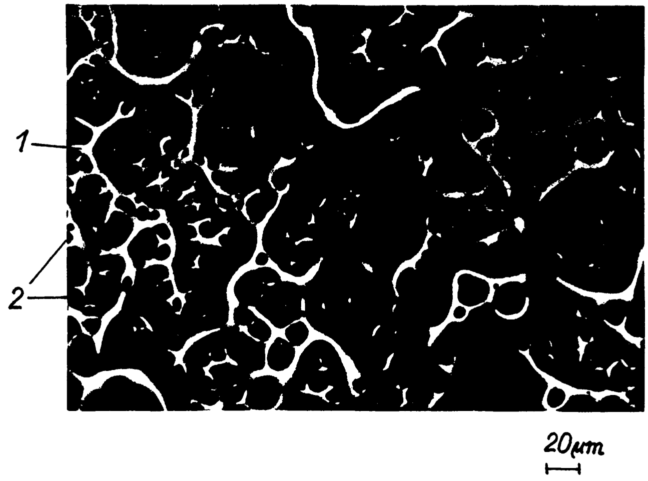

Fig. 7.8. Structure of the surface layer of UHMWPE-based gel and Vaseline oil: 1 - polymer matrix, 2 - pores containing liquid.

Micropore filling is a serious problem solved by regulating charge state of the porous polymer matrix. The polymer implant porous layer is treated by plasma, gas discharge or immobilization is performed on the pore walls of lyophilic molecules. Three methods are considered in work [75] for regulating solid body wetting through surfactant molecules adsorption on the wetted surface, adsorption of macromolecules whose segments are polar and have affinity with the surface, or polymer brushes (Fig. 7.9). In all the three cases change of wetting parameters is attributed to regulation of the surface charge state.

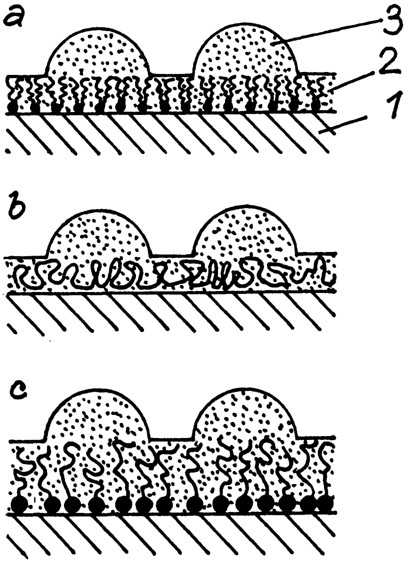

Fig. 7.9. Regulation of wetting by adsorbed layers consisting of: a - surfactant, b - polymer chains, c - polymer brushes; 1 - backing, 2 - adsorbed layer, 3 - liquid.

Endoprostheses with a polymer element having cartilage-simulating porous layer with medicinal or synovial liquid show the following advantages.

1. Wear of polymer parts follow predominantly adhesive or abrasive mechanism. Any signs of fatigue wear in the porous layer imitating cartilage were not found.
2. One of the arguments against polymer use in endoprostheses is the formation of a great number of wear debris. This overloads phagocytic mechanism of protecting synovial cavity and intensifies cell reactions in the space between the implant and bone [76] leading to endoprosthesis loosening. The microscopic analysis have shown that the gel porous structure serves as a vessel at friction which adsorbs UHMWPE debris. Withdrawal of particles from the friction zone decreases with the growing charge density on the friction surface.

3. Isolation of drugs from gel polymer matrix takes the syneresis mechanism. The process kinetics depends on the drug molecules polarity and the polarizing charge distribution in the porous layer. Thus, the prolonged action of drugs liberated into the operative wound from the micropores of cartilage simulating antifrictional element can be regulated.

The synovial liquid composition is known to include cholesterol derivatives belonging to the liquid crystalline group [77] which structure responds to changes in electric field. Using pendulum friction machine the friction coefficient of the steel-UHMWPE pair was studied as dependent on the polarizing charge density in polymer samples (Hostalen GUR, Germany). The load was similar to the range of human joint loading. The friction was lubricated by a physiological solution with added 2 % of liquid crystalline compositions (a 1:1 blend of oleic and linolenic acids).

When the friction pairs are lubricated with the physiological solution, the friction coefficient does not react on the presence of the polarizing charge in the samples. Lubrication with a composition containing liquid crystals imparts the pair sensitivity to the charge state of the polymer sample. The dependence was established between the friction coefficient and the polarizing charge density (Fig. 7.10). The negative charge effect is more efficient than that of the positive.

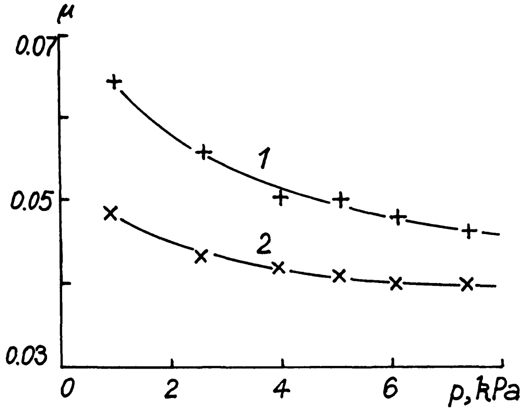

Fig. 7.10. Steel-UHMWPE pair friction coefficient versus loading and presence of polarizing charge (σ) in the polymer sample at lubrication by a liquid-crystalline composition: 1 - $\sigma = 0$; 2 - $\sigma = 10^{-8}$ C/cm^2.

7.2.2. Regulated drug transport.

Any drug consists of two main parts, i.e., an active medicinal substance (MS) and components of the medicinal form (MF). The latter ensures favorable conditions for the active substance behavior in the organism.

Traditional MF involving tablets, capsules, ointments and injection solutions are not optimum by this criterion. They do not provide the regulated MS delivery to the part they are to heal.

The modern concept of drug formulation treats MF as a system for a prolonged and continuous, according to a given program MS, transportation to the sick organ, the target. Some elements of the system consist of polymers, so the new generation of MF is called the macromolecular therapeutic system (MTS) [78]. Their development is an actual problem connected, particularly, with chemotherapeutic oncology which needs drugs able to hamper toxic reactions and create antitumoral effect [79].

MTS size ranges from millimeter fractions to several centimeters. They are introduced into the organism perorally, as injection or implantation, and can be fixed on the skin or mucous membrane. MS is not, as a rule, chemically connected with MTS, so its isolation is a physical process accompanied, in a number of cases, by the change in MF charge state. This serves grounds for the electret use in MTS.

The peculiarities of MTS healing action are shown in Fig. 7.11 in contrast to traditional MF [80]. The latters provide uneven MS introduction into the organism (curve 1). Rapid isolation of the main mass of MS often approaches its critical concentration and may cause side effects. Most of the present day MS participate actively in metabolism. In this connection their concentration *C* in the organism rapidly drops and necessitates another dose of the drug. Non-optimal for therapy saw-tooth diagram of *C* dependence on time is characteristic for patients with chronic diseases. The simplest MTS program is provision of a steady MS isolation at a given time period (2). Often, ejection of the elevated content of MS is useful at the beginning of MTS work with transition to the regime of drug isolation at a constant or decelerating rate (3). The principle of self-programming systems, where the rate of MS isolation depends on organism reaction was formulated in 1979 [81]. MTS for curing diabetes which controls insulin ejecta and responds to glucose concentration in blood were developed on this base [82]. The program is assigned by a specific MTS structure, design and its polymer units charge state.

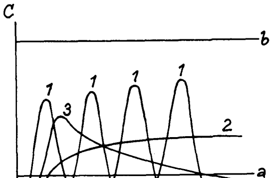

Fig. 7.11. Kinetic dependence of drug concentration in blood plasma at using different medicinal forms: 1 - a periodic introduction in traditional MF; 2 and 3 - continuous feeding from MTS; a and b - lower limits of efficient and toxic concentrations.

The idea of electret use in MTS consists in electrostatic interaction between MS molecules and the electret field. The more polar is the molecule the more strong is interaction. Neutral molecules polarize in the electret charge field and then interact with it. This assists in most cases MS retaining in MTS. Electret charge relaxation under the action of factors predetermining the organism state accelerates liberation of MS molecules. Realization of this idea in different MTS groups has features of its own.

MTS with a nondestructive in the organism porous polymer frame-vessel for MS is its simplest type. The frame is fabricated from biocompatible polymers, for e.g., silicon rubber, ethylene and vinyl alcohol copolymers (EVA), polymethyl methacrylate and other MS which are introduced into MTS in the form of powders at the stage of the frame formation. The liquid-phase MS (solutions, suspensions) saturate the formed frame. MTS as spheres or rods are inserted into the organism cavity or implanted. Upon diffusive removal of MS the frame is withdrawn from the organism.

Transformation of the frame into the electret state decelerates MS isolation and its molecules are held-back on the frame walls by electrostatic adsorption (Fig. 7.12). Charge relaxation accelerates MS diffusion. The kinetics of MS transportation from such MTS in the organism is described by diagram 3 in Fig. 7.11. The maximum here corresponds to MS removal from the frame surface layer followed by diffusion deceleration due to the electret field effect. This is confirmed by the following facts.

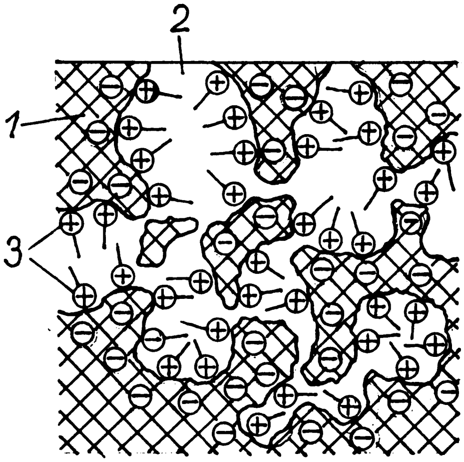

Fig. 7.12. MTS structure with nondestructive polymer frame: 1 - frame, 2 - pores filled with MS, 3 - MS molecules.

The kinetics of diffusive liberation of 5-fluororasil (anticancerogenic MS) and hydrochloride pilocarpine (ophthalmological MS) from the frames on EVA copolymer base have been studied. The velocity of diffusion depends on the ethylene to vinyl alcohol link ratio in the copolymer macromolecule, i.e. on the polarizability of the polymer frame.

In the 80-s in GDR a Kallocryl MTS was developed based on polymethacrylate and sulfate gentamicine for local pharmacotherapy of infected wounds. Introduction of decreasing polarizability plasticizer (polyethylene glycol - 400) into the polymer frame intensified MS liberation. Addition of a surfactant (butandiol dimethacrylate) diminishing wetting and rising polarizability of the polymer frame reduced the velocity of gentamicine diffusion.

MTS on the base of biologically soluble and destructive polymers is functioning in conditions of mass exchange with the organism liquid media.

Most of modern MF on the biodegrading polymers base are formed by heterochain macromolecules (synthetic or natural). If to exclude emergency cases (e.g., curing of malignant tumor) all MTS components must leave the organism during a reasonable period as a result of excretion or metabolite assimilation of the organism.

The degree of MS bounding to such a polymer carrier defines the MTS physiological activity. Most frequently MS is retained on the carrier through the hydrolytic labile link decomposing in the presence of enzymes. MS liberation is accompanied by breakage of the links and formation of -ON, $-H_2$, -CHO, -COOH groups causing the carrier electric polarization [83]. The forming radicals neutralize according to the chemical kinetics laws leading to surface charge decrease. Thus, MS liberation is accompanied by the formation and neutralization of charge carriers in dynamic equilibrium. During MTS functioning the equilibrium shifts to the side of surface charge increase. The latter drops then with MS consumption and approaches zero. This group MTS are dynamic electret systems which lifetime is commensurable with that of MS liberation.

Kinetic dependencies of the structural and charge parameters of the polymer carrier during MTS operation are given in Fig. 7.13. The carrier biodegradation is accompanied by exponential mass decreasing (curve 1). Simultaneously with this, the quantity of radicals formed at degradation rises at first and then drops passing the maximum (2). This curve corresponds to variation of the degrading charge carrier mass. Curve (3) of radical neutralization is analogous to the second curve but relative to it curve 3 maximum is shifted by the period Δt equal to time from radical formation to neutralization. The dependence of surface charge density formed at degradation also passes the maximum which abscissa is inside Δt.

Frequently, electret charge is initially created on the polymer carrier. It assists electrostatic bonding between the carrier and the cell surface or functional groups alleviating MTS penetration into the organism [84].

The compositions of biologically destructive MTS are, as a rule, patented [85].

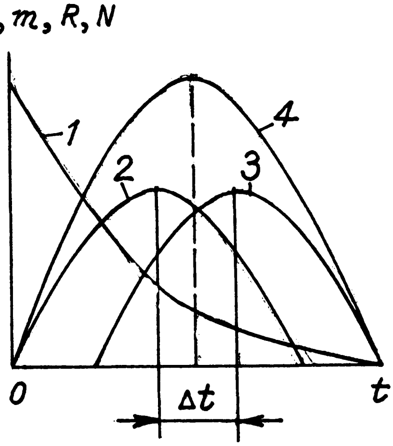

Fig. 7.13. The dependence of polymer carrier mass (m, 1), radical number (R, 2) formed at macromolecule degradation, number of neutralized radicals (N, 3) and surface charge density (σ, 4) formed at degradation versus time of MTS functioning.

Hydrogel MTS have polymer carrier from hydrophilic polymers adsorbing water till an equilibrium value and are insoluble in water due to a three-dimensional net. They are used when not swelled or as a ready gel. Hydrogel MTS have been developed able to decompose in the organism.

Probable applications of electric polarization in hydrogel MTS can be illustrated using the example of already mentioned systems for controlling insulin isolation. A complex of lectine and saccharum-containing derived insulin are placed into the polymer matrix that is permeable for both glucose and insulin but not permeable for lectines (Fig. 7.14). Glucose from the environment penetrates into the hydrogel polymer matrix and replaces insulin derivative in it. Electric polarization of the matrix is a helpful means of regulating rate of the processes. It can change the degree of hydrogel swelling, strength with which the matrix electrostatically attracts or repulses glucose and insulin molecules as well as the intensity of polymer matrix degradation.

It can be anticipated that the last generation of hydrogel MTS intended for osteosynthesis and curing of posttraumatic diseases [86] would take the path of regulating drugs release (bone morfogenic protein, fibrin-degrading agents etc.) using methods of hydrogel polymer matrix polarization.

Hydrogels constitute the base of materials for contact lens of prolonged usage. Tough and rather contradicting requirements are imposed on the lens, i.e. suitable mechanical properties (low elasticity modulus and high tear strength), optical transparency, chemical and thermal stability, and biocompatibility. Along with this the material should be permeable to oxygen and wettable by tears [87]. Satisfaction of the latter requirement hampers in many situations realization of other hydrogel properties ensuring lens serviceability. Electric polarization of hydrogel polymer matrix helps to differentiate and regulate in a wide range wettability of lens not practically affecting other hydrogel parameters.

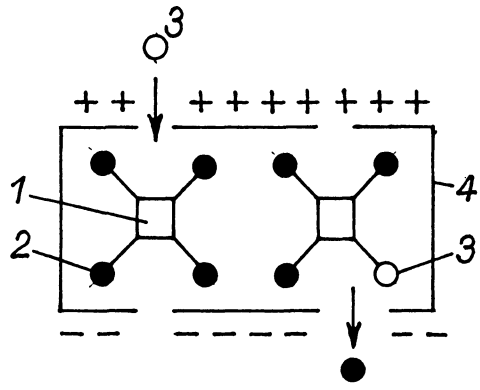

Fig. 7.14. Diagram of a hydrogel MTS for regulated insulin isolation: 1 - lectine complex (conquinamine A), 2 - carbon-containing insulin derivative, 3 - glucose, 4 - hydrogel polymer matrix with polarizing charge.

Membrane MTS is a reservoir containing MS which walls are formed by a 10-100 μm thick membrane controlling MS diffusion velocity from the reservoir. Regulation of permeability is an important task in creating membrane MTS. It is necessary to balance membrane permeability and that of the mucous coat (or skin) of the organism. MS flow through the membrane should be such as to maintain in blood MS concentration close to the minimum therapeutic for a long time (from a week to a month).

Use of electrets in these systems is based on regulation of diffusive permeability of the polymer membrane by electric polarization. It's equally effective for both types of used in MTS membranes, namely continuous (diffusive), usually made of silicon rubber and polyurethane, and microporous ones (pore size 0.1-1.0 μm) from cellulose ethers, polyoxyethyl methacrylate hydrogels, polyvinyl acetate, polycarbonates.

Membrane MTS structures are versatile ranging from the simplest microcapsules to complex systems involving many elements and realizing programs with variable in time MS feeding.

Cutaneous therapeutic systems (CTS) are aimed at prolonged and continuous MS feeding through the skin according to a given program. By its design CTS is a thin (below 1 mm) manylayered lamella structure (Fig. 7.15).The upper cover layer 1 is usually made of a metallized polymer film.

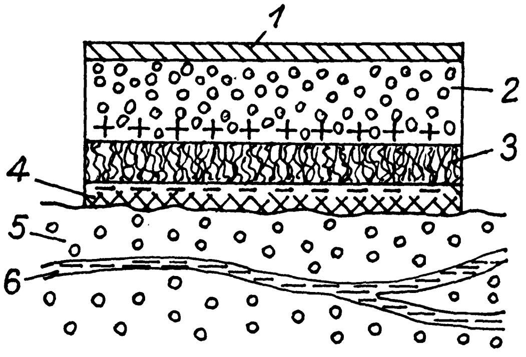

Fig. 7.15. Cutaneous therapeutic system. Explanations in the text.

The next is reservoir 2 in the form of a layer containing MS in the liquid-carrier. The reservoir is divided by a polymer microporous membrane 3 which controls MS consumption owing to its porosity and electret charge. With adhesive layer 4 the system is fixed on the skin 5. Through the skin MS is brought to local circulation vessels 6.

The amount of fed to the skin MS is regulated by membrane 3 permeability and relaxation of the formed in it polarized charge. For creation of the initial elevated MS ejection it is introduced into the adhesive.

The first CTS were worked out in the 70-s at American company «Alza» by A. Zaffarony with collaborators [78]. The formation of polarized charge on membranes was attached little importance at that time. Considerable discrepancies in MS isolation kinetics confirmed, however, the presence of spontaneous charge in the membranes. Systems with scopolamine (antiseasickneess means), nitroglycerine (antianginous) and clonidine (hypotension drug) have undergone clinical tests. CTS included anti-infectious, antiallergic and analgetic drugs. CTS helped many of chronic patients to avoid hospitalization and to undergo ambulant therapy.

Microcapsules with MS in the membrane shell are extensively used in medical practice.

Among this class goods a contraceptive system «Progestasert» (Alza) is known. It contains progesterone - a natural hormone. The latter diffuses through the membrane and occurs in the target organ (uterus). The membrane penetrability is finely regulated. This provides for the minimum but sufficient for contraception excretion of hormone during several months.

The preparation «Ocusert» is inserted under the eyelid. Drugs, for e.g., pilocarpine are isolated through the hydrogel membrane. Owing to accurate dosage of drug penetration, such a system efficiency is much higher than that of drops, ointments and other traditional MF.

Electric polarization is a convenient means for regulating membrane permeability. Figure 7.16 shows the diagram of a system displaying spontaneous polarization to control insulin feeding. The microcapsule shell is made of hydrogel based on amino-containing polymer with immobilized glucoseoxidase (GO) which is a ferment randomly catalyzing glucose oxidation to gluconic acid:

$$C_6H_{12}O_6 \xrightarrow[O_2]{GO} HO-CH_2-(CHOH)_4-COOH + H_2O$$

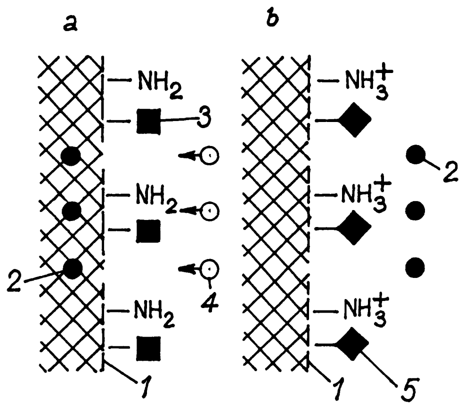

Fig. 7.16. Operation mechanism of microcapsule with self-polarizing membranes for regulated insulin diffusion: a - before, b - after glucose penetration into the capsule;
1 - membrane, 2 - insulin, 3 - glucoseoxydase (GO), 4 - glucose, 5 - the product of GO transformation.

The system works as follows. Glucose appears in the medium surrounding the capsule and diffuses into the hydrogel membrane. GO oxidizes glucose and hydrogel pH decreases leading to ionization of hydrogel aminogroups. Due to electrostatic repulsion of the charged aminogroups the degree of hydrogel swelling increases. This speeds up insulin diffusion through the membrane to the organism.

Osmotic minipumps are a specific type of MTS. They are reservoirs from a semipermeable membrane containing MS and a solid osmotic agent (usually NaCl). Water diffuses from the organism through the membrane to the reservoir. MS and osmotic agent solution is formed there generating osmotic pressure which is proportional to the amount of entered water. MS solution is ejected under the pressure action through a special hole in the membrane. Osmotic minipumps are used perorally, placed in the organism cavity or implanted on the skin.

The company Alza manufactures two types of minipumps. The simplest type is «Oros» intended for peroral use. It is covered by a membrane of the matrix tablet consisting of solid MS and salt. A more complex type «Alzet» is a cylinder inside a cylinder. In the outer cylinder a solid osmotic agent is placed, in the inner one there is MS solution. The inner cylinder has a microhole for MS releasing outwards. This takes place when water from the organism penetrates into the outer cylinder and osmotic pressure develops there.

Time and place of minipump actuation are defined by the membrane properties. It could permit inside predominantly acid or alkali media or partially destruct in the presence of certain ferments. This offers an opportunity for regulating the membrane permeability using electric polarization. The base of structurally sensitive to electric field membranes are PVC compositions with polyacids. Their permeability is connected with polarizing processes in the amorphous part of the polymer matrix and depends on stereoregularity, molecular mobility and presence of acidic groups in the composition [88].

The given review proves that the problem of regulated transport of drugs stands in the abutment of medicine, biology, chemistry and engineering. Its solution is characterized in the 90-s by a wide use of physical methods for monitoring processes of drug liberation from its carriers. This is essentially associated with the carrier charge state control and electret effect application.

7.2.3. Electrotherapy.

Electrotherapy is a general term for curing methods based on dosed effect of electric current, electric and electromagnetic fields on the human organism.

Most spread methods are using low-voltage current. The current is directed through the apparatus terminals and by wires on the electrodes fixed on the patient. The current passes continuously (*galvanization*) or by pulses alternating with pauses. In this way ion motion as well as physico-chemical processes are stimulated at the cell level. This excites reactions in the organism and its systems and enhances blood circulation, sleep, relieves pain and inflammatory processes, heals injured tissues, and so on. The action of currents intensifies if to wet the seal under the electrode by a drug solution. It penetrates to the tissues and effects in its way the organism. This method is called *medicinal electrophoresis*.

Application of high-voltage pulse current has obtained the term *darsonvalization* by the name of a Frenchman D'Arsonval who suggested this method. The therapy makes use of glass electrodes filled by a luminous gas. Between the skin and electrode a small spark discharge is generated. It irritates nerve endings in the skin due to which blood circulation and tissue feeding improves, and pain attenuates.

Franklinization is the method employing a constant electric field of high voltage. Spicular electrodes are placed above the head or the affected area (wound or ulcer). Molecules of the air ionize in a strong electric filed and inhalation of ions imposes positive effect at a number of diseases.

UHF-therapy makes use of the alternating electric field of ultra-high frequency. The exposure is conducted through condenser plates installed over the affected area. It is accompanied by the feeling of heat and results in antiinflammatory action, vasodilatation, improved tissue nutrition, relieved pain.

Microwave therapy utilizes ultra-high frequency electromagnetic field (of centimeter or decimeter band). Energy of radiation penetrates into the organism tissues to the depth of a few cm causing vasodilatation, pain relieving and improving tissue feeding.

The above-mentioned methods do not involve direct action of electret field on the sore organs. They are, nevertheless, realized with the help of medical electronic instruments and devices incorporating electret transducers, switches, meters and other units described in ch. 2. Besides, there exists a medicinal field directly connected with application of electret effect. This includes, first of all, methods of diagnostics based on recording biopotentials of separate organs and the methods where electric polarization of medical preparations or organism systems is used.

Diagnostic methods making use of recording biopotentials have been developed for a rather wide group of organs displaying a powerful biofield.

Most known and popular among the biofield diagnostic methods is *electrocardiography*. This procedure for functional analysis of heart is based on graphic registration of its biopotentials variation in time. *Electrocardiogram*, which is the kinetic curve of potential difference of the heart electric field at its systole, is taken by the instrument called electrocardiograph. Depending on the method of recording biofield parameters the following types of instruments can be discriminated. *Electrocardioscope* records data on biological activity of the heart by reflecting its electric field variations on display of the electron-beam tube (oscilloscope). *Electrocardiophone* transforms heart biopotentials into sound signals. Most accurate technique of investigating heart activity and visualizing its defects in interatrial and interventricular septum is *intracardial electrography*. The procedure consists in recording the dependence of heart biopotentials in time using electrodes located on its cavity walls. *Intracavitary electrogram* of the heart is the kinetic curve of its electric field potentials recorded using electrodes introduced into the heart cavity through blood vessels.

A vast set of diagnostic methods have been developed for the functional state of brain. They fall into the following groups of investigation depending on the means of recording brain biopotentials. *Electroencephalography* conducts graphic recording of biopotentials variation in time. By means of electroencephaloscopy biopotentials of numbers of brain sites are fixed on display as a mosaic of dots continuously varying their brightness and size. *Electroencephalophony* is based on transformation of infrasound oscillations of biopotential into the sound frequency oscillations. The corresponding electronic instruments have got the names of electroencephalograph, electroencephaloscope and electroencephalophone. *Electrocorticography* is the method for investigating cerebral hemispheres cortex. It consists in recording cortex biopotentials using electrodes placed just on its surface. It's used mainly during surgical operations or in experiments on animals. The method is realized by *electrocorticograph* - a special instrument completed with small electrodes fixed precisely on certain sites of the cortex. The diagnosis is determined using *electrocorticograms* - the curves of cortex biopotential dependence on time. *Electrosubcorticography* is the method to investigate brain subcortical structures. It is based on recording biopotentials using introduced in these structures electrodes.

Electroneurography studies nervous system based on graphic recording in time the varying bioelectric activity of peripheral nerves. The sum of axon potentials constituting the nerve (neurogram) is recorded by *electroneurograph.*

Electrogastrography investigates motor activity of the stomach by recording its biopotentials. A special instrument is used with this aim named *electrogastrograph* which registers biofield variation in time. Electrointestinography similar to *lectroneurography* analyzes intestine functioning. Electrogastroenterograph estimates biopotentials of separate gastroenteric tract sections. This is attained by generating signals with 0.04-0.06 Hz frequency for the stomach, 0.1-0.3 Hz for small and 0.015-0.03 Hz for big intestine.

Special diagnostic methods are devoted to investigating *nystagmus* which is involuntary two-phase rhythmic (with fast and slow phases) eyeball motion. *Electronystagmography* is the method investigating nystagma based on recording variations of eyeball biopotentials. Sensors transmitting signals to the electronic device *electronystagmograph* are fixed on the eye orbit edges. The functions of ocular muscles and the functional state of retina outer layers are investigated by *electrooculography.* Using *electrooculograph* the eye biopotentials are registered by fixing electrodes on the outer edges of the eye. The analogous method of investigating retina functional state is called *electroretinography.* The curve of retina biopotentials variation emerging at eye irritation by light (electroretinogram) helps to define retina diseases.

Electromanometry is measurement of pressure variation in the body cavity or in the lumen of a large blood vessel using a manometer with an electronic pressure sensor. The latter is very miniature necessitating application of predominantly electret transducers in the electromanometers.

Functional diagnostics of muscle system is at present unthinkable without *electromyography*, the method for graphic registration of skeletal muscles biopotentials. The kinetic curves of biopotential variation (electromyograms) are obtained using special devices *electromyographs*. *Electromyomasticatiography* is a simultaneous recording of biopotentials of both chewer and the lower jaw movement.

In the recent years a new diagnostic method has been worked out for investigating blood diseases. It is based on the electret application technique. Aqua molecules are known to be connected with proteins playing an essential role in biological processes. Hydration of two important oxygen carriers in the organism, i.e., hemoglobin (Hb) and myoglobin (Mb) stabilizes the structure of red pigment thus assisting reversible bonding of oxygen [89]. Dehydration is accompanied by Fe oxidation which enters carrier composition and formation of hemochromic particles. The latters are composed of coordinately bonded with red pigment Fe atoms and show a characteristic UV adsorption spectrum [90]. Structural recombination of Hb and Mb is accompanied by the varying functional state of all significant systems in the organism. Prompt information on aqua molecules relation to Hb and Mb and on stability of these hydrated structures is valuable to diagnose a number of diseases.

In work [91] a characteristic is given of the linkage between aqua molecule, Hb and Mb using TSD. In Fig. 7.17 TSC spectra are shown taken for Hb (1) and Mb (2) samples. These are general spectra obtained by sample polarization in a wide temperature range. The components of general spectra have been separated and interpreted by making-and-breaking the field in the narrow band boundaries of the given temperature range. A conclusion has been made on the existence of several hydrate shells round Hb and Mb featuring wide distribution of relaxation times and activation energy. A supposition have been put forward on conformation protein changes at dehydration.

Methods utilizing electret effect are not numerous as compared to diagnostic ones, but are widely applicable today.

Electroaerosol is the aerosol which particles carry electric charges. *Electroaerosol therapy* uses electroaerosols with curing or therapeutic aims. *Electroaerosol inhalation* is a curing procedure during which electroaerosol of a drug reaches the organism through respiratory tracts. The procedure

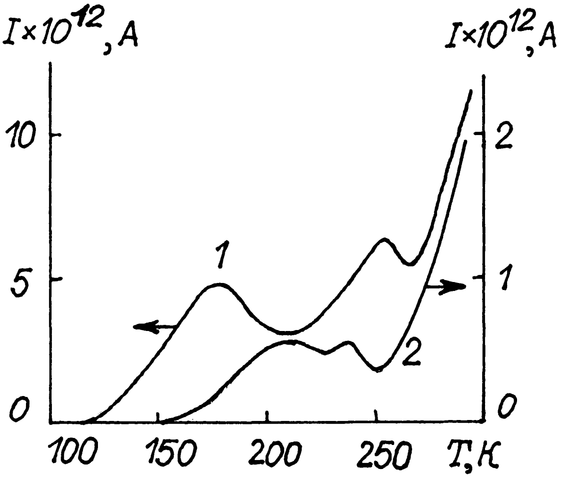

Fig. 7.17. TSC-spectra of hemoglobin (1) and myoglobin (2). Degrees of sample hydration, correspondingly: 0.08 and 0.025.

employs an electroaerosol generator - the source of aerosol. It incorporates a device imparting electric charge to the aerosol particles. Electret effect during inhalation provides for the highest curing effect. Fine particles of a drug possessing large surface and carrying the electric charge are electrostatically attracted to the mucous coat in the respiratory tract. So, they almost fully cover the surface, their charge dissipates and the drug is rapidly absorbed by the blood. The curing effect is thus composed of MS and electric charge actions on the organism.

Electroanelgesia relieves pain at electric field or current effect on the central nervous system or directly on the site of painful sensation. *Galvanopuncture* is one of its variants. It exerts the electric field or current effect on biologically active points using acicular electrodes or field source. A device has been proposed by the present authors of segmental reflexotherapy (Fig. 7.18). It consists of an elastic base with fixed on it needles [92]. The base is made of magnetic material with different-pole magnetized surface. The needles are made of a ferromagnetic and dielectric polarized materials. The latter ones are installed on magnetic poles, the electret needles are placed between opposite poles. Thus, the applicator becomes the source of both magnetic and electric fields. This offers synergetic action of different physiotherapeutic factors on the organism. The applicator ability to relieve painful sensation increases considerably.

Use of electrets in medicine is connected with realizing multidisciplinary research programs, combining biology, chemistry and engineering. Research is required in cellular mechanisms of healing,

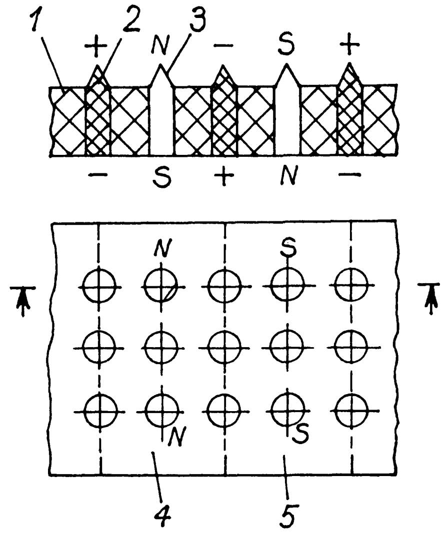

Fig. 7.18. Electret-magnetic applicator: 1 - elastic magnetic base, 2 and 3 - electret and ferromagnetic needles, 4 and 5 - magnetized oppositely sites on the base.

synthesis of new materials and the development of new technologies for clinical applications. Most effective means of advancing tissue-engineering technologies will be in enthusiastic cooperation [93]. Many advances have been made in the past decade, with a number of commercial products already available for medical applications, and the next decade promises to yield even greater innovations.

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CHAPTER 8

ECOLOGICAL AND ECONOMIC ASPECTS OF ELECTRET APPLICATION

Use of electrets in machines influences technicoeconomic aspects of machinery production and durability, as well as on ecological and social problems. Some of these questions are treated in this chapter.

At present the range of electret industrial application is commensurable with that of dielectric materials. In this connection, time of electret charge conservation has become one of the most important factors of machinery efficiency. Most of electrets are in nonequilibrium state that disappears at operation due to the polarizing charge relaxation. When in operation or production stage, often an unexpected spontaneous polarization of dielectric occurs. Its effect on operation properties of articles is ambiguous. It leads, in a number of cases, to reduction of equipment serviceability.

Electrets contribute into solution of some problems connected with ecology, since electric field is an ecologically safe technological means. Electrets can be used to disinfect industrial emissions and waste waters, reduce corrosion of materials, clean air and running water, solve other problems of environmental pollution.

All the above mentioned facts form the basis of technical and economic benefits favoring electret application. In this chapter the principles of economic analysis are considered used to estimate the expediency of electric polarization and the results are discussed of electret application in machinery with account for their action on environment and social sphere.

8.1. TERMS OF ELECTRET CHARGE PRESERVATION.

Electret performances undergo changes due to relaxation of polarized charge leading to impairment of machine parts containing electrets. So far, the problem of time of electret charge preservation, or in other words, stability of electrets is of major importance when selecting electret materials and forecasting their efficient operation conditions.

8.1.1. Charge relaxation.

Kinetics of electret charge relaxation (i.e., discharge or depolarization) is characterized by kinetic dependencies between electret potential difference $U_e(t)$, total charge per unit electret area $\sigma(t)$ and discharge current density $j(t)$. Time and velocity of charge relaxation in isothermal conditions differ much for various dielectrics and depend on conditions of electret charging and storage (operation). Relaxation mechanisms of dielectric charge electrified in different conditions may also differ.

As it has been noted in 1.2, the method of thermally stimulated depolarization (TSD) or thermally stimulated discharge (TSDc) is highly popular with researchers in investigations of polarization and charge relaxation mechanisms. Discharge occurs in nonisothermal conditions when electret is heated under constant velocity. TSD advantage is a relatively short duration of experiment not exceeding one test hour. It should be considered although, that it is not always easy to establish the relation between isothermal and nonisothermal test results. It is possible to interpret TSD-produced results on the base of this or that notions on discharge nature [1].

It has been found out that the velocity of U_e reduction is the higher the larger is the initial value of electret potential difference U_e^0 (Fig. 8.1). Time of the original area relaxation reduces with increasing U_e^0.

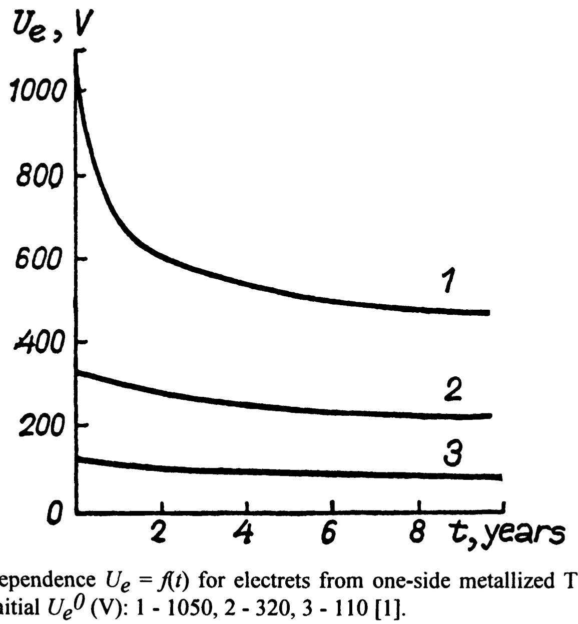

Fig. 8.1. The dependence $U_e = f(t)$ for electrets from one-side metallized Teflon FEP films with different initial U_e^0 (V): 1 - 1050, 2 - 320, 3 - 110 [1].

At *elevated temperatures* the process of charge relaxation in isothermal conditions runs rather intensely and terminates in a few hours or even minutes. In this case the dependencies $U_e(t)$, $\sigma(t)$ and $j(t)$ are studied continuously and the electret is discharged just between the measuring device electrodes. It has been already shown in [2] that with rising temperature the rate of depolarization increases (Fig. 8.2).

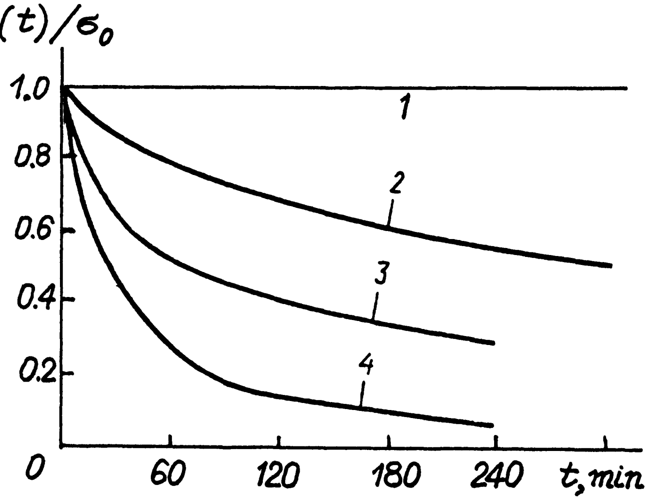

Fig. 8.2. Charge relaxation in polycarbonate electrets under different storage temperatures (°C): 1 - 25, 2 - 90, 3 - 10, 4 - 120.

In the course of a few first days or hours (depending on storage temperature) a relatively fast charge reduction is observed. Then, the charge stabilizes and the second stage is characterized by not less than a 8-10 years relaxation period.

Charge variation with rising temperature is defined by temperature dependence of dielectric conductivity. When electrets are heated at a 3-4.5 °C/min rate, HDPE space charge quickly breaks already at a 70 °C temperature. In ceramic materials a noticeable charge is preserved till 200-250 °C, while in pyrolytic boron nitride space charge diminishes below 10 % at 300 °C [3].

Despite the fact that electret storage at elevated temperatures leads to a faster space charge relaxation, there are data evidencing that charge stability for the majority of electrets can be increased by their heating during, upon or even before electrization [4, 5]. As for e.g., charge relaxation time constant of annealed after charging Teflon FEP-based electret is about 200 years at room temperature [6].

Durability of polymer film electrets is conditioned by the polymer origin and depends most of all on its *specific conductance* γ. The less γ, the higher stability shows one-side metallized electret at room temperature (Fig.

8.3). It is seen from the figure, that an extremely high stability display one-side PTFE electrets negatively charged in this case (by electron beam or corona discharge). Relaxation of positively charged samples proceeds much quicker. This can be attributed to a more mobile holes in contrast to electrons in the negative Teflon [7].

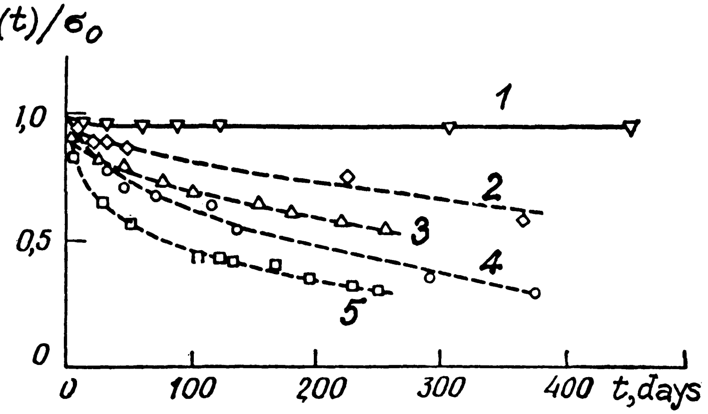

Fig. 8.3. Charge relaxation in dry atmosphere at room temperature for electret films from: 1 - PTFE, 2 - PC, 3 - PP, 4 - poly-2,6-diphenyl-1,4-phenyleneoxide, 5 - PETF [4].

Electret stability depends, to great degree, on environment *humidity*. Homocharge relaxation time in polymer films is specified by their specific surface conductance which increases by several orders in humid medium [8]. Electrets from fluorine-containing polymers are most durable in humid atmosphere. The polymers can be placed in the following order according to decreasing stability [1]:

Teflon FEP > PP > PTFCE > PS > PETF > PI

Screening of electrets hampers outer charge relaxation because of settled from air ions [9] or any other adjacent medium, for e.g., moving electroconducting liquid. The process of electret discharging is considered to be strongly retarded if the samples are stored or in operation between short-circuited electrodes. Such state is characteristic of metal-polymer electrets (MPE) working as a M1-P-M2 system with short-circuited or closed through resistance electrodes [10].

8.1.2. Effect of additions.

Filled polymers display, in a number of cases, a complex of indispensable for technical application properties. So, to obtain a material with given mechanical, electric, heat and physical properties, compositions are widely used consisting of a polymer binder, filler and other additives, as well as heterogeneous polymer-polymer blends and plasticized polymer materials. Fillers (different nature fibers, talc, fabric, metal oxides, etc.) improve mechanical properties of polymers, while powder ceramic materials rise dielectric permeability of compositions. Composite materials are not molecular-level blends as compared to solutions and plasticized polymers, but present heterogeneous systems. Each of the mentioned material possesses the properties of their own influencing formation and relaxation of the electret charge.

Plastification is an efficient technological method of regulating deformation and strength characteristics of polymer materials. The most spread type of plastification is introduction of low-molecular substances compatible with polymers at molecular level. This changes some parameters of dipolar-segment and dipolar-group losses which effect dipolar orientation and ion shift accompanying electret state formation.

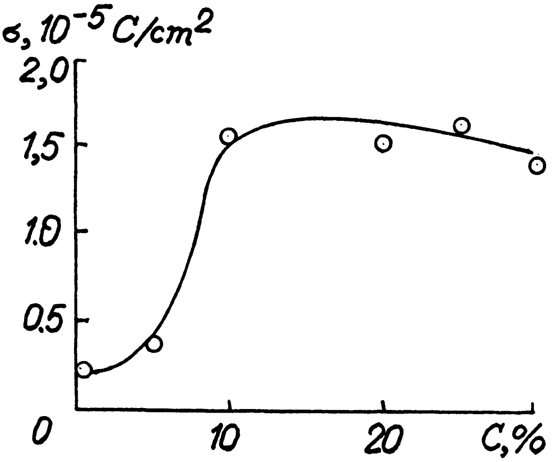

Fig. 8.4. TSD charge density in plasticized PVB samples depending on DMP content in polymer material. Polarization between Cu-Al electrodes.

Figure 8.4. presents TSD charge density dependence in PVB-based MPE versus dimethyl phthalate (DMP) plasticizer amount in the sample. The presence of maximum corresponding to 10-20 % of DMP concentration can be explained by competing effect of two factors. With increasing content of plasticizer there grows the amount of additives serving as traps for charges and initiators of dipole and quasi-dipole formation. At the same time, increase in DMP concentration causes weakening of molecular interaction and rise in electric conductivity of the polymer material. These reduce rigidity of polarized elements bonding inside the structure.

Despite wide nomenclature and expanding application of *filled polymer materials*, there is no strictly theoretical or experimental basis of their polarization parameters. Calculation formulas ε and tan δ for layered materials and a number of theoretical formulas for dielectric characteristics of matrix systems and statistic blends with different by shape inclusions are given in [1]. Accumulation of experimental data in this field makes it possible to understand and verify electric properties of multicomponental materials.

The influence of filling on electret charge has been discussed in 4.3 (see Fig. 4.17). Nonmonotonous dependence of charge versus concentration is governed by several factors. Introduction of a small amount of filler (0.5-1.0 mass %) contributes to formation of more perfect structures, notice that, electret charge value is a structurally sensitive characteristic of material [2]. With increasing concentration of conducting filler further charge growth seems to be illogical since rise in conductivity is to impair the polymer material electret properties. Some polarization peculiarities of polymers in MPE can, however, explain such charge growth. Apparently, the main role in this case is played by the mechanism of electrochemical polarization (see ch. 1.2.5) as far as polarization process involves both electrodes of unlike metals (Cu-Al) and metal filler particles distributed in the polymer bulk. At a still further increase of filler content, charge formation is compensated by its neutralization (discharge) due to growing conductivity of the polymer composite and at a high filler concentration (10-20 %), current-carrying bridges appear in it.

Charge growth and rise in its stability is also observed in electrets from heterogeneous materials on *polymer blend* base. HDPE and PVC blends have been studied. The longest time of charge relaxation has been recorded at a ratio 75 % of HDPE to 25 % of PVC. This can be attributed to additional polarization generated in heterogeneous systems at the interface between two different dielectric permittivities (Maxwell-Wagner's polarization) [5].

Electret charge in MPE is rather stable. The values of efficient charge surface density in electrets formed between Cu-Al electrodes were controlled during 100 days and the charge did not practically show changes.

From the summarized data it can be stated that electret life time, i.e. time of charge preservation, is mainly conditioned by chemical structure of dielectric. Life of electrets from carnauba wax or its blends constitutes several years. Ceramic electrets in dry atmosphere do not change their charge during a few years either. Polymer electrets display a lower charge stability, their life, however, can be considerably prolonged by using special technological means.

8.1.3. Effect of irradiation.

Outer action effect on electret durability (temperature, humidity, deformation, friction, etc.) have been partly considered in previous chapters (see 1.2.4, 6.1.2, 8.1.1). The question of electret stability at different types of exposure to radiation is of great practical significance.

Effect of γ-radiation on polymer electrets results in TSD charge variation. Notice that, radiation dose influences both the value of depolarization current and density of defined by Compton's current space charge [11]. Penetrating radiation is known to increase polymer conductivity because of formed by ionogenic radiolysis products and raised concentration and mobility of charge carriers due to macromolecular destruction. Carriers displace in the electret field causing charge compensation and reduction of its surface density. From the other hand, processes of radiation-induced crosslinking of macromolecules are observed at polymer material irradiation. They lead to space network formation, reduction of electrical conductance and amorphization of structure which gains electric conductivity [12-14]. Thus, γ-radiation of polymer electrets makes it possible to simultaneously vary the material structure and the number of free charge carriers. Both the total effect governing change of material physic-mechanical properties and stability of polarizing charge are dependent on what process dominates under a certain dose exposure.

Increased conductivity of polymer films at irradiation accelerates electret charge relaxation and varies TSD current spectra character. These regularities were obtained during investigations of electret polymer films exposed preliminary to electron and γ- irradiation of different intensity [15]. With increasing dose the film conductivity grew and relaxation time of electret potential difference U_e reduced (Fig. 8.5).

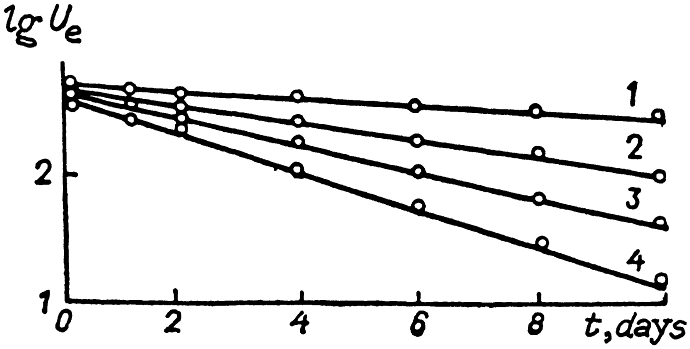

Fig. 8.5. The dependence $U_e = f(t)$ for PTFE films after exposure to different dose ionization radiation (Gy): 1 - 100, 2 - 500, 3 - 700, 4 - 1 000 [15].

Some inorganic materials are able to preserve space charge during many months and even years (Fig. 8.6).

Structural changes and charge carrier formation under irradiation influence MPE polarization and depolarization. Particularly, activation energy of TSD process in exposed material changes (Fig. 8.7). This can l attributed to expanding spectrum of dipole relaxation time and reducing

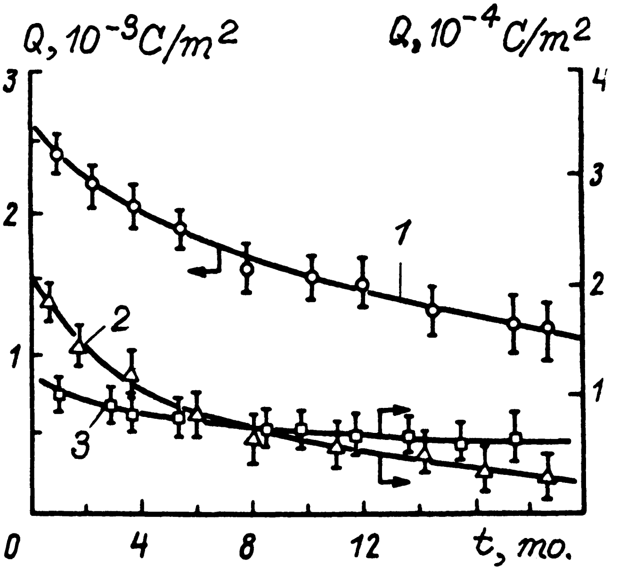

Fig. 8.6. Charge relaxation in samples exposed to protons of 9.8 MeV energy: 1 - aluminum phosphate glass, 2 - corundum ceramics microlite, 3 - pyrolytic boron nitride [3].

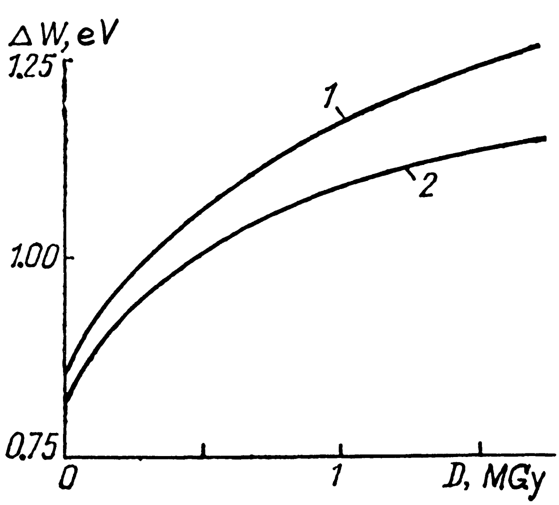

Fig. 8.7. The dependence of TSD activation energy on dose of γ-radiation for MPE based on PVB (1) and PPl (2).

segmental mobility of macromolecules as a result of crosslinking. Apparently, redistribution of charge traps across thickness takes place at irradiation, i.e., depth trap concentration increases and charge release occurs at higher temperatures. Radicals forming at macromolecular destruction can serve as depth traps as well as crosslinks and impurities.

It should be also mentioned that, with increasing radiation dose the polarizing current is generated under lower temperatures, which means that, TSD current depends on the absorbed dose. This circumstance helped to develop a method for estimating the absorbed dose of γ-radiation judging by the change in TSD activation energy for the exposed film in contrast to nonirradiated one [16].

8.2. SPONTANEOUS ELECTRET EFFECTS.

Electret fields used at machine manufacture or operation can lead to an accidental spontaneous polarization of dielectric parts.

Space charge (SC) generated at spontaneous polarization of dielectric parts most often impairs their performances and those of conjugated machine elements.

Already at the end of the 20-s a supposition was put forward in Ioffe's work [17] about SC effect on electro-physical properties of solid dielectrics. This concept on SC role in such processes remained a hypothesis till recent years in spite of a great number of works devoted to dielectric breakdown and aging. The main reason was the difficulty in experimental determination of SC parameters in solid dielectrics. This was underlined in practically all publications and scientific reports on the problem. Gaps in methodology were bridged at the end of 70-s and beginning of 80-s when the radiation diagnostic [3, 18] and deformation wave methods [19-22] were shown to be most promising for SC studies in polymers.

Probing of SC in polymers under electric voltage (e.g., pulse one) supported the supposition on electric instability of dielectrics. A discrete (oscillating) in time and space character of SC motion and fixing in traps [23-25] has been detected.

Many of qualitative regularities characterizing both short-term and long-term electric stabilities of solid dielectrics can be consistently interpreted only by using notions on SC accumulation and effects. The importance of SC storage in polymer aging is confirmed by a number of phenomena occurring in materials at a prolonged electric field action. They include the formation of polymer degradation zones near the injecting electrodes, luminescence and recombination radiation [26, 27], lowering of field intensity in dielectric and arising from it polarity effect [28], strong influence of applied voltage on dendrite formation in materials [29], and etc.

The analysis is given in work [30] of the stored in polymer dielectric (PP, PETF, PC) negative SC influence under strong electric fields on the dependence between polymer durability τ, electric field intensity E, breakdown intensity E_{br} and the rate of the mean field intensity $\acute{E}$ increase in conditions of partial discharge suppression. Because of nonlinear character of the dependence between local field intensity in polymers and mean field intensity determined experimentally, break of charts lg $\tau(E)$ and E_{br} (lg $\acute{E}$) may occur. Supposing that at a linear rise of intensity an additional factor accelerating electric damage of polymers appears, the authors of [30] explain the phenomenon by recombination of charges accompanied by additional heat generation.

SC leads to analogous effect induced by electron bombardment of polymers which provides for partial discharge action, i.e., reduction of electric strength and a considerable change in the polymer structure [31].

Spontaneous generation of SC in dielectrics can be a cause of spoiled elements in optical systems. Niobate-based ($LiNbO_3$, Ba_2Na, Nb_5O_{15}, etc.) laser radiation control devices show a high electro-optical coefficient. They are characterized by a rather low, as compared to water-soluble crystals, intensity of guide fields. Working elements of electro-optical parts (shutter, deflector, lens, etc.) must possess high optical homogeneity at operation in electric fields. Prolonged action of guide fields results, however, in redistribution of electric intensity in optically active crystal and, consequently, in its optical heterogeneity and instability.

Relaxation polarization of hermetizing polymer materials in the edge field of MDP structures may be one of the reasons of electronic structure failure. Decline of semiconducting instrument characteristics under elevated temperatures is usually attributed to charge instability at the polymer-crystal surface interface [32]. Charge redistribution on the crystal surface can arise from the sealant polarization in the edge field of the instrument active parts. Often, inverse layer forms over the multi-emitter transistor, being the main reason of circuit breakdown.

Static electricity brings about spontaneous polarization in dielectrics, so far its emergence in machines leads, in majority of cases, to unwanted consequences. Stored electrostatic charges might disturb production process of articles from dielectric materials or become dangerous for operators [33].

Boost in polymer output dictates the necessity in reducing electric charges generated during manufacture to the extent not violating technological process nor producing spark discharges able to explode combustible gas mixtures.

To dissipate and reduce static electric charges during dielectric article processing and operation, the following precautions are made: humidity in works is raised, electric charges of opposite polarity are created and directed to the charged object, air conductivity is increased by ionization, conducting composites and coatings are applied, and etc. A detailed analysis of protecting means against static electricity in different fields the reader can find in devoted to the theme monographs [33-39].

Triboelectrization is the most spread type of electrization generated at sliding friction in different technological processes (cutting, grinding, polishing, etc.) and friction joints containing dielectric units. It has been noted in ch. 5.2 that triboelectret state is formed in polymer materials due to intensive electro-physical processes occurring in metal-polymer movable joints during operation. These processes are spontaneous and are determined by the friction joint operation conditions (origin of friction joint materials, load and velocity regime, humidity, temperature, lubrication, etc.). Triboelectret state of polymer materials can strongly effect frictional characteristics of a friction joint. Data obtained during nylon frictional electrization studies [40] support that the intensity of electrization and friction parameters are interrelated. It is seen from Fig. 8.8 that a certain correlation exists between electrization current I and friction force F dependence versus time for the nylon-metal friction pairs. At the initial period both dependencies are of a smooth character. Upon current inversion (after 1.3-1.4 ks) they acquire a synchronous jerky character. With increasing time of interaction the friction force grows. The dependence I(t) passes the maximum corresponding to nylon glass transition temperature. In the ideal case a coordinated variation of I(t) and F(t) dependencies must be observed at increasing time of interaction. But, as a result of temperature effect at friction and accompanying physic-chemical transformations, the dependence I(t) shows the maximum, then decline and inversion of current.

Triboelectret state exerts a considerable effect on electro-physical, mechanical and frictional properties of polymer materials. Particularly, as a result of electret state effect on friction and wear processes the polymer structure undergoes transformations which can lead to impairment of its strength and working capacity. Recommendations how to reduce wear in metal-polymer friction joints using electric fields are given in ch. 5.2.

Decreased mechanical strength under electric field and discharge action has been experimentally recorded for many polymers. Thus, PTFE film exposed to glowing or high-frequency discharge shows mass loss, separation of monomers as gases and by 25-30 % strength reduction. Data on high-frequency oxygen effect on some polymers are presented in Table 8.1.

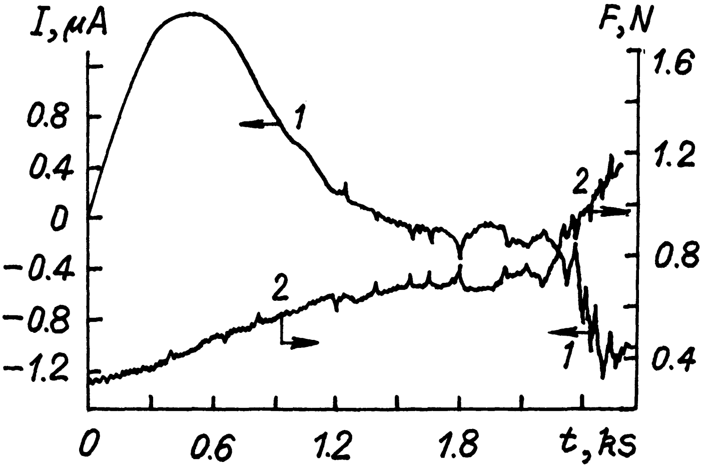

Fig. 8.8.

One of the results of electric field action on polymers is accelerated capillary and surface diffusion of hostile media with the consequent reduction of polymer strength. If a polymer part surface is moistened in electric field, arc discharge can occur leading to material damage. In a cooled nonpolymerized epoxy resin containing dispersed water and glycerin, dendrites start growing under the electric field effect. They stretch in direction of electric field action. Similar dendrites have been discovered in polyethylene insulation of power cables with reduced electric strength.

Table 8.1. Destruction of polymers at electric discharging [41]

Polymer	Rate of destruction, mg/(cm^2/h) for discharges:		
	high-frequency oxygen discharge	arc discharge	activated in high-frequency discharge oxygen
PTFE	0.10	-	0.077
PS	0.11	0.02	0.160
PA	0.15	-	0.340
PE	0.20	0.30	0.307
PETF	0.20	0.03	-
PP	0.22	0.32	0.427
PVC	0.30	-	-
PMMA	0.43	-	0.270

An efficient means for suppressing dendrite and increasing polymer insulation resistance to them can serve introduction of additives which either prolong incubation period of dendrite origination or reduce its growth rate [42]. They involve antioxidants (for e.g., diphenylamine), aromatic hydrocarbons [43] and plasticizers. To increase resistance of high-voltage pulse cable with polymer insulation to dendrite formation the following methods can be used: laying of semiconducting screens on the core and insulation, application of oil (or glycerin) coatings on the wire before insulation and substitution of monolithic insulation by a multilayered or combined one.

8.3. ELECTRET MATERIALS AND ECOLOGY.

The processes occurring in the global ecological system mankind-nature are interrelated. V. I. Vernadsky, for e.g., investigated nature evolution in interdependence with the history of society and singled out man's activity as a crucial factor influencing biosphere [41]. The scientific and technical revolution of the 20th century has practically eliminated restrictions in utilization of natural resources. Rise of public material culture and growth of population on the Earth has lead to commensurability between processes running in technology and those in nature. These caused changes in water, air and soil which violated biological balance. A contradiction appeared between unbounded prospects in development of production and confined natural resources. Mankind survival is now probable only in conditions of reasonable control over technological processes within rigidly defined limits.

Adherence to ecological principles is at present an objective necessity of material production. Methods of environment protection are formulated by the scientific domain named *population* and *engineering ecology*. The former formulates standards for vegetal-animal world, the latter defines reasonable extent of human activities. Electrets are highly efficient means in solving problems raised by engineering ecology (Fig. 8.9).

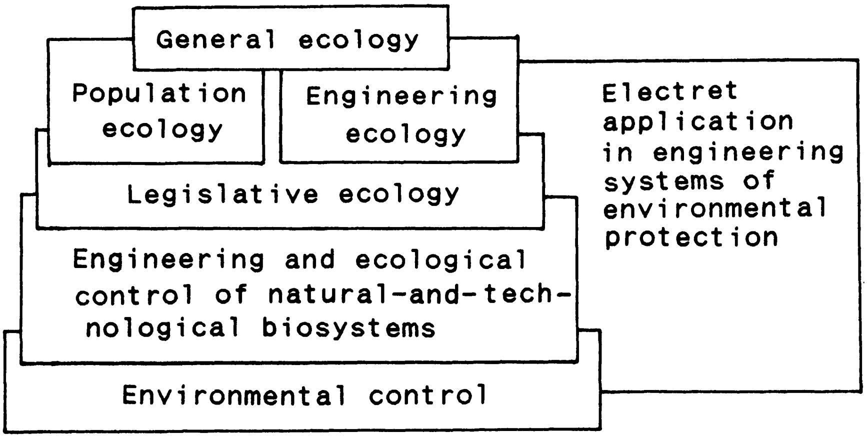

Fig. 8.9. Interrelation between electret application and ecological spheres.

Electric fields as a technological and technogenic factor are attractive owing to their ecological purity since environment is not contaminated by any waste. In Table 8.2 values are presented of technogenic effects on *geosphere*, i.e., concentric shells from which the Earth is composed of: atmosphere, hydrosphere, lithosphere (earth's crust) and biosphere (the zone of active vitality in the first three geospheres). These data are the result of a many year experience in construction and exploitation of the oil-gas system facilities. It is seen from the Table that the total effect of electric fields causes the minimum degradation consequences as compared to other technogenic factors.

The traditional industrial conservatism expresses itself in tendency to minimum changes in the adopted techniques. Use of electric polarization is convenient because of its simple methods easily included into any technological scheme. Field function at material forming and article production is the major criterion determining polarization place inside the technological process. Such electric fields are able of modifying the initial components of the material or their intermediate products. Furthermore, the induced by such treatment polarizing charge aftereffect on the following technological stages or component interaction is not excluded. Examples of such effects are given in Fig. 3.1. In a number of cases the formed material

Table 8.2. Severity of technogenic effects

Type and character of technogenic action	Index of ecological severity of technogenic action on biosphere			
	atmosphere	hydrosphere	lithosphere	biosphere
Mechanical	0.23	0.15	0.28	0.05
Shorterm (S)	0.34	0.20	0.34	0.18
Longterm (L)	0.18	0.25	0.14	0.08
	0.37	0.20	0.21	0.2
Heat				
S	0.12	0.05	0.28	0.31
	0.19	0.35	0.39	0.46
L				
	0.10	0.15	0.17	0.20
Biochemical	0.12	0.20	0.26	0.23
S				
	0.10	0.15	0.17	0.20
L	0.12	0.20	0.26	0.23
Electrochemical				
S				
L				
Electromagnetic				
S				
L				

or article treatment in electric fields is a terminating operation of the technological process. There are techniques where electric field treatment takes place at each stage of material processing. Such technological process schemes are shown in Fig. 8.10.

Special precaution measures for such polarization are aimed at reducing electric field action on operators. Modern electric techniques rarely use powerful electric fields leading sometimes to different severity *traumatic injury* (from negligible pain to tissue carbonization). However, electrostatic fields spontaneously forming at dielectric polarization can become an inadmissible accidental factor occurring at production. Most of

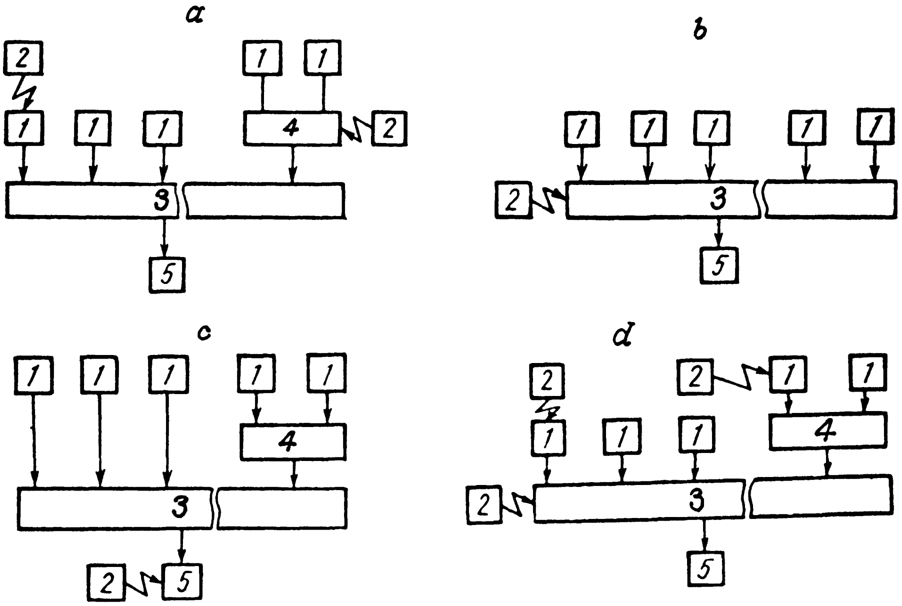

Fig. 8.10. Flow diagram to manufacture composites and their articles using electric fields.
a, b - modification of original components and intermediate products of their reaction, c - final product, d - initial components, intermediate and final products.
1 - initial component, 2 - electric field source, 3 - zone of physic-chemical interaction between components, 4 and 5 - intermediate and ready products.

ceramic and plastic components, first of all binders, mineral and organic fillers including organic liquids, are not conductors. Their behavior in contact with other components or parts is not, however, limited to only mechanical contact, pressure redistribution or contact deformation. Contacting is accompanied by charge carrier transfer, space charge storage in dielectric and draining along conducting components. The problem of electrostatic charge neutralization or useful utilization in the mentioned technologies is an urgent problem from the viewpoint of engineering ecology.

Standards have been worked out in every country regulating precaution means for technologies using electrostatic fields. Compliance with the standards is especially important at electrostatic deposition of dispersions, material exposure to electric corona-, gas- or glowing discharge, and high-energy electron and ion beams.

In interrelation between electric field and ecosystem, positive influence of fields on living beings should be noted. Already in the 18th century L. Galvany detected the relation between metabolism and charge transfer. *Bioelectret effect* is the property of men's animals' and plants' tissues to stay in an electret-like state characterized by quasi-stable bioelectret field, piezo- and pyroelectric effects. Electret state has been discovered in practically all important classes of biopolymers (polypeptides, polysaccharides, polynucleatides). Natural electrets, like keratins are present in vivo in many biological tissues, bones, sinews etc. (see ch. 7). Two peculiarities of bioelectret effect, i.e., lasting preservation of electric field and thermally stimulated current (TSC), are displayed by living tissues of plants. They vary similarly at dehydration of vegetable tissue. As one of physiological fields *electrophysiology* studies electric phenomena (bioelectric potentials) in living organisms and the mechanism of electric current action on them. Medicine has long been utilizing electric methods to cure patients. Among them are *electrostimulation* which uses electric pulses to maintain nutrition and normal functioning of damaged nervous-muscular apparatus, *electric theurapy* and its modifications (faradization, galvanization, dorsonvalization, diathermy, etc.) which use electric and electromagnetic fields as a therapeutic method, *electric sleep* that is caused by weak electric current action on man's brain, and etc.

So, intrinsic for ecosystem electric fields can efficiently, from engineering ecology viewpoint, be adopted in industrial technologies. They can reduce technogenic effects down to permissible limits.

Inhibition of metal corrosion is also an actual problem of engineering ecology. The degree of environment pollution by the products of continuously corroding machines, buildings, structures is progressing in time and is at present strongly hazardous for biosphere. Scientific grounds of the problem alleviation by using electrets is based on the following ideas.

Electrochemical corrosion imposes physic-chemical solution of metals accompanied by electric current generation in the corroding system, or vice versa, it takes place when current passes in a metal. Naturally, charged particle transfer can be regulated by the electret field which hampers or ceases corrosion damage. Most important directions in corrosion inhibition by electret effect are discussed in ch. 3. It is significant from the point of view of engineering ecology that corrosion suppression does not necessitate the continuous generation of current. The protective effect is reached in terms of electret energy stored in the process of electric polarization.

Disinfection of industrial emissions and waste water cleaning are indispensable precaution measures in protecting nature against industrial technogenesis. Prospects of the problem solution are to a great degree connected with electret effect.

Industrial *ejections into atmosphere* are subjected to short-wave irradiation and undergo chemical transformations, i.e., photolysis (at sunlight radiation), ozonolysis (at reactions with ozone), hydrolysis (at interaction with water vapor), pyrolysis (decomposition at heating) and etc. Their products are able of reacting with initial contaminants. Secondary products are, as a rule, more toxic than initial ones and more hazardous for flora and fauna.

Most efficient gas purification methods from impurities (gaseous and aerosol) are based on adsorption and catalysis. Section 6.4 of the present book describes how to use electrets in adsorption filters. The filters purify gases from sulfurous compounds (SO_2, H_2S), water vapor, acids (H_2SO_4, HCl) and carbon oxides. Electret filters are most economical in closed technological cycles where adsorbed substances are used as raw material aimed at further processing. Catalytic purification of gases is free of liquid waste utilization. Oxides (vanadium catalysts) are often used as catalysts, as well as complex dielectric compounds (complex catalysts) or catalysts applied onto dielectric powder carriers (acidic and main catalysts). Their efficiency can be regulated by electric polarization methods. Electret catalysts show wide potentialities in sanitary cleaning (high-degree cleaning) of air.

Sewage (atmospheric and contaminated by domestic and industrial waste waters) are cleaned by mechanical, physic-chemical, chemical and biological methods.

Mechanical separation of mineral and organic contaminants using centrifugal and gravitation forces proceeds more efficiently as compared to that by electric fields. It is advisable to use electret elements in strain and filtration plants, centrifuges and hydrocyclones.

Examples of physic-chemical treatment of suspensions using flotation, coagulation, extraction and sorption under electric field action are given in ch. 1.3.

Biological methods occupy a special place in the system of waste water cleaning. They simulate innate oxidation processes occurring in nature. As it has been already shown in 6.4, polymer electrets, which are biomass carriers, show a higher sorption capacity in relation to microbicidic cultures as compared to common polymers. They provide for the biofilter most fast attaining its stationary operation regime. Biofilters with electret carriers belong to the new generation of purification systems which governs prospects of engineering ecology development.

Contamination of the earth's depths and their irrational utilization affect all the geospheres. In the negative anthropogenic variation of lithosphere dominate the following factors [45]:

a) growing scale of mining mineral resources,
b) nuclear tests,
c) burial of radioactive waste,
d) large-scale industrial construction.

The role of electrets in weakening ecological consequences of such effects consists in improving hermetizing systems. Oil and gas well drilling often results in depressurization of seams and causes oil spread, salinization and swamping of soils. Depressurization of main oil or gas pipelines leads to global pollution of water and soil causing large-scale ecological losses. Nature suffers great losses from evaporation or filtration leakage from underground oil, gas or condensate reservoirs. The main directions and examples of electret use in hermetizing accessories are quoted in ch. 6.

Air and drinkable water cleaning is an essential factor of mankind survival in conditions of global technogenesis. The range of air and water contamination is characterized by the following data [45].

At present power plants eject into atmosphere above 100 million tones of dust-like substances yearly, about 150 million tones of SO_2, 300 million tones of CO, more than 50 million tones of NO, and etc. At the beginning of the 20th century these values were by an order less. Experts of the World Health Organization consider these ejections to be the main reason of chronic bronchitis, pneumonia, emphysema (being often the cause of lungs' cancer) and other diseases. Besides, technogenic pollution of atmosphere disturbs ozone layer which is a specific protecting shell preserving the Earth's flora and fauna from cosmic rays. Pollution can also bring about warming which might violate ecological balance up to global ice melting and rise of world ocean level. Naturally, the latest achievements in science and technology are directed to overcome these consequences. It has been shown in ch. 6.4, that electrets, being one of the most efficient gas purification means, play an important part in regulating atmospheric purity.

Contemporary enterprises spend water for their technological needs in amounts not less than 10-12 % of the world hydrological cycle volume. Another 30 % of water goes to dilute wastage at disinfection, being although not always efficient. The state of fresh water stores is strongly impairing due to disposal of wastage containing oil, chlorine, phenolic compounds, heavy metals and radioactive substances into rivers. Hazard of water radioactive pollution increases with the growing output of nuclear power engineering and the absence of reliable methods of radioactive waste liquidation. In the recent years the border between industrial failure and natural calamity has leveled. Chernobyl disaster is an evidence to this fact.

Preservation of fresh water stores is somehow or other related to hermetic sealing. Advanced, from the standpoint of ecology, industrial systems involving circulating water supply, closed heat regulation cycles, reactors for biological neutralization of waste, and etc. insulate technological media from natural waters. Use of electrets, being a unique, having no analogues hermetizing means, shows wide prospects and is constantly expanding.

There are some other aspects of electret application aimed at solving ecological problems, namely, rise of power plant efficiency and utilization of industrial waste outside the Earth limits.

Ecologically safe energy sources have been developed based on electrets. The review cited in 2.2 proves that both nomenclature and sphere of such objects application is limited because of low power of generated by them electric field. Nevertheless, they are indispensable parts of a great number of instruments and radioelectronic devices. A hypothesis has been put forward on the probability of regulating combustion process and reduction of disposals into atmosphere by transforming solid fuel into the electret state [10].

Generators on electret films have found their application in cosmic techniques due to their small mass, simple design and reliability at operation in vacuum. The ideas of carrying industrial waste outside the Earth's orbit and their burning up by the Sun energy are also connected with electret application. In the near-term outlook, the construction of enterprises is probable contaminating geospheres on orbital stations.

Thus, electret is ecologically safe means able to reduce global technogenic aftereffects. Its creation and application is ecological contribution of natural sciences into the challenge of preserving nature.

8.4. ECONOMIC ASPECTS OF ELECTRET APPLICATION.

Electric polarization of engineering materials and machine parts requires, as a rule, additional power consumption. Merits of electret parts are, nevertheless, so significant that excel expenses on electret production. These advantages are less prominent on the stage of production and are clearly displayed at machine operation. They provide for improvement of machine performances and often result in positive social changes. The latter estimation is difficult because of the gaining specialization of sciences, as well as separateness of technical and economic scientific branches. Below the principles of cost estimate are considered for electret application in engineering.

Advantages of electrets used as machine parts can be observed at all stages of technical article production and service life.

In contrast to other engineering materials, the distinctive feature of electrets is their ability to generate electric field. Realization of the feature in machines allows changes in their traditional design philosophy and joints operation, improves service characteristics, simplifies structure, reduces expenses and rejects auxiliary materials. Electret unit as a structural element can improve operation conditions and reduce maintenance cost. These happen because of improved tightness of sealing, prolongation of lubrication cycle and corrosion reduction. Production of engineering articles containing electrets can lead to changes in social sphere expressed in better general conditions (air and running water cleaning, rise of sanitary and hygiene efficiency) and working conditions (simplified maintenance of machines, lowered leakage, reduced pollutant gas content in workshops, etc.). An essential social effect is produced by electrets in medicinal equipment which helps to keep people healthy and fit for work. The importance of electrets in solution of ecological problems has been discussed in 8.3.

Polarization as a technological process for electret production is characterized by low energy consumption. Owing to low electric conductance of dielectric, polarization current density does not exceed 10^{-8}-10^{-12} A/cm^2. Even at tens of kV voltage, the polarization source power is about mWt. So, the main portion of expenses goes on technological attachments in electric insulation and development of high-voltage power sources. The latters, as showed the examples of radio-, photo, metal-polymer and other electret types, are far from being always necessary.

It is surprising, that such a negligible action of energy provides for a deep physic-chemical restructurization of dielectrics which results in the electret material anisotropy. This makes it possible to reinforce physical, chemical and mechanical properties of electrets in desirable direction. Polarization is also advantageous due to feasibility of local modification not effecting the material bulk.

Polarization easily enters any technological cycle of production. It can be combined with article forming accompanied by heating. It is seen from Fig. 8.10 that polarization can be performed at any technological stage. This proves once again that electric polarization of dielectrics should become as mass technological operation as metal quenching and tempering, plastics welding, coating application, and other processes have turned to be. The only, easy to overcome for polarization obstacle could be the demand for technological equipment and observance of special precaution measures.

Preparation of production intended for electret use has its peculiarities related to this class material specifics.

The criterion for the choice of electret material and its production method is based, as a rule, on imposed by the customer requirements concerning article cost at minimum expenses. Request for proposal usually includes higher performances of the being developed electret article as compared to common designs. Grounds in favor of electret use in articles are the following: simplification of design, reduction of metal content, improvement of performances, maintenance cost lowering and streamlined manufacture. These values are experimentally verified in laboratory, bench and service tests for both electrets and their articles. Both the method and criteria for selecting design and technological variants would change in case electret article application leads to social affects.

In the process of technological preparation of production, problems arise related to deficiency of dielectrics which are the basic raw material for electrets. The majority of problems solved at this stage are directed to correct facilities, management and to finding new partners for cooperation. This is because polarization usually rises article cost, so economy of resources starting from the stage of technological design predetermines the efficiency of future production. To perform polarization the corresponding technological equipment and specialists in electric machining of materials are needed. Changes in the staff effect, in a certain manner, production relations in the firm, as well as moral and psychological climate of the personnel. Adoption of electret articles at an enterprise is also connected with increasing technological effectiveness and automation degree promoting intensified movement of basic production assets.

The combination of factors visualizing expediency of electret use in articles is shown in Fig. 8.11. It is impossible to indicate how to make a generalized analysis of such a complex set of factors. The strategy of selecting optimum variants consists in orientation of the chosen estimates using the criteria of social expediency. With this aim, the correlation between expenses spent on electret production and level of its performances is estimated. Thus, grounds are created for elimination of some constituents of the article cost. The experience in industrial production evidence that the most efficient way of reducing article cost is connected with economy of the labor, i.e., materials. Electrets produced by polarization combine several functions in one material. This is achieved without practically any auxiliary technological efforts and commonly results in reduction of materials consumption.

Economic analysis of research, design, technological and management solutions in production of engineering electret articles is based on comparing the resultant cost estimate and total expenditures for their rated service life.

Only in a few cases the advantages of electret article performance are apparent as compared to nonelectret ones since the former production is characterized by lower daily and capital costs. More often situations occur when electret application is connected with additional capital investments on design and purchasing of equipment for electric polarization. Nevertheless, it promotes economy in current expenses because of simplified electret article design. Commonly, electret production is of a certain social importance related, for e.g., to improvement of environment associated with purification of wastage using electret filters, and etc. Efficiency of such production is evaluated using cost indices expressing social results. In this case unbiased estimate depends rigidly on reliability of data on induced by electret application social aftereffects.

Choice of decisions is based in these cases on the economic analysis of variants involving standard methods with account for above ideas. Economic analysis is the first step in the combination of measures in managing such science consuming processes as electret article production is.

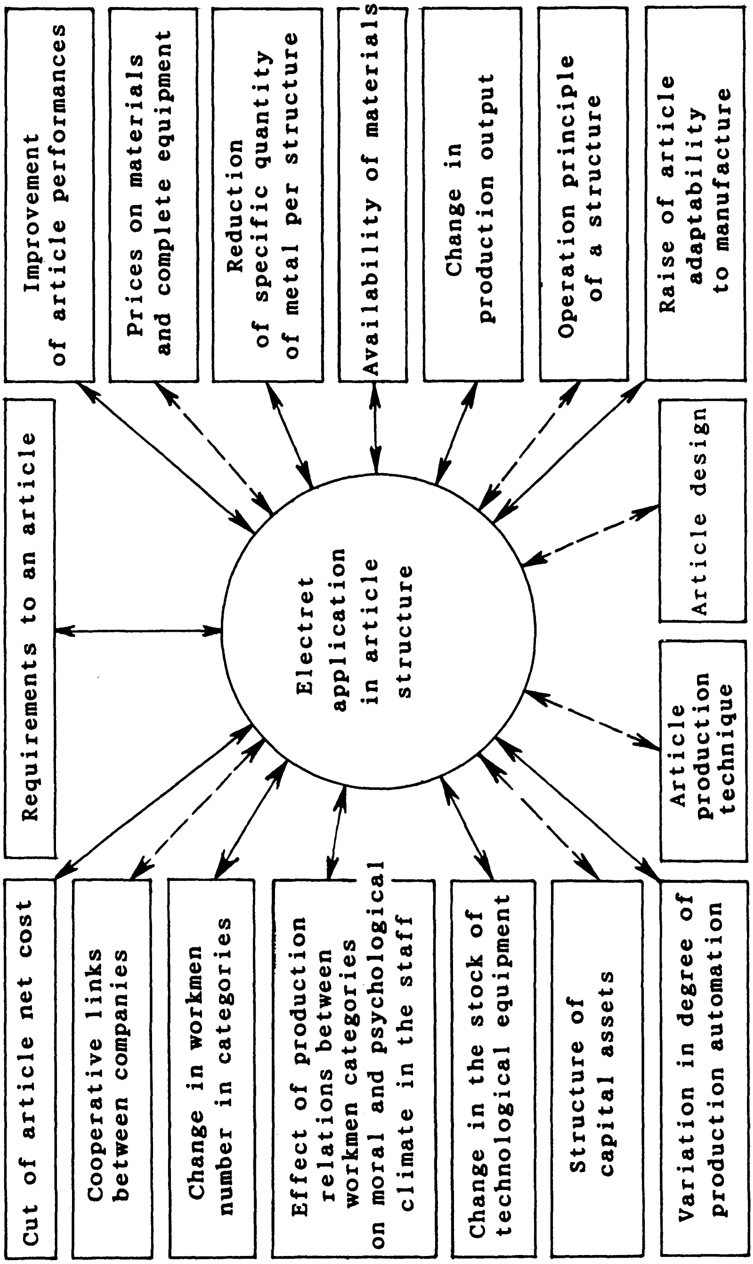

Fig. 8.11. Combination of factors determining electret application in engineering articles. Unbroken arrows - direct influence, dotted arrows - oblique.

The results of analysis serve as efficiency criteria for all kinds of works, i.e., research, design, technological and managing (choice of credit, co-workers, cost establishing, etc.) preceding start of article production. They are the basis of business-plan for each particular enterprise aimed at engineering electret article production.

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