Triboelectrization as a mechanochemical reaction. Molecular mechanisms of electrization.

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In this book the new theory of the triboelectrization is described. Contrary to the old theories, the main emphasis is given to the mechanochemical modification of the triboelectrified surfaces. In addition to the created by the author radical theory of the triboelectricity all other possible mechanisms of the electrization are described.

Contents.

Introduction. A historical overview (of the mechanisms of the triboelectrization).

Triboelctricity is a well known fact, probably the first electromagnetic phenomenon of the artificial origin, discovered by the humanity. Of course, lightning was known by the humans from the ancient prehistoric times (long before any signs of civilisation), but this is a natural phenomenon, demonstration of electromagnetism, not the artificial one. We don’t know, whether magnets or triboelectrization were found first, but it might be triboelectricity. Ancient Greeks (and may be inhabitants of Egypt) knew that phenomenon and electron is named after the amber (the Greek word for amber is electron).

A lot of study was done later during centuries in the field of electrostatics. But mainly physics were concentrated in the field of investigation of the laws of the charge interactions. Many famous scientists, among them Coulomb, Franklin, Maxwell, Helmholtz, Landau discovered many underlying the surface laws, that govern the behaviour of the electric charge with respect to another electric charges, metal surfaces and dielectrics. Many problems were solved and Coulomb law was found to be valid even on subatomic level. Nevertheless, despite a huge progress in the field of electromagnetism (all the achievements of the electronics and many other disciplines were impossible without progress in this field) the molecular mechanisms of the charge separation are not understood fully, since they are not of the primary interest for the microelectronics. About a century ago the time of electrostatic generators was over – the van der Graaf generator was the last example of useful electrostatic device. Since that the interest for the problem of the electrostatic charge separation was over and at the present time the interest to the problem of the tribologic laws is how to prevent dangerous charge accumulations, what might lead to sparks and fire.

But the huge progress in the field of solid state physics and in the band theory of conductors and semiconductors would probably explained all the possible phenomena that might happened in the solid state and in the place of the contacts between the different solids. And it looks like this for the triboelectrization as well, being the simple touching of two different solids should be explained very easily, since it looks like a straightforward application of the band theory. Nevertheless even very modern calculations of the work functions for many polymers and dielectrics can't explain the tribological row (known from middle ages) in the case of dielectric and metal-dielectric contacts. It is strange to note, that for the case of metal-metal and metal-semiconductors contacts that band theory works absolutely, that is, it explains everything very well, including charge transfer.

Historically the first explanation of the charge separation was that by the mechanical action something is introduced into the solids, thus forcing them to contact or to push each other [1]. Later, at the time of Faraday, conception of charges appears and it was established, that negative charge recombine with the positive one, thus leading to the neutral state of the solid body [1]. At that time the idea of electric current appears, but the scientists were thinking that it is positively charged particles, that are moved by the electric field and create the current.

In 1785 Charles Augustin Coulomb discovered the main law of electrostatics – Coulomb law, that looks exactly as Newton law for the gravitational forces. The most important contribution to the theory of the molecular mechanism of the charge separation was made by Helmholtz in 19th century [2]. He proposed the theory of the double layer, that appears in the contact between the two dielectrics with the thickness of the layer much smaller then the characteristic dimension of the system. Being separated, those two dielectrics receive a rest charge – positive onto one of them and negative on the other dielectric. The idea of the double layer was further developed and the structure of it was investigated very thoroughly – it was found how it is organised [3-5]. That double layer in the liquid can explain the charge separation at moving of one liquid with respect to another or at moving of the solid out of the liquid very easily – part of the layer is deleted away by the moving body. And therefore, part of the charge, that was not succeeded to recombine with the opposite charge on the second liquid is rest on that body or liquid – the charge separation occurred.

As it was proved later by the development of the physics, that theory was found very useful and it easily explains (together with other laws of electrostatics) the further behaviour of the charges in the bulk of the solids or liquids, but the origin of that double layer was unclear. Much more advanced was the theory of the charge separation, that was developed being based upon the band theory of solids, especially for metals and semiconductors, where that theory was found very satisfactorily. Band theory is described in many books, among them in [6,7] there are just a couple of examples.

Double layer theory created by Helmholtz was successfully applied to the theory of the adhesion. In Russia academician B.V.Deryagin during many years developed that theory and with the help of it he explained why the adhesion works so well and how it might depend upon the internal electric field. In one of his books [8] the following formula for the energy, necessary for the separation of the two surfaces of 1 cm^2 is given (formula of the energy of the capacitor):

$A_o=(2\pi \sigma ^2{}_o h)/\varepsilon$ (1)

where σ_o - $1/cm^2$ - surface density of charges, h- separation of the two electrified solids, ε - the mean value of the dielectric constant. The formula is in SGSE units and it is assumed, that the value of the contact surface is $1cm^2$.

Another important problem, that is connected with the electrostatics is the problem of the lubrication and trapping of the charge, received by the triboelectrization process. This phenomenon is known as Landau autolocalization, or more general, autolocalization [9]. That phenomenon consists in the decrease of the energy of the charge, trapped inside the solid (in the near surface layer) due to the polarisation of the nearby atoms or molecules in the vicinity of the trapped charge. If the electron is transferred from one surface (one solid) to another and it is trapped inside, due to the presence of the molecules with some dipole moment (both inherent and induced) some of them are reoriented in such a way, that the real charge is surrounded by the cloud of the dipoles and thus the overall energy of the charge is lowered. This phenomenon is extremely important for the case of the triboelectricity, since in this case the idea of the charge, trapped in the solid state is important because of the necessity to observe that charge. To do it, it is necessary to have it trapped, otherwise it will not be possible to observe it at all – it will be dissipated too easily and we could not be able even to detect the rest charge (triboelectric charge). Landau autolocalization would lead to deeper minimum of that charge, thus the recombination is braked and the charge is possible to detect in a straightforward manner – through the detection of the electric charge.

All those scientists, including A.Einstein contribute to the general development of that important field of electromagnetism. (A Einstein proposed the idea of the new device for multiplication of the small amount of electric charges, the device, that would allow to help somebody to measure smaller then usually triboelectric charges).

B.When the charge separation occurs?

In practice there is a lot of possible mechanisms, that would lead to microscopic charge separation, it takes place in the case of the absorption of the quantum of the light (photochemical charge separation), that has a huge “application” in nature in the case of photosynthesis (inside the chlorophyll molecules). According to the theory of dissolution of Arrhenius charge separation takes place even in the process of the dissolution of the compounds, that have an ionic mature, for example NaCl, by the polar solvents like water. But this case should lead to the creation of the ions in the solution, that have counterions very close to the main ion, that was dissolved in the water. In many other interactions of the radiation with the solids and the liquids the charge separation occurs, with the ions being stabilised nearby due to the strong Coulomb interactions between the charges. One more possible mechanism of the charge separation, that allows the microscopic charge separation are some other mechanisms, that include interaction of the high energy particle with the compound (β -ray irradiation should lead to the heterolythic bond breakage with the ions formation, the ions are localised one nearby the other). But all those mechanisms should lead to the microscopic charge separation, when a couple of charges form an ion pair in the solid or in the liquid. Some temperature increase may also lead to the creation of the liquid, that consists from ions, for example, NaCl melting would give a liquid, consisted from ions, that are created an ionic liquid, that can conduct electricity (one of the methods of the metals like Na or K production is an electrolysis of the melted salts). According to [8], double electric layer is created also by the process of adhesion, but here this layer might be of a microscopic nature (in molecular scale distance between the separated layers) or it might have a macroscopic nature, that is, the distance between the charged layers is much higher then the microscopic distance (no more then 10 A) and reaches the value of ~ 100 A, where the real macroscopic charge separation may be detected by some macroscopic methods.

We are much more interested in the processes of the macroscopic charge separation with the help of the different methods, that would lead to the production of two bodies one of them is positively charged (macroscopically); another is negatively charged (also macroscopically). One of those processes is the main topic of the present book – this is triboelectricity, triboelectrization. But this is not the only possible mechanism of such macroscopic charge separation. Another mechanisms are photoeffect (studied by Stoletov and Einstein) electrization by the electric beam (β -radiation), with one solid, that was irradiated is charged negatively, and another one, that emits β -rays – positively, Dorn’s effect (establishing of the voltage between the two electrodes introduced in the liquid, in which sedimentation of the colloid particles takes place) other colloid phenomena, when the colloid particle (a macroscopic body) is charged, despite it is surrounded by the counterions. Electrization was observed also during some phase transitions (creation of a liquid from the gas or frozen liquid) and mechanisms of piezoelectrification, including the process of the mechanoelectrets creation. Below all the processes of the macroscopic charge separation will be considered in more details.

Triboelectrization takes place when the couple of materials is rubbed against each other. Part of that book is devoted to the molecular mechanisms underlying this process.

Photoeffect is the process of the electron’s knocking out by the light quanta from some solids, which include some semiconductors and metals. This process was studied by Russian physic Stoletov. There are two main types of photoeffect – internal and external. Internal photoeffect can take place in some semiconductors and dielectrics [1,6]. Under the action of the light the electron is transferred from valence band to the conduction band and the resistivity decreases – this effect is used in the simplest photoresistors. More complicated is the idea of the creation of the voltage difference between the two contacts on the boundary between the two difference dielectrics or semiconductors at light. This photovoltage is the main mechanism, that lies in the basis of the photodiods and phototransistors functions.

The external photoeffect was discovered by G.Hertz in 1887 as the phenomenon of the alleviation of the discharge between the two electrodes, charged by any other methods (triboelectric device, for example) when the negatively charged electrode is irradiated by the violet light. This phenomenon was later investigated by Halvaks, Rigi, A.G.Stoletov, A.Einstein. The phenomenon of the external photoeffect was one of the main proves of the quantum nature of the light [11]. The law, discovered by A.Einstein, can be found in any textbook on electromagnetism:

$1/2m_ev^2_{max}=h\nu - A$ (2)

where A is the work function for the material chosen for the experiment, $h\nu$ - is the energy of the light quantum absorbed, m_e – is the mass of the electron, v_{max} - is the maximal velocity of the electron, that leaves the solid under investigation.

Biloelectricity is the electricity received as the result of the disintegration of the water flow. Because of the fluctuations of the number of the ions, which belong to one or another drop received as the result of disintegration of the water stream in some drops the amount of positive ions should be different from the amount of negative ions, thus leading to charging.

Colloid particles and nanostructures. Those macroscopic entities are charged because of some surface phenomena (colloids) [4] or because of some special properties of the nanoscale particles [12].

Macroscopic charge, created by β -radiation. An intensive ray of electrons (β -radiation) should charge any surface in a straightforward manner, since the incident ray of elementary particles (electrons) should be trapped in a surface layer of the solid under investigation, thus leading to the surface charge.

Phase transitions. It might be considered as an established fact, that phase transitions might lead to the macroscopic charging of the solids [13]. The mechanism of that process will be considered below (Chapter 3).

In general, all those phenomena may be subdivided into three main groups. The most trivial group is when the charging is created by “painting” of the surface with electrons (β -rays) or protons (from particle accelerator, for example). To the second group those phenomena may be assigned, where the presence of the outer input of high energy quanta is necessary. The external source of the energy is a beam of light (for the case of the photoeffect). The energy of the quantum is more then for the electron excitation to the unbonding orbit and for the deletion of it later from the solid surface layer. The energy of the quantum is more then A in formula (2). As the result of the interaction of the quantum with the molecule (it is not a collective phenomenon) the electron leaves the molecule and creates a positive charge on the surface. The third group consists of the triboelectricity, biloelectricity and charging through the phase transitions. As the result of the energy input some collective phenomenon takes place, that either accumulate the energy from a lot of small quanta to one large quantum, enough for the excitation of the electron. Another possible explanation that will be developed below consists in participation of some intermediates, that has lower ionization energy (radicals). That intermediates are created by some mechanochemical reactions, when the molecules are distorted by the forces, created by the lattice in such a way, that the free radicals generation takes place.

C.Some useful formulas from electrostatics.

In the present book CI system will be used . The formulas of interest are:

$F=1/(4\pi\ \varepsilon\ o)[q_1q_2/(\varepsilon\ r_{12})]$ (3)

The force, with which two plates of the plates of the plane capacitor attract each other:

$F=qE=S\sigma\ \sigma\ /(2\varepsilon_{o\varepsilon})=q^2/(2\varepsilon_{o\varepsilon}S)$ (4)

assuming that both plates are charged equally.

Chapter 2. Triboelectricity.

A.Main laws of triboelectricity.

A lot of scientists during many centuries studied the laws of the triboelectricity, that is, those rules, that the triboinduced charge should observe. Since the positive and negative charges were discovered in the Middle Ages, primarily the signs of the tribocharges were measured were measured by many famous scientists, including Coulomb and Helmholtz. In the 20th century many ideas about how to study the surface phenomena were devised, including Ozhe-spectroscopy, that for the first glance should be very useful for the investigation of the triboinduced charges, mass-spectroscopy at the end of the 20th century atomic force spectroscopy and tunnelling spectroscopy. It was almost obvious, that finally a lot of efforts in that direction, the efforts, that lead to many applications of the solid-state physics (mainly electronic devices) would lead to the full understanding of the phenomenon of the triboelectricity. Nevertheless, it is necessary first to sum the main laws of triboelectricity. The most frequently in connection with the triboelectricity the triboelectric rows are mentioned. In [14] several triboelectric rows or series are mentioned. The authors of that series does not mentioned the absolute value of the charge generated during the friction of the two surfaces. , they mentioned just the signs, received on the two surfaces. In that series, the material in the upper part of the row being subjected to the friction to the lower in the list material is charged positively (the lower in the list material is charged negatively). For example, in the row …A…B…C…At friction A over B (friction means stirring of the flat surfaces) A is charged positively, B is charged negatively, at friction A over C A is charged positively, C is charged negatively, at friction A over C A is charged positively, C is charged negatively, at friction B over C B is charged positively, while C is negatively charged. The triboelectric series described in [14]:

Vilke series: Faraday series:

Glass + Fur +

Wool Flannel

Fur Ivory

Feather Feather

Wood Quartz (Crystal)

Wax Flint glass

Dull glass Silk

Lead Wood

Sulphur Metals

Metals - Sulphur -

For some series the correlation was found between the rigidity and the charge induced. For example, Gesehus series:

Diamond (rigidity =10)

Topaz (rigidity = 8)

Crystal (rigidity = 7)

Smooth glass (rigidity = 5)

Mica (rigidity = 3)

Calcite (rigidity = 3)

Sulphur (rigidity = 2)

Wax (rigidity <1)

Another, more full tribological series are published in Internet [15]:

Human hands +

Asbestos

Rabbit fur

Glass

Mica

Human hair

Nylon

Wool

Fur

Pb

Silk

Aluminium

Paper

Cotton

Steel

Wood

Ivory

Sealing wax

Hard rubber

Ni, Cu

Brass, Ag

Au, Pt

Sulphur

Acetate, Rayon

Polyester

Styrene (Styrofoam)

Orlon

Saran

Polyurethane

Polyethylene

Vinyl (PVC)

Silicon

Teflon -

Some other useful and interesting charging pairs are described in [8]. The experiment described in [8] is as follows: the powder of the crumbled up solid is spilled upon the solid surface. At bending of the plate the powder is shaken off either under the influence of its own weight or at tapping on the plate. The plates from the material, that demonstrate neutral behaviour (neither acid or base), pH ~ 7, such as Pt or paraffin are charged positively by the powders of the organic acids and they are charged negatively by the base dyes, amidol, methol, and inorganic bases ($Ba(OH)_2$, NaOH). The plate from glass (glass has a weak base behaviour) is usually charged positively, but the strong bases give the negative charge. The sulphur, that has an acid reaction usually gives negative charge, but the organic acids (benzoic, salicylic) give the positive charge.

Some other rules, that were definitely established by many generations of the scientists are as follows [15]: at friction of a pair of the chemically identical solids more dense solid receive a positive charge. Let us made two ebonite plates, which are later bent (deformed by bending), so we may rub a concave surface of the bent ebonite plate against a convex surface of the bent ebonite plate (the second one). If the concave ebonite surface is rubbed against the convex ebonite surface, the positive charge is generated upon the concave surface. Among many dielectrics one interesting general correlation was observed: the dielectric with the higher dielectric permeability is charged positively (when it is rubbed against the dielectric with the smaller ε).

Dielectric liquids are also capable to carry the triboelectric charge received during moving of the liquid inside the dielectric or metal tube. At pouring of the oil (petrol) through the steel tube the oil is charged negatively. Some interesting facts about the value and the sign of the charge induced in the jet fuel are outlined in [16]. The jet fuel was charging at passing through the polyurethane foam (porolon), polyether-type foams, polyester-type foams. The highest charge was received during passage of the jet fuel through the paper filter. The charge received was equal to 4000-5000 $mkC \cdot m^{-3}$. Polyurethane (polyester) give very small charge and of the different signs. The charge is 6 times higher at passage through polyether foams and sometimes is reaches the value of 213 $mkC \cdot m^{-3}$.

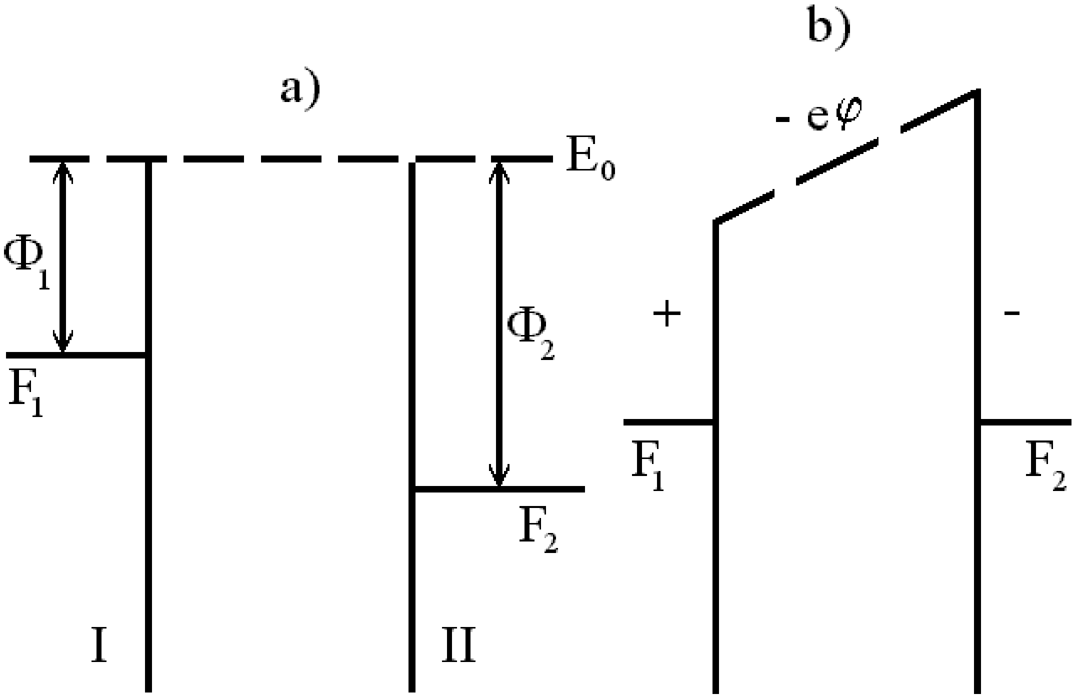
B.The classical theories of the triboelectricity.

The most earlier theories of the triboelectricity were trying to describe the charge law using the ideas of the chemically intact surfaces. That is, in addition to Helmholtz double layer the authors of the early theories tried to found correlations between the sign of the triboelectric charge in the triboelectric series and the certain chemical properties of the solid. For example, the correlation between the rigidity and the sign was found it is described in [14] (Gesehus series). The most pronounced idea was received soon after the discovery of the free electron and consists in the attempt to find the correlation between the donor-acceptor properties and the sign of the triboelectric charge. The main point of those theories is that there is a straightforward correlation between the difference of the ionisation energy of the donor I_D and the electron affinity of the acceptor E_A and the value (and sign) of the charge transferred. That is, the process of the electrization might be described by the chemical process – electron transfer between the initial chemically intact compounds, donor of the electron D and the acceptor of the electron A:

$$D + A \rightarrow D^+ + A^- \quad (5)$$

In this process one of the initial compounds works as a donor D, another one works as an acceptor A (depending upon of the difference I_D-E_A – this difference determines the direction of the process). Every compound might be considered as a donor or as an acceptor and the comparison of the difference of both directions allows somebody to determine the sign received). Triboelectrization was considered as a primary process between the chemically intact surfaces.

But for the description of the tribological series between the dielectrics this idea failed.



Another theory used the band theory as the initial step for the consideration of the process of the electron transfer from one material to another one. This was found to be the perfect description of the process of the contact charge transfer between the metals. The contact phenomena for the conductors (metals) and semiconductors are described in many textbooks [6]. The scheme of the appearance of the charge transfer between the different metals with $F_1 \neq F_2$ – two Fermi-levels is shown in Fig.1A.

Fig.1 The scheme of the charge transfer in the metals and in the semiconductors.

In this figure E_o means the energy of the free electron in the vacuum, Φ_1 – ionisation energy (work function) of the first metal, Φ_2 – ionisation energy (work function) of the second metal, at the beginning of the experiment $F_1 \neq F_2$. After the beginning of the experiment, when two metals are in contact with each other, Fermi-levels are now equal to each other, but the charge transfer between two metals leads to the creation of the potential between two metals in the contact (Fig.1B). Some electrons comes from one metal to the second one (since there are metals, there is a lot of the free energy levels in the continuum just above F_1 and F_2 and the electrons can move from one metal to another). Therefore, in one metal positive charge is generated and another one is negatively charged. In principle, quick separation may trap those charges but more easily they can be registered with the help of the electric field measurements in the contact. For the case of the less conductive materials – semiconductors – those effects lead to the creation of the diodes, transistors and virtually all the modern electronics!

Many scientists tried to apply this theory in a straightforward manner to the problem of the contact of the two dielectrics. For example, in [18] the idea of work function in the polymers is applied to the problem of the electrization of the polymers. It was supposed, that some additional surface energy levels exist in the polymers (polyethylene, polypropylene) [18]. Those traps work in the way, analogous to the case of the metal. But without such a supposition about the surface energy levels that idea of the application of the band theory should failed. Being considered for the case of the dielectric, it is necessary to consider the following: for the case of the metals and semiconductors as the result of the overlapping of the wave functions of the neighbouring atoms or molecules (in the case of the organic metals) delocalization of the electrons take place and it is possible to understand, how the additional charge distribution in the vicinity of the contact takes place over the whole volume of the semiconductor or the metal. But this theory is inapplicable to the case of the intact molecular dielectrics. Since the energy of the interaction between the molecules in the molecular crystal is much less then the energy of the intermolecular bonds, in the molecular crystal the delocalization length of the electrons is small and in fact it should be localised onto some molecular orbits. Actually no delocalization similar to metals is present. Being considered the autolocalization phenomenon, that would mean that just a few molecules will be involved in the process of the delocalization of the charge. In this case the energy levels, from which and to which the electron transfer can take place at the contact of the two dielectrics, in fact coincide with the energy levels of the isolated molecules but in the potential, created by the crystal field in the place of the contact of the two given molecules [19]. Therefore, in the present case the phenomenon of the triboelectrization would be determined mainly by the energy levels of the isolated molecules, not by the band properties of the solid state (in real live because of the weak interaction between the molecules the bands should be of a width ~ Δ E, and therefore, vary narrow, in fact, coinciding with the energy levels of the separated molecules (taken out of any crystal lattice). At ambient temperatures. In order to be observed the band width should be at least comparable (or more) with kT at ambient temperatures. Just at T=0 band width might be of any width. If the band width comparable with kT because of the thermal motion the band structure through the sample should disappear easily, just some islands with interacting molecules remains instead of the band structure. At consideration of the two immediately contacting molecules the difference between the ionization potential of the first molecule and the electron affinity of the second molecule should be considered. For the intact molecules from any tribological series this value is very high and therefore, the amount of the transferred charges should be very small. Indeed, it is not so easy to overcome the energy difference in several eV and to put the electron from the donor molecule to the acceptor molecule. More to the point, the charge should be localized in the surface layers. The time of the charge transfer in a real dielectric may be estimated as follows. If the potential difference is equal to 1 V, the for the paraffin with the resistivity $\rho = 10^{15}\ \Omega \cdot m$ and for the distance of 10 nm , for 1 cm^2 the resistance is $R=10^{11}\ \Omega$ and the charge received at triboelectrization is ~ $6,4 \cdot 10^{-9}\ C/cm^2$ should flow during t=630 seconds [20]. Therefore, even if the charge transfer between the bands was possible, it would demand too much time for the completion. It is necessary to emphasize, that those considerations are valid for the intact dielectrics, in the mechanochemically treated dielectrics some new levels appear, which may create additional level’s density above the highest occupied levels inside the gap.

C)The author’s theory of the triboelectricity.

Despite in the literature I did not find the exact description absolutely similar to my theory, there are some articles, where some ideas, underlying my theory are outlined. In [21] the experiment conducted by T.Urbanskii is described. During milling of the Baltic amber (polyabeitic acid) he observed both free charges and free radicals. T Urbanskii believed, that investigation of the phenomenon of the generation of the free radicals through the mechanical milling or breakage, through scratching or polishing can elucidate such phenomenon as charging of the of the solids and triboluminescence, which are not yet fully explained. Generation of the free radicals and free charges both takes place through the bond cleavage and generation of the intermediates.

The idea of the correlation between the mechanoelectrons and the free radicals is mentioned in [22]. The correlation between the mechanoemission (mechanoelectrons may be considered as one more mechanism of the tribocharge and therefore, it should be an indirect correlation between the radicals and charging) and stirring of the polymer in the vacuum (energy of the mechanoemission >100 keV) is outlined in [23].

The idea, very close to my theory is outlined in [24]. The authors of [24] consider the process of the triboelectrization as the result of the reaction of the machanoradicals, generated on one polymer surface (homolythic bond breakage) and of the mechanoanions, generated on the surface of the second polymer due to the heterolythic bond breakage. The electron transfer between the secondary products takes place, what lead to the triboelectrization. That mechanism, from the author’s point of view is also possible, but it is not the main one, another mechanism predominates, when the charge transfer takes place between two radicals, with the radicals itself generated as the result of the mechanochemical reaction in the contact.

The main points of my theory are:

1.The process in the contact is a very complicated mechanochemical reaction, when the free radicals are generated in many possible ways: rupture of the chemical bonds, donor-acceptor interactions in a potential well, created by the other molecules from both surfaces in a microscopic contact (where the donor-acceptor reaction itself takes place).

2.All the generated products, including ions, radicals, pieces of the macromolecules, and some nondestructed pieces of the initial compounds has a different affinity (adhesion) to the different surfaces (both intact and treated) – this is responsible for the macroscopic mass transfer in the friction contact [25].

3.After the disrupture of the contact, the ions and other products remain bounded to the surfaces, where they were attached with the help of the adhesion forces. This is true for all products, including ions and radicals.

4.There are several processes, that are responsible for the triboelectric charging of the surfaces. Among them are: primarily electron transfer, generation of the ion-radicals (both signs) on one surface and then withdraw of the electron by either acceptor molecule or another radical from the second surface [24], generation of the two free radicals with electron transfer between them, assuming both radicals (and consequently ions) are chemically attached to the initial surfaces (the author wants to prove, that this is the main mechanism of the triboelectrization), tearing away of the pieces of the molecules with the generation: first free radicals, then ions and adhesion of those ions to different surfaces one ion mainly to one surface, another ion mainly to the second one, what would give after the separation of the surfaces positive charge on one surface and the negative one on the another one.

Therefore, the main idea of the mechanochemical processes responsible for the triboelectrization is that the real process, responsible for the charge is just one of the whole bunch of many mechanochemical reactions in that contact. Even selective adhesion of the ions onto the different surfaces is just one of the few adhesion processes, many of them lead to the mass transfer of the products to one or another surface. As the result of that process of the mass transfer, some of the products (or, for example, pieces of the initial macromolecules) can be found on one surface, some products onto the another one after the separation of the stirred surfaces.

Every item of that theory needs to be theoretically and experimentally substantiated. The first principle of my theory is that a mechanochemical reaction in the contact takes place – the chemical bonds broke, the new compounds appear, with the whole row of the new compounds are generated in the reactions, that may have their own rules, different from the ordinary chemistry in the solution. In this consideration the solid dielectric – solid dielectric contact, metal – solid dielectric contact, solid dielectric – liquid contacts are chosen. Many experiments were conducted with the help stirring of the solid dielectrics, specially important in the case of the solid molecular dielectrics. It is a well known fact, that during the milling of many inorganic solids the mechanochemical reactions take place. Therefore, at mutual stirring of the chosen dielectric couple (let both of the compounds are inorganic dielectrics) the mechanochemical reaction should take place as well. Despite the intensity of the mechanochemical reactions in that case is much lower (compare to the case of the powerful desintegrators and milling aggregates), their intensity in the case of the milling in a mill or a mortar because of the much lower energy input (the pressure applied is lower, the energy of the impact between the molecules is lower), some mechanochemical reactions should take place in this case as well. From another point of view, comparison of the triboelectric yield (charge on the surface) as a function of the intensity of stirring (the fact, mentioned in many publications [14, for example]) and the mechanochemical yield as a function of the intensity of milling show, that both processes have a similar function dependence – the higher the intensity of the action, the higher the yield. This similarity is of a significance! It allows to eliminate easily the charge transfer mechanism between bands responsible for the electrization charge of the metals in the contact (assuming quick electron delocalization). Of course, the contact surface also should depend upon the intensity (applied force, for example) but that should be a saturated dependence (like in friction laws), while mechanochemistry usually demonstrates another type of the yield dependence as a function of the intensity, similar to the process of the triboelectrization and different from the friction laws. According to [14], there is a dependence between the electric charge, accumulated onto the surface during the process of the triboelectrization and the velocity of rubbing. But according to Coulomb law for friction, the friction force (and therefore, the real contact between surfaces) does not depend upon the relative velocity (in the reasonable velocity range, say 1 cm/s – 10 cm/s), therefore, triboelectricity is not proportional to the real contact, as it is assumed in many old theories ([14], for example). If it were proportional, no dependence upon the velocity would be observed. Contrary to this, mechanochemical reactions strongly depend upon any velocity parameters [27] (velocity of balls in a mill, for example) since it increases the intensity of the action.

More complicated question is the question of the mechanochemistry of the low-molecular weight organic compounds. For many years it was assumed that the mechanochemistry of the low-molecular weight organic compounds is a very rare case (contrary to polymers, where many chemical reactions are easily initiated due to the polymer bond rupture at stretching). Now it is clear, that the mechanochemistry of the low-molecular weight organic compounds, despite it is not thoroughly investigated part of the science, poses some interesting chemical reactions with unusual mechanisms [26]. In this book [26] a lot of the mechanochemical reactions is described, including those, that are responsible for the free radicals generation and some other mechanochemical reactions, that have a different mechanism compare to the reactions between the same compounds in the liquid state. That demonstration of the many reactions, which have a different mechanism, also points out, that some reactions, which might lead to charge separation (reactions, that have Δ H>0, thermodynamically unprofitable, can, nevertheless, take place in mechanochemistry, since a lot of other chemical reactions with Δ H>0 indeed take place in mechanochemistry). Among those reactions the reactions, that demonstrate the appearance of the free radicals are of the special interest, since they, as it will be shown later, lead to the generation of the free charges through the interaction between the radicals.

Since the low-molecular weight organic compounds are capable to interact easily in a mortar or in a mill, they should also interact mechanochemically with the generation of the many products, including radicals, when a bulk of one material is stirred with respect to the bulk of another material (instead of investigation of milling of the mixed powders in a mortar). Unfortunately, this supposition is not so easy to check, since in this case all the generated compounds are on the surface and their concentration is too low to be detected by the usual method, they are usually invisible and visible and UV-spectroscopy can not be applied (except for some special cases, see next subchapter). Just some very sensitive methods can detect those compounds (EPR, infrared spectroscopy, Ozhe-spectroscopy should be applied).

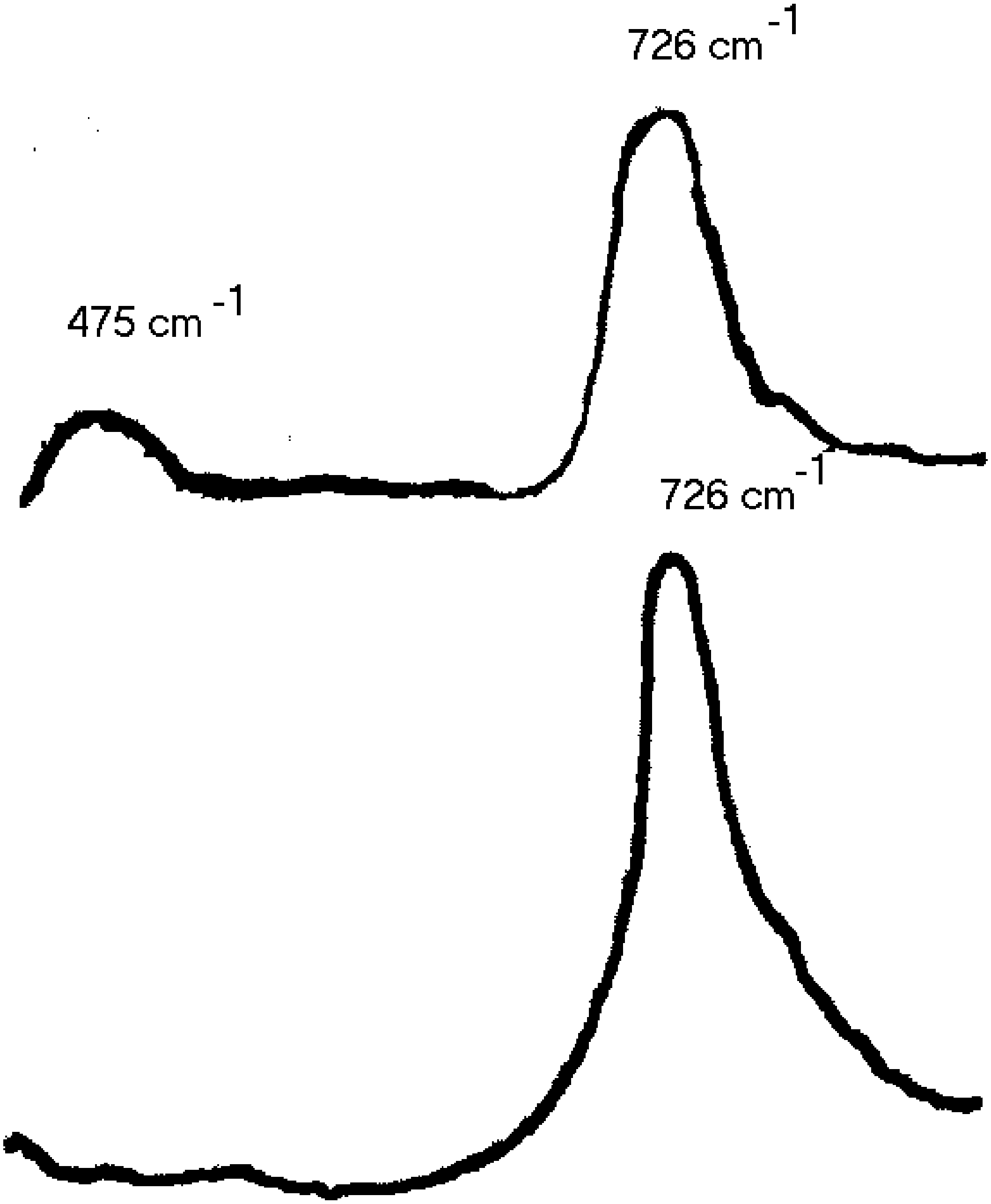
I. Mechanochemical reactions of some polymers. (The mechanochemical reactions, which does not connected with the bond rupture).

Before the presentation of the main idea, that generation of the free radicals on both surfaces of the friction pair strictly precedes the generation of the free charges, some results are outlined, that demonstrate higher reaction ability of the polymers, those polymers, that are of main interest later in the case of the mechanochemistry. Polymers are very well charged at rubbing and usually possess negative charge (see triboelectric series higher). Mainly paraffin and polyethylene were investigated by author both theoretically and experimentally [20] and their enhanced reactivity is discussed here. Some data are described concerning the mechanoactivation of the reaction of the polyethylene teflon with iodine, confirmed by infrared spectroscopy data and EPR-spectroscopy data. The possibility of the mechanogenerated complexes of teflon and polypropylene is discussed. In general, this subchapter supports strongly the main idea – on the surface of solid dielectrics the mechanochemical reactions at friction are extremely common, almost inevitable. It was shown in many examples of low-molecular weight organic compounds, described in [26]. As it was shown in [20], mechanochemical generation of the free radicals – very reactive species in chemistry – takes place at triboelectrization of the different polymers, including polyethylene and paraffin, what also tells about the possible mechanoactivation of alkanes. In addition in [20] the influence of the iodine as an inhibitor of the triboelectrization at friction of the polymers is discussed, polymers like paraffin (polyethylene), and therefore in this part of the book an additional data about how this process may take place are discussed (exactly how the iodine may prevent the triboelectrization).

In order to do so the reagents were used: iodine (chemically pure) and industrial powder of polyethylene and films of polyethylene, teflon, polypropylene, EPR-spectrometer EPR-21i and IR spectrometer Karl Zeiss 311982. Stirring of the powders was conducted in a porcelain mortar (the powder of the iodine and the powder of the polyethylene) or the crystalline iodine was poured onto the teflon film and it was stirred with the force, at this process the brown scales, that include some amount of the product of the interaction of the iodine with the teflon. Then for the registration of the EPR-spectra the products received are placed into the ampoule for the EPR-spectroscopy and the registration of the EPR-spectra in the air at room temperature was conducted for the reaction products and the initial compounds. For the registration of the IR-spectra the film was made from the mechanochemically treated powder polyethylene + iodine (with the help of melting of the corresponding powder at the temperature around the temperature of melting of polyethylene, with all the additional iodine was sublimed as a violet vapor; it was checked in advance, that the same procedure for merely mixed powders of the iodine and the polyethylene does not lead to the generation of the product – the iodine is completely evaporated and the film is not received). As far as the teflon is concerned, the scales, containing the product are placed between the two polyethylene films and the registration was conducted of that sum film. IR-spectrum of the initial sample of the adamantane and the adamantane, stirred with the iodine, was registered with the help of the preliminary preparation of the suspension in the vaseline oil.

IR-spectra received tell about the generation of C-I bonds at stirring. It is clearly seen in Fig 2., where the upper IR-spectrum corresponds to the sample, received at stirring of the iodine with the polyethylene, and below – IR-spectrum of the initial polyethylene film (received by mere melting of the initial polyethylene powder). A new band is seen clearly at 475 cm^{-1} what exactly corresponds to the band, that appears at production of C-I bond.

Fig.2 IR-spectrum of the polyethylene film before the mechanochemical reaction with I_2 (lower spectrum) and after the mechanochemical reaction (475 cm^{-1} corresponds to C-I bond)



For the control of the importance of the molecular mass for that effect of the mechanochemical generation of C-I bond it was conducted stirring of the adamantane powder with the same crystalline iodine. In this case both IR-spectroscopy and chromatography show unequivocally that generation of C-I bond does not take place, that is, it is possible to activate mechanochemically just high-molecular weight alkanes like paraffin and polyethylene, while relatively low-molecular weight alkanes such as adamantane, can not be activated in such a way (but, as it was demonstrated in my book [26], many other chemical reactions between the low-molecular weight organic compounds are possible through the mechanochemistry). Apparently, either C-C bonds rupture in polyethylene, induced by the mechanical energy [28] responsible for the generation of C-I bonds, or at stirring of polyethylene activation of C-H bonds take place because of the deformation of C-C bonds, as it should be for the strained neighboring bonds [29].

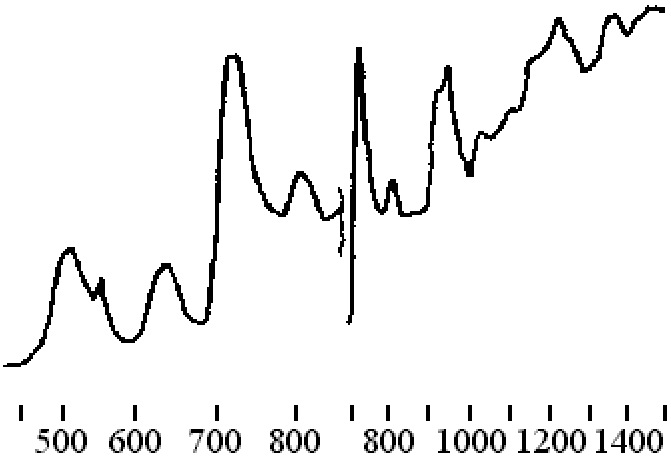


Fig.3 IR-spectrum of the mechanochemical reaction of teflon with I_2

As far as the teflon is concerned, at stirring of it the process of the generation of the brown scales, which give a row of the new bands in IR-spectrum, namely at 805 cm^{-1}, 920 cm^{-1}, 955 cm^{-1}, 1030 cm^{-1}, 1100 cm^{-1}, 1260 cm^{-1} (see Fig.3). Those bands may in principle correspond to the different chemical bonds, that are received as the result of the generation of the chemical bonds between the radicals, received at bond rupture C-C in teflon, further reaction of the oxygen addition to the place of the rupture, and then the addition reaction of the iodine to the oxygen atom, for example (two first reactions are well known for the chemistry of teflon) :

$$-CF_2\text{-}CF_2\text{-}O\text{-}O^{\cdot} \rightarrow -CF_2{=}O + CF_2{=}O + I_2 \rightarrow -CF_2\text{-}O\text{-}I\ (I) \rightarrow -CF_2\text{-}O\text{-}IO_2\ (II)\ (6)$$

(it is the compounds of the acid HIO_3 that are the most stable, that is, the ester of the acid HIO_3 should be the most stable compound (II), while the ester of the acid HIO (compound I) should quickly disproportionate into the ester of the acid HIO_3, exactly as it takes place in the case of the inorganic compounds [30].

Therefore, it is possible to consider as proved, that at stirring of the iodine in the crystal state with the teflon film the production of some chemical compounds take place, that may be registered with the help of IR-spectroscopy.

Besides that the registration of the EPR-spectra of the received products of the chemical reactions was conducted. As it was expected, in the case of stirring of I_2 and polyethylene no EPR-signal was observed, while for the case of stirring of teflon with the crystalline iodine the EPR-spectrum was observed, shown in Fig.4. The signal itself is not the signal of the peroxide radical. About that radical it is known, that it is received according to the following mechanism [31]:

$$-CF_2-CF_2- \rightarrow -CF_2^{\cdot} + O_2 \rightarrow CF_2-O-O^{\cdot} \quad (7)$$

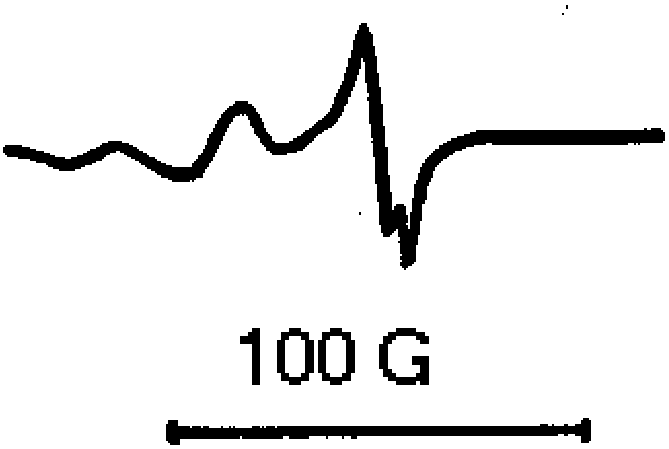


Fig.4 EPR-signal of the mechanochemically treated teflon with I_2.

The problem is in the experimentally observed fact, that the parameters of the EPR-spectra received does not coincide with the data about the peroxide radical outlined [31], what tells about the participation of the iodine in the reaction. At stirring of teflon over the glass pilling of the teflon from the film also takes place, but in the products received no EPR-signal was observed.

It is necessary to mention also the unsuccessive attempt to understand the nature of those radicals (teflon + iodine, mechanochemistry) with the help of the following technique: I put the teflon powder nearby the γ -source (radioactive Co) for a time period of 6 months together with the iodine powder in one closed vessel. The idea was that as the result of the free radicals generation together with the chemical reaction with the iodine vapor the same chemical compounds, as in the case of the mechanochemistry between the crystalline iodine and the teflon can be generated. (The identification would be performed with the help of IR-spectroscopy). Unfortunately, the experiment failed – no reaction was observed despite the teflon powder was transformed by such a strong dose of the radiation so great, that the mechanical properties of the powder changed (the powder become less adhesive and more dry to the touch). Nevertheless, no change of the color was observed – probably the iodine vapor does not reached the reactive centers (radicals). This experiment emphasizes the real difference between the mechanochemical method of the reaction conduction and the radiation chemistry ideas.

In addition, it is necessary to outline one more important observation, that take relation to the generation of some new compounds at the mechanochemical reaction of the crystalline iodine with teflon. It is a well known fact [10], that teflon at friction over practically any surface charges negatively, but if this surface is treated by the crystalline iodine, then the treated teflon surface is charged positively (at friction over wood, for example). It means, that the mechanochemistry takes place (both iodine and teflon separately should give negative charge). To explain that effect numerous explanations were considered, in particular, the phenomenon of the electron transfer from created on the teflon surface compounds, like $–CF_2$-O-I or $–CF_2$-O-IO_2, but the value, that is equal to the ionization energy, in any case turned out to be very large, and according to the theory, developed below and in [20], it is more profitable to charge the teflon surface negatively. The only possibility, from my point of view, is either to consider the withdraw of the molecule I_2^-, received as the result of the production and disappearance of the charge transfer complex between the teflon molecule and the iodine molecule (see below about the complex and in the following subchapters about the possibility of the mechanism of charging, connected with the ions transfer from one surface to another) or to use the chemical reaction of the electron withdraw from the molecule I_2^-, that is, transition $I_2^- \rightarrow$ I2 + e-, since it is that process, that is the least energetically disadvantageous (ionization potential is Ia=2.33 eV quantum chemistry calculations [34]).

The key for understanding of the fact, how the molecule I_2^- may be generated is perception of the possibility of the generation at friction of the covered by the iodine teflon surface of the complex: teflon (part of the polymer molecule) + iodine:

$$-(CF_2)_n- + I_2 \rightarrow [-(CF_2)_n^+-\ldots I_2^-] \rightarrow \text{friction} \rightarrow -(CF_2)_n^+- + I_2 + e^- \quad (8)$$

Indeed, the iodine is known as giving complexes with many organic molecules, such as benzene, numerous ethers etc [32]. As it was found, at stirring with force of the iodine at the surface of the teflon the generation of the dark-violet strips was observed, disappearing during 2-3 seconds, that is under the action of the friction production of the unstable complex teflon+iodine takes place, which appears as the result of the mechanochemical reaction between the iodine and the teflon (influence of the matrix, Chapter 5 of [26]). After the end of the matrix influence onto the chemical reaction, the complex becomes thermodynamically unprofitable and it disappears during the time of the order of several seconds. This phenomenon is exactly analogous to the phenomenon of the observation of the bright crimson trace disappearing in 0.5-1 sec at stirring of p-quinone with glicine [33]. The only difference is that in the case of the complex p-quinone – glycine without any mechanochemistry it will be received by itself because of the volatility of the quinone, during approximately half an hour, that is, the complex is thermodynamically profitable (Δ H <0), and mechanochemistry leads to the short time increase of the modulus of $|\Delta H|$ during the time of the action of the mechanical energy, while after the end of the action of the mechanical load, after 0.5-1 seconds the complex disappears (the matrix influence is over, time of the delay is connected with the characteristic time of the relaxation of the pressed microcrystals, most likely this is the time of the existence of the induced adhesion contact, but it is also possible to talk about the production of the new phase, consisted from the complexes). Contrary to that complex the complex between the iodine and teflon (and also the complex of the iodine with polypropylene [the crystalline iodine was spilled over the polymer and stirred by the pestle with the force – one stroke, another one – and dark crimson trace appears]) the generation of the complex between the teflon molecule and the iodine molecule in the absence of the mechanical energy is thermodynamically unprofitable, that's why the complex exists for the short time period only (it was specially checked, that even at ~ 100 ^{o}C the iodine vapor does not give this coloring with teflon).

An alternative explanation of that fact is the effect of the diffusion acceleration because of the input of the mechanical energy, that is the explanation might be turned into the phenomenon of the mechanoactivation of the diffusion (a simple increase of the contact surface). This explanation is not valid because for the case of p-quinone with glycine (the complex is profitable thermodynamically) the complex is destroyed nevertheless after the end of the mechanical load (temporarily), but it is a mere diffusion acceleration, the complex should remain (the color should persist), but the complex is over. Of course, it will be back later, in a natural diffusion way, but initial destruction of the complex in the case of diffusion acceleration is impossible, once created, whether it is a quick diffusion or slow one, it should remains. It was possible to suppose that in the case of the complexes iodine + teflon and p-quinone + glycine the different mechanisms works, (and it is possible, in a general consideration) but one more argument against acceleration of the diffusion is: in reality in a well ground powder of the teflon with the iodine the color remains brown, that is, the diffusion does not lead to the change of the color, to the production of the complex, and therefore, the complex is not stable for the thermodynamical reason and diffusion bear no meaning here, (but it is temporarily stable, under load, that's the main application of mechanochemistry here). Indeed, as it was established, teflon has a very complicated structure, what is connected with the large amount of the double layers (ions of F^- in teflon are polarized very strong, and in teflon the complicated structure of the double energetic layers appears), that's why in reality at the action of the mechanical energy) the freeze of that structure can take place, what leads to the improvement of the ability of the iodine molecules to penetrate inside the polymeric conglomerates, what might in principle be called the acceleration of the diffusion, but in reality the increase of the concentration of the complexes takes place not because of the increase of the surface at the constant energy of the affinity of the iodine molecule to the surface (artificial mobility, mechanoactivation), but because of the increase of the energy member in a diffusion coefficient (the activation energy E_a of the diffusion drops at the action of the mechanical load at the moment of the load application), but in this case it would be very difficult to explain, why in the mixture of the powders the diffusion does not take place at all and why the complexes generated are coming apart. More realistic is the explanation, that at friction the lot of defects is generated, near them the enthalpy of the complex becomes more negative and during the time of the existence of the defect (1-2 sec) the generation of the complex takes place, that is, the generation of the mechanostimulated complex iodine plus teflon is observed, what gives back the electron, that's why the treated by the iodine teflon surface is charged positively.

Indeed, the experiments described showed unequivocally, that the mechanical energy, applied to the contact of the two dielectrics, is able to conduct the mechanoactivation of the surface of such low-active compounds as teflon and some alkanes. In addition, by the straightforward experiments the possibility of the production of the mechanostimulated complexes is demonstrated (probably with charge transfer between the molecules). The complex between those molecules can not exist without mechanochemistry at all.

About the possibility of the activation of C-H bond in the alkanes at deformation of C-C bond in the alkanes.

About the possibility of the activation of C-H bond in the alkanes at the deformation of C-C bond in the alkane it is said in a great amount of the publications (see review [29]), but mainly this fact bear some relation to the reaction of the polymer oxidation, when, for example, the process of the oxidation of the polypropylene (ozone consumption and the free radicals generation) is accelerated 2-5 times at application of the stretching load in the load's range from 33 to 145 GPa. As far as the activation of the C-H bond in the general case is concerned, it was shown, that at stretching of the molecule of the alkane the energy of the initial state increases in the higher extent, then the energy of the transition state, what leads to lowering of the activation energy of the reaction [29].

The author of the book was concerned about the potential energy surface that corresponds to the tearing away of the hydrogen atom from ethane at shortening or at elongation of C-C bond, that is, calculation of the enthalpy of the reaction was conducted:

$$C_2H_6 \rightarrow C_2H_5^{\cdot} + H^{\cdot} \quad (9)$$

for the case of the infinite separation of the radicals, generated as the result of the process.

In this case, as it turns out, contrary to other reactions, described in [29], (the transition complex of the C-H bond rupture has a small distance of the elongation of C-H bond), the distance of the elongation of C-H bond is high – it is literally hydrogen atom withdraw to infinity. In the cases, described in [29], the longer C-C bond, the easier C-H bond activation (not simple rupture!) occurs. In the present case, for the longer distances the energy of H-atom withdraw increases, for the shorter distances of C-C bond the energy of C-H bond decreases. GAUSSIAN program was used, method SLYP and basis 6-311g** [34]. The results of the calculations are as follows: at stretching of C-C bond in ethane for 6.1 % the enthalpy of the C-H bond rupture decreases for 3,2 %. This behaviour of the enthalpy of C-H bond rupture well correlates with some limiting cases: at full rupture of C-C bond $CH_3^{\cdot}$–radicals would be received, that has more strong C-H bond, then ethane (it is 11,5 % higher, 457,7 kJ/mol in $CH_3^{\cdot}$ versus 410,5 kJ/mol in C_2H_6 [35]), at the same in the second limiting case, when C-C bond becomes equal to the double bond, the possibility of the change of the hybridization appears and a couple of H-atoms should be selected. That is, the bonding energy should decrease, what was confirmed by the calculations.

The main conclusion is that stretching of the polymer leads not only to C-C bond rupture (it was known for many years, this is the part of the classical mechanochemistry of the polymers [36], but also to the activation of C-H bond in the polymer (and other bonds, immediately placed to C-C bond) [29].

II Impregnation of the dielectric surface – the way to control the mechanochemical reaction and to prevent the process of the triboelectrization.

Usually the specialists in the triboelectrization investigate the intact surfaces, clean of any dirt and other compounds. I decided to study experimentally the idea of the impregnation of the solid dielectric surfaces by some radical traps, bearing in mind the possible change of the triboelectrization. Indeed, the change in the triboelectrization was observed. At doping of the crystalline iodine and some powder like $CoSO_4$, $CuCl_2$ the easily observable decrease of the triboelectric charge was received. Thus the initial idea about the radical nature of the triboelectrization was confirmed [20].

For the investigation of the phenomenon of the triboelectrization of static electricity the compounds were chosen, which are capable to generate strong (in the absolute value) electric charges: paraffin (polyethylene) and animal bristle (pig bristle) and human hair, and polyurethane (taken as porolon). In fact, pig bristle and human hair are protein (keratin) with large content of the sulfur. The painting brush was used, made out of pig bristle and paraffin sticks (household candles, made out of paraffin with some of them were colorless and others were yellow, with a very small difference between them). For some control experiments the chemically pure paraffin was used. Another reactives include the chemically pure iodine, $CuCl_2 \cdot 6H_2O$, $MnSO_4 \cdot 10H_2O$, $CoSO_4 \cdot 7H_2O$, $Ni_3(PO_4)_2 \cdot 7H_2O$, $Co[Cl(NH_3)_5]Cl$, $FeSO_4 \cdot 7H_2O$, TEMPOL, $Mg(AlO_2)_2$, K_2SO_4, ZnO, NaCl, oxalic acid, citric acid, chalcone (benzalacetophenone), p-chloranil, 1-aminoanthraquinone, p-quinone. Some other reactives of the industrial purity include: starch, chalk, Al-fillings, coal, Fe-fillings, fructose, 1,3,5-trioxane (meta-formaldehyde, trioxymethylene, $C_3H_6O_3$). Some standard oil paints were also used in order to cover different polymers with the radical-absorbtive chemicals (to impregnate the polymer surface). In addition, polyethylene powder with the particle size $7 \cdot 10^{-3} \div 0.2$ mm was used. Paraffin and polyethylene easily develop even at very insignificant action, as brushing with the weak force by the paint brush (clean out of fat with the help of the acetone) quite a strong electrical charge and, as it turns out, easily registered EPR-signal. For the registration of the EPR-signal the EPR-spectrometer EPR-21i was used. In order to register the electric field, created with the help of the dielectrics, used in the experiment a special equipment was applied, constructed from the field effect transistor and light-emitting diode. This device is shown in Fig.5. The scheme of the device is depicted in [37]. As a second, independent method of the registration of the electric field intensity the weighting method was used, based upon the application of the pieces of the metal foil of the different weight (in the electric field the conducting foil, taken as a flat surface (flat plane) starts to be attracted to the charged dielectric).

Procedure of the impregnation of the paraffin is as follows: on the surface of the candle or melted paraffin 50-100 mg/cm^2 of the compound for the impregnation was placed (as a powder, uniformly through the whole surface). Then that surface was heated with the help of the flow of the hot air to the temperature just higher then the melting temperature (it is possible to hold the candle over the red-hot stove) in order to receive at melting of the upper layer of the paraffin the uniform distribution of the impregnant in the upper layer of the paraffin (1-2 mm thick). After cooling of that surface to the room temperature at stirring the impregnant does not leave this layer any more (with time, of course, the impregnant leaves that material together with the upper layer of the paraffin and the procedure should be repeated). Since the iodine can be dissolved in paraffin, impregnation of the paraffin by the iodine can be made not only on the surface, but also the whole volume of the paraffin can be doped. The procedure of the dissolution of the iodine in the paraffin consists in melting of the piece of the paraffin in a cylindrical vessel (placing the vessel in a hot water in order to prevent an ignition of the paraffin itself, the procedure was taken in the air) addition of a necessary amount of the crystalline iodine in the paraffin and stirring of the crystals with the help of the glass stick. After several minutes all the iodine is uniformly dissolved in a paraffin, a pink melt is formed. (Up to 0.12 M/kg solution has been easily received by the author). After cooling of the vessel the cylinder of the doped solid paraffin inside the glass cylinder was received. But the adhesion forces are too large to delete it from the glass vessel. A very accurate heating allows to melt just surface layer of the doped paraffin and the rest cylinder easily leaves the glass vessel. The uniformly doped paraffin cylinder is ready for the experiment. A series of the doped by the iodine paraffin cylinders was made, with the concentrations of 0.48; 1.074; 2.863; 5.30; 8.574; 16.34; 40.10; 112.56 mM/kg.

Electrization of the compounds was conducted with the help of brushing by the paint brush, made from pig bristle of the items under investigation (for example, of the paraffin disk), or through stirring of that compound or another one over the human hair (actually alive hair of the author was used, I just stirred the paraffin stick over my head) or over the polyurethane (porolon). The sensing unit, shown in Fig.5, consists of the field-effect transistor KP303A (with p-n junction and n-channel), light-emitting diode AL307DM, AL307BM and 9 V battery) for the registration of the negative charge and an analogous to it sensing unit for the registration of the positive charge consists of the transistor KP103E (with p-n junction and p-channel), light-emitting diode AL307DM, AL307BM and 9 V battery. Those field-effect transistors, that were used for the sensing unit, were made in Russia, and the equal to them transistors made in US are described in [37]. That sensing units were used to obtain the information about the relative remoteness of the charged surface from the sensing unit. The sensing unit works in such a way, that the continuously emitting light sensing unit is switched off when the electric field intensity on the small antenna (as that antenna in both cases the bent up electrode of the transistor of a length of 1 cm was used [37]) reaches the certain value. Two main methods of the investigation of the triboelectric charge with the help of that sensing unit were applied. Assuming that at experiments with the triboelectricity the error in the definition of the charge obtained is usually high, registration of the maximal charge (from approximately 30 experiments of successful stirring) was conducted. In every attempt the charged surface was approaching the sensing unit before the light-emitting diode is switched off. Then the relative charges might be measured with the help of a Coulomb law:

$$E=\{1/(4\pi\ \varepsilon_o)\}\cdot q/r^2 \quad (10)$$

here E is the value of the field, at which the light-emitting diode is switched off.

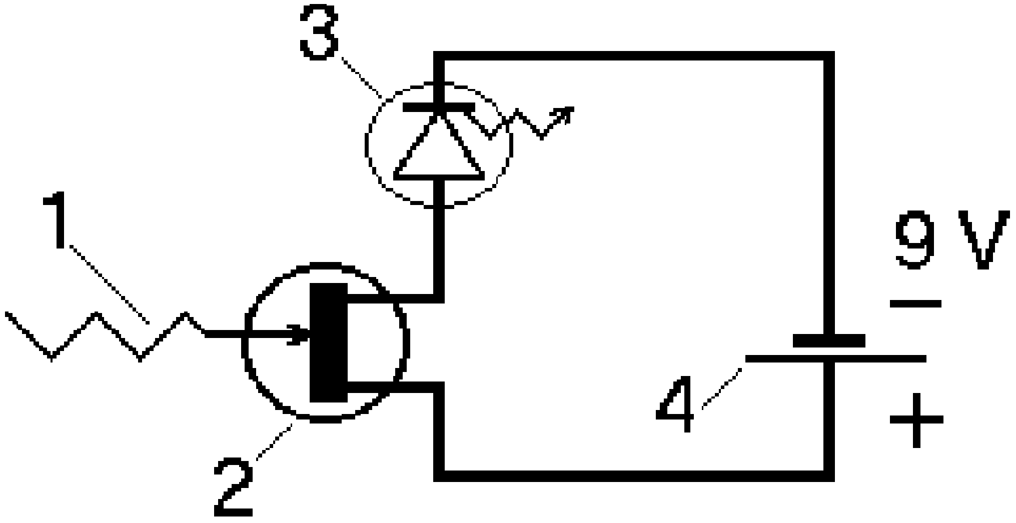


Fig.5 The scheme of the sensing unit of a high sensitivity for the registration of the permanent electric fields. 1 - antenna, 2 - field effect transistor, 3 - light emitting diode, 4 - battery.

In the second experimental method (also with sensing unit) the accumulation curve was recorded. Every stirring (for example, paraffin stick over porolon or paraffin stick over human hair) was separated by the equal time periods (around 5 sec). Then along x-axis the number of stirrings is plotted. Actually one stirring consists of 3 seconds of stirring itself and 2 s registration. Despite the seemingly simple idea, that method allowed me to obtain nice (for electrostatic) accumulation curves. Those curves are shown in Fig.6. Along the y-axes the surface charge, taken in an arbitrary units, is shown. The charge was calculated with the help of a formula (10) (in a real life I just squared the distance r, in cm, at which the light-emitting diode switches off). Curves 1 and 2 corresponds to stirring of the paraffin stick (undoped) with the help of the human hair. Actually two different sticks were taken from the same set of sticks and the difference between curves 1 and 2 characterizes the error in an accumulation curves for the same material. This error is not very large, taking into consideration, that the electrostatic usually has very large errors.

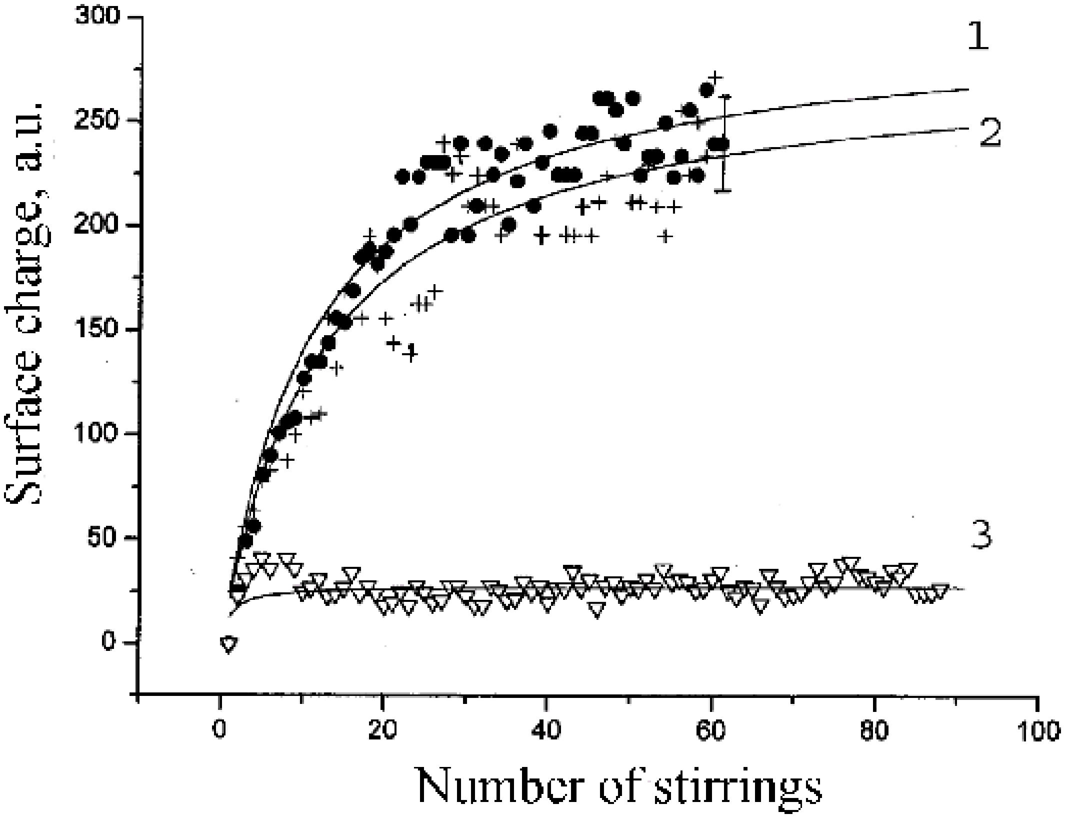


Fig.6 The curves of the accumulation of the triboelectric charge: at stirring of the paraffin stick (nonimpregnated) over the polyurethane - curves 1,2; at stirring of the paraffin stick, impregnated by the crystalline iodine over the keratin - curve 3.

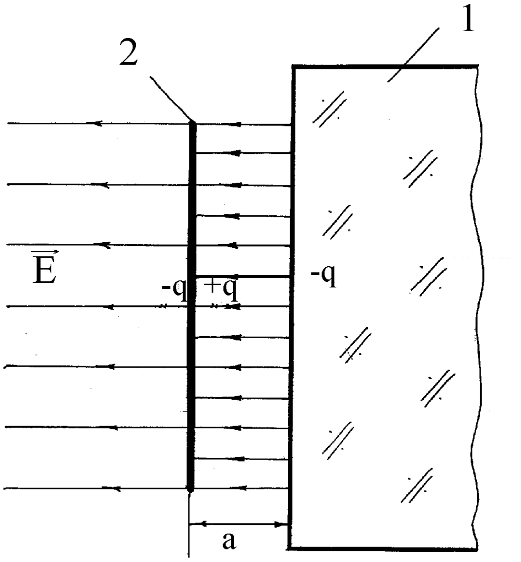


Fig.7 The scheme of the creation of the induced charge onto the surface of the metal foil near the surface of the charged dielectric.

In addition to the method of the determination of the electric field intensity with the help of the sensing unit, another direct method of the determination of the electric field intensity has been applied. I use the direct weighting method of the determination of the electric field intensity. In order to perform it, many pieces of the metal foil of the different weight were manufactured. In Fig.7 it is shown schematically, how the charge is redistributed on that metal foil when the piece of the foil is in the vicinity of the charged dielectric. It is clearly seen, that on the surface pointed toward the charged dielectric (with the charge –q) the opposite charge +q is induced, and the charge –q is on the opposite surface of the foil. In Fig.7 1 means the charged dielectric, 2 – the metal foil. Under the action of the charge –q, generated with the help of the triboelectrization, on the surface of the metal foil the positive charge +q is induced (as it was already mentioned) and it will be a force like a force between the plates of the plane capacitor, that should attract the metal foil to the charged dielectric. Using the formula for the flat capacitor I obtained that the attraction force between the foil and the charged dielectric is equal to:

$$F=1/(2\varepsilon_o)\cdot q^2/S \quad (11)$$

where S should be the surface of one of the plates of the capacitor. In the approximation of the flat capacitor (neglecting the edge effects, where the electric field intensity is different from the electric field intensity in the middle of the plate). That force does not depend upon the distance between the dielectric and the foil. For the horizontal position of the foil, using the formula:

$$mg=1/(2\varepsilon_o)\cdot q^2/S \quad (12)$$

it is possible to determine the charge q onto the dielectric. This charge corresponds to the surface charge density q/S. If the surface of the plate is higher than the charged dielectric surface, then it is necessary to consider as S the smaller surface, that is, the surface of the charged dielectric.

The formula (12) is received for the ideal case of the neglect of the edge effects. Generally speaking, the field E is distorted strongly from the ideal case, shown in Fig.7 in the presence of the metal foil on its edges (like in a real capacitor). But, as it is shown in [38], the influence of the distortion does not exceed the zone of a dimension a (here a is the distance from the foil to the dielectric) and therefore at condition $a<<(S)^{1/2}$ the formula outlined should work satisfactorily. In the present case the distance a was chosen to be equal to 1 mm, and the least surface S was equal to 1 cm^2. Therefore, the second method is also quite possible for the investigation of the effects of the impregnation of the dielectrics. In the present case it appears the possibility of the measurement of the absolute value of the surface charge, expressed in C/cm^2 or in $1/cm^2$ (number of the electrons for 1 cm^2).

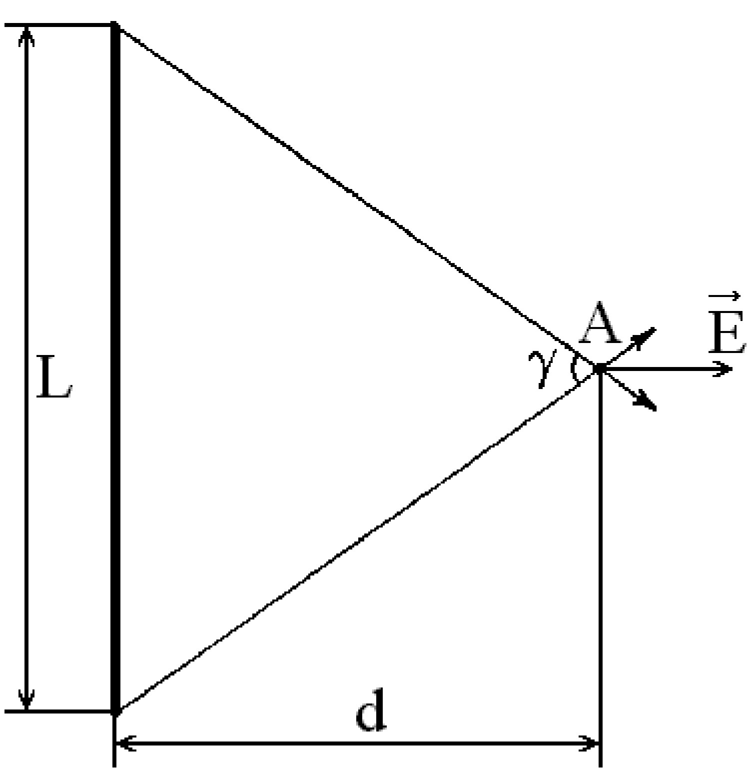


Fig.8 Scheme of calculation of the electric field in the vicinity of the uniformly charged line.

Some implications of the formula (10) are necessary. For the very close distance between the charged surface (if it is not point source) and the antenna of the sensing unit the Coulomb law for the point charges is inapplicable. In Fig.8 it is shown, how the electric field in the point A, placed at a distance d perpendicular to the center of the uniformly charged line of a length L is formed. According to [38], if the angle γ is the angle, at which the charged line is seen, then the electric field is given by:

$$E= \tau /(2\pi\ \varepsilon_O d)\cdot \mathrm{Sin}(\gamma /2)= \tau /(2\pi\ \varepsilon_o d)\cdot (L/2)/(d^2+(L/2)^2)^{1/2} \quad (13)$$

It was measured, that in our case the charged part of the stick is a rectangle of 5 cm length and 1 cm width. Assuming the uniform charge of it, I considered it as a line and for a short distances (less then 5 cm) I used (13) instead of (10). This will be especially important for the case of the observation of the charge decay in the air, when the last traces of the charge are observed at the very small distances between the antenna and the charged surface.

Curve 3 corresponds to the sample, doped by the crystalline iodine, and it is possible to observe, that the effect is large. The accumulation curve can be considered as due to two different processes. In the first process the equation, describing the accumulation of the charge is:

$$dQ/dt=P-aQ \quad (14)$$

here Q is the charge on the surface, P – rate of the charge accumulation, a – rate of the charge decrease due to the discharge processes.

In the second process the equation, describing the accumulation curve may be depicted by the formula:

$$dQ/dt=P-bQ^2 \quad (15)$$

From the point of view of physics the first case corresponds to the following recombination idea: the charges are generated in pairs (say from radicals) and then they have some probability to recombine in a pair (predominating process) $A^{\cdot} + B^{\cdot} \rightarrow A^{+} + B^{-}$ $\rightarrow$ recombination in a pair.

Since this is a pair of the charges, recombination takes place according to the first order kinetic law:

$$[A^{+}\ldots B^{-}] \rightarrow [A\ldots B] \quad (16)$$

and then the equation (14) should be applied.

Contrary to this idea, if the charges are well separated before the recombination, then the kinetic of the recombination should follow the second order kinetic law: charges are generated in a pair, one charge (positive) is on one surface, another one (negative) is on the another one, so $[A^{+}] \equiv [B^{-}]$, and, since every negative charge at stirring has some probability to recombine with some portion of the charges (positive) on the another surface, it should be, that the recombination rate is proportional to the production of the concentrations:

$$A^{+} + B^{-} \rightarrow A + B$$

$$dQ/dt=P-b[A^{+}][B^{-}] =P-bQ^2 \qquad (17)$$

That idea may be checked with the help of the accurate simulations of the accumulation curve in Fig.6. In Fig.9 it is shown how the accumulation curve 1 from Fig.6 may be simulated with the help of either equation (14) or equation (15). Equation (14) leads to the following curve:

$$[Q]=P_1[1-\exp(-N/P_2)] \quad (18)$$

while the equation (15) leads to the following curve:

$$[Q]=P_1\{\exp(P_2{\cdot}N)-1\}/\{\exp(P_2{\cdot}N)+1\} \quad (19)$$

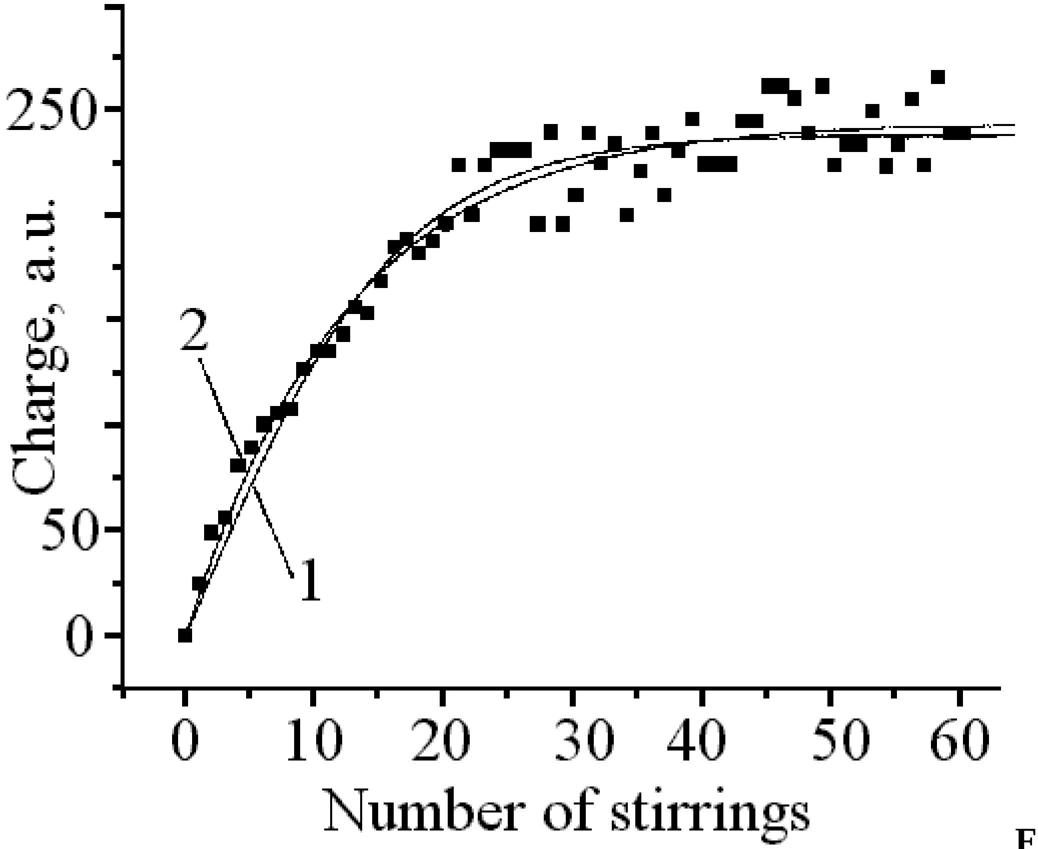


Fig.9

Simulation of the accumulation curve by the first (2) or second (1) order kinetic curve.

Simulation of the experimental curve, conducted by both equations (18) and (19) is shown in Fig.9. Curve 1 corresponds to (19) and the curve 2 to (18). Despite the error is quite large, it is possible to see, that for the initial part of the accumulation curve (18) fits a little better, while the plateau is fitted by both equations (18) and (19) with approximately the same quality. So I choose the equation (16) to work with throughout the book.

Before I continue the description of the triboelectrization chemistry, I should consider the problem of the applicability of the chemical laws (the law of mass action) in the case of the triboelectrization and in the case of the mechanochemical reactions between the radicals. Let's consider two planes, one is impregnated by the radical $A^\cdot$, another one is impregnated by the radical $B^\cdot$ (see Fig.10). If for certainty the plate 1 is covered by the radical $A^\cdot$ and the plate 2 is covered by the radical $B^\cdot$, then at movement of a plate 2 with respect to 1 the radical $B^\cdot$ chosen may react with some amount of radicals A onto plate 1. That number is proportional to the surface concentration of those radicals onto plate 1, that is, if the cross-section of the reaction (5) is l, then, if the plate is L, the surface, swept by the radical B. is $S=L^\cdot l$, and the amount of the radicals in this surface, met by the radical $B^\cdot$, is equal to:

$$N=S/S_o{}^\cdot[A^\cdot] \quad (20)$$

where S_o – the general surface of the plate 1 and $[B^{\cdot}]$ – surface concentration of the radical $A^{\cdot}$. Therefore, in that assumption (uniform distribution of $A^{\cdot}$ throughout the surface of 1) the main law of chemistry is valid, the probability of the reaction is proportional to the concentration of $A^{\cdot}$. The rate of the reaction itself can be written:

$$V=kS/S_o{\cdot}[A^{\cdot}]{\cdot}[B^{\cdot}] \quad (21)$$

since every radical $B^{\cdot}$ independently reacts in the same manner.

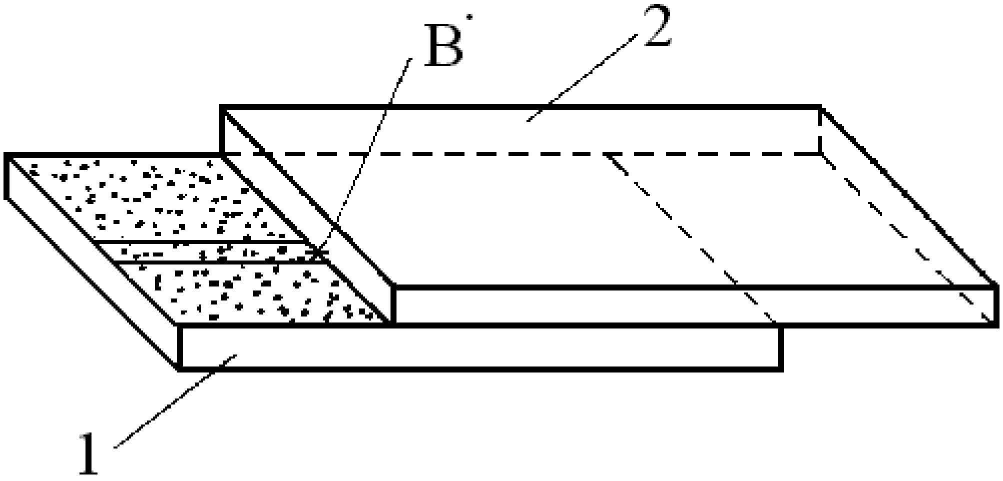


Fig.10.

Scheme of the calculation of the probability of the radicals encounter.

Now let's suppose that the radical's distribution changes from a uniform one to a heterogeneous one. Then, if the radicals are associated into groups of N_o radicals in one group with the full amount of groups $N/N_o=K$, then the overall amount of the radicals meet by $B^{\cdot}$ should be:

a)The probability to meet a group P_1~K.

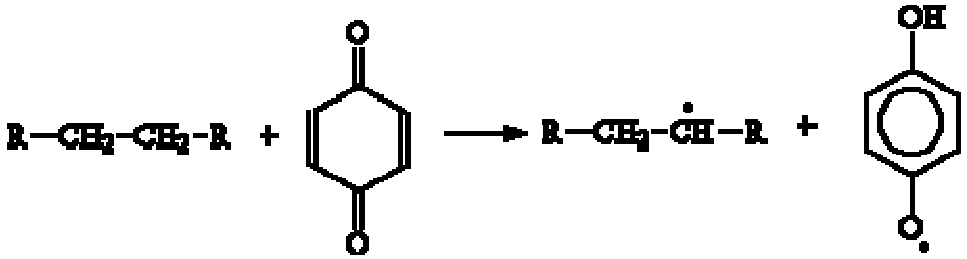
b)The probability to react in a group P_2~N_o.

(I can again paint the same trace, like in Fig.10). Then the overall probability should be proportional to: $K{\cdot}N_o=N$, that is, again to the concentration of the radicals A. on the surface. Therefore, a very important statement is proved: even if the shape of the radicals distribution changes from a heterogeneous one (on a plate) the rate of the reaction does not feel that and it should be proportional to the concentration of the radical $A^{\cdot}$.

Nevertheless, the change of the distribution in the direction, perpendicular to the surface (in the layer, immediately under the surface) should influence the chemical reaction since the probability to meet a radical for B. depends on the amount of those radicals immediately under the surface. In the next consideration I suppose that distribution in the perpendicular direction does not change.

In order to maintain all other parameters the same, stirring was conducted with the same relative velocity all the time, that is, in every case, for every system the relative velocity of sliding is the same. In this case, assuming that the distribution in the perpendicular direction does not change, we should observe that the rate of the reaction is proportional to the concentration of every radical. I suppose that the distribution is the same for every concentration of the iodine dissolved inside the paraffin. This is very important for the case of the different concentrations of the iodine as it doped the paraffin.

This supposition allowed me to apply the classical theory of the chemistry, the law of mass action. I suppose, that the iodine acts not onto the free charges, but instead, onto some predecessor of those charges, actually free radicals. How might free radicals be generated at such a weak mechanochemistry? Higher some observations about the donor-acceptor interactions with such polymer as teflon were outlined. In reality the same idea is applicable for the free radicals as the result of the mechanochemically promoted reaction between the donor and the acceptor. For example, at mechanical stirring between the polyethylene powder (the same as mentioned above) and p-quinone a strong EPR-signal was recorded ($2\cdot10^{19}$ 1/g). The signal is shown in Fig.11. It is possible to observe that signal at stirring of a mixture at room temperature. The signal is quite wide and it definitely possesses some unresolved hyperfine structure. That experiment is a demonstration of the fact, that the acceptor properties of quinone and the donor properties of the paraffin were so enhanced by the mechanochemistry, that a strong radical is accumulated at a reaction with a weak donor (polyethylene). Probably, the reaction takes place:



The alkyl radical should quickly die, while the semiquinone radical is very stable in a solid matrix and the result of the mechanochemical reaction, probably, is the accumulation of the semiquinone radical. The question arises, whether it is possible to observe the appearance of a semiquinone radical at stirring of the quinone itself. The answer is no, despite some weak signal, on the level of 10^{16}-10^{17} 1/g is observed, nevertheless, even in a pure quinone. If somebody took the mixture of the quinone and hydroquinone, the intensity of EPR-signal never exceeds 10^{18} 1/g, therefore, that idea of the appearance of the signal merely from a pure quinone is also out of a consideration.

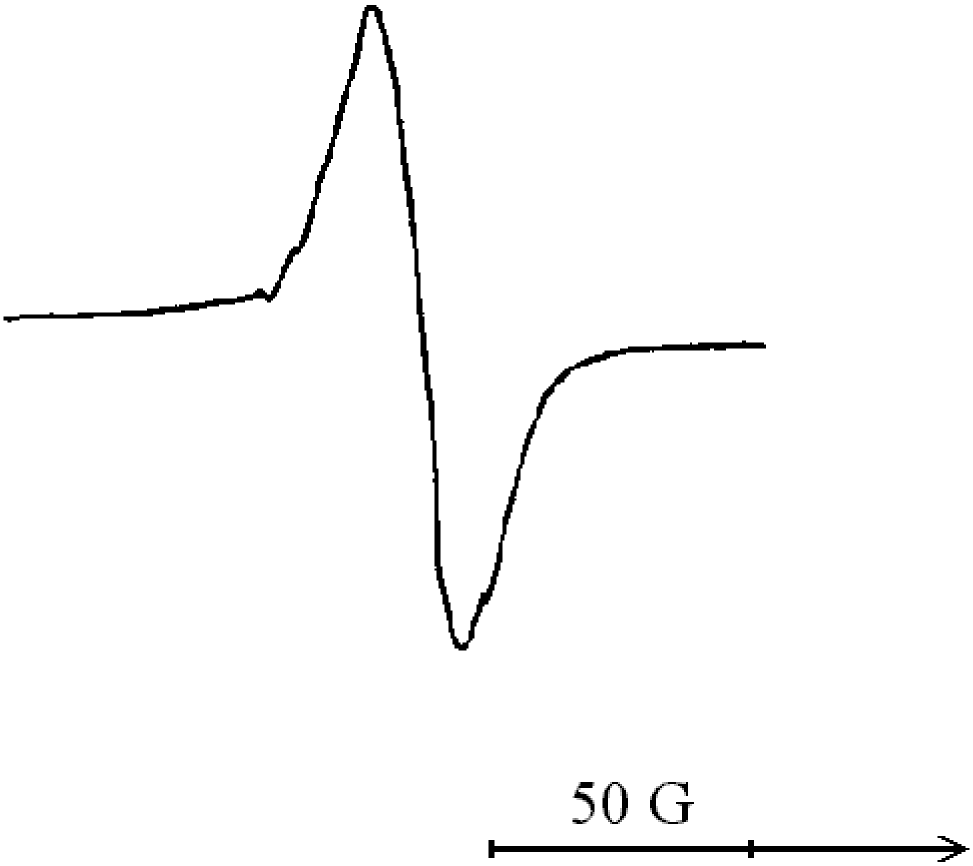


Fig.11

EPR-signal after stirring of polyethylene with p-quinone.

The same idea was applied to the case of the mechanochemical action between adamantane and quinone. Contrary to the case of the action of the mechanochemistry upon the mixture adamantane + $KMnO_4$ [26] (no reaction), the appearance of the EPR-signal ($1.5 \cdot 10^{17}$ 1/g) after 10 minutes of stirring was observed. In the polymers the distortion of the main chain alleviates the chemical reactions of the side groups and atoms [60,61], but this is not the polymer, nevertheless, the reaction still takes place, since the radical (most obviously semiquinone one) has a tendency for accumulation. But whether it is a radical, generated through the mechanochemical reaction with the adamantane or just the quinone itself is responsible, is not clear.

The mass action law is inapplicable for the case of the mechanochemistry, since the relative concentrations on both stirring surfaces are given and the mean concentrations in a thing layer, where the mechanochemical reaction takes place, is determined not by the relative concentrations on every surface, but by the crystal structure of that layer, by the relative arrangement of the molecules from both layers in the reaction cage [26]. Therefore, for the reaction of the initial generation of the radicals I should write just P – rate of the radicals generation, while for other chemical reactions, bearing in mind, that all the parameters except for the iodine concentration are constants:

$$A + DH \xrightarrow{P} AH^{\cdot} + D^{\cdot} \quad (23)$$

$$\left.\begin{array}{l} D^{\cdot} + I_2 \rightarrow DI + I^{\cdot} \\ AH^{\cdot} + I^{\cdot} \rightarrow HAI \end{array}\right\} D^{\cdot} \ldots AH^{\cdot} + I_2 \xrightarrow{k_3} DI + HAI \text{ (quenching) } (24)$$

$$D^{\cdot} \ldots AH^{\cdot} \xrightarrow{k_1} D^{-} + AH^{+} \quad (25)$$

$$AH^{+} + D^{-} \xrightarrow{k_2} \text{recombination of the charges}$$

Therefore I suppose that the free radicals are the source of the free charges, the predecessor of the free charges. I suppose that the free radicals create first a complex, which later transfers into a couple of charges (see below the conception of the radical pairs of association). The action of the iodine onto the ultimate behaviour of the accumulated charge confirms it. For the free charges I have the differential equation:

$$d[D^{-}]/dt=k_1[D^{\cdot}\ldots AH^{\cdot}]-k_2[D^{-}] \quad (26)$$

here the reaction of the generation of the free charges is a monomolecular one (with the reaction constant of k_1) and the reaction of the recombination of the charge is also monomolecular one (see higher).

The quasi-stationary process for the free radicals generation yields:

$$d[D^{\cdot}]/dt=P-k_3[D^{\cdot}\ldots AH^{\cdot}][I_2]=0 \quad (27)$$

here P – generation of the free radicals due to the mechanochemistry, k_3 – recombination constant.

From equation (27) it follows:

$$[D^{\cdot}\ldots AH^{\cdot}]=P/(k_3[I_2]) \quad (28)$$

From equation (26), (28) it is possible to obtain the equation:

$$[D^{-}]/dt=k_1P/(k_3[I_2])-k_2[D^{-}] \qquad (29)$$

After the simulation of the curves like shown in Fig.6 for all the iodine concentrations I obtained the following results (see Table 1). Now in equation (18) $P_1=k_1P/(k_3k_2[I_2])$; $P_2=1/k_2$, but in Table 1 $P_1=k_1P/(k_2k_3[I_2])$ and $P_2=1/k_2$ are shown.

Table 1.

Dependence of the parameters P_1 and P_2 upon the iodine concentrations.

I_2 concentration	0	0.48	1.074	2.863	5.300	8.574	16.34	40.10	112.56
P_1, a.u.	172.86	142.27	153.46	118.18	119.27	95.711	82.255	33.576	0
ΔP_1, (error of P_1)	2.22	2.601	1.986	2.675	1.959	2.040	1.846	0.946	-
P_2, a.u.	1.223	1.599	0.303	0.558	0.993	1.692	1.056	0.848	-
ΔP_2, (error of P_2)	0.188	0.318	0.192	0.228	0.207	0.357	0.335	0.368	-

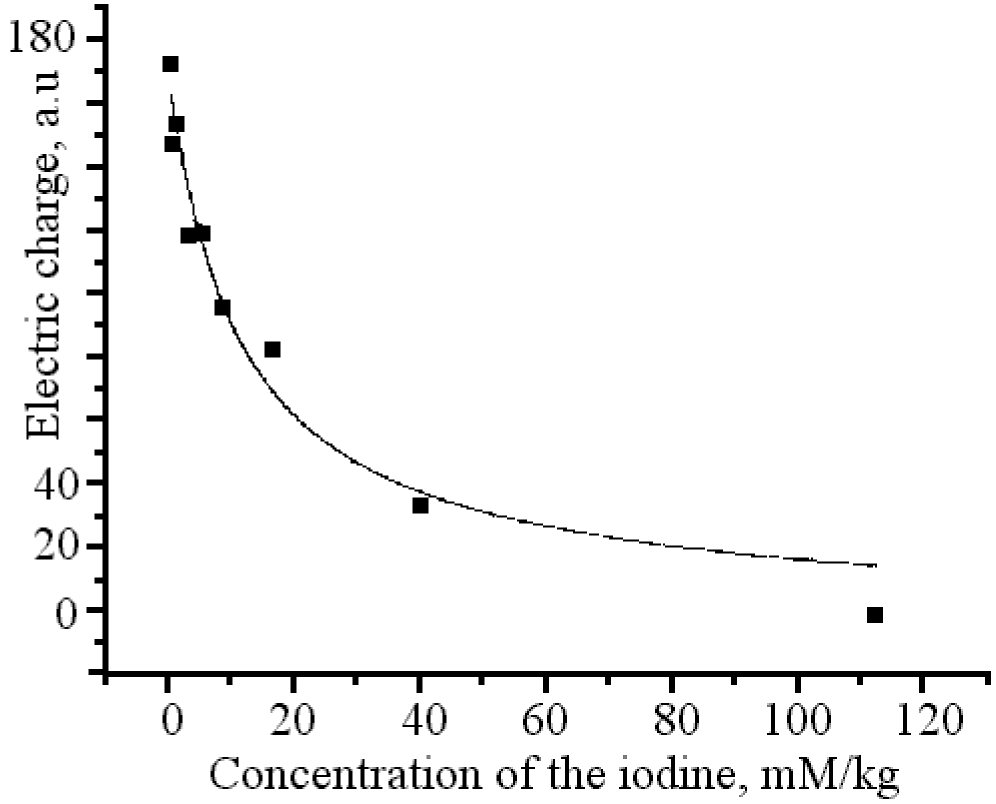


Fig.12.

The dependence of P_1 as a function of the I_2 concentration.

In Fig.12 the dependence of P_1 is plotted. It is possible to see, that the points are well fitted by the law: $y=1/(a+b[I_2])$ with the parameters: a=0.00618+/-0.00024; b=0.00048+/-0.00007. In Fig.13 the dependence of P_2 upon the iodine concentration $[I_2]$ is shown. It is possible to see that actually no dependence exists, that is, the error is so high, that the most reasonable supposition that k_2 is a constant. Then from Fig.12 it is possible to see, indeed, the right dependence of the value P_1 from the concentration of the iodine $P_1 \sim 1/[I_2]$. The value of a in the dependence $y=1/(a+b[I_2])$ means the presence of all the other (except for the iodine) radical traps (any dirt should also decrease the concentration of the radicals). As far as k_1 and k_3 constants is concerned, I don't see any possibility of them to depend upon the iodine concentration. Indeed, no obvious mechanism of the dependence of the probability of the generation of the ions from the radicals upon the presence of the iodine molecules nearby is possible. Actually, the iodine itself, or its complex with the polyethylene should give some additional triboelectrization paths, but in this case the dependence in Fig.12 should reverse the sign (as in the case of teflon, for example) and it should be a linear dependence – the higher the iodine concentration, the higher the admixture of the opposite sign in the system.

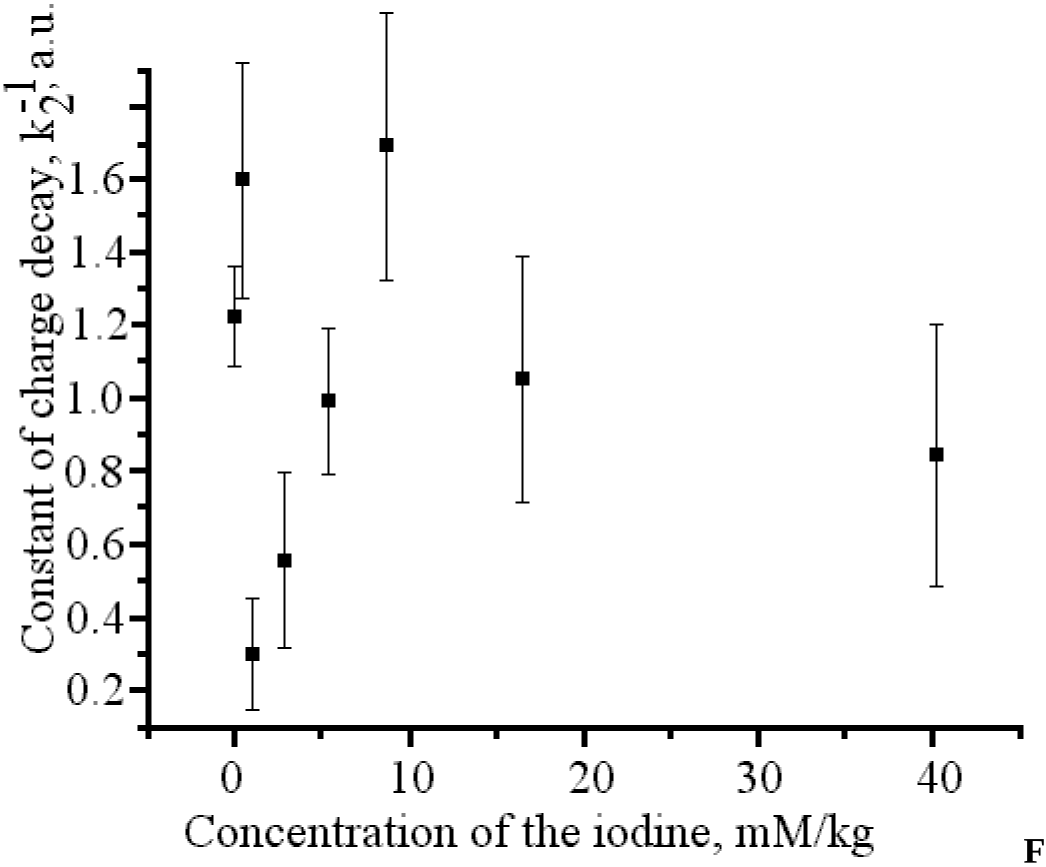


Fig.13

Dependence of charge decay constant upon I_2 concentration.

From the consideration of the possibility of usage of mass action law it seems to me, that the mechanism described is valid. Nevertheless, it is possible to fit the dependence in Fig.12 also as a curve $y=A/(B+x)^2$, that is, the reaction order for $[I_2]$ can be different from (29). I devoted a special discussion of that fact before the discussion of the mechanisms on the molecular level of the charge transfer between the radicals. Here it is proved, that in any case (any order of the dependence from $[I_2]$) the generation of the free radicals precedes the generation of the free charges.

Now let's consider the real order of the chemical reaction (24). I am really interested in a right order of that reaction, since in (26) from that dependence it might be received 1st or 2nd order with respect to the iodine. Since from the simulation of the curve from Fig.12 it is possible to obtain both orders, the accurate consideration should allow me to infer some information about the mechanism.

Let’s consider accurately the reactions of the radicals quenching (24):

$$D^{\cdot} + I_2 \xrightarrow{k1} DI + I^{\cdot}$$

$$AH^{\cdot} + I_2 \xrightarrow{k2} AHI + I^{\cdot} \quad (30)$$

$$D. + I. \xrightarrow{k3} DI$$

$$AH. + I. \xrightarrow{k4} AHI$$

Since the radicals are very unstable, the problem is to obtain the true order of the reaction with respect to the iodine – whether it is first, like in (28) or second. I use quasistationary procedure to obtain the order of the reaction with respect to the iodine.

$$d[I^{\cdot}]/dt= k_1[D^{\cdot}][I_2] + k_2[AH^{\cdot}][I_2]-k_3[D^{\cdot}][I^{\cdot}]-k_4[AH^{\cdot}][I^{\cdot}]=0 \quad (31)$$

$$[I^{\cdot}]=(k_1[D^{\cdot}]+k_2[AH^{\cdot}])[I_2]/(k_3[D^{\cdot}]+k_4[AH^{\cdot}]) \quad (32)$$

$$d[D^{\cdot}]/dt=P-k_1[D^{\cdot}][I_2]-k_3[D^{\cdot}][I^{\cdot}]=0 \quad (33)$$

$$d[AH^{\cdot}]/dt=P-k_2[AH^{\cdot}][I_2]-k_4[AH^{\cdot}][I^{\cdot}]=0 \quad (34)$$

After replacing of $[I^{\cdot}]$ with (32) it is possible to obtain from (33), (34):

$$P-k_1[D^{\cdot}][I_2]-k_3[D^{\cdot}](k_1[D^{\cdot}]+k_2[AH^{\cdot}])[I_2]/(k_3[D_{.}]+k_4[AH^{\cdot}])=0 \quad (35)$$

$$P-k_2[AH^{\cdot}][I_2]-k_4[AH^{\cdot}](k_1[D^{\cdot}]+k_2[AH^{\cdot}])[I_2]/(k_3[D_{.}]+k_4[AH^{\cdot}])=0 \quad (36)$$

Now I transform those equations (35), (36) as follows:

$$(P-k_1[D^{\cdot}][I_2])(k_3[D^{\cdot}]+k_4[AH^{\cdot}])-k_3[D^{\cdot}](k_1[D^{\cdot}]+k_2[AH^{\cdot}])[I_2]=0$$

$$(P-k_2[AH^{\cdot}][I_2])(k_3[D^{\cdot}]+k_4[AH^{\cdot}])-k_4[AH^{\cdot}](k_1[D^{\cdot}]+k_2[AH^{\cdot}])[I_2]=0$$

$$Pk_3[D^{\cdot}]+Pk_4[AH^{\cdot}]-2k_1k_3[D^{\cdot}]^2[I_2]-k_1k_4[D^{\cdot}][AH^{\cdot}][I_2]-k_2k_3[D^{\cdot}][AH^{\cdot}][I_2]=0 \quad (37)$$

$$Pk_3[D^{\cdot}]+Pk_4[AH^{\cdot}]-2k_2k_4[AH^{\cdot}]^2[I_2]-k_2k_3[D^{\cdot}][AH^{\cdot}][I_2]-k_1k_4[D^{\cdot}][AH^{\cdot}][I_2]=0 \quad (38)$$

After substitution of one equation from another one I obtained:

$$-2k_1k_3[D^{\cdot}]^2[I_2]=-2k_2k_4[AH^{\cdot}]^2[I_2] \quad (39)$$

From (39) it is follows:

$$[AH^{\cdot}]=(k_1k_3/k_2k_4)^{1/2}[D^{\cdot}] \quad (40)$$

Now I substitute (40) into (37), (38) and obtain:

$[D^{\cdot}]=\{P/[I_2]\}(k_3+(k_1k_3k_4/k_2)^{1/2})/\{(k_1k_4+k_2k_3)(k_1k_3/k_2k_4)^{1/2}+2k_1k_3\}$ (41)

$[AH^{\cdot}]=\{P/[I_2]\}(k_4+(k_2k_3k_4/k_1)^{1/2})/\{(k_1k_4+k_2k_3)(k_2k_4/k_1k_3)^{1/2}+2k_2k_4\}$ (42)

The most important question, that will be discussed later is whether the process of the generation of the free charges from the free radicals is a monomolecular one or bimolecular one, that is, whether the production of the complex $[D^{\cdot}\ldots AH^{\cdot}]$ precedes the generation of the radicals and the reaction inside the complex is a limiting step (monomolecular reaction) or the limiting step is meeting of those radicals. In the first case the quenching process:

$[AH^{\cdot}\ldots D^{\cdot}] + I_2 \rightarrow DI + AHI$ (41)

and the corresponding reaction of the generation of the free charge:

$[D^{\cdot}\ldots AH^{\cdot}] \rightarrow D^- + AH^+$ (42)

gives the equation:

$d[D^-]/dt=k_1[D^{\cdot}\ldots AH^{\cdot}] - k_2[D^-]$ (43)

$d[D^-]/dt=k_1P/\{k_3[I_2]\}-k_2[D^-]\}$ (44)

what coincides with (28) and yields the first order of the reaction (29) with respect to the iodine.

In the second case the quenching process (30) gives (41) and (42) and, since the reaction of the generation of the free charges is a bimolecular one:

$d[D^-]/dt=k_1[D^{\cdot}][AH^{\cdot}]-k_2[D^-]$ (45)

$d[D^-]/dt=k_1PK/[I_2]^2 - k_2[D^-]$ (46)

here K means the combination of the constants from (41) and (42). It is possible to see, that the second order of the reaction with respect to the iodine is obtained.

In Fig.14 the parameter P_1 is simulated by the expression $y=A/(B+x)^2$ and I obtained: A=171367 +/- 49875, B=32,82 +/- 5,16. That curve describes the data obtained much better, but it is necessary to remember, that in reality the error is very large and the difference between the curves in Fig.12 and Fig.14 should be inferred from the accurate consideration of the nature of the stage of the generation of the free charges (25).

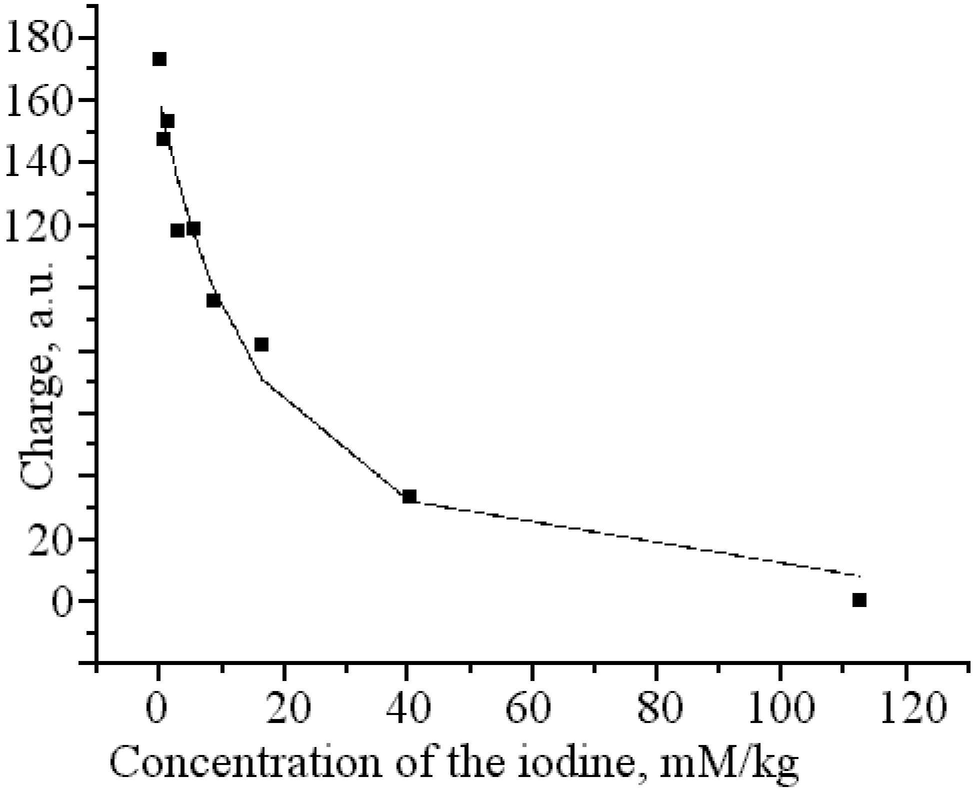


Fig.14. Dependence of the charge upon concentration. Simulation by (46).

I <u>must</u> emphasize, that in real mechanochemistry the mass action law does not work and I applied that law just with respect to the change of $[I_2]$ (concentration of the iodine) assuming, that all other parameters are the same. That is not true and the deviation from curve in Fig.12 for the high concentrations of the iodine may be depicted with the help of the consideration of the rigidity of the sample doped with the iodine.

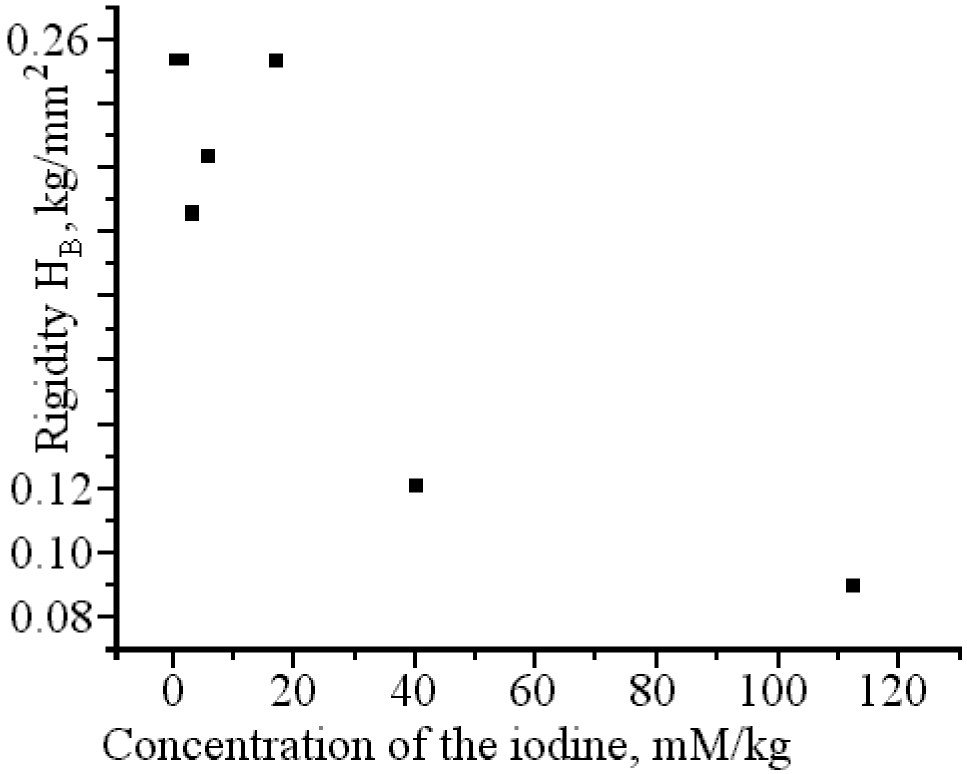


Fig.15

Brinell hardness as a function of the iodine concentration.

Deviation from the simulated curve y=1/(a+bx) in Fig.12 at high concentrations of the iodine is possible to explain by the presence in the system of the effect, connected with the increase of the plasticity of the polymer at doping. It is known [39], that at increase of the plasticity of the polymer because of doping of it with the monomer alleviation of the movements of the polymer chains with respect to each other and as a consequence, lowering of the rates of all the mechanochemical reactions, connected with the polymer. Indeed, in Fig.15 the brinell hardness of the samples investigated is shown as a function of the iodine concentrations. Lowering of the brinell hardness is clearly seen, what allows somebody to come to the conclusion, that the plasticity of the samples increases at high level of doping with the iodine. Since the plasticity increases, it is possible to expect, that the value of P in (23) becomes lower as well. Since the plasticity of the matrix is less, the value of the potential of the matrix (see influence of the matrix, Chapter 5 of [26]) is less and the generation of the radicals due to the donor-acceptor interactions is less. There is a temptation to explain the whole curve in Fig.12 as the result of the decline of the brinell hardness at doping. Indeed, the lower the hardness, the less the radicals generation. But I conducted some control experiments, for example, at doping with 1-amino-anthraquinone I did not observe any change at triboinduced charge [20], while the brinell hardness lowered from 0,254 to 0,167, what should lead to very appreciable change in the tribocharge (up to 10 times), if somebody suppose that just the brinell hardness responsible. Therefore, despite it is a well established fact, that there is a deviation from a curve in Fig.12, and in Fig.14 the law $A/(B+x)^2$ works much better, it is possible also to explain that deviation through the influence of the change of the plasticity as the result of doping of the sample with the iodine. There is a lot of other examples of the influence of the rigidity of the matrix onto the mechanochemical reactions (see [20]) and the observed very nice dependence of the kinetic parameters from the concentration of the iodine is more probably an exception, then the rule.

Other radical traps can also work as the obstacle of the charge accumulation. I considered compounds of Co, Fe, Cu. Those salts of metals of variable valency (I mean Cu^+/Cu^{2+} , Fe^{2+}/Fe^{3+} , Co^{2+}/Co^{3+} transitions) works very well as the radical scavengers in the different reactions with the organic radicals in liquids, for example:

$$Cu^{2+} + R^{\cdot} \rightarrow R^{+} + Cu^{+}$$

$$Fe^{3+} + R^{\cdot} \rightarrow R^{+} + Fe^{2+}$$

$$Fe^{2+} + R^{\cdot} \rightarrow R^{-} + Fe^{3+} \quad (47)$$

$$Cu^{+} + R^{\cdot} \rightarrow R^{-} + Cu^{2+}$$

Many reactions of that type are described in [40]. As it was established, those compounds decrease the triboelectrization through the quenching of the free radicals in the case of the mechanochemistry as well. Many of the compounds were investigated, all of them were impregnated in the near surface layer and actually many of them decrease a little the electric field intensity, but the strong effect is observed just for the radical traps. All the data are summarized in Table 2, here the sensing unit and the weighting methods were used.

<u>Table 2.</u>

The relative surface charge onto the impregnated and non-impregnated paraffin sticks (stirring over the keratin), measured with the help of a sensing unit and with the help of a weighting method

Impregnant	The sensing unit	Weighting method
None	1.0	1.0
$Co[Cl(NH_3)_5]Cl$	0,316	0.076
$CoSO_4$	0,219	0,228
$FeSO_4$	0,078	0,144
I_2	0,078	0
$Ni_3(PO_4)_2$	0,66	0,671
TEMPOL	0,472	0,676

Al-fillings	0,316	0,879
$Mg(AlO_2)_2$	0,563	0,886
Starch	0,473	0,446
Benzalacetophenone + p-chloranil	0,711	-
Coal	0,390	0,518
Fe-filings	0,983	0,944
Oxalic acid	0,516	0,830
Citric acid	0,563	0,687
K_2SO_4	0,660	0,682
ZnO	0,711	0,752
Chalk	-	0.938
$CuCl_2$	-	0.048
Sugar	-	0,546
NaCl	-	0.546

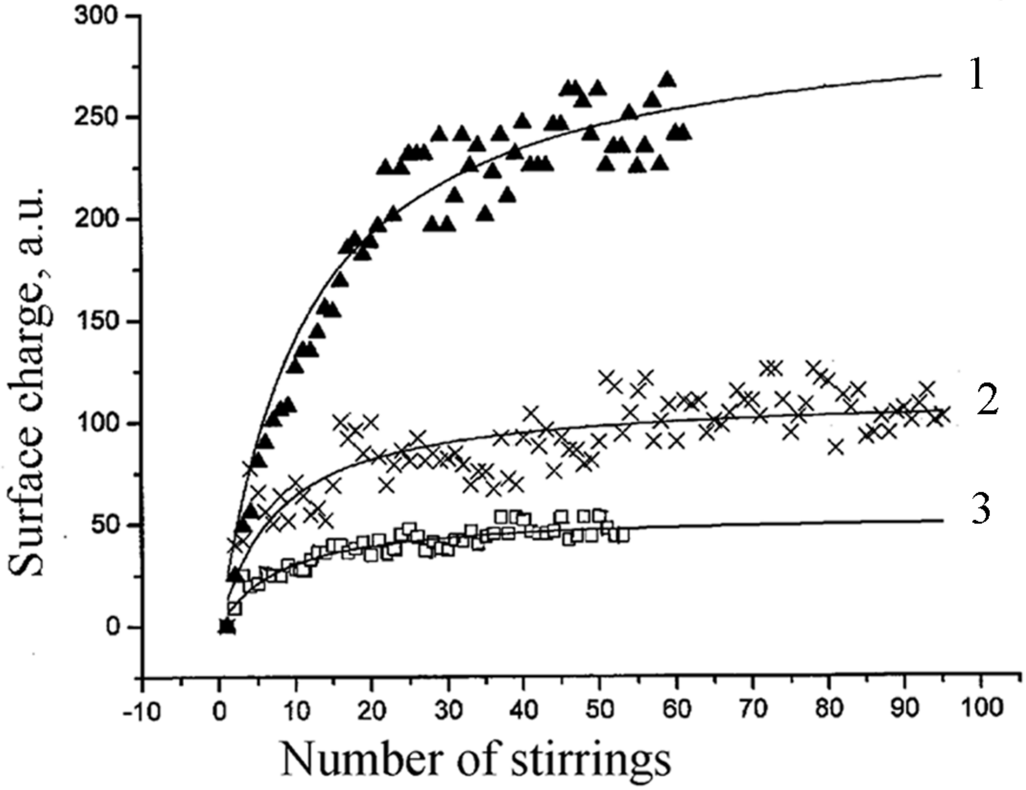


Fig.16

The accumulation curves at stirring of the paraffin stick over polyurethane: the curve 1 - the impregnant is absent, the curve 2 - impregnated by $Ni_3(PO4)_2$, the curve 3 - impregnated by $CoSO_4$.

In order to show, how the presence of the impregnant influences the accumulation curve, in Fig.16 some accumulation curves are shown, with the paraffin was used of another quality, of a more yellow color, different from the paraffin, used for the experiments, which results are outlined in Table 2. The curve 1 coincides with the curve 1 from Fig. 6, curve 2 corresponds to the case of the impregnation with the salt $Ni_3(PO_4)_2$, and the curve 3 corresponds to the case of the impregnation with the salt $CoSO_4$. The curves were fitted with the equation (18). For the curve 1: P_1=245,387+/-3.193, P_2=11,23+/10,594 (this is the curve 1 from Fig.6); for the curve 2: P_1=99,464+/-1,99, P_2=9,65+/-1,11; for the curve3: P_1=46,0488+/-0,951; P_2=9,349 +/- 0.796. Accordingly it is necessary to take for the clean (nonimpregnated) yellowish candle the value of the surface charge 245 a.u., at impregnation with the Ni-salt 100 a.u., with the Co-salt – 46 a.u.

In addition it is necessary to mention (and this is a very well known fact [14]), that the absolute value of the charge accumulated depends strongly upon the weather. That’s why the control experiment was usually performed onto the clean surface and the fixation of the relative values (the impregnated surface versus clean surface). For example, for the case of the impregnation with K_2SO_4 two accumulation curves were measured for the contact pair (stirring pair): paraffin (colorless)/human hair (curve 1) and paraffin (colorless) (+K_2SO_4)/human hair (curve 2) and they have the parameters:

Curve 1: P_1=74,91+/-2,52, P_2=1,288+/-0,391

Curve 2: P_1=83,69+/-2,44, P_2=3,24+/-0,72

Therefore, it is possible to see, that for the case of the impregnation with K_2SO_4 any lowering of the intensity of the electric field of the charge accumulated is absent (in the experiments with other compounds a weak effect has been observed nevertheless, see Table 2).

Some of the control experiments were performed in a nitrogen gas atmosphere, and the signs were the same, and the values of the triboelectical charge were approximately the same. I checked: paraffin, doped with I_2 + pig bristle and undoped paraffin + pig bristle.

It is necessary to emphasize, that some compounds, bearing some relation to the free radicals, for example, p-benzoquinone and 1-amino-anthraquinone at impregnation, contrary to other compounds, increase the triboelectric charge to some extent. Below in Table 3 some data are outlined for the friction pair paraffin stick (yellowish) / polyurethane, with the paraffin stick was impregnated with the compounds (quinones and the lignin for comparison) or the stick was not impregnated at all.

Table 3.

The parameters of the accumulation curves for the paraffin sticks for the cases of stirring of the impregnated and nonimpregnated paraffin sticks over the polyurethane.

Impregnant	P_1, a.u., negative charge	P_2, times
None	113.455 +/-2,726	8,123 +/-0,8158
p-benzoquinone	167,43761+/-3,102	3,69011+/-0,4093
1-aminoanthraquinone	133,8863+/-2,861	5,67214+/-0,5855
Lignin	102,0056+/-1,719	1,79619+/-0,30363

From the Table 3 it is possible to see a small increase of the effect of the generation of the negative electric charge onto the surface in the case of the impregnation of the surface with the compounds, inclined to withdraw the electric charge (electron) from the donor, that is accepters. Besides at comparison of the data of the Tables 2 and 3 it is possible to see, that the value of the charge itself upon the nonimpregnated paraffin changed ~2 times in the absolute value, what might be explained by the fact, that the experiments were conducted in the different days, and the temperature, and the humidity influence the electrostatic effects very much (it is known from the classical publications made in the ages of Coulomb, Helmholtz, Maxwell). That's why just relative values, obtained in the same day (during 1-2 hours) bear some meaning for the experimentalist (or the very strong effects, of 1-2 orders of the magnitude, which are reproduced at any circumstances, since they much larger then the scattering of the data obtained because of the influence of the temperature and (or) the humidity).

Up to this point the discussion of the triboelectrization concerned the compounds, in which the phenomenon of the triboelectrization has a mere scientific interest. Indeed, such systems as paraffin / polyurethane and paraffin / human hair never used in the industry. The beauty of those systems is that the effect of the triboelectrization is relatively large and it is easy to interpret it – even the small change of the triboelectric charge at the impregnation leads to an appreciable change of the electric field registered. Indeed, it would be interesting to investigate the influence of those impregnants (radical traps) onto the triboelectrization of the compounds, which have a high practical (industrial) applications. The polyurethane sponges (porolon sponges) were investigated, that were impregnated (painted with a thing layer) by the oil paints, that include different compounds of the metals of the variable valency.

The results of the successive stirring are outlined in Table 4 (it is necessary to remember, that polyurethane, like the pig bristle, as well as the human hair is charged positively over the paraffin). In the Table 4 the charge is outlined in a.u. (those a.u. approximately, +/- 40 % coincide for the both sensing units "+" and "-" , see higher , that is, the absolute sensitivity is approximately the same for the both signs). The charge, mentioned in Table 4 was measured with the help of a sensing unit, described higher (see Fig.5). The same effect is clearly seen – the strong lowering of the charge received (value P1) for those paints, that include the salts of the metals of the variable valency, in particular Cr, Fe, Mn and also I_2. Again, similar to the case of the compounds, outlined in the Table 2, some lowering of the charge (much smaller) was observed at covering of the polyurethane with the other paints (ZnO and ultramarine).

Table 4

The surface charge, received onto the polyurethane (the charge is positive), impregnated by the different compounds at stirring over the paraffin stick.

Impregnant (paint)	P_1, a.u. (positive charge)	P_2, times
None	84,99 +/- 2.88	12,52+/-1,48
ZnO (zinc white)	34,204+/-2,73	4,32+/-1,37
$Na_9Al_6Si_6O_{24}S$ (ultramarine)	42,013+/-1,696	2,528+/-0,55
FeO + Fe_2O_3 (25%) + MnO (7-10%)	7,3698+/-1,189	4,365+/-

(umber)		1,96
Cr_2O_3 (chrome oxide)	16,895+/-0,754	0.737+/-0.30
FeO, Fe_2O_3 (up to 66%) (ochre)	<1	-
I_2	<1	-

One more important material, that may be used for packing is polyethylene film and it would be great if the electrostatic charge was diminished on it. It occurs, that if the polyethylene film is painted by the certain paints (the usual oil paints were used), such as “chrome oxide” (the name of the green oil paint that include the corresponding compound Cr_2O_3), then the sharp decrease of the triboelectric charge is observed. This phenomenon is shown in Fig.17 and the data obtained are reflected in the Table 5. (the industrial polyethylene film was used).

Table 5.

The surface charge, received onto the polyethylene film, painted by the different paints, at stirring over the polyurethane sponge.

Impregnant (paint)	P_1, a.u. (negative charge)	P_2, times
None	180,516+/-9,14	20,988+/-2,64
ZnO (zinc white)	121,5908+/-5,84	10,23376+/-1,36
Cr_2O_3 (chrome oxide)	40,72044+/-1,08	3,12951+/-0,44

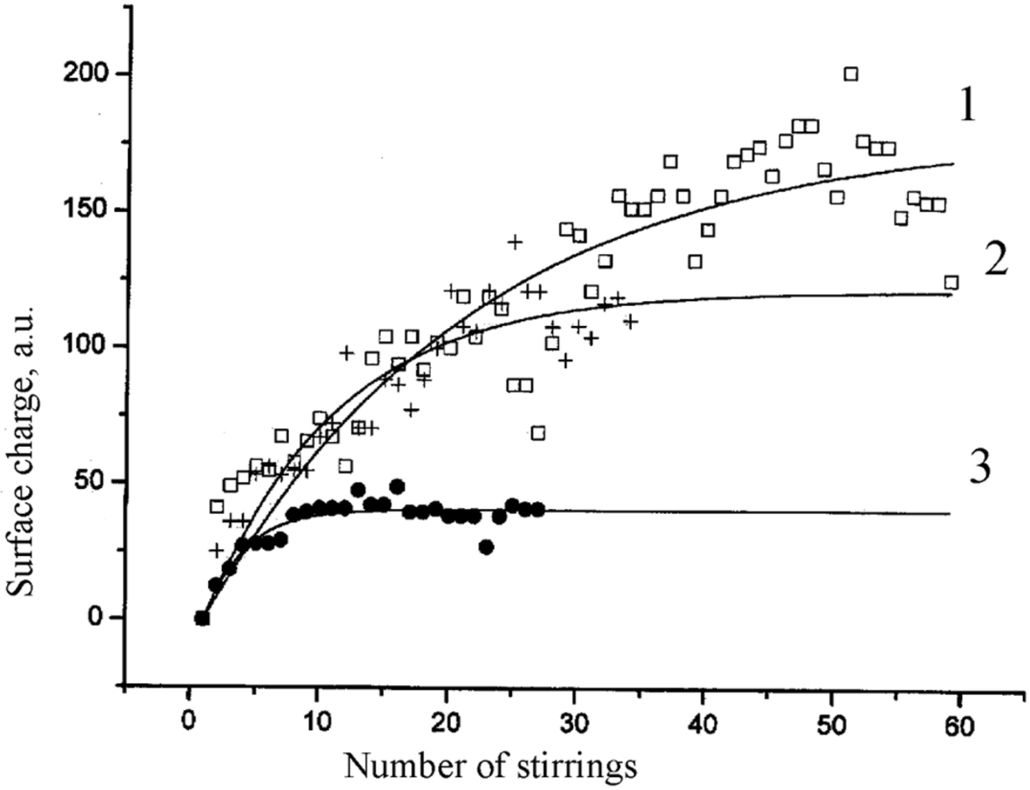


Fig.17

The accumulation curves of the triboelectric charge for the samples of the industrial polyethylene film: the curve 1 - clean film, the curve 2 - painted by ZnO (zinc white), the curve 3 - painted by Cr_2O_3 (paint, named “chromium oxide”).

Again it is possible to see the same phenomenon: any paint lowered the charge, but the most strongly it is diminished by the paint (impregnant), which contains the ions of the metals Cr^{3+} , Fe^{2+} or Fe^{3+}.

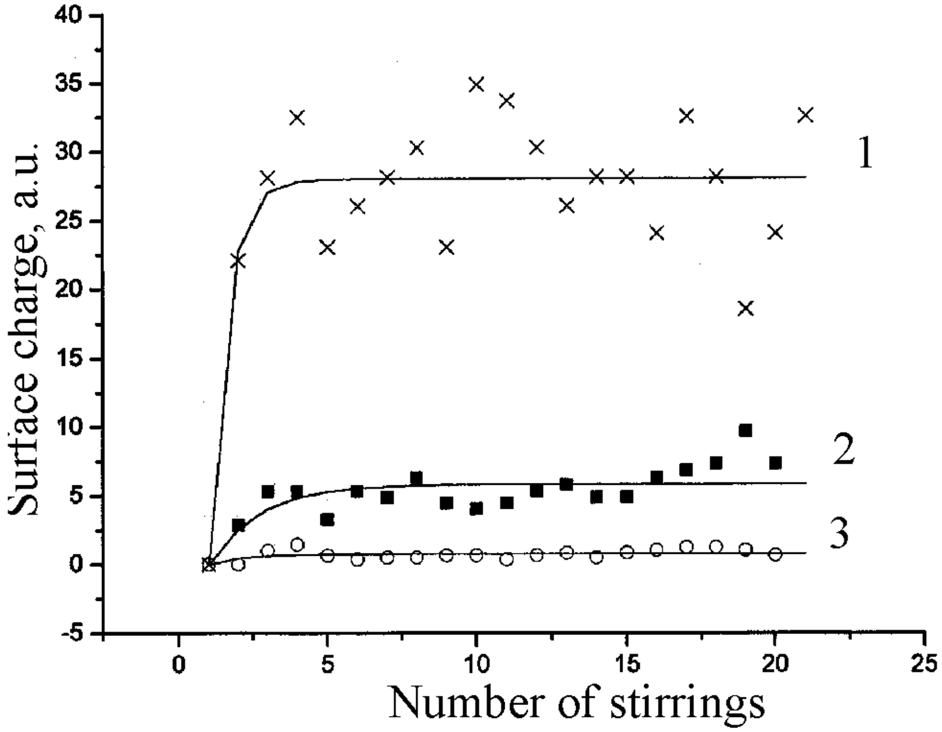


Fig.18 The accumulation curves of the surface charge for the case of painting of the antistatic polymer bag: the curve 1 - one polymer layer of the three-layered bag (without conducting foil between the layers), the curve 2 - the three-layered bag (the assembled bag), the curve 3 - the three-layered, painted by the paint "dark ochre" (contains the iron oxides of both valences).

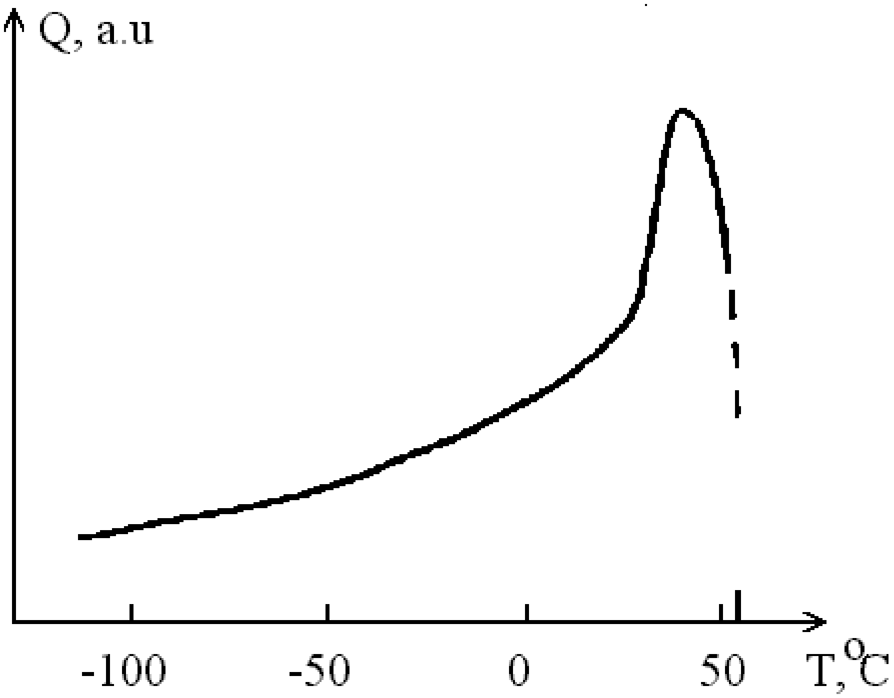
Very important is the question about the possibility to improve in such a way the electrostatic properties of the industrially used polymer bags. For the experiments the antistatic bag "Supershield" DY3850 was chosen, manufactured by the firm DOU YEE Singapore, that is built from three layers: two polymeric layers and a metal foil between them. At consideration with respect to electrostatic of the polymer (without foil, the polymer was obtained through the careful separation of all the three layers, what is allowed by the construction of the bag), then at stirring over the human hair, the curve 1 from the Fig.18 was obtained. At stirring at the same conditions of the three-layered polymer bag material the curve was obtained, plotted as a curve 2 in Fig.18. Finally after being painted the polymer bag material with the dark ochre (the paint, that contains the oxides of the iron FeO, Fe_2O_3 in the amount up to 60-66 %) the curve 3 is obtained (Fig.18). The parameters of all the curves are outlined in the Table 6. From the comparison of the curves 1,2,3 in Fig.18 it is possible to draw a conclusion, that, despite the insertion of the metal foil (merely physical method of the prevention of the electrostatics) itself leads to the essential lowering of the triboelectric surface charge, combination of both the physical (foil) and the chemical (impregnant – radical trap) methods of the prevention of the charge accumulation lead to the very strong lowering of the triboelectrization onto the surface of the solid dielectrics. This is a practically ready technology, under the seemingly simplicity of which there is a deep understanding of the mechanism of the triboelectricity and the mechanochemical generation of the radicals at the friction.

Table 6.

The surface charge, received at stirring of the antistatic polymer bag (painted or not) over the keratin.

Polymer film	P_1, a.u. (negative charge)	P_2, times
1 layer of the polymer (no paint)	27,999+/-0,982	0,592+/-0,275
Assembled bag (without paint)	5,8187+/-0,388	1,644+/-0,713
Assembled bag, painted by the dark ochre (FeO, Fe_2O_3).	0,758+/-0,084	0.998+/-0.961

Fig.19. The scheme of the charge change as the function of temperature.



It is very important to emphasize, that the relative surface at stirring has some influence onto the triboelectric charge. Part of any effect of lowering of the charge accumulated is because the surface becomes harder and the surface of the contact becomes smaller. That fact immediately leads to lowering of the charge accumulated. For example, the temperature dependence of the charge accumulated onto the paraffin stick at friction over the human hair may be schematically shown in Fig.19. Such a strong increase of the charge accumulated at the surface as the result of stirring over the human hair near the melting temperature (53 ^{o}C) of the paraffin can be explained by the great increase of the contact surface. Of course, at even higher temperatures no charge is observed – charging of a liquid is much smaller, then charging of a solid. That's why any compound that makes the surface a little harder (including salts of Co, Fe, Cu of course) make the charge accumulated a little lower (30-50 %), what is seen in Table 2. Actually almost all the compounds, used for the impregnation, were harder then the paraffin at room temperature and that effect partly explains also the influence of the radical traps (salts of Co, Fe, Cu) but just in part. As far as the starch and the coal is concerned, the action of those compounds is probably similar to the action of the low-effective radical traps, that's why the decrease is just a little higher, then for the non trapping compounds.

Actually addition of the radical traps (I_2) can be demonstrated in an impressing experiment – lowering of the tribocharge of the industrial powder at mixing. The tribocharge, generated onto the powder, does not allowed to tackle them easily because of a strong scattering, repulsion of the particles of the powder. I used the industrial powder of the polyethylene with the grain size in the range $7\cdot10^{-3}$ mm – 0,2 mm. At mixing of that polyethylene powder with the help of a pig bristle in a porcelain mortar the following phenomenon was observed: because of the electrization the particles of the polyethylene soar up from the region of mixing as a sol, generating like the dust cloud to the height up to 10-20 cm, settling on the nearby items, including the hand of the experimenter. From that data it is possible to estimate the surface charge, generated onto the polyethylene particles. For estimations it was chosen, that polyethylene particles are spheres of a diameter 10^{-2} mm with the distance between the centers $r_0=1{,}1\cdot10^{-2}$ mm (what allows to conform the bulk density of the polyethylene and the density of the polyethylene powder). Then, the knowledge of the fact, that approximately 20% of the whole polyethylene mass at mixing during 1 minute overcome the height of 5 cm (a mortar wall) allows to estimate roughly the charge onto the every polyethylene particle from the energy consideration, assuming, that two particles charged with the same sign repel and that pushing apart gives the energy for the particle to leave the mortar:

$$[1/(4\pi\,\varepsilon_o)]q^2/r_o=mgh \qquad (48)$$

where q is a charge onto the surface of the both balls of mass m and with the distance of r_o between the centers, g=9,83 m/c^2, h=0,05 m, h – the height of the mortar.

Assuming the mass m equal to $5\cdot10^{-3}$ g, we receive $q=1{,}7\cdot10^{-16}$ C, that is, approximately 1000 electrons for 1 particle of the polyethylene, what corresponds to the charge surface $1{,}3\cdot10^{11}$ 1/cm^2. Then, the knowledge of the fact, that the general amount of the particles of the polyethylene in 1 g is equal to ~ $2\cdot10^{11}$ and just ~ 20% leaves it, the general charge, generated for 1 min turns to be equal to $4\cdot10^{13}$ 1/(g$\cdot$min).

At addition of a small amount of a crystalline iodine (around 15 mg for 1 gram of the polyethylene) at mixing with the help of a pig bristle of the polyethylene powder in a mortar the phenomenon is observed: the whole polyethylene is turned to be purple by the iodine vapor (assuming the weak complexes are formed of this type or that) and then at mixing the so expressed effects of the electrization does not observed – the sol almost does not appear and the polyethylene powder does not pass onto the nearby items as a dust cloud. The polyethylene powder behaves itself as if it is almost did not electrified (but nevertheless to some extent the effects of the electrization are present nevertheless – the crystalline iodine just lowered for 2-3 orders of magnitude the static tribological charge, but does not delete it completely, as in the case of addition of, for example, water). If the iodine is added in the process of mixing (instead of the start of mixing experiment), then the polyethylene powder that was accumulated strongly in the pig bristle (since particles of the polyethylene are charged negatively; and the pig bristle (keratin) is charged positively), is pouring down into the mortar. At following mixing, the iodine is consumed quickly (35 mg – for the time ~ 10 min at the mass of the polyethylene around 0,8 gram) and the rate of it's expenditure was possible to calculate, with knowledge of a time of the full decolorization (in the linear approximation), and the mass of the crystals added. It was found to be equal to $0{,}6 \cdot 10^{19}$ (molecules of I_2)/(g·min). In the special experiment it was checked , that the rate of the natural iodine evaporation (at mixing once in a several minutes for imitation of the same diffusion conditions) equals at room temperature at the same conditions to several hours (> ~ 4 hours), that is, the natural iodine evaporation does not explain the decolorization of the mixture for such a short time period.

III Estimation of the diffusion coefficient (I_2 in paraffin).

Since the mechanochemical reaction of quenching of the free radicals with the iodine takes place in a thin layer near the surface, it is possible to expect, that after some time of keeping of the impregnated by the iodine paraffin (the iodine was dissolved in the paraffin, several concentrations, see higher) should lead to the decrease of the iodine concentration in the layer near the surface. Therefore, right after keeping for a long enough period (I choose 3 months) the accumulation curves should change and from the difference of the parameters of the initial accumulation curves and the accumulation curves after keeping the real change of the iodine concentrations can be exactly calculated and the diffusion coefficient can be estimated.

After 102 days the parameters of the accumulation curves looks as follows:

Table 7.

Dependence of the parameters P_1 and P_2 upon the iodine concentrations (102 days after preparation and keeping at room temperature).

C, mM/kg	0	0,48	1,074	2,863	5,300	16,34	40, 10	112,56
P_1, a.u.	322,2593	278,288	305,150	235,642	241,356	202,249	83,805	1,4125
ΔP_1	11,64364	10,50952	7,15981	4,55075	4,58885	5,2382	2,33749	0,23528
P_2	4,18748	1,63576	0,09298	1,53772	1,8301	3,98612	-	-

Δ P_2	0,57924	0,3767	0,21485	0,25137	0,24635	0,50232	-	-

Again it is possible to see, that the value P_2 does not depend upon the concentration of the iodine dissolved in the paraffin. Dependence of the parameter P_1 as a function of the concentration of the iodine is plotted in Fig.20. That dependence was simulated by the curves:

Simulation $y=1/(a+bx)$ a=0,00326+/-0,00018; b=0,00018+/-0,00005

Simulation $y=a/(b+x)^2$ a=729421,7953+/-307996; b=49,19927+/-11,02789

The simulation $y=1/(a+bx)$ is shown in Fig.20.

Now it is possible to compare the relative change of the concentrations after the recalculation of the value P_1 of the samples after waiting for 102 days. I take the value P_1 at zero concentration after keeping equals to the value P_1 at zero concentration of the freshly prepared samples (Table 1).

Table 8.

Relative change of the value P_1 as a function of the concentration of the iodine dissolved in the paraffin.

C,mM/kg	0	0,48	1,074	2,863	5,300	16,34	40,10	112,56
P_1 old	172,856	147,270	153,455	118,178	119,272	82,255	33, 576	0
P_1 new	322,2593	278,2882	305,1497	235,6422	241,3557	202,2486	83,80545	1,4125
P_1 new norm.	172,856	149,270	163,679	126,396	129,4603	108,484	44,9522	0,7576
C effective	0	0,45	0,50	2,40	3,0	8,0	32,5	110,5
Relat. change	1,0	0,9375	0,4655	0,8382	0,566	0,4896	0,8105	0,9817

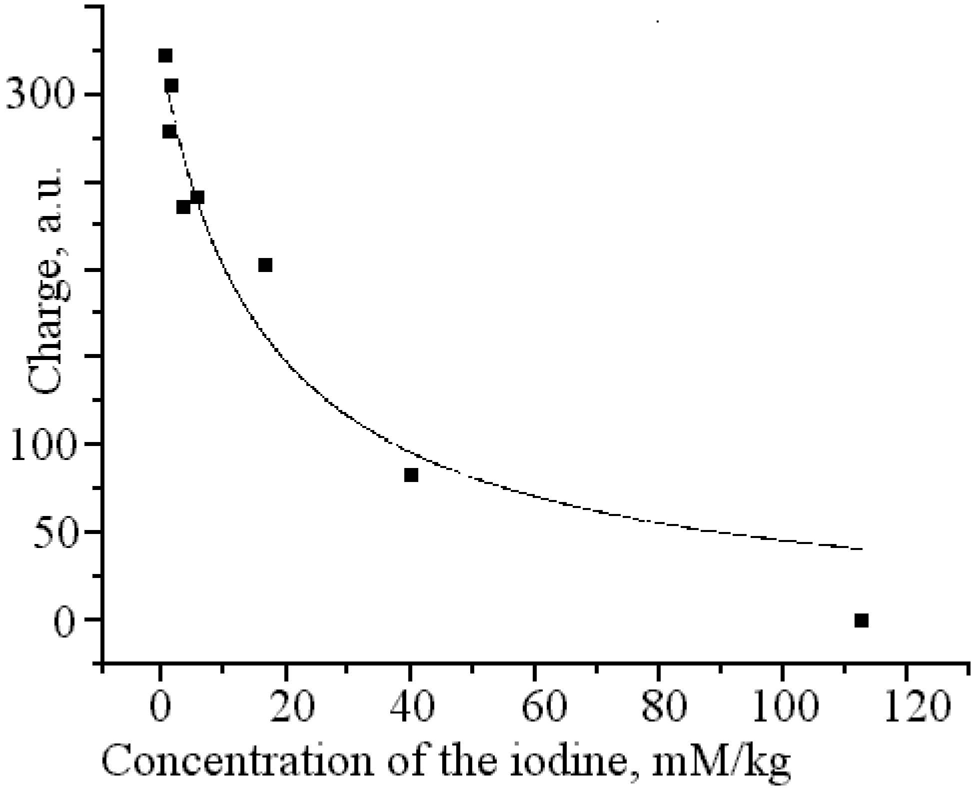


Fig.20

Dependence of the value P_1 upon I_2 concentration after keeping in the air.

After the normalization I obtained the higher values of P_1 for all the concentrations except for zero. It means, that the effective concentration of the iodine in the near surface layer diminished. I obtained the effective value of the concentration from the Fig.12. I found the value of the concentration what corresponds to the value P_1 new norm. in the Fig.12. The mean relative change of the concentration (except for the near error point C=112,56) for all the concentrations is 0,68457.

The equation of the diffusion should be solved in order to obtain the time dependence of the concentration of the iodine in the near surface layer.

$$dC/dt=Dd^2C/dx^2 \qquad (49)$$

For the step-like initial profile of the concentrations the solution is outlined in [41]. The solution is:

$$dC/dx=C_1/\sqrt{\pi Dt}\ \exp[-x^2/(2Dt)] \qquad (50)$$

After substitution $y=x/\sqrt{\pi Dt}$ it is possible to obtain:

$$C=C_1\sqrt{2/\pi}\int_0^z \exp(-y^2)dy \qquad (51)$$

here z is the distance from the surface deep into the sample or for the relative concentration the equation is valid (In Fig.21 the function erf(z), necessary to investigate the effective concentration in the thin layer at triboelectrization is shown).

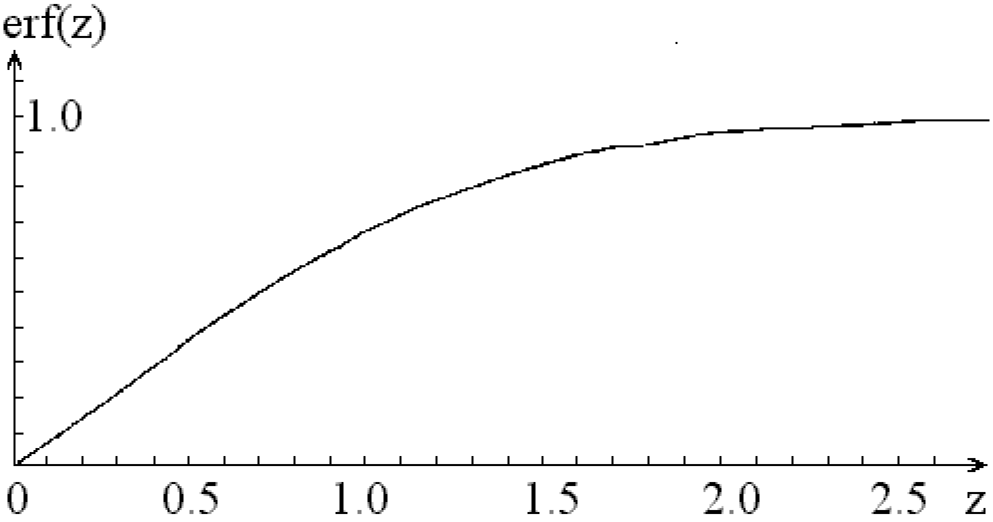


Fig.21

Function erf(z) as function z.

$$C_{rel}=C/C_1=\sqrt{2/\pi}\int_0^z \exp(-y^2)dy=\mathrm{erf}(z) \quad (52)$$

The value of the substituted (y instead of x) deepness of the effective layer I obtained from the equation:

$$0,68457=\int_0^a erf(z)dz\,/a \qquad (53)$$

and the value of a=2.5. Then, from the equation:

$$a=x/\sqrt{2Dt} \qquad (54)$$

Accepting x=0,5 mm, I obtained: $D=2,3\cdot 10^{-11}$ cm^2/c.

The same value can be estimated from the straightforward observation of the iodine diffusion in the paraffin. I observed the penetration of the iodine into the depth of the paraffin r=0,3 cm for 1 year and 6 months. Then, from Einstein equation:

$$r^2=2Dt \qquad (55)$$

I obtained $D=9{,}5\cdot10^{-10}$ cm^2/c.

Therefore, estimation for the value of D is: $D \sim 10^{-9} \div 10^{-11}$ cm^2/c.

IV Proofs of the free radicals generation.

It was already mentioned that the triboelectrization process is hindered by the presence of some compounds known as the radical traps (I_2, salts of Cu^{2+}, Co^{2+}, Cr^{2+}, Fe^{2+}/Fe^{3+} etc.). Nevertheless it is necessary to give some additional proofs of the generation of the free radicals during such a process (mechanochemical action onto the mixtures of the different compounds, for example, donor+accepter).

I investigated the phenomenon of the generation of the free radicals and radical pairs at the mechanochemical reaction between the solid dielectrics, one of them is a donor, another one is an acceptor [42-46]. At stirring with the force a couple of those compounds I have observed, in addition to the process of the generation of the free radicals and radical pairs also the generation of a considerable amount of the electrostatic charge. Actually the whole powder was triboelectrified through stirring and the powder has been splashed over the whole porcelain mortar and part of the pestle. In addition, as it was already discussed, I observed also a very good EPR-signal at stirring of a couple of the dielectrics each of them neither donor nor acceptor (teflon + I_2, for example). Usage of EPR and spin traps allowed me to investigate the production of the free radicals in the case of stirring of different other chemical compounds. Since the most experiments in the field of the triboelectrization were performed with the help of the compounds like paraffin and keratin (human hair) and also polyethylene, polyurethane, the same compounds were chosen for the experiments in the field of the generation and the investigation of the free radicals.

I observed the generation of the free radicals in the case of stirring in a mortar with the force of the mixture: keratin + paraffin and polyurethane + paraffin. The spectrum obtained is shown in Fig.22 (B). In the same figure (Fig.22) spectrum A corresponds to the initial signal EPR of the human hair (the intensity is equal to $9\cdot10^{17}$ 1/g). Line C on the Fig.22 B corresponds to the signal from the quartz. The EPR-signal of the human hair (from melanin), shown as a spectrum A after the beginning of stirring disappears, then the signal B appears. Concentrations of the free radicals in the system, what corresponds to the spectrum B is $1\cdot10^{16}$ 1/g. Time of stirring is 5 minutes. For the system paraffin-polyurethane the signal is exactly the same (but the polyurethane-porolon-the initial EPR-signal, contrary to the case of the human hair, is absent), that is, it's width and g-factor coincide with the parameters of the signal in the case of the system paraffin+keratin, but it's amplitude after stirring for 20 minutes is approximately 2 times smaller, then in the case of stirring of the paraffin and the human hair.

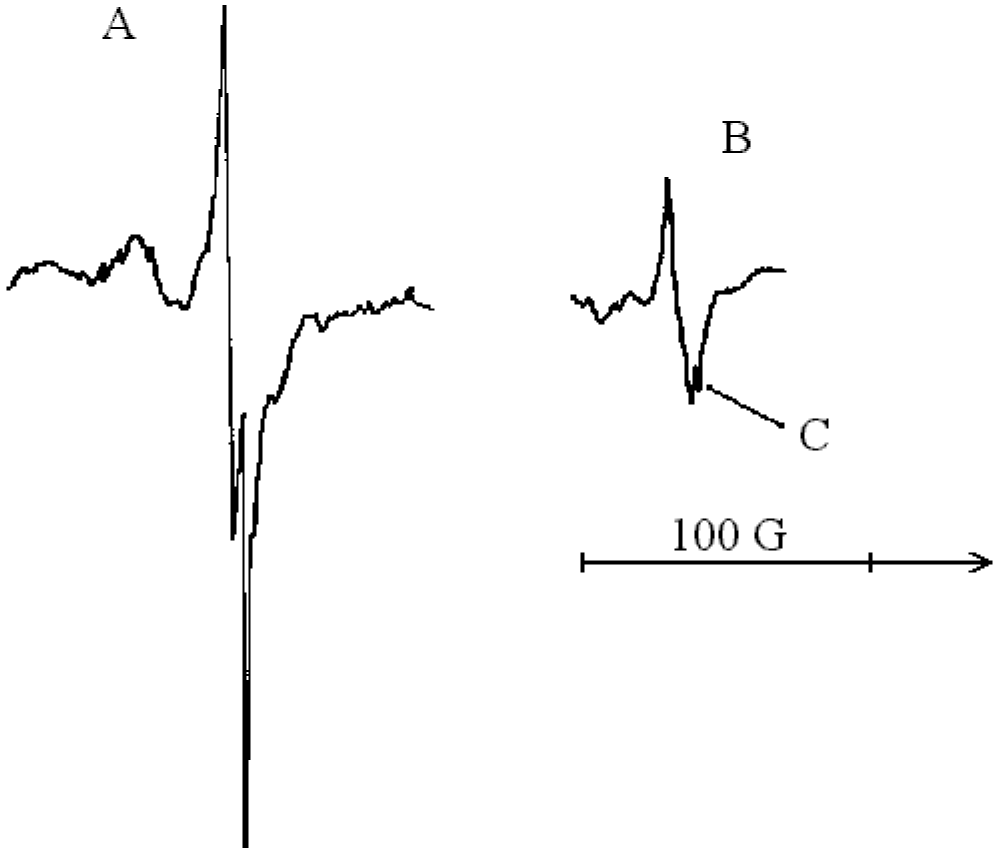


Fig.22

EPR-spectrum of keratin (human hair) (A) and EPR-spectrum of mechanochemically treated keratin+paraffin

The radical shown in Fig.22 B is most probably, a secondary one and that radical is obtained as the result of the very complicated chemical processes. In order to obtain the concentration of the initial radicals, the methods of the inhibition by the radical traps were used [47], namely, I_2, $CuCl_2$, stable radical TEMPOL, lignin, phenoxyl radical. The process of the decolorization of the pink polyethylene powder through the stirring with the help of a pig bristle in a porcelain mortar was already described. Actually the crystalline iodine does not interact with the polyethylene at heating. (it must not react with alkanes without some compounds, eliminating HI [48]). The expenditure of the iodine, assuming that every iodine molecule react with a couple of the radicals from the polyethylene corresponds to the rate of the free radicals generation $1{,}2 \cdot 10^{19}$ 1/(g·min). Frankly speaking, this is not the ultimate proof of the radical path of the mechanochemical reaction, it might be some other mechanisms (unexpectedly). But, since the homolityc bond cleavage. Is much more profitable in mechanochemistry (in the absence of any polar solvent) [49] and since it is a well known fact, that the process of the reaction of the halogens with the alkanes is the radical one, the probability of the radical mechanism in this case is overwhelming:

$$R^{\cdot} + I_2 \rightarrow RI + I^{\cdot}$$

$$R^{\cdot} + I^{\cdot} \rightarrow RI \qquad (56)$$

Usage of the salts of the metals of the variable valency can also reveal the presence of the free radicals. Usage of them as the radical traps is depicted in many details in [40]. About some of the salts of those transition metals it is known, that they may react with such polymers as polyethylene and some others [50]. Again it is assumed [47] that the mechanism of the reaction consists in the reaction of the reduction-oxidation of the ion of Cu^{2+} in accordance with the analogous reactions of the salts of the transition metals in the solution [40]. The salt of Cu^{2+} has been used $CuCl_2{\cdot}6H_2O$. This blue salt at the mechanochemical reaction with the polyethylene in the porcelain mortar starts to enter the chemical reaction (simultaneously it starts to be dissolved in it with the polymer turns to be green), and the chemical reaction is possible to see as the rate of the decrease of the signal from Cu^{2+}, registered with the help of EPR. The intensity of the EPR-signal from Cu^{2+} at usual stirring with the force in the porcelain mortar lowered two times at stirring just for 1 minute, keeping approximately this level during approximately 13 next minutes of stirring, what might be explained partly by the fact of the reaction hindering (since the crystals of $CuCl_2$ reacts just from the surface), and partly by the fact, that in the real live more light polyethylene particles rather leave the mortar as the result of the electrization, what leads to the partial enrichment of the rest mixture by the copper salt. Besides that, the rate of the initial diameter of the crystals as well – at very careful preliminary milling of the copper salt this rate increases.

An analogous experiment was performed also for the much less intensive action, consisted in stirring by the pig bristle of the polyethylene powder, in which the salt $CuCl_2{\cdot}6H_2O$ was added. In Fig.23 the curve 2 shows, how the relative intensity of the EPR-signal from Cu^{2+} ion changes at action of such a type. Of course, at this, less intensive, (compare to stirring force) action the rate of the decrease of the EPR-signal from Cu^{2+} is much less.

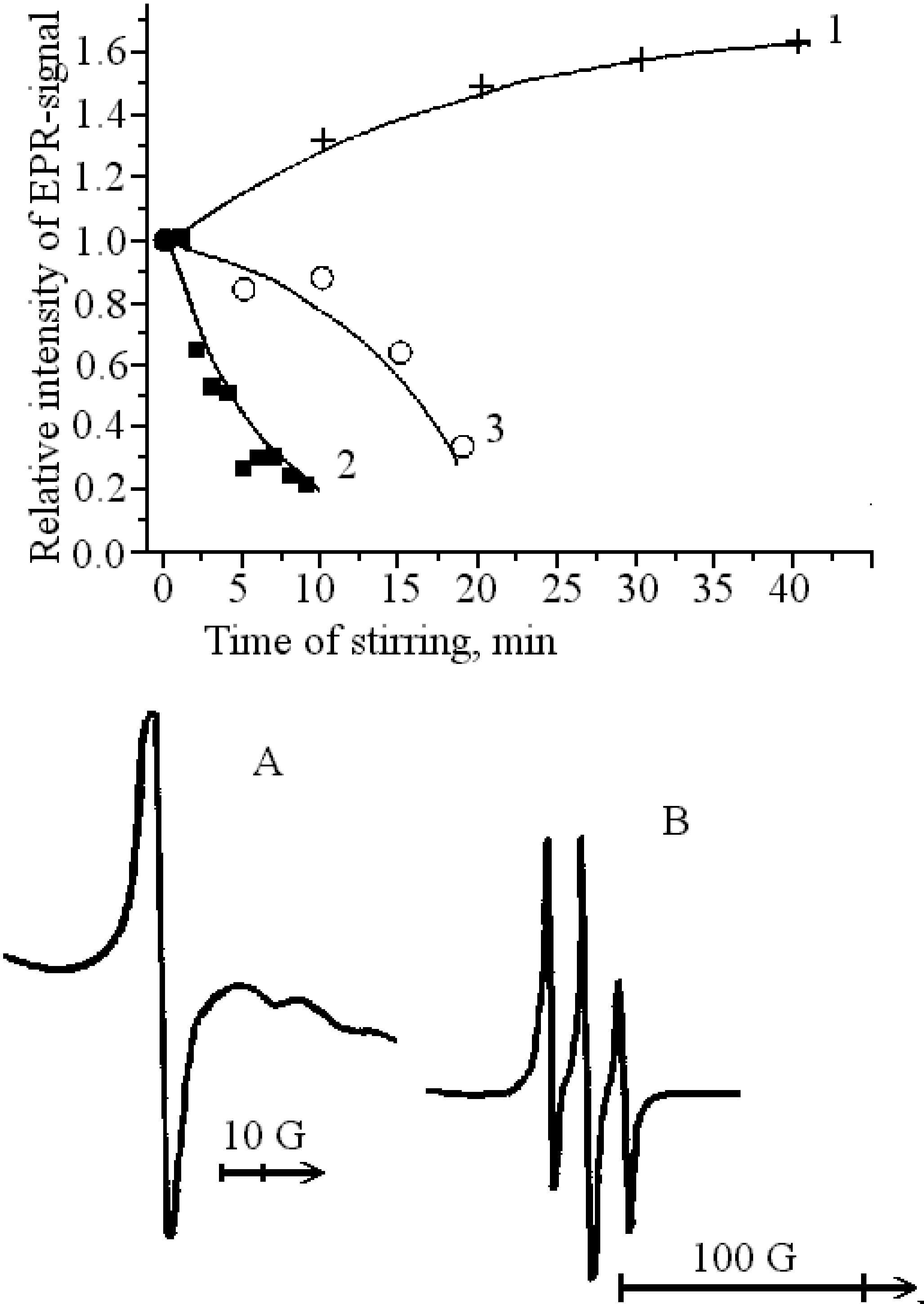


Fig. 23

Accumulation curves for some mechanochemical systems (see text).

Finally, some stable radicals were used, such as phenoxyl radical, obtained from the ionol and TEMPOL (the nitroxide radical, what dies at capturing of the alkyl radical). It is necessary to note, that the similar phenomenon of the reaction of the nitroxide radical due to the presence of the mechanochemically generated radicals in the polymer was already described in [51,52]. In Fig.23 the curve 3 shows how the relative intensity of the EPR-signal changes at mixing with the help of the pig bristle of the polyethylene in the porcelain mortar, where preliminary the solution of the nitroxide radical TEMPOL in heptane was poured (added to the polyethylene powder) and the whole mixture has been dried. The spectrum of the EPR-signal obtained is shown below (spectrum b) and it is possible to see that the nitroxide radical does not aggregate in the polyethylene and it is mobile enough – three distinct lines are closer to the high-viscosity solution, then to the solid state. The initial concentration of the nitroxide radical was $1{,}2\cdot10^{18}$ 1/g. An analogous experiment was performed by soaking of the porolon by the nitroxide radical solution. Again at stirring the concentration of the EPR-signal diminishes. Since polyethylene usually gives the negative charge at triboelectrization and porolon yields the positive charge at triboelectrization, both types of the radicals are capable to catch the nitroxide radical. It is also possible to measure the rate of the decrease of the nitroxide radical concentration, when that radical is taken as a powder, mixed together with the polyethylene. Again as the result of the free radicals generation in the polyethylene the stable radicals TEMPOL are captured.

One more method of the investigation of capturing of the neutral radicals is the usage of such a radical trap as lignin. In Fig.23 on the left (spectrum a) the EPR signal in lignin is shown and the curve 1 in the Fig.23 demonstrates, how the intensity of the EPR-signal in lignin changes at mixing (stirring) of the lignin powder in a mortar by the pig bristle during the time outlined along X axes. In the present case for the generation of the free radicals the process of stirring of the lignin particles with the help of the pig bristle was used. EPR-spectrum of the lignin is a singlet line with a width of 5,5 G and the initial concentration $3.9\cdot10^{16}$ 1/g. The rate of the line intensity increase (shown in Fig.23) corresponds to $1{,}9\cdot10^{15}$ 1/(g·min). Nevertheless, in another experiment the rate of the spins generation was equal to $5{,}5\cdot10^{15}$ 1/(g·min). It is possible to see, that the rate in this case much lower, then measured with the help of the crystalline iodine, probably, the polyconjugated system of lignin is much less effective with respect to capturing and stabilization of the free radicals generated, then the iodine.

Nevertheless, those experiments demonstrates absolutely clearly, that the amount of the free radicals generated in the case of the triboelectrization is by far exceeds the rate of the free charge generation.

It is necessary to discuss one more possible mechanism of the influence of I_2 and O_2 molecules in the near-surface layer onto the mechanism of the free charges recombination

$R^- + I_2 \rightarrow R + I_2^-$

$R^- + O_2 \rightarrow R + O_2^-$

and I_2^- and O_2^- leaves the near surface layer because of the high diffusion rate of both ions. The O_2^- influence was excluded through the experiment in the oxygen-free atmosphere (Ar or N_2 atmosphere). Despite in such an atmosphere O_2 molecules are still present in the near surface layer, their concentration should be less in this case. No observable effect of the change of the atmosphere was present, therefore, O_2 does not work. One more possible process is an electron transfer from ion R^- onto I. And then quick diffusion of I^- due to the strong electric field near the surface. For the reaction of the electron transfer from the ion onto the $I^\cdot$ atom:

$CH_3\text{-}CH_2\text{-}CH^-\text{-}CH_2\text{-}CH_3 + I^\cdot \rightarrow CH_3\text{-}CH_2\text{-}CH^\cdot\text{-}CH_2\text{-}CH_3 + I^-$

the enthalpy ΔH (method AM1) is equal to $\Delta H=-167{,}17$ kJ/mol

For the reaction of the recombination of the radical and the atom:

$CH_3\text{-}CH_2\text{-}CH^\cdot\text{-}CH_2\text{-}CH_3 + I^\cdot \rightarrow C_5H_{11}I$

ΔH calculated with the help of AM1 method gives $\Delta H=-135{,}86$ kJ/mol.

Therefore, it is very profitable to transfer the electron from the ion onto the atom $I^\cdot$ in order to obtain I^-, even more profitable, then the recombination.

The diffusion rate of I- in the paraffin lattice (crystalline polyethylene lattice) can be estimated as follows. GAUSSIAN calculations shows that I- interacts with 4 chains at the same time (the distance, at which it stabilizes near the polymer molecule, allows it). Therefore, calculations, conducted with the help of the different methods (AM1, MNDO, MINDO3, PM3) necessary to multiply by 4. Reaction of the capture of the ion I^- by the molecule of C_5H_{12} according to the reaction:

$C_5H_{12} + I^- \rightarrow C_5H_{12}I^-$

$\Delta H=-27{,}604$ kJ/mol (AM1), $4^{\cdot\Delta}H=110{,}4$ kJ/mol. Other methods yield: 88 kJ/mol, 58,68 kJ/mol (for 4 bonds). The average value is equal to: $\Delta H=85{,}7$ kJ/mol. Now it is time to calculate the electric field contribution to the activation energy of a jump between two adjacent positions (sites). In order to do it, I considered the electric field distribution created by the charge (I considered point charges). If at the initial moment the charge was placed in the point $\underline{r}_o$, and then it was a jump into $\underline{r}_1$, then the electric field changes onto the value $\Delta \underline{E}=\underline{E}(\underline{r}_1)-\underline{E}(\underline{r}_o)$. But the field $-\underline{E}(\underline{r}_o)$ is equal to the field, created by the charge with the opposite sign, placed into $\underline{r}_o$. That is, the field $\underline{E}(\underline{r}_1)-\underline{E}(\underline{r}_o)$ is equal to the sum of the field of the charges +q and –q, separated by $\underline{r}_1-\underline{r}_o$, that is, to the field of an electric dipole with $\underline{l}=\underline{r}_1-\underline{r}_o$.

$E=3(\underline{pr})\underline{r}/r^5 - \underline{p}/r^3 \quad E^2=(3(\underline{pr})\underline{r}/r^5 - \underline{p}/r^3)^2=9(\underline{pr})r^2/r^{10} - 6(\underline{pr})^2/r^8 + p^2/r^6=3(\underline{pr})^2/r^8+p^2/r^6$

The energy is equal to:

$$W=1/(8\pi)\int E^2dV=1/(8\pi)\int (3(\underline{pr})^2/r^8+p^2/r^6)dV$$

The first term is equal to:

$$W=1/(8\pi)\int 3(\underline{pr})^2/r^8 dV=1/(8\pi)\int [3p^2r^2\mathrm{Cos}^{2\theta}\, 2\pi\ \mathrm{Sin}\theta\ d\theta\ dr]/r^8$$

(since $\underline{pr}=pr\mathrm{Cos}\theta$).

$$W=3/4p^2\int_{r_o}^{\infty} dr/r^4 \int_{0}^{\pi} \mathrm{Cos}(\theta)\mathrm{Sin}(\theta)d\theta=(1/6)p^2/r_o^3$$

In an analogous way I calculated the second integral:

$$1/(8\pi)\int E^2dV=p^2/2\int dr/r^4=p^2/6r_o^3$$

I take value r_o equal to the distance of jump (the distance between two neighboring chains in a crystal, $4,954\cdot 10^{-10}$ m):

$$W=(1/6+1/6)p^2/r_o^3=1/3\ e^2r_o^2/r_o^3=1/3e^2/r_o=93,3\ \mathrm{kJ/mol}$$

Therefore, for the diffusion coefficient I obtained $\Delta H=85,7$ kJ/mol –specific interactions, $\Delta H=93,3$ kJ/mol – electrostatic interactions.

Using formula [49]:

$$D=10^{-5}\ m^2/s\ \exp(-E_a/RT)=10^{-5}\exp(-E/RT)=6,6\cdot 10^{-37}\ m^2/s$$

The electric field on the surface is around $1\cdot 10^6$ V/m and the velocity can be obtained using Einstein formula for mobility: $\mu=D/kT$, then:

$$V=\mu F=\mu eE=D/kTeE=3,65\cdot 10^{-29}\ m/s$$

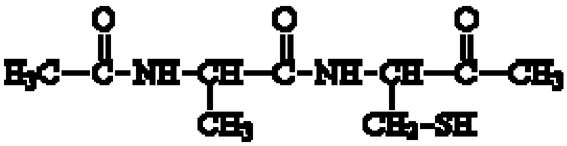
This too small for any observable charge decay, for example in the layer of 10 Å the time is equal to $3\cdot 10^{19}$ s.

If I consider I_2^- molecule, the problem will be the same. So no discharge due to the presence of I^- or I_2^- is impossible, they are moving too slow.

V How the mechanochemistry changes the mechanism of the chemical reaction?

In a classical chemistry the reaction between the paraffin and the keratin (human hair) is prohibited. Nevertheless, at mechanochemistry EPR method and the spin traps method proved that a lot of free radicals is generated. The question arises, how it is possible to change the mechanism of the chemical reaction or to induce a reaction between the keratin and the paraffin via the influence of the mechanical energy. In many books and chemical publications [27] the problem of the elevated temperature in the case of the mechanochemical reaction is discussed. Some assumptions were mad, that it is high temperature, that is responsible for the free radicals generation in a sliding contact (as well as in the case of the mechanochemistry of the low-molecular weight organic compounds). I also touched this problem in two of my publications [53,54]. It was measured with the help of a thermocouple, that the average increase of the temperature at a moderate mechanical action (stirring by the pestle with a moderate force, ~ 50-100 N) does not lead to an increase of the temperature more then, say 5-10 K, that is, the negligible increase. As far as the so-called local hot spots is concerned, I made some calculations in [54] and I proved that the percentage of the chemical transformation, exhibited by the spiropyrane, what would be talked about as coming from high temperature (melting of the solid) is negligible with respect to the real yield of the mechanochemical reaction of the spiropyrane transformation. Moreover, when the liquid nitrogen has been poured into the mortar, the rate of the mechanochemical reaction increases (but the percentage of the hot spots should be less). In some other publications, written by famous soviet mechanochemists A.A.Zharov [55] this problem is discussed as well. A.A.Zharov mentioned, that even for the case of the much more powerful action of high pressure combined with shearing deformation both global and local temperature increase are negligible. Therefore, the temperature increase can not be responsible for the generation of the free radicals.

In some publications [56,57] in the field of sonochemistry the problem of the change of the mechanism (SN_2 versus radical) was already discussed and it was discovered, that sonochemistry, as well as the mechanochemistry, promotes free radicals generation in the chemical reactions. In general features the idea of the possibility to change the mechanism of the chemical reaction is outlined in [19] and in my book [26]. In a few words, since the solid state support stress, the reacting molecules are placed in a strong anisotropic cage, created by the other molecules. Despite a single intermolecular bond of the crystal lattice in the case of the low-molecular weight organic compounds is weak (~ 20-30 kJ/mol), around the energy of the crystal lattice, usually the reacting molecules are surrounded by many of the neighbours and as the result many intermolecular bonds should be rearranged in order to obtain quasiliquid freedom of the molecules – therefore, they must react in a predetermined positions and stressed by the other molecules (the defect). The reaction in such an energy well leads to the change of the mechanism, as it will be shown below.



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\underset{\underset{\displaystyle CH_2-SH}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

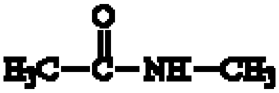
$$H_3C-CH_2-CH_2-CH_2-CH_3$$

In the present book I tried to calculate more accurately (compare to my book [26]) the possibility of the free radicals generation in the case of the low-molecular weight organic compounds. As a model compounds for the reaction between the keratin and the paraffin I choose:

Keratin Paraffin

(57)

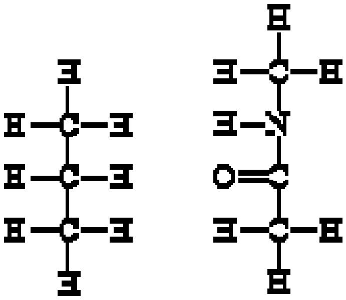
$H_3C-CH_2-CH_3$



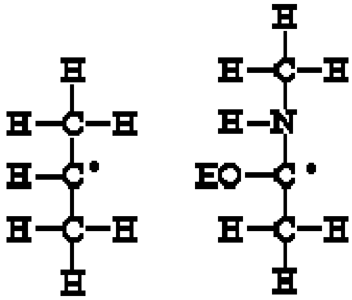
$H_3C-\overset{\overset{O}{\|}}{C}-NH-CH_3$

But for the estimation of the possibility of the influence of the matrix (change of the molecule structure) I choose:

I calculated the following geometry.



Singlet



Triplet

(58)

fixing the distance between the O-atom and the middle C-atom of the propane molecule (r-distance), allowing the computer program GAUSSIAN to optimize all other parameters for both singlet and triplet states (AM1 semiempirical method was used). It is necessary to remember, that the triplet state between two radicals, separated by a large enough distance is situated just higher the lower singlet state. The exchange integral between them for a radical pair is usually very small (compare to the values, normal in chemical thermodynamics, say 1 eV). The distance between the singlet and triplet levels was calculated in a famous paper [79] for the hydrogen molecule. I calculated triplet level because GAUSSIAN program exhibits some difficulties in optimization of the singlet levels for large distances – it starts to recombine radicals.

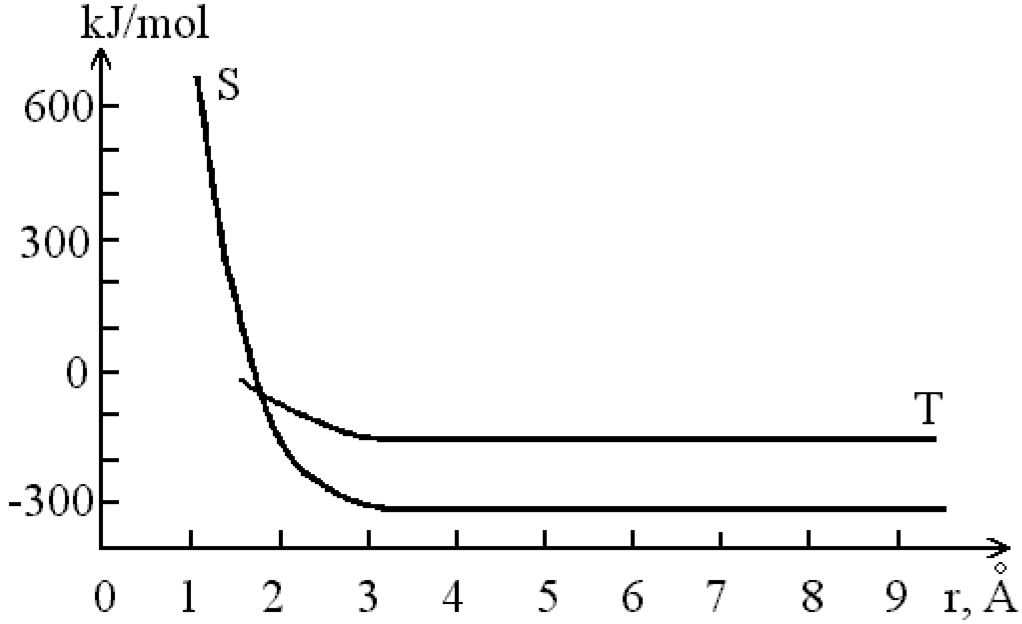


Fig.24

Singlet and triplet levels of a pair of molecules (see text).

The results obtained are shown in Fig.24. The curve S corresponds to the singlet level of the molecular pair and the curve T corresponds to the triplet level of the radical pair, received after hydrogen atom transfer. Even at an equilibrium distance of around 3 Å the energy difference is not very much (~ 150 kJ/mol) and it is easily achievable in the mechanochemistry (see [26]). How it is possible to concentrate that energy onto a couple of molecules near the defect, if the energy of the crystal lattice is around 20-30 kJ/mol? Indeed, it is possible. The defect in a molecular crystal has a definite three-dimensional structure (let it be an additional molecule). The crystal structure far from the additional molecule is unperturbed (see Fig.25). In this figure a) corresponds to the schematic picture of the unperturbed crystal (two-dimensional) and b) corresponds to the picture of the crystal with one additional molecule inside the lattice. I supposed that the outer layer of the region around the defect is unperturbed (no displacement of the molecules should be present). I considered the second coordination sphere as nonmoving (of course, in the real live the second coordination sphere also exhibits some displacements and another spheres as well), but for the purposes of the explanation this is a good idea.

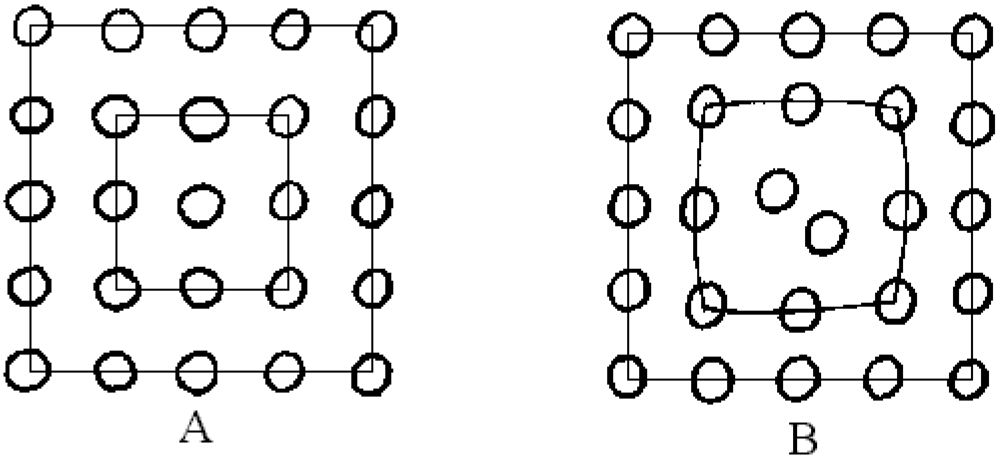


Fig.25

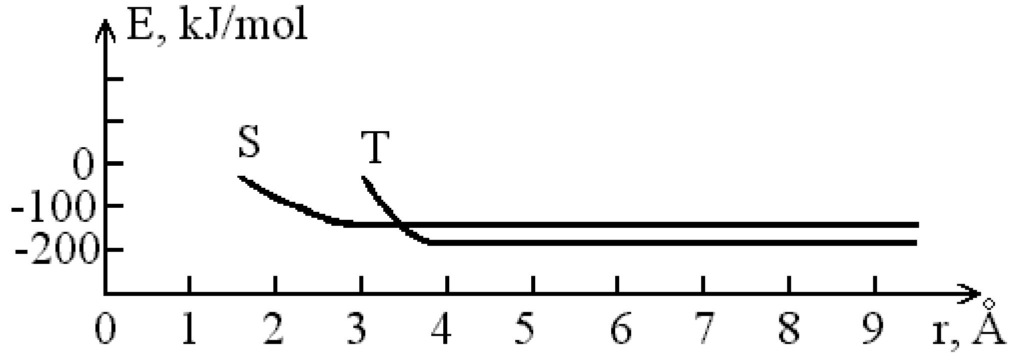
Schematic representation of the perturbed and unperturbed crystal lattice.

Comparison of the figures a) and b) allows somebody to see, that in the vicinity of the additional atom the crystal lattice is distorted. I want to prove that the energy of the interaction between the two molecules in the center of that defect might be several times higher, then the energy of the crystal lattice. If it were the gas molecules inside the unperturbed volume, it would be possible to say, that the energy of the interaction of the central molecule is of the order of the crystal lattice energy: the energy of the repulsion can not more then approximately the crystal lattice energy: the energy of the repulsion can not be more then approximately the crystal lattice energy, and in this case all the molecules of the defect continue to rearrange itself before that additional energy is distributed equally between them. But in the real live the internal layers of the molecules are rigid layers, not the gas, so they create some additional stress onto the centers of the defect. Really it is not so easy to estimate the real ΔE for the defect, but I can consider it as a number of the immediate neighbours of the two reacting molecules (first coordination sphere times the energy of the crystal lattice, that is, $\Delta E=(6-9)^{\cdot\Delta}E_1$, that is, in the range 120-180 kJ/mol.

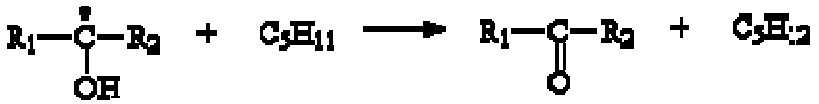
In addition to that, static influence of the matrix onto the chemical reaction, that is, when the surrounding molecules are in a static equilibrium, another, even more powerful mechanism of the energy concentration is possible. I mean the dynamic influence of the matrix. In [26] I estimated the time of the relaxation of the first two coordination spheres as ~ 10^{-5} s (it means, that the more molecules are involved in the process of the transformation of the crystal lattice near the defect, the more time demands such a rearrangement. Usually the time of the strike of the balls in a mill also around 10^{-5} s [49], so, the times are comparable. Therefore, in this case the system does not have enough to reach the full equilibrium around the defect and the energy improved onto the molecules is even more, then for the static influence of the matrix. The time of the matrix relaxation after the shock wave action was also considered in [58,59]. The figures are mentioned 10^{-8}-10^{-5} s. (For the first time, connected with the phase transitions, induced by the shock wave, was found to be equal to $0,2-0,3^{\cdot}10^{-6}$ s [59].

It is possible to see, that since those times are comparable, it is necessary to consider the reaction inside the nonequilibrium defect. In this case the value of the energy, which might lead to the transition to the another molecules (radicals) is even more and the unusual reaction is even more probable. This mechanism of the energy concentration, which appears in the case of the polymer, when the energy concentrates because of the long polymer chain. Even the rupture of the chemical bond is possible in the case of the mechanochemistry of the polymer, what means, that in the case of the mechanochemistry of the polymers the value of Δ E reaches 400-500 kJ/mol (that's enough for the rupture of the bond in the case of the polyethylene).

Fig.26 Energy levels for deformed molecules (see text).



From the publications [60,61] it is follows, that the stretched (or in the more general case distorted) polymer chain supports some reaction with the side groups or atoms (H-atom, for example, see also higher). Now it is possible to check it for the present case. I considered the energy levels of the molecules singlet (but with the frozen geometry of the triplet). In Fig.26 it is clearly seen, that the energy levels intersect in the vicinity of 3,5 Å. Therefore, since Δ E=20-30 kJ/mol, the problem of the mechanochemical reaction is now solved – it is inevitable. The only problem now is, whether the activation energy of the transfer of the hydrogen atom from the polyethylene molecule (propane molecule in my case) is very high (much more then, say 30 kJ/mol, the energy of the crystal lattice) or not. If it were very high, the reaction would be impossible with the help of the mechanochemistry. GAUSSIAN calculations (AM1 method) show, that the energy of the barriers of the hydrogen atom transfer is around 50 kJ/mol, that is, not very high. Some other estimations, made with the help of some semiempirical methods [62] give the values of around 6 kJ/mol one method) and 31 kJ/mol (another method). One more method of the estimation of that value is to consider the reaction of the recombination. In the case of the reaction:



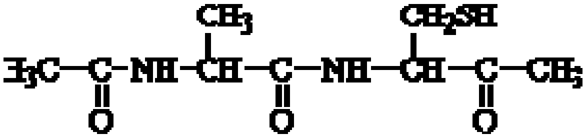
$$R_1-\overset{\bullet}{\underset{OH}{C}}-R_2 + C_5H_{11} \longrightarrow R_1-\underset{O}{\underset{\|}{C}}-R_2 + C_5H_{12}$$

The activation energy is 2-4 kJ/mol [63].

Now it is time to discuss the possibility of the alleviation of the charge transfer between the free radicals. As it was already mentioned, if the filled band of the donor were higher (or nearby) the empty band of an acceptor, Frenkel's theory would work satisfactorily [14]. Unfortunately, usually in the case of the dielectrics the empty level is much higher in energy then the filled one (the gap is very large), so no possibility of such an electron transfer is possible. In order to prove that and to find, how the radicals generation alleviate the process of the triboelectrization, quantum chemical calculations were performed. Just the chemical mechanisms of the electron transfer with the help of the GAUSSIAN [34] were considered. As a model system the interaction between the molecules C_5H_{12} (DH, donor) (model of the paraffin) and CH_3-C(O)-NH-CH(CH_3)-C(O)-NH-CH(CH_2SH)-C(O)-CH_3 (A, acceptor) (model of the keratin, the protein, being the base of the pig bristle and the human hair).

$H_3C-CH_2-CH_2-CH_2-CH_3$

(DH, donor)



$$H_3C-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{CH_2SH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

(A, acceptor)

The energies were calculated of the following molecules, ions, radicals and the radical complexes: CH_3-CH_2-$CH_2^{\cdot -}$-CH_2-CH_3 ($DH^{\cdot -}$); CH_3-CH_2-$CH_2^{\cdot +}$-CH_2-CH_3 ($DH^{\cdot +}$); CH_3-CH_2-$CH^{\cdot}$-CH_2-CH_3 ($D^{\cdot}$); CH_3-CH_2-CH^{+}-CH_2-CH_3 (D^{+}); CH_3-CH_2-CH^{-}-CH_2-CH_3 (D^{-}); CH_3-C(O)-NH-CH(CH_3)-$C^{\cdot +}$(O)-NH-CH(CH_2SH)-C(O)-CH_3 ($A^{\cdot +}$); CH_3-C(O)-NH-CH(CH_3)-$C^{\cdot -}$(O)-NH-CH(CH_2SH)-C(O)-CH_3 ($A^{\cdot -}$); CH_3-C(O)-NH-CH(CH_3)-$C^{\cdot}$(OH)-NH-CH(CH_2SH)-C(O)-CH_3 ($AH^{\cdot}$); CH_3-C(O)-NH-CH(CH_3)-C^{+}(OH)-NH-CH(CH_2SH)-C(O)-CH_3 (AH^{+}); CH_3-C(O)-NH-CH(CH_3)-C^{-}(OH)-NH-CH(CH_2SH)-C(O)-CH_3 (AH^{-});

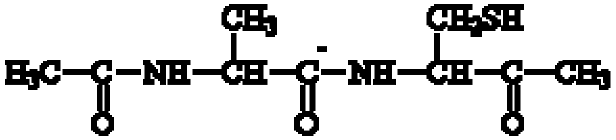
$H_3C-CH_2-CH_2^{\cdot-}-CH_2-CH_3$ (DH$^{\cdot-}$)

$H_3C-CH_2-CH_2^{\cdot+}-CH_2-CH_3$ (DH$^{\cdot+}$)

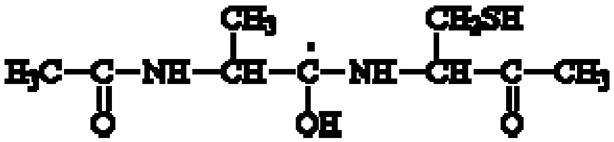
$H_3C-CH_2-\dot{C}H-CH_2-CH_3$ (D$^{\cdot}$)

$H_3C-CH_2-CH^{+}-CH_2-CH_3$ (D^{+})

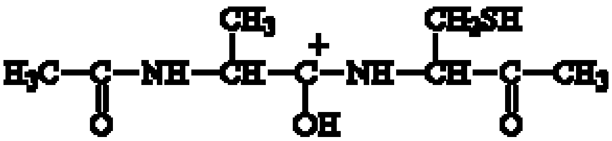
$H_3C-CH_2-CH^{-}-CH_2-CH_3$ (D^{-})



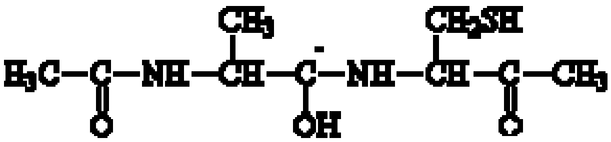
$H_3C-C(=O)-NH-CH(CH_3)-\overset{-}{C}(=O)-NH-CH(CH_2SH)-C(=O)-CH_3$ (A$^{\cdot-}$)



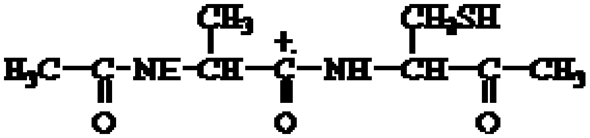
$H_3C-C(=O)-NH-CH(CH_3)-\dot{C}(OH)-NH-CH(CH_2SH)-C(=O)-CH_3$ (AH$^{\cdot}$)



$H_3C-C(=O)-NH-CH(CH_3)-\overset{+}{C}(OH)-NH-CH(CH_2SH)-C(=O)-CH_3$ (AH^{+})



$H_3C-C(=O)-NH-CH(CH_3)-\overset{-}{C}(OH)-NH-CH(CH_2SH)-C(=O)-CH_3$ (AH^{-})



$$H_3C-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{\overset{+\cdot}{C}}-NH-\overset{\overset{CH_2SH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

(A^{+})

and also the complex $[AH^{\cdot}\ldots D^{\cdot}]$ with the help of the five semiempirical methods (AM1, MNDO, MINDO3, PM3, CNDO). The results obtained are summarized in the Table 9.

Table 9.

The enthalpies of the production of the different radicals, ion-radicals, ions combinations from the molecules of donor and acceptor, and also the energy of the radical complex (the energy of the initial donor+accepter is taken to be equal to zero). The energies are expressed in kJ/mol [20].

Method	AM1	MNDO	MINDO3	PM3	CNDO
A+ DH	0	0	0	0	0
$A^{\cdot+}$ + $DH^{\cdot-}$	1031,66	1005,24	601,524	-	-
$A^{\cdot-}$ + $DH^{\cdot+}$	943.309	1003,31	661,62	945,275	1729,85
$AH^{\cdot}$ + $D^{\cdot}$	157,87	116,26	147,0	132,283	691,87
$[AH^{\cdot}\ldots D^{\cdot}]$	130,471	102,572	109,64	-	-
AH^{+} + D^{-}	784,22	751,84	358,54	794,72	1288,73
AH^{-} + D^{+}	849, 20	865,96	493,4	803,42	1014,6

The next consequence is clearly seen: all the methods, except for CNDO, give the close energies (assuming that these are the semiempirical methods) and it allows to make the following conclusions:

1)The straightforward electron transfer is extremely unprofitable in energy (and, in addition, it is a little more profitable in energy for the paraffin to be charged positively).

2)The process of the hydrogen atom transfer, despite it is also unprofitable in energy, can be conducted via the mechanochemical route (see higher), taking into account the production of the radical complex $[AH^{\cdot}\ldots D^{\cdot}]$ costs just ~ 110 kJ/mol.

3)As it is seen from the Table 9, the process of the backward transfer of the electron from $AH^{\cdot}$ to $D^{\cdot}$, despite it is very unprofitable in energy (~ 500 kJ/mol), but nevertheless it is much more probable (with respect to ~ 1000 kJ/mol for the electron transfer between the initial molecules). In addition, the rule of signs is observed here – stabilization of the electron is much more suitable for the paraffin, what is in accordance with the experimental data.

I should emphasize that the idea of the surface states as extremely important for understanding of the triboelectrization was already mentioned in the literature. In [65] the role of the modern surface analysis techniques in understanding electrification phenomena was considered. The author mentioned several experiments. At investigation of the electrization between mercury and polyethylene it was found, that the surface oxidation of the polyethylene may increase the surface charge up to twenty times. Transmission IR-spectroscopy shows, that the reaction of the oxidation yields ozonides and the carbonyl compounds, what produce the charge-transfer dots on the surface.

A very important observation was made in the experiment, conducted by Salanek [65]. He found, using XPS that the double mass transfer takes place between all the combinations PTFE, PET, PC and between the polymers and the metals Au, Ag, Pt. The surface spectra of PET demonstrated the presence of CF_2 carbon (C_{1s}) spectrum and F_{1s} spectrum after friction of that surface by PTFE. It was checked, that F^- is absent when there is just a contact without friction (a very good demonstration, that it is really mechanochemistry, not mere contact, what is responsible for the tribocharge). The estimations performed of the amount of the material transferred showed, that the amount of the material transferred several orders of the magnitude higher then it is necessary to charge the surface (if somebody would considered the ratio one atom of the material is transferred ↔ one elementary unit of charge s transferred). Exactly as in the case of the ratio of the free radicals and the free charges for the case of the dielectric charging. The authors [65] made a real conclusion, that the material transfer should be considered in all the models of the contact charging. The idea of the material transfer at friction was also considered in [25].

It is necessary to describe another experiment where the importance of the defects with the energy levels in the middle of the gap was clearly demonstrated. In [66] the solid rare gases were investigated. Solid rare gases are shown by the experiment to provide a useful system for investigating the fundamental processes of contact electrification of insulators. Pure solid rare gases do not acquire charge when contacted by metals, but the ability to acquire charge can be conferred by doping the rare gas solids with electron-accepting molecules [66].

The idea of the experiment follows from consideration of the energy levels in a solid rare gas and in a metal. In Fig.27 the energy levels of the metal and the argon atom are shown. It is a well known fact, that the vacuum level is very close (within 1 eV) to the bottom of the conduction band of insulators (including Ar, taken as a solid). The value ΔE_I is typically 10 eV or more and, therefore, the full valence bond is really deep below the vacuum level. The work function $\hat{O}_m$ of metals (typically about 4 eV) is considerably less, then the energy gap ΔE_I. Consequently, the Fermi level of the metal lies deep in the energy gap of the insulator and so, when the metal and insulator are brought into contact electrons does not transfer from the metal into the insulator, because there are no unoccupied levels into which they can go [66]. The temperature is too small to provide the energy enough for the thermal excitation ($kT \sim 3 \cdot 10^{-2}$ eV at room temperature) into the empty conduction band. Similar arguments show that electrons can not transfer from the insulator to the metal.

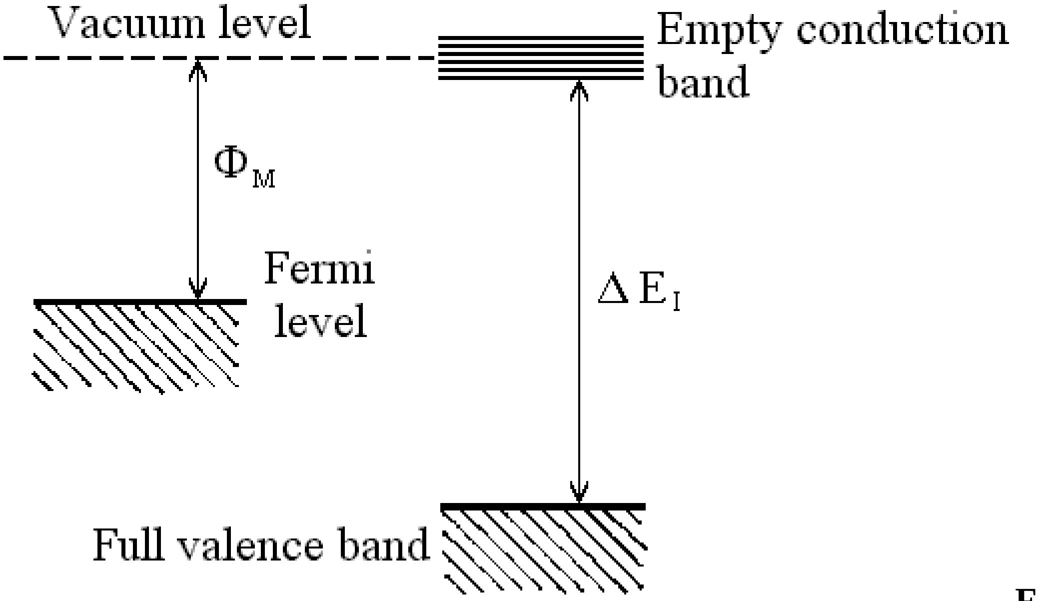


Fig.27

The scheme of energy levels of a rare gas matrix and a typical metal.

The electronic band structure of solid rare gases is known, they have an electron gap, which is greater then 9 eV and the bottom of the conduction band lies close to the vacuum energy. Because the force between atoms is weak the atoms keep their identities in the solid and so the authors [66] do not expect crystal defects to provide deep donor or acceptor centers no do they expect the surface states which are normally associated with “dangling” bonds. Consequently, it is possible to expect that, unlike most insulators, solid pure rare gases would not be charged by contact to metals and should be an excellent system for studying the basic mechanisms of contact electrification.

The experiments, conducted in [66] showed, that pure rare gas solids (neon, argon, krypton, xenon) are not charged by the spheres of gold, aluminum, cadmium. No contact charging was detectable, i.e. contact charge density was less than $5^{\cdot}10^{-14}$ $C^{\cdot}mm^{-2}$ (for comparison the contact charge density on a typical insulator, such as a polymer, is usually on a typical insulator, such as a polymer, is usually about 10^{-11} $C^{\cdot}mm^{-2}$). The authors [66] used poly(tetrafluoroethylene) to check their apparatus.

Experiments, performed in [66] was to put electron accepting centers into a pure rare gas and see, if this doped solid now charges on being contacted by a metal. The Cl_2 molecules is highly electronegative; in [66] they added some chlorine gas to argon gas, condensed this mixture onto the copper table in the cryostat and then made contact electrification measurements in the same way as for pure rare gases. It was found that, as predicted, the chlorine-doped argon samples receive a negative charge on contact to metals (Au, Cd, Al). The charge is from 10^{-12} $C^{\cdot}mm^{-2}$, concentration of Cl_2 0,01% to 10^{-10} $C^{\cdot}mm^{-2}$ at concentration 1-10% Cl_2.

The experiments were repeated with solid argon doped with another electronegative molecule O_2. O_2 is somewhat less electronegative than Cl_2. Charge is from 10^{-13} C·mm^{-2} for 0,001 % of O_2 to 10^{-11} C·mm^{-2} for 10% of O_2. It can be seen, that O_2-doped solid argon samples also charge negatively though the magnitude of the charge density is less than that of the Cl_2-doped samples.

The experiments were repeated with argon doped with molecules which are not highly electronegative: N_2, CH_4, CO. No contact electrification could be detected, i.e. any contact charge density was less than $5 \cdot 10^{-14}$ C·mm^{-2} [66].

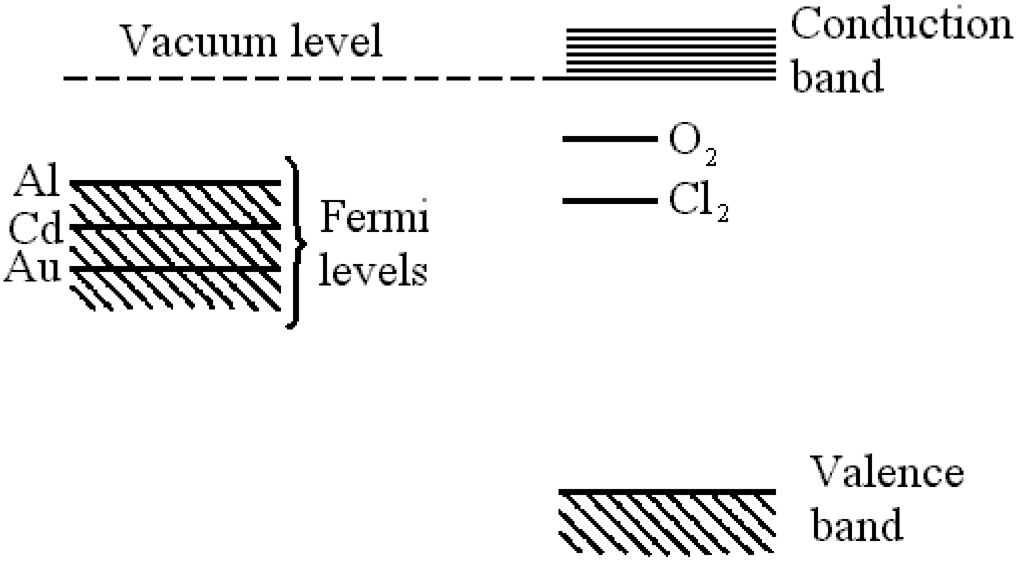


Fig.28

Energy levels of dopants in a rare gas matrix (see text).

In Fig.28 the approximate positions of the energy levels of O_2 and Cl_2 molecules are shown. It is possible to see, that, indeed, Cl_2 molecules have an energy level below Fermi level of many metals and it should be charged easily. The authors [66] can however confer the ability to acquire contact charge by introducing suitable impurities. The energy levels of those molecules should not be very distorted through the action of the rare gas matrix. Some puzzles were also discussed in [66] – just one out of 1000 suitable molecules was charged (in the near surface layer). Those results are very well correlate with my own, where I demonstrated, that 1 out of 10^6-10^8 radicals (active centers) is charged. Another puzzle is that for the molecules of Cl_2 and O_2 the energy levels can not be perturbed strongly by the influence of the matrix, so, electronegativity of Cl_2 molecule and O_2 molecule should be 2.5 eV and 0.4 eV respectively, what is much less then the work function of gold (around 5 eV). Nevertheless, the authors [66] mentioned that polarization of the surrounding rare gas solid may increase the ionization potential of an impurity by up to 2 eV. It seems that in this case the energy level of Cl_2 should reach the Fermi-level of gold and the energy level of O_2 molecule should be just higher that level. I actually also used this idea in my work [19].

The publication [66] is really a very well manifestation of the point of view that the impurities what are responsible for the triboelectrization of the solid dielectrics.

In my another publication [64] it is described in great details, that in reality the value of the energy distance between the charge transfer levels $AH^+ + D^-$ and $[AH^{\cdot}\ldots D^{\cdot}]$ is even less (it is 500 kJ/mol for the infinite separation of the ions). For the distance, at which the complex is stabilized, it is equal to $2|V_{12}|$ and it is exponentially small for large r (distance between the radicals). In the following subchapter I rewrite it ones more.

VI Production and decay of the charge transfer complexes as an explanation of the generation of the triboelectricity in the case of the friction of the two dielectrics.

In this subchapter I developed a well known theory of the charge transfer complexes for the case of the two radicals (contrary to, for example, case of the two molecules) the energy level, which correspond to the charge transfer between the two agents of a complex (radicals or molecules), as a rule, approaches close enough the ground energy level, what allows the generation of the triboelectricity in high concentrations. Since the static triboelectrization of the two dielectrics is greatly influenced by the radical traps, it would be possible to suppose the presence of the donor-acceptor interactions as the reason for the generation of the free radicals [20] and then charges [64]. The donor acceptor approximation to the generation of the triboelectricity is mentioned in some publications [17,67], but just as an explanation of the appearance of the double electric layer (without investigation of the details of how that layer appears). Therefore, the problem of the generation of the static charges at friction of the two dielectrics is a very important one and essentially necessary for the fundamental and applied problems. In the present subchapter the donor-acceptor theory of the generation of the triboelectricity is developed.

In the basis of the Malliken’s theory of the complexes production the idea is placed of the electron transfer from the donor to the acceptor and at this process at formation of the energy levels, responsible for the bond in the complex, the essential role will be played by the level of the Coulomb interaction between the molecules.

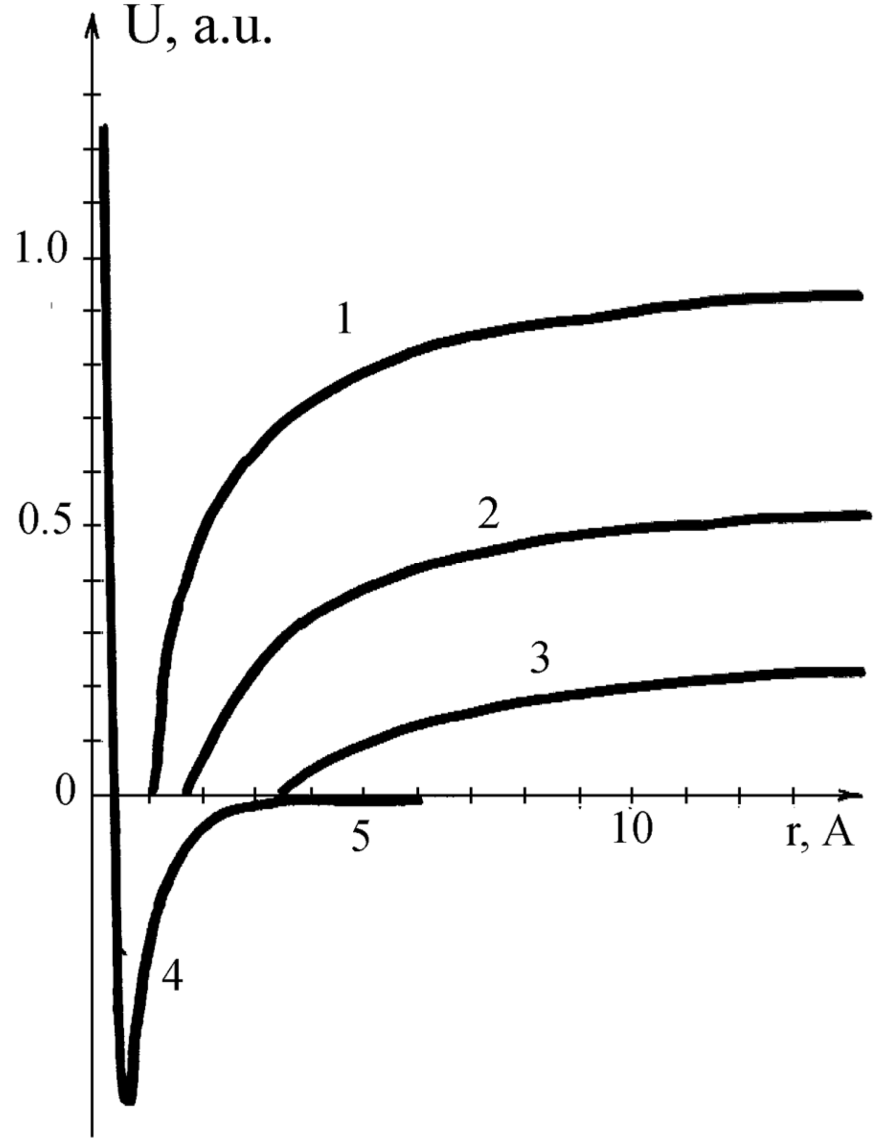
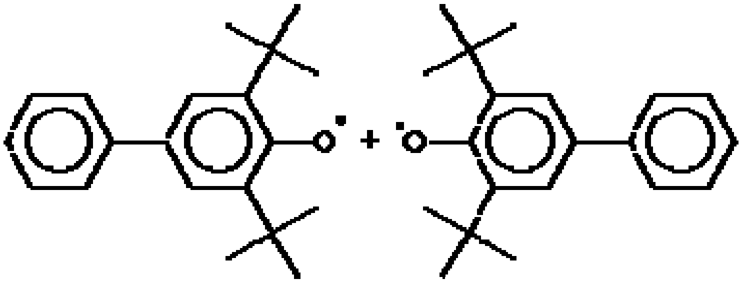


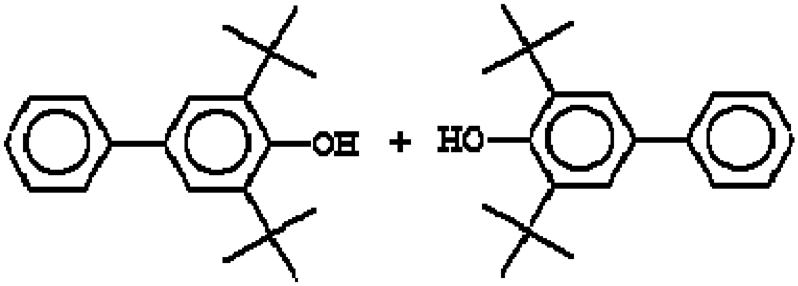
Fig.29 The potential curves of the Coulomb interaction between the molecules (curves 1,2,3), for the different values of the difference between the ionization energy and electron affinity (Δ E=I-E_o, see the text); and the curve 4 is a schematically shown the molecular singlet term of the ground state.

In Fig.29 the corresponding levels of the Coulomb interaction for the three different systems are shown. For the first system the value Δ E=I-E_a (ionization energy minus electron affinity, the Coulomb term reaches that value Δ E as r→ ∞) is equal to the relatively large value (curve 1) so, that the level of the Coulomb attraction crosses the level U=0 in the place, where the potential well for the bond (curve 4) is situated (approximately); For the second system it is equal to some “medium” value (curve 2), so that the level of the Coulomb term crosses the energy level U=0 in the vicinity of the "tail" of the potential curve 4; For the third system Δ E is equal to a "small" value (the curve 3), so, that the level of the Coulomb interaction intersects with the line U=0 in the place, where the energy of the singlet level ~0, very "far" from the potential well. According to the general conception [68] the curve 1 (taking into account the repulsive part of the term, which appears in the vicinity of r→ 0 and it will be placed very high in energy) corresponds to some excited state of the molecule (for example, state CH_3^- …CH_3^+ in ethane) and it will not play a major part at consideration of the low-energy interactions; the curve 2 should correspond to the level, realized between the good donor and acceptor and it gives either ionic bond ($BF_3…NH_3$) or charge transfer complex ($I_2{\cdot}C_6H_6$, in this case the main minimum on the curve 4 without influence of the curve 2 is small or absent completely); the curve 3 corresponds to the term, that is realized between two radicals and it corresponds to proximity, almost meeting of two levels 3 and 4 with the production of the shallow minimum on the curve 4, since at high distance r, where the levels 3 and 4 intersect, the interaction between them is small (here just complicated organic molecules are considered, where the steric hindrance starts to appear for the level 3 already at distances ~ 1-2 Å , the problem is that, for example, for the molecule NaCl the level 3 is simply below 4, what gives in this case a very strong ionic bond, not disturbed by the steric hindrance repulsion.

Why it is namely the case of the two radicals, for example [69]:



(61)



what corresponds to the small value of Δ E, and for example, for the two molecules of a type:

the value of Δ E in the general case should be higher (as an average over all the more or less complicated molecules)? The explanation in the general features is possible to give, using MO LKAO method (molecular orbits, linear combination of the atomic orbits) (Fig.30).

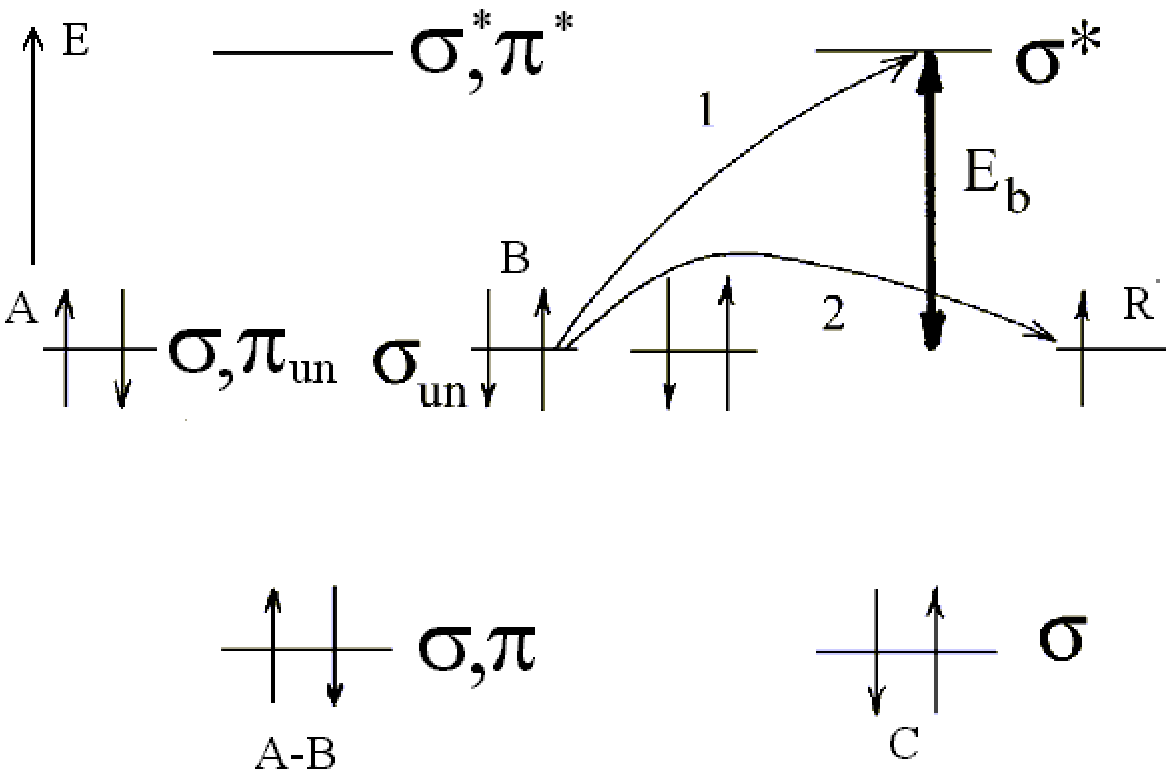


Fig.30. The energy diagram, showing the scheme of the energy levels, received with the help of the method MO LCAO for the bond between the two parts in the molecule (on the left there present bonding σ , π orbits; unbonding occupied orbits σ $_{un}$, π $_{un}$; and free anti-bonding σ *, π * orbits) and for the bond between the two groups in a radical (on the right, there is a free place on the unbonding orbit, since it is a radical), the path 1 shows the scheme of the electron transfer at production of a donor-acceptor bond in the case of the interaction of the molecules, which has all the occupied orbits, and the path 2 - the scheme of the electron transfer at production of a donor-acceptor bond between the two radicals.

Lets consider the pair of the organic molecules, which give the bond A-B. At this point I consider the general case of the molecules, which include atoms o, N, so that there is always a lot of nonbonding orbits (they are shown schematically in the center of the figure). At production of the bond in the general case bonding (σ ,π) and antibonding (σ *,π *) orbits appear, which are separated from unbonding (nonbonding) (σ_{un}) by the value E_b, and an approximate value of the bond in the molecules is ~ 150-200 kJ/mol, for the averaged bond. If now it is necessary to consider the electron transfer from the molecule like A-B to the molecule C, for example, according to the principle $A\text{-}B^+ \ldots C^-$, it is possible to see, that the most profitable in energy path (according to the Pauli principle) – the path from the nonbonding orbital of A-B to the antibonding orbital of the molecule C, what is connected with the energy loss in ~ E_b (path 1). If the case of the two radicals is considered, then they always have one unpaired electron onto the unbonding orbit, what tells, that in the case of our simple scheme the energy $\Delta E=I-E_a \sim 0$ (path 2). In the reality, of course, for the radicals $\Delta E>0$ as well, but if it is necessary to consider in the general case the two molecules and the two radicals, it is possible to write:

Two radicals: $R_1^{\cdot} + R_2^{\cdot}$: $\Delta E \sim \Delta$

Two molecules: A + B: $\Delta E \sim \Delta + E_b > \Delta$

that is, from the very beginning the value of E_b is included in a value of ΔE for the molecules and not for the radicals.

Of course, from that approximate consideration there are thousands of exceptions and in the every specific case of the interaction of the two molecules or the two radicals it is necessary to conduct the accurate quantum-chemical calculations, but in the general it is possible to see, that in the case of the two radicals the undisturbed Coulomb level will cross the ground level at higher distance r (the case 3 from Fig.29), then in the case of the two molecules with the electronic shells (the cases 1 and 2 from Fig.29). This general law will have important consequences for the triboelectrization of the dielectrics, what will be shown below.

First of all, it is necessary to consider the case of the quasi-intersection of the singlet Coulomb term with the ground singlet term [68]. The problem for the Coulomb term is solved in many textbooks [68] and it is necessary to use the perturbation theory in the second order.

Let's consider the case, when the level of the charge transfer state intersects the ground term so far from the minimum (the curve 4), that it is possible to consider that term U=0 (Fig.30).

Let for the clarity the term is considered:

$$E_1=C_1-e^2/(\varepsilon r) \quad (63)$$

where for example C_1=4 eV, ε =1, that is E_1=4-14,4/r, E – in eV, r – in Å, and the term U=0 (ground state far from any chemical bond).

The terms are intersect in the point r=3,6 Å. Let's for the clarity V_{12}=1 eV.

Let's complete the solution with the help of the successive approximation method [70]. Because of the term intersection it is not possible to use the second order of the perturbation theory for the whole term from 0 to infinity. But in the intersection point itself it is possible to receive [70]:

$$\begin{vmatrix} V_{11}-E & V_{12} \\ V_{12} & V_{22}-E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0 \quad (64)$$

$$E_{1,2}=(V_{11}+V_{22})/2 +/- [(V_{11}-V_{22})^2/4+(V_{12})^2]^{1/2} \quad (65)$$

that is the distance between the levels will be equal exactly to $2V_{12}$=2 eV (for $V_{11}=V_{22}$) (estimation of V_{12} see below). At a large distance from the intersection point it is possible to use the second order of the perturbation theory [70] and then it is possible to receive:

$$E_n^{(2)}=\sum_m (V_{mn})^2/(E_{no}-E_{mo}) \quad (66)$$

$$E_n^{(2)}=(1)^2/[0-(4-14{,}4/r)] \quad (67)$$

that is

$$E_o=0+r/[14{,}4-4\cdot r] \text{ for } r>>2{,}6\ \text{Å} \quad (68)$$

Let's consider this approximation up to the point, where the second order does not work any more, where V=Δ E=E_n^o – E_m^o=1 eV. This point is situated in the point:

$$1=4-14{,}4/r;\ 3=14{,}4/r \Rightarrow r=4{,}8\ \text{Å}$$

According to (68), in this point the well appeared of a depth: E_o=4,8(14,4-4·4,8)=-1 eV (roughly, since the real approximation does not work properly).

That is, in the crude approximation it is possible to receive, that the well depth in the point of the intersection will be approximately equal to V_{12} ~ 1 eV and the minimal distance between the levels (singlet ground level and the singlet charge transfer level) will be equal to $2V_{12}$=2 eV.

Schematically those terms (perturbed and unperturbed) are shown in Fig.31. Unperturbed terms are shown by the dotted line near the point of the intersection, and $2V_{12}$ means the gap width in the point of the maximal approaching of the levels. The value V_{12}=1 eV was chosen on purpose – it is the typical value of V_{12} for the charge transfer complex between the radicals, as it will be shown below. Then, for the following considerations it is necessary to know how the value V_{12} depends on the distance.

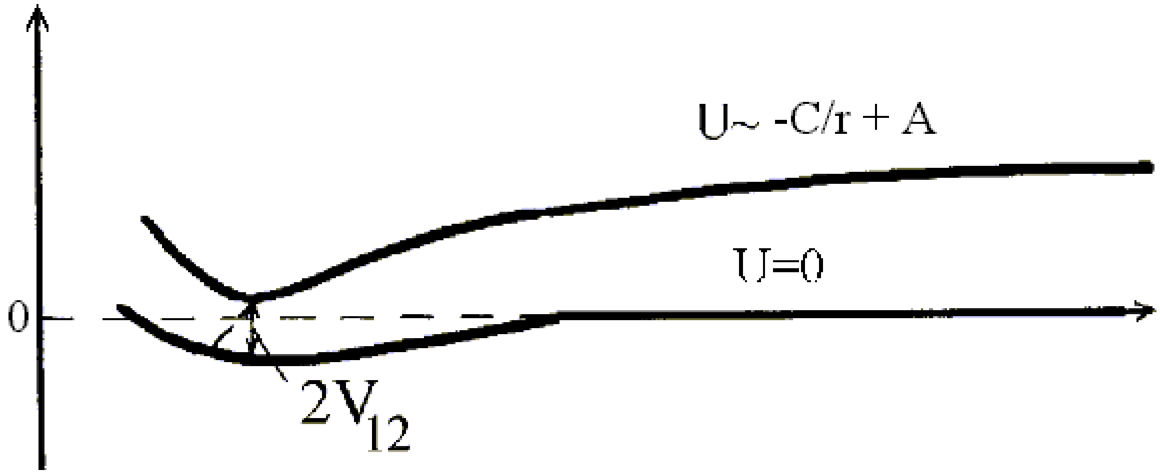


Fig.31 The scheme of the interaction of the Coulomb term U=-C/r + A and the ground term.

In order to estimate this term of an equation, which is responsible for the interaction of the singlet charge transfer term with the singlet level of the ground term, it is possible to use several approximations.

1st approximation consists in the calculations with the help of the variational method for the description of the interaction of the singlet charge transfer term and a singlet term of the molecule, similar to the molecule of the hydrogen. It is a well known method of the determination of the coordinate and wave function of Haitler and London in a molecule H_2 for the ground state [71]. It is possible to use the same method for the calculation of the admixture of the state H^+…H^-. Let’s consider the hypothetical, but every important in the applications method of a small difference between those term, that is, the case of a small value of the ionization potential. All the integrals and symbols are taken from [71].

The wave function of the ground state has a form:

$${}^1\hat{O}_1=1/(2)^{1/2}[\Psi_a(1)\Psi_b(2)+\Psi_a(2)\Psi_b(1)]=\Psi_1 \quad (69)$$

and symmetrical (singlet) wave function of the charge transfer term:

$${}^1\hat{O}_2=1/(2)^{1/2}[\Psi_a^-(1,2)\Psi_b^+ + \Psi_a^{+\Psi}{}_b^-(1,2)]=\Psi_2 \quad (70)$$

In principle it is possible to solve the whole task with the help of a standard variational method, but I am interested in just one term of the interaction between Ψ_1 and Ψ_2. For that purpose I rewrite the wave function in a form:

$\Psi_1=1/(2)^{1/2}[\Psi_a(1)\Psi_b(2)+\Psi_a(2)\Psi_b(1)]$; $\Psi_2=1/(2)^{1/2}[\Psi_a(1)\Psi_a(2)+\Psi_b(2)\Psi_b(1)]$ (71)

where $\Psi_a(1)$ means, that 1st electron is situated on the atom a; $\Psi_a(2)$ – that 2nd electron is situated on the atom a etc.

Let's calculate the interaction term H_{12}:

$H_{12}=\int 1/2(\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1))\hat{H}(\Psi_a(1)\Psi_a(2) +\Psi_b(1)\Psi_b(2))\, dV_{12} =1/2 \int [(\Psi_a(1)\Psi_b(2)\hat{H}\Psi_a(1)\Psi_a(2) + \Psi_a(2)\Psi_b(1)\hat{H}\Psi_a(1)\Psi_a(2) + \Psi_a(1)\Psi_b(2)\hat{H}\Psi_b(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)\hat{H}\Psi_b(1)\Psi_b(2)]dV_{12}$ (72)

Then, taking into the consideration, that the Hamiltonian is equal:

$\hat{H} =\hat{p}_1^2/(2m) + \hat{p}_2^2/(2m) – e^2/r_{a1} – e^2/r_{a2} – e^2/r_{b2} + e^2/r_{12} + e^2/R_{ab}$ (73)

I obtain (the symbols of the integrals are omitted):

$\Psi_a(1)\Psi_a(2)\hat{H}\Psi_a(1)\Psi_b(2)=\Psi_a(1)\Psi_a(2)(\hat{p}_1^2/(2m) + \hat{p}_2^2/(2m) – e^2/r_{a1} – e^2/r_{a2} – e^2/r_{b2} + e^2/r_{12} + e^2/R_{ab})\Psi_a(1)\Psi_b(2)=S_{ab}E_H + \Psi_a(1)\Psi_a(2)E_{H\Psi\,a}(1)\Psi_b(2) + \Psi_a(1)\Psi_a(2)(-e^2/r_{ab})\Psi_a(1)\Psi_b(2) +\Psi_a(1)\Psi_a(2)(-e^2/r_{b1})\Psi_a(1)\Psi_b(2) +\Psi_a(1)\Psi_a(2)(e^2/r_{12})\Psi_a(1)\Psi_b(2) + \Psi_a(1)\Psi_a(2)(e^2/R_{ab})\Psi_a(1)\Psi_b(2) = S_{ab}E_H+ S_{ab}E_H + K + JS_{ab} +(e^2/R_{ab})S_{ab}+ \Psi_a(1)\Psi_a(2)(e^2/r_{12})\Psi_a(1)\Psi_b(2)$ (74)

where $K=\Psi_a(2)(-e^2/r_{a2})\Psi_b(2)$ – exchange term for the molecule H_2^+ (see [71]) $J=\Psi_a(1)(-e^2/r_{b1})\Psi_a(1)$ – Coulomb term for the molecule H_2^+ (see [71]), the symbols are taken from [71], S_{ab} – transition integral.

Let's calculate the second part of the sum:

$\Psi_a(1)\Psi_a(2)\hat{H}\Psi_a(2)\Psi_b(1)=\Psi_a(1)\Psi_a(2)(\hat{p}_1^2/(2m) + \hat{p}_2^2/(2m) – e^2/r_{a1} – e^2/r_{a2} – e^2/r_{b2} + e^2/r_{12} + e^2/R_{ab})\Psi_a(2)\Psi_b(1)= S_{ab}E_H+ S_{ab}E_H + K + JS_{ab} +(e^2/R_{ab})S_{ab}+ \Psi_a(1)\Psi_a(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)$ (75)

Let's calculate the third element of the sum:

$\Psi_b(1)\Psi_b(2)\hat{H}\Psi_a(1)\Psi_b(2)=\Psi_b(1)\Psi_b(2)(\hat{p}_1^2/(2m) + \hat{p}_2^2/(2m) – e^2/r_{a1} – e^2/r_{a2} – e^2/r_{b2} + e^2/r_{12} + e^2/R_{ab})\Psi_a(1)\Psi_b(2)= S_{ab}E_H+ S_{ab}E_H + K + JS_{ab} +(e^2/R_{ab})S_{ab}+ \Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(1)\Psi_b(2)$ (76)

Let's calculate in an analogous way the fourth element of the sum:

$\Psi_b(1)\Psi_b(2)\hat{H}\Psi_a(2)\Psi_b(1)=\Psi_a(1)\Psi_a(2)(\hat{p}_1^2/(2m)+\hat{p}_2^2/(2m)-e^2/r_{a1}-e^2/r_{a2}-e^2/r_{b2}+e^2/r_{12}+e^2/R_{ab})\Psi_a(2)\Psi_b(1)=S_{ab}E_H+S_{ab}E_H+K+JS_{ab}+(e^2/R_{ab})S_{ab}+\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)$ (77)

The final element is equal to:

$H_{12}=2[2S_{ab}E_H+K+S_{ab}J+(e^2/R_{ab})S_{ab}+\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)]$ (78)

since it is possible to show, that the last elements in all sums are equal.

The origin of a multiple 2 before the sum in a square brackets is as follows. Since there is a symmetrical case, in reality it will be two regions of the interaction near the left atom a and near the right atom b. It will always be valid for the pair of two equivalent radicals. But for the nonsymmetrical, more general case such an interaction zone will be just one – near the atom or the molecule of a donor. In the real case it will be, of course, a pair of them, but the second term, what is responsible for the interaction with the electron on a donor, does not play any role for the ground state (according to Mulliken's theory, it corresponds to the excited complex with the charge transfer). Therefore, in the reality it is necessary to write:

$$H_{12}=H^1_{12}+H^2_{12} \quad (79)$$

and in the general case, when the donor and the acceptor are determined clearly:

$H^1_{12}=2S_{ab}E_H+K+S_{ab}J+(e^2/R_{ab})S_{ab}+\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)$ (80)

with the very high accuracy.

Let's consider first the last term:

$$\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1) \quad (81)$$

For the hydrogen molecule, created from two atoms of the hydrogen, as a wave function Ψ the wave function of 1S electronic state may be considered, namely:

$\Psi_a(1)=\pi^{-1/2}a_o^{-3/2}\exp(-r_{a1}/a_o)$ $\Psi_b(2)=\pi^{-1/2}a_o^{-3/2}\exp(-r_{b2}/a_o)$ $\Psi_a(2)=\pi^{-1/2}a_o^{-3/2}\exp(-r_{a2}/a_o)$

$\Psi_b(1)=\pi^{-1/2}a_o^{-3/2}\exp(-r_{b1}/a_o)$ (82)

Then, we have: term of a kind $\Psi_a(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)$ have been calculated in [71] and determined as J'. Since, as it will be shown below the term $\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)$ is not the largest in the sum for H_{12}, it is possible to write:

$\Psi_b(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)=\Psi_a(1)\Psi_b(2)(e^2/r_{12})\Psi_a(2)\Psi_b(1)\cdot[\Psi_b(1)/\Psi_a(1)]$ (83)

But the last ratio is equal to $\exp[(r_{a1}-r_{b1})/a_o] \sim \exp(-R_{ab}/a_o)=Const$, then all the integrals are written in [71] and it is possible to find:

$H_{12} \sim 2S_{ab}E_H + K + S_{ab}J + e^2/R_{ab} + \exp(-R_{ab}/a_o)J'$ (84)

Finally, I have ($D=R_{ab}/a_o$, R_{ab} – the distance between a and b; a_o-the Bohr's constant, all the symbols are taken from [71]):

$H_{12} \sim 2e^{-D}(1+D+[1/3]D^2)\cdot E_H - [e^2/a_o]e^{-D}(1+D) + e^{-D}(1+D+[1/3]D^2)(e^2/(Da_o))[1- e^{-2D}(1+D)] + (e^2/R_{ab})e^{-D}(1+D+[1/3]D^2) + e^{-D}[(e^2/a_o)(1/D-e^{-2D}(D+11/8+3/4D+1/6D2)]=e^{-D}(2E_H+2E_HD+2/3E_HD^2-De^2/a_o + e^2/a_o +e^2/R_{ab}) + e^{-3D}[\ldots] +\ldots$ (85)

The asymptotic will be determined by the term e^{-D}. Using values: E_H=13,6 eV, e^2/a_o=27,21 eV, $a_o=5,292\cdot10^{-11}$ m=0,5292 Å, we receive $H_{12} \sim e^{-D}(2\cdot13,6 +2/3(R_{ab}/a_o)^2\cdot13,6 +27,21 + 27,21\cdot a_o/R_{ab})$ (86)

The data on the dependence H_{12} from R_{ab} are placed in Table 10.

Table 10.

The relation between the interatomic distance in the molecule H_2 and the interaction term between the singlet state and the charge transfer state.

R_{ab}, Å	H_{12}, eV
2	4,38
3	1,218
4	0,303
5	0,0691
6	0,01478
7	0,0030096
8	0,0005909
10	0,000021002

The second approach consists in the usage of the Malliken theory in order to determine the value of V_{12} for the different values of the distances between the components of a complex and to use the law e^{-D} for the long distances between the molecules or the radicals in the complex (since, undoubtedly, it is this law, determined by the overlapping of the wave functions, will take place for all molecules, not just for the pair $H^+\ldots H^-$).

In book [68] the data are outlined for the complexes calculations $I_2{\cdot}C_6H_6$ (H_{12}=-0,57 eV, r=3,5 Å) and $(CH_3)_3N{\cdot}I_2$ (H_{12}=-1,82 eV, r=2,37 Å). In addition, in papers [72] the data are outlined for a large number of the charge transfer complexes and, using the formulas [73]:

$b/a=-(H_{01}-E_oS_{01})/(E_1-E_0)$; $\Delta\ \mu\ /(er)=b^2+abS_{01}$; $a^2+2abS_{01}+b^2=1$; $\Delta\ H_o=[(E_1-E_0)(1+(b^*/a^*)^2 + (b/a)^2]/[a^2(1+(a/b)S_{01})(1+(b^*/a^*)^2+(b/a)^2]=(E_1-E_0)/[a^2(1+(a/b)S_{01}]$

$b/a=(H_{01}-E_0S_{01})/[\Delta\ H_0(a^2(1+(a/b)S_{01})]$; $b/a{\cdot}\Delta\ H_0 - a^2(1+(a/b)S_{01})=H_{01}-E_0S_{01}$ (87)

from that equations:

$H_{01}=(a/b){\cdot}\Delta\ H_0(b^2+abS_{01})+E_0S_{01}=ab\Delta\ H_0(1+(a/b)S_{01})$ (88)

symbols see [73], in particular H_{01} – the interaction term, $\Delta\ H_0$ – the enthalpy of the complex production [72,73], S_{01} - the transition integral, E_0 – the energy of the ground term, a and b the coefficients, that are responsible for the presence of the ground and the admixture of the charge transfer state, respectively.

For the simplification of the calculations let's consider just the complexes with the long distances between the molecules or the radicals, so that E_o is taken to be equal to 0 [68], S_{01}=0,1 [68], and all the other data taken from [72,73]and quantum chemical calculations using GAUSSIAN program. The data received shows, that for the complex $I_2{\cdot}(C_6H_5)O$ with r=5,9 Å, H_{12} ~ -0,07 eV and for the complex $BF_3.(CH_3)_2O$ with r=4,2 Å, H_{12} ~ -0,3 eV. Therefore, with the help of all the data received it is possible to obtain the following estimations, summarized in the Table 11.

Table 11.

The value of the term, that is responsible for the interaction between the ground state and the charge transfer state for some of the donor-acceptor complexes.

R_{ab}, Å	$\lvert H_{21}\rvert$, eV
2,37	1,82
3,5	0,57
4,2	0,3
5,9	0,07

It is interesting to note, that the sign of the term H_{12} does not have any influence, since in the formulas for the repulsion of those terms that term enters as a square $(H_{12})^2$. In the reality the sign of the corresponding term in the molecule $H^+ \ldots H^-$

might be positive, what does not contradict to the negative sign for the complicated molecules, since at calculation of $H^+ \ldots H^-$ just 1S functions of H-atoms were considered. In both cases two methods give similar estimations for $|H_{21}|$ depending on the distance.

The values of the term $|H_{21}|$ has a crucial meaning for understanding of the possibility of the triboelectrization of the dielectrics. The idea is that even for two interacting radicals, where the value $\Delta E = I - E_a$ is already quite small (see higher), it occurs to be equal for example, for the pair:

CH_3-CH_2-$CH^{\cdot}$-CH_2-CH_3 ($R_1^{\cdot}$) + CH_3-C(O)-NH-CH(CH_3)-$^{\cdot}$C(OH)-NH-CH(CH_2SH)-C(O)-CH_3 ($R_2^{\cdot}$) (89)

to the value ~ 630 kJ/mol (=6,53 eV), see [20], what is almost unattainable for any mechanochemistry. In reality it is necessary to take into the consideration, that in the solid state this value should be 2-3 eV lower [74,75] because of the fact, that in the solid state the effective value of ε changes strongly with the distance and it is necessary to take into the consideration the influence of the nearby molecules, but even for the value ΔE=4,53 eV in the point r=3,2 Å, I receive the value $|V_{12}|$ ~0,5-1 eV, and the distance between the levels in the point of the maximal approaching ~2$|V_{12}|$ ~1-2 eV, the value, that may be overcome with the help of the mechanochemistry (as it is known, the bond with the energy ~ 1 eV might be in principle ruptured with the high probability [75]). Namely, at sliding apart of two dielectrics (increase of r in Fig.31) it will take place the jump (according to Landau-Zeener formula [70] or through the activation mechanism) onto the higher level (charge transfer state) and separation of the charges will occur (triboelectrization).

Therefore, the mechanism outlined of the charges generation at triboelectrization overcome at least the most strong, energetic barriers onto the mechanogeneration of the free charges through the production of a radical pair of association:

$$A + DH \rightarrow A^+ + DH^- \ (\Delta H \text{ – high, ~ 1000 kJ/mol}) \quad (90)$$

$$A + DH \rightarrow AH^{\cdot} + D^{\cdot} \ (\Delta H \sim 100 \text{ kJ/mol}) \rightarrow [AH^+ \ldots D^-] \ (\Delta H \sim 100 \text{ kJ/mol}) \rightarrow$$

$$\{\text{double electric layer}\} \rightarrow AH^+ + D^- \ (\text{mechanical separation of the double electric layer}) \quad (91)$$

It is interesting to note, how the mechanism proposed is in accordance, from one point, with the theory of a double electric layer, proposed by Helmholtz [14], and, from another point, the dynamic of a grow of the energy from $2V_{12}$ to ΔE (for several eV), is in a good accordance with the theory of the adhesion layer, proposed by academician Deryagin [76], the main postulate of which is the fact, that for the adhesion of the two surfaces the electrostatic forces are responsible.

In the proposed subchapter a new conception of the fact, how the explanation of the appearance of the radical pair of association because of the admixture of a charge transfer state may help to understand the phenomenon of the triboelectrization of the dielectrics, if one of them has a donor and another – an acceptor nature.

It is necessary to remember, that the so-called dangling bonds on the surface are considered by the physics as generating the so-called Tamm's levels. Those levels for the crystals with strong covalent bonds (like Ge, Si, diamond)are situated somewhere in a gap between the valence band and the conduction band and may, in principle, be responsible for triboelectrization of the solid dielectrics. The problem of the appearance of the energy level with E=0 exactly in the middle of the gap between the conduction band and the valence band is described in [78]. For the simplest case of the molecular orbitals (sp-hybridization) interaction in [78] it is written, how in addition to energy levels +/-β (in the limit of band width $\Delta \rightarrow 0$) one more level with energy E=0 in the center appears. For the case of the band width nonequal to zero in [78] some calculations are made, but the principle is the same – some energy levels in the middle of the gap start to exist. According to Fig.30, the level of the radical is exactly in the middle of the gap. In reality in [78] the levels might be shifted by some interactions, and, as it follows from my explanations, the levels are not exactly in the middle of the gap, but again the theory of physics [78] and the theory of chemists (my own, for example) roughly coincide – the levels in the middle of the gap are because of the defects (and they may be responsible for the triboelectrization).

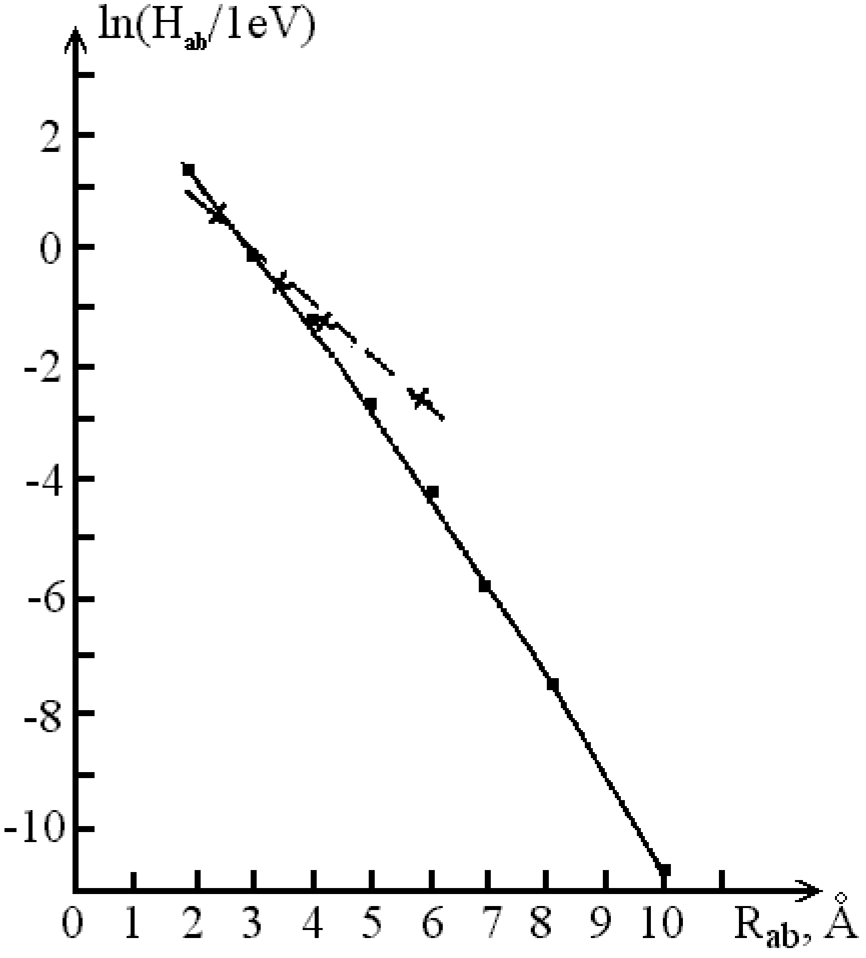
VII Charge transfer inside the complex between two radicals.

As it was proved higher, in the complex the charge should overcome the barrier in ~ 1 eV for the suitable distance between the radicals in the complex, what is definitely below the difference between the ionization potential and the electron affinity. The stronger acceptor properties of the radical generated, the easier for it to withdraw the electron from the second radical, the large the distance between the radicals in the complex and therefore, the smaller the value $2H_{12}$ (see Tables 10 and 11), the separation between the levels. But still it is necessary to remember about that value – it should be overcame and it is positive, that is, the reaction is thermodynamically unprofitable. In Fig.32 the logarithm of the value $H_{12}=V_{12}$, expressed in eV versus the distance between the radicals, expressed in $\mathring{A}$ is shown. For example, for the case considered here (paraffin + keratin), using formula (63) and taking the energy difference between the ground term and the charge transfer term to be equal to 4,53 eV, I obtained r=3,18 $\mathring{A}$ and H_{12}=0,67 eV, separation between the levels in the point of the maximal approaching is $2H_{12}$ ~ 129 kJ/mol.

How it is possible to overcome that value? A consistent approach should be to apply again the mechanochemical rule, that this energy can in principle be overcame due to the distortion in energy created by the crystal lattice field. The only difference is that at any distortion the charge transfer level should be higher then the ground level and the value H_{12} probably does not change very much at distortion. It might be possible, nevertheless, that ionization potential changes greatly at stress (as it was proved for polymers [29]), thus alleviating the charge transfer path. Indeed, even sonochemistry can alleviate charge transfer path compare to SN_2 mechanism due to some mechanical energy [56,57].

But some other mechanisms also can work in this case, and I conducted the theoretical estimation of their possibility. Since there is a movement of one radical with respect to another in the vicinity of the terms intersection, Landau-Zeener problem can be applied [70]. Another possibility is the straightforward electron transfer due to thermal activation (according to Arrhenius law $k_o\exp(-E/RT)$, where k_o – the collision rate of pairs of the radicals, E – activation energy).

Fig.32 Dependence of H_{12} from distance.



A very interesting question is: even if the electron is transferred by any of the mechanisms described onto the charge-transfer level (see Fig.31), how is it possible for it to hold there for a time span enough for the couple of the just generated ions to be separated for a large enough distance? The following estimation shows, that this is possible. It is a well known fact, that the energy transferred onto the electronically excited state (for example, in the case of the fluorescence process) is hold onto the excited state for 10^{-8} s. Now it is possible to estimate, how far is the ions separation for that time. I measured the relative velocity of sliding of one surface in a friction pair with respect to another as equal to 1,4 m/s (the mean velocity). In reality the velocity changes approximately according to the law $v=A\sin(\omega t)$, and A should be $\pi/2$ times higher then the averaged velocity, actually $|A|$. Therefore, I assume the velocity as changing according to the law $v=2{,}2\mathrm{Sin}(\omega t)$. It is necessary to mention here, that, according to the modern understanding of the process, taking place in the vicinity of the surfaces of the friction pair, sound waves are excited onto the surface of those friction surfaces, thus leading to much higher relative velocities of the molecules one with respect to another. Actually it will be discussed later, together with self-oscillations (auto-oscillations, stick-slip phenomenon). But even 2.2 m/s gives the free charges separation of $2.2\cdot 10^{-8}=220\ \mathring{A}$, what is impossible to reach by backward electron tunneling process [84].

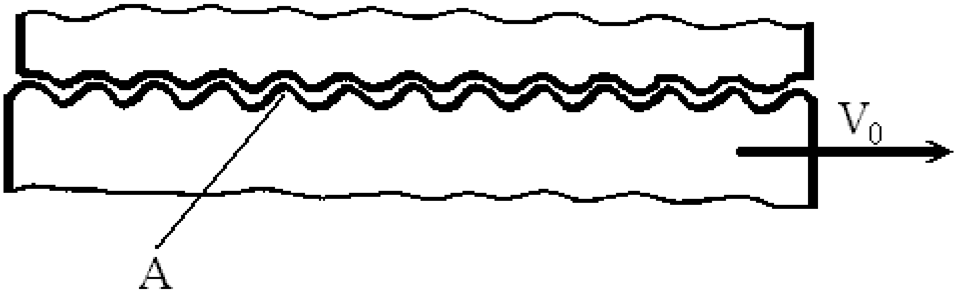


Fig.33 The schematic representation of the friction surfaces.

A very complicated problem to be solved in order to find the answer to the question about the possible way of the free charges generation is how much is the relative velocity of the molecules on the surface (molecules on one surface versus the molecules on another surface) with the possibility of the self-oscillations process and the sound waves on the surface. In order to do it, it is necessary to consider the maximal possible velocity of the molecules that are participating in the process of the generation of the sound waves in the parts, that are to relax after the end of the stress. In a few words, the process of the relaxation with the subsequent sound waves generation and self-oscillations is as follows: At the beginning after the stress relaxation of every small contact region (say A in Fig.33) in that small region sound waves are excited on the surface of that region, and the velocity of that waves is equal to V_2 (velocity of sound of the longitude waves). Actually along the surface of the friction pair also self-oscillations are inevitable with some frequency ν_o (usually in the range 600 Hz – 5000 Hz [80]). So the overall velocity of the molecules is described by the equation:

$$V=V_o\mathrm{Sin}(\Omega t) + A_{1\omega_1}\mathrm{Sin}(\omega_1 t) + A_{2\omega_2}\mathrm{Sin}(\omega_2 t) \qquad (92)$$

here V_o stands for the sliding velocity (measured by the experimentalist, V_o=2,2 m/s in our case, Ω is around 12,6 – the frequency is around 2 Hz, A_1 – the amplitude of the self-oscillations with some frequency around ω_2 ~5 kHz (stick-slip phenomenon) and A_2 – the oscillations with the frequencies, corresponding to the frequencies, presented in the sound waves (up to Debye frequency). The last reveals itself in the relaxation of a small, but still macroscopic region, named A in Fig.33.

How much is the amplitude of the oscillations of each type? Estimation of the maximal possible displacement of the molecules in the sound wave onto the surface is as follows - I estimate it as the displacement in the case of melting of the solid (paraffin in my case). Exactly in the case of melting that displacement should take place. It is known, that in Debye model there is a limitation onto the frequency of phonon oscillations, equal to:

$$\hbar\omega_m=k_{B\theta} \qquad (93)$$

If the one-dimensional model of the lattice is considered, then it is possible to obtain:

$$\omega(f)=2\sqrt{k/M}\,\left|\,\mathrm{Sin}(fa/2)\right| \qquad (94)$$

The maximal frequency is equal to:

$$\omega_m=2(k/M)^{1/2}\Rightarrow k=(1/4)M\omega^2_m=(1/4)M(k\theta/\hbar)^2$$

If the melting temperature $T_m>T_D$ (Debye temperature) I obtained: for 1 degree of freedom the energy is $k_BT_m/2$. Then:

$$K_BT_m/2=kx^2/2\Rightarrow x=[(k_BT_m)/k]^{1/2}(\hbar/k_{B\theta})=2\hbar/(k_{B\theta})=[2\hbar/\theta][T_m/(k_BM)]^{1/2} \qquad (95)$$

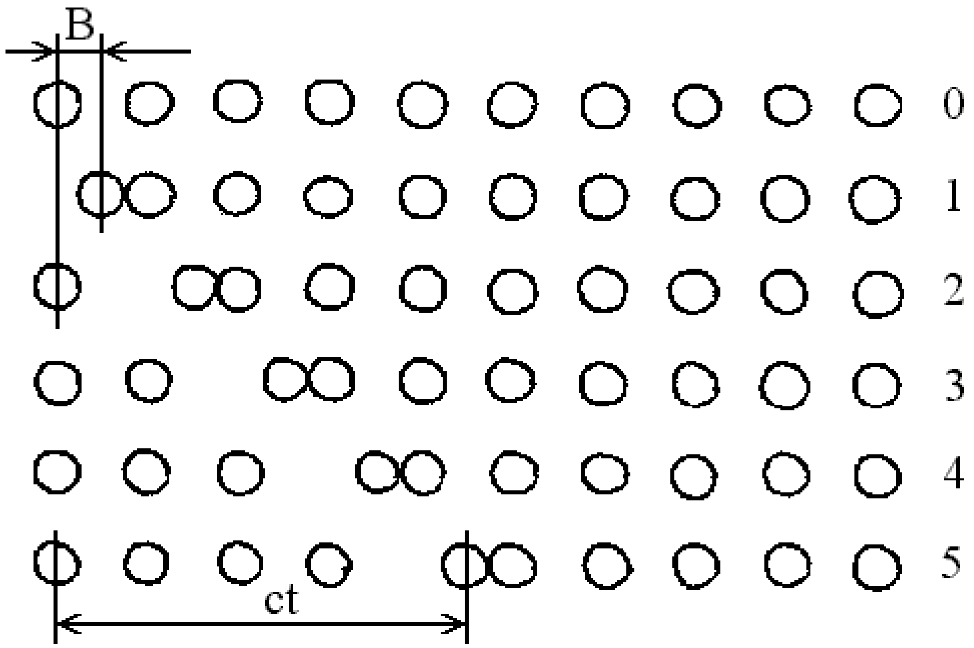


Fig.34

The scheme of the sound wave propagation.

For the organic solid I obtained (θ =150-300K), Tm=400 K, $M=4{,}73\cdot10^{-25}$ kg, $x=0{,}07338$ Å, and if the crystal lattice parameter a=6 Å, x/a=0,01223.

I consider this value of the displacement (mean displacement) as reached at the upper layer of the paraffin because of the melting (or quasimelting) of the lattice (at least in the upper layer) during the friction of a pair of two dielectrics.

Now it is time to calculate the maximal velocity of the molecules due to the relaxation of the macroscopic parts of the body (sound waves on the surface). In Fig.34 the process of the propagation of the sound wave in one-dimensional lattice is shown for several time periods starting from zero. The value B demonstrates the maximal possible amplitude of the molecules oscillations due to sound waves. It is equal to the intermolecular distance (I considered the waves with the shortest possible wavelength, equal to the molecular separation). Then the velocity is equal to:

$$V=(A\sin(\omega t))'=A\omega \operatorname{Sin}(\omega t)=A2\pi \nu \operatorname{Sin}(\omega t)=2\pi\, 0{,}01223a\nu \operatorname{Sin}(\omega t)=0{,}0768c_2\operatorname{Sin}(\omega t) \quad (96)$$

(since the maximal value of A is equal to 0,01223 from (95)).

In [81] the value of the longitude waves in polyethylene was published. It is equal to 1950 m/s. Thus the maximal value of the velocity of the molecules one with respect to another is equal to: V_{max}=150 m/s (around 100 times higher, then the velocity of sliding).

Now it is possible to estimate a collision rate of pairs of both radicals, what should lead to the chemical reaction of generation of a pair of ions. From the above estimations it is follows, that the number of free radicals generated for 1 s exceeds the amount of free charges: $1,2\cdot 10^{19}/4\cdot 10^{13}=3\cdot 10^{5}$ times. For estimations I considered $3\cdot 10^{5} – 1\cdot 10^{7}$. The surface radicals concentration is $1,6\cdot 10^{10}\cdot(3\cdot 10^{5} – 1\cdot 10^{7}) \sim 4,8\cdot 10^{15} – 1,6\cdot 10^{17}$. It means, that if the sliding takes place in one direction, the real amount of radicals every certain radical encounters is equal to the ratio of the effective surface, covered by the radical during the sliding divided 1 cm^2. That is, if one radical has an effective distance of the reaction (capture cross section) around 1 Å , the effective velocity of 150 m/s the covered surface for 1 s is equal to $150\cdot 10^{-10}=1,5\cdot 10^{-8}$ m^2 and the ratio of the surfaces for 1 cm^2 is $1.5\cdot 10^{-4}$. Therefore, every radical meets $N_1=4,8\cdot 10^{15} – 1,6\cdot 10^{17})\cdot 1,5\cdot 10^{-4}=7,2\cdot 10^{11} – 3,8\cdot 10^{13}$ radicals. Now, taking into the consideration the activation energy as equal to 129 kJ/mol, I obtained: $N=(3,5\cdot 10^{27} – 3,8\cdot 10^{30})\exp(-129000/[8,31\cdot 300])=1,2\cdot 10^{5} – 1,3\cdot 10^{8}$ $1/[cm^2\cdot s]$. Now, since, the rate of the free charges generated is known (free charges per second), it is possible to obtain the stationary concentration (from equation (10)) as the value P/a. The constant of free charges decay is taken from Table 1 as $1/\langle P_2\rangle$ (it is necessary to remember, that in Table 1 the number of stirrings is considered and the time between the stirrings is 3 s, that is $\tau = P_2\cdot 3=3,102$ s. Then stationary concentration is: $3,6\cdot 10^{5} – 4,9\cdot 10^{8}$ 1/s. This value is in principle not enough for the explanation of the generated charges, but since I prove the possibility to reduce activation energy due to the matrix effects, this explanation (together with the influence of the mechanochemistry) is suitable. In reality, of course, free radicals are distributed onto the layer of a finite depth of the surface of the solid dielectric, and therefore, the collision rate of pairs seems to be overestimated. Despite the diffusion rate in a paraffin is very small, it is that value, that allows to consider the volume estimations, not the surface one.

The reaction path of a radical during strike I consider as a thread of a length of 150 m (the effective velocity) and the capture cross section is to be estimated. From (63) I found the distance of the terms intersection is 3,18 Å (for a pair paraffin-keratin) and capture cross section is $S=\pi r^2=31,8$ Å^2 $=3,18\cdot 10^{-19}$ m^2. Therefore, the effective volume of the reaction is $4,77\cdot 10^{-17}$ m^3. Since the free radicals are distributed in a layer of approximately $l=(Dt)^{1/2} \sim (1\cdot 10^{-10}\ cm^2/s\cdot 3\ s)^{1/2}=1,73\cdot 10^{-5}$ cm. The free radicals is in an amount of $4,8\cdot 10^{15} – 1,6\cdot 10^{17}$ are distributed, therefore, in a volume of $1,73\cdot 10^{-5}$ cm^3 (the volume of the reaction). The ratio of the effective volume to the volume of the reaction is: $3,18\cdot 10^{-19}\cdot 10^{6}/1,73\cdot 10^{-5}=1,84\cdot 10^{-8}$ and every radical meets $8,8\cdot 10^{7} – 2,9\cdot 10^{9}$ radicals, what is 10^4 times lower then the upper estimation, what should lead for the final case of the free charges to $3,6\cdot 10^{1} – 4,9\cdot 10^{4}$ $1/cm^2$ not enough without matrix effect, that lowers the activation energy.

Since the free radicals move one with respect to another, it is also possible to consider Landau-Zeener problem in order to find the effective constant. Instead of $\exp(-E_a/RT)$ I should use the formula [70]:

$$P_{12} \sim \exp(-[\pi (\Delta U_{min})^2]/[2\hbar\ V_{r\Delta} F]) \qquad (97)$$

here ΔU_{min} is the minimal separation between the levels (see Fig.31), V_r – relative velocity of the interacting radicals, ΔF is the influence $\partial U/\partial r$ in the point of intersection for the diabatic terms. Since from (63) it is follows, that:

$$E=0=C_1-e^2/[4\pi \varepsilon_o r] \quad (98)$$

Here $C_1=\Delta V\infty$ - the difference between the charge transfer state and the ground state in the case of the infinite separation between the terms. For the case of the friction pair paraffin-keratin $\Delta V\infty$ =4,53 eV=$7{,}258 \cdot 10^{-19}$ J. For the force I received:

$$F=\partial U/\partial r=e^2/[4\pi \varepsilon_o r^2]=e^{2|} {}^{\Delta}V\infty|^2(4\pi \varepsilon_o)^2/[4\pi \varepsilon_o e^4]=|\Delta V\infty|^2(4\pi \varepsilon_o)/e^2 \quad (99)$$

The difference ΔF will be equal to the same value (the ground level is considered to be flat, F=0. Therefore, $\Delta F=|\Delta V\infty|^2(4\pi \varepsilon_o)/e^2$. The value Δ Umin=1,34 eV=$2{,}144 \cdot 10^{-19}$ J and taking V_r=150 m/s, I obtained:

$$P_{12} \sim \exp(-2001) \sim 0 \quad (100)$$

Therefore, Landau-Zeener process in this case is impossible. But, if the $|\Delta V\infty|$ = 3 eV, then $|\Delta U_{min}|$ =0.0821 eV, and $P_{12} \sim \exp(-17{,}12)$ and the probability, according to Landau-Zeener is much larger then the value $\exp(-E_a/RT) \sim \exp(-51{,}74)$. Therefore, despite in the present case this idea is definitely out of the question, it should work at lower ionization potential of the donor.

One more interesting idea, that should be considered. The relative velocities of those radicals are 300 m/s. Then the energy released in the impact is $(m_1+m_2)V^2/2$, where m expressed in kg/mol. For the pair in (57) I obtained: $E=(72+225) \cdot 10^{-3} (300)^2/2=13{,}4$ kJ/mol, that is, quite a considerable energy, that should be subtracted from 129 kJ/mol in order to obtain the true estimation of the energy splitting between the levels in the interaction point.

The time of the interaction is $2 \cdot 10^{-12}$ s (for the velocity of 150 m/s, the distance of the effective interaction is ~ 3 Å . This is too small to establish any thermodynamic equilibrium and, therefore, in the real live Arrhenius formula $k_o\exp(-E/RT)$ is applicable for crude estimations only.

That's why I mentioned both monomolecular (43) and bimolecular (45) mechanisms of the charge generation. According to experimental data, second order is obtained and this is in agreement with the time of the interaction. I obtained 10^{-12} s – hardly possible to expect the complex generation during such a short time. Such a short time of the real interaction also allows to consider the lattice as a rigid one and therefore, more mechanochemistry ideas applicable. Those estimations shows, that mechanochemistry is between the molecular beam and usual chemistry for the time of the interaction of the molecules. More probably, that again matrix influence should be considered as responsible for the chemical reaction of the charges generation from the radicals.

As far as the mechanism, outlined in [24] is concerned, in principle, it is possible, but the proof of that mechanism, outlined in [24] – generation of $TCNE^-$ anion radical as the result of the reaction between the mechanoanion and TCNE is incorrect. The authors considered the reaction between the TCNE and polymer as in a liquid, but in reality, as it was shown for similar reagents in mechanochemistry [82,83], just charge transfer complexes are generated and as the result TCNE- is observed. It is generated not because of the reaction between the anion-radical and TCNE, but because of the reaction between the initial compounds. I think, that for both donor and acceptor surfaces in triboelectricity the key role belongs to free radicals.

VIII Mechanochemical theory of triboelectrization of the ionic compounds.

It is a well known fact, that in chemistry of the ionic compounds usually the proton transfer or OH^--group transfer takes place. According to this conception and assuming, that for the interaction of the ionic compounds the ions transfer might be more easier then the free radicals (because of the strong polarity of the interacting solids), it is possible to try to classify those dielectrics, that are capable to give or accept H^+ or OH^- according to acid-base principle.

In [8] it is described, that the plates from the material that has a neutral reaction are charged positively by the powders of the organic acids and negatively by the base dyes (acceptors of proton), and also by such bases as amidol (2,4-diaminophenol dihydrochloride), metol, and inorganic bases $Ba(OH)_2$, NaOH. The glass is almost all the time is charged positively, but some strong bases charge it negatively (again acceptors of the proton). Sulphur, that has an acid reaction (donor of the proton) usually is charged negatively, just the organic acids (benzoic, salicylic) give it the positive charge.

Therefore, it is possible to suppose, that at friction of a pair of the compounds one of them is necessary to consider as a donor of H^+ or acceptor of OH^- and another – acceptor of H^+ or donor of OH^-. According to the process that predominates, the compounds, charged positively can: accept H^+ or give OH^- and the compound, charged negatively: accept OH^- or give H^+.

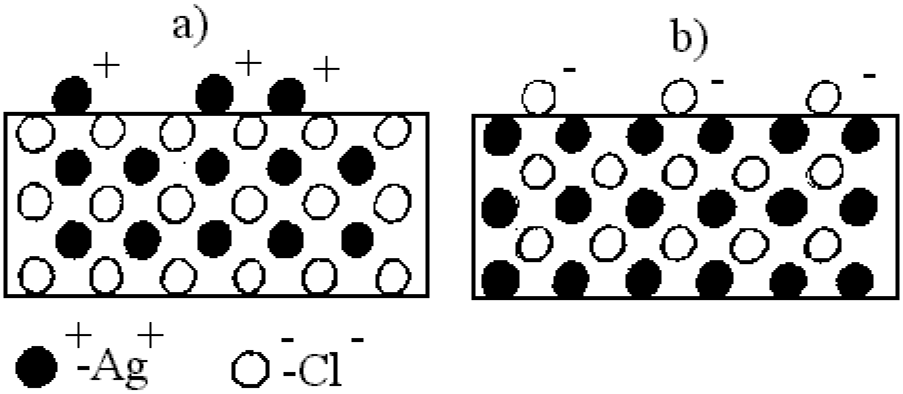
For example, bases give OH- and charged positively, acids give H+ and charged negatively. The known fact, that strong bases at friction with glass give the negative charge, might be attributed, I think, to the following chain of the reactions:

$$NaOH + Na_2SiO_3 \rightarrow Na^+ + OH^- + Na_2SiO_3 \rightarrow Na^+ + NaOH + NaSiO_3^- \quad (101)$$

that is, as the result of the bond rupture $Na\ldots SiO_3\text{-}Na$ it will be the positive charge onto NaOH (bulk) and negative – onto glass and some compound (OH^-) will be transferred onto glass.

In reality it should be a complicated chemistry between the ionic compounds, that might lead to the reaction, similar to present in the polar solvents. This is not contradict to the usual understanding of mechanochemistry – the radicals generation is more profitable, then the ions generation. At first, the strong crystal lattice in the place of the contact is an ionic one and according to [26] it might be even stronger polar lattice, then the water – dissociation will be onto ions due to the polar environment. And also, according to Fig.31, the ionic path is very unprofitable onto the long distances (in infinity, since e^2/r is a very slow function with distance). Usually the reaction products and reagents are within a cage 2-3 Å and that term (e^2/r) is definitely far from the maximal value.

Fig.36 The scheme of charging of colloids.



This idea is very close to the idea, described in [4], how the colloid particles are charging. The colloid particle of the ionic compound, say AgCl, can be charged positively if it is placed into the solution of $AgNO_3$. In this case Ag^+ ions finish building the lattice of AgCl (see Fig.35a), thus charging the colloid particle positively. If the same colloid particle is placed into the solution of NaCl, Cl^- ions also build the crystal lattice of the AgCl, charging it negatively (see Fig.35b). I think, that the same process can take place in the case of the triboelectrization of the ionic compounds (like (101)), but it is conducted mechanochemically.

IX Decay of the triboelectric charge for the case of the solid dielectrics.

The triboelectric charge, generated onto the surface of the solid dielectrics is unstable and tends to decay with time. What is the time dependence of that decay? From the usual consideration it should be an exponential law (exp(-kt)). In the simplest case of the surface onto the air the potential is $\varphi = 0 + q/\varepsilon r$, that is, voltage $U = \alpha q$, where n is the number of the electrons and then for the constant air resistance R it is possible to obtain: $I = U/R$, $dq/dt = -\alpha q/R = -\beta q$. From that equation it is possible to receive the exponential law $q = q_o \exp(-\beta t)$, that is, the first order of the reaction.

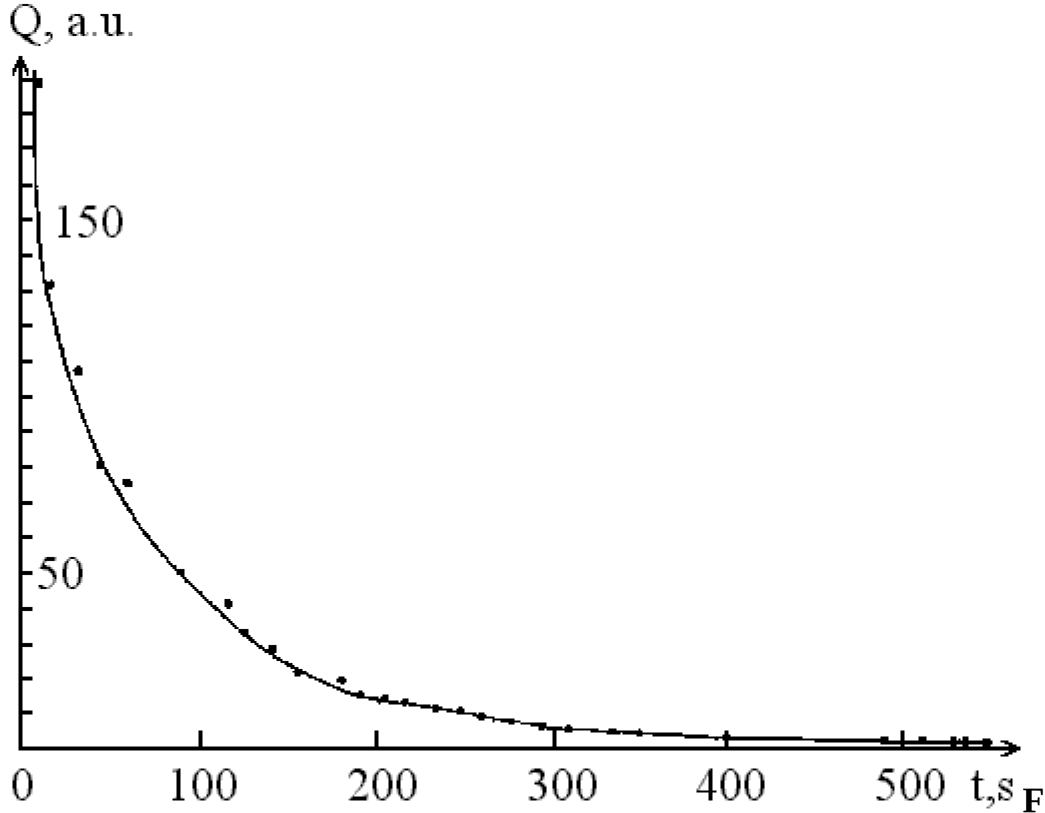


Fig.36

The decay curve of the triboelectric charge.

The real experimental curve is shown in Fig.36. At measurement of this curve I used the sensing unit (the charge is nonimpregnated paraffin and the electric field was calculated with the help of formula (13) for nonpoint charges). I tried to simulate this curve with the help of the different laws. Exponential decay does not work properly. I tried to use the following idea. From [1] it is known that for the decay of the triboelectric charge the ions in the air are responsible. I investigated the decay of the negative charge on the air. It decays due to the inevitable presence of the positive ions in the air, which strike the surface. In reality the negative charges has some activation energy to be overcame for the recombination process. Those activation energies are different for the different sites and the distribution over the activation energies should be applied. For the rectangular distribution the decay law is logarithmic [84]. No such curves were observed. It was established, that the best fit was done by the curve:

$$q=1/(a+bt) \quad (102)$$

what corresponds to the second order kinetic curve:

$$dq/dt=-bq^2 \quad (103)$$

I investigated just decay of the negative charge (positive charge decay is too quick for my experimental setup). Due to presence of the positive ions in the air when an additional flow is created (by heat-gun) the decay is much faster. At T=17,5 °C without additional flow from the heat-gun (in this flow due to the presence of the red-hot heater a big amount of positive ions is present, so the discharge is much faster) the kinetic parameters obtained were (for (102)): a=0,00082+/-0,00004; b=0,00022+/-0,00001. For less time of stirring before the experiment: a=0,00181+/-0,00007; b=0,00028+/-0,00001.

In the experiment, when the flow from the heat-gun was used: a=0,00002+/-0,00003; b=0,00067+/-0,00002 (a great increase in b value is present).

For another type of paraffin (yellowish one) the results are summarized in the Table 12.

Table 12

The kinetic parameters of the negative charge decay onto the impregnated and nonimpregnated paraffin (T=12 °C).

Impregnant	a	b, s^{-1}
None	0,00106 +/-0,00003	$0{,}00023 +/- 7 \cdot 10^{-6}$
I_2 (sample A)	0,00742	0,01084
I_2 (sample A)	0,001604	0,01847
I_2 (sample A)	0,0027	0,01947
I_2 (1 year of keeping)	0,00256	0,00946
I_2 (1 month of keeping)	0,03028	0,00082
Aminoanthraquinone	0,00115	0,0003
Lignin	0,00112	0,00035
$Ni_3(PO_4)_2$	0,00202+/-0,00007	$0{,}00022 +/- 9{,}8 \cdot 10^{-6}$
$CoSO_4$	0,00131+/-0,00004	$0{,}00019 +/- 6{,}6 \cdot 10^{-6}$

In the case of the impregnation by I_2 the increase of b value is two orders of magnitude, this is enough for the explanation of the decay of the charge but it does not depend upon the concentration (see also Table 1). From Table 1 it follows that time of charge decay is something like 3 s, while in my equipment in the air it also around 3-5 s for sample A. Nevertheless, for another one (1 month of keeping), taken from the same set as in Table 1, the time of the charge decay (2.718 times) was found to be equal to 66 seconds (like for nonimpregnated paraffin and impregnated by some indifferent to radicals stuff). For one more sample (1 year of keeping) the time decay is again small, but the value of a is high, what means, that the iodine is evaporated from the near surface layer. The increase in b value for impregnated by I_2 samples is present, but probably, the mechanisms are different for decay in contact and in the air. I think, that (sample A) was too much doped and actually this is the charge onto the crystalline iodine (the crystal of the iodine itself is also charged negatively with the similar time decay). But I am sure, that the inevitable presence of I_2 vapor near the surface alleviates somehow the charge decay due to the positive ions in the air – I_2 molecules might be ionized very easily, for example.

I found in the literature [85,86] some experimental curves, made by more modern equipment of charge decay in the air. In both cases I made the simulation of the experimental data by myself, using the published curves. I found the same law 1/(a+bt) as the best fit, contrary to expected exponential decay.

How is it possible to explain the kinetic law (103)? It should be this law if the charges are generated by the discharge in the air (both positive and negative), say $A^+ \ldots B^-$. Then the recombination step is $A^+ + B^- \rightarrow AB$ and the kinetic law is :

$$d[A^+]/dt=-k[A^+][B^-]=-kq^2$$

since from charge conservation law $[A^+]=[B^-]$.

But I used to investigate the discharge of the charged solid in the air. From the usual consideration it follows, that it should be exponential law, not the law (103). In reality the distortion of the concentration of the ions in the air near the surface of the dielectric takes place (they are attracted by the charged dielectric) and it is possible to show, that near the surface of the dielectric: $n=n_o\exp(-e\varphi/kT)$ (in more general case $\exp(-B\varphi/D)$, B-mobility, D-diffusion coefficient, φ -potential of the surface) I obtained: for the charged surface $E=\sigma/(2\varepsilon_o)$, and then:

$$n=n_o\exp(-eEx/(kT))=n_o\exp(-enx/(2\varepsilon_o kT))=n_o\exp(-\alpha q) \quad (104)$$

Then I have:

$$\int dq/[q\cdot\exp(-\alpha q)]= - \int kn_o dt \quad (105)$$

This is the so-called exponential integral and in [87] it is outlined:

$$Ei(x)=\int_{-\infty}^{x}[e^t/t]dt = -\int_{-x}^{\infty}[e^{-t}/t]dt \sim [e^{-x}/x](1-1!/x+2!/x^2-3!/x^3+\ldots)\ x\rightarrow\infty \quad (107)$$

Using (107), I obtained:

$$\int [(e^{-\alpha q})/q]dq=-\int [(e^{-\alpha q})/q]dq \sim [\exp(-\alpha q)]/\alpha q=kn_o t \quad (108)$$

If $\exp(-\alpha q)\sim 1-\alpha q$, then $1/[\alpha q]=kn_o t$ – the necessary dependence.

Another possibility for the nonlinear dependence (the second order of the reaction) is the secondary electron emission. In order to ionize the gas, an electron should obtain on its way the energy, no less then the ionization energy of the molecule, that is, for 10 eV and electric field of 10^6 V/m it should be 10^{-5} m, but the mean free path is (at normal pressure) $\lambda = 1/(\sqrt{2}\ n\sigma) = 0{,}707/(2.69 \cdot 10^{19} \cdot 7{,}548 \cdot 10^{-16}) = 3{,}48 \cdot 10^{-5}$ cm – much less then it is necessary to reach 10 eV and the process of that type at normal pressure and small electric field is impossible.

Chapter 3. Electrization, induced by phase transitions.

According to numerous most modern publications, there should be a connection between the charge transfer (not merely dielectrics, but also some liquids) and phase transitions [88]. Indeed, at phase transitions (some of them) the energy is released. According to the general rules of the nature (like Gauss law), this energy release can not be represented just by one process, with one certain energy, for example, just heating. Some energy should accumulate via some molecular mechanisms (like in nonequilibrium thermodynamic) and lead to accumulation of the energy, enough for the electron or ion transfer, what should lead to triboelectrization. But what are those molecular mechanisms?

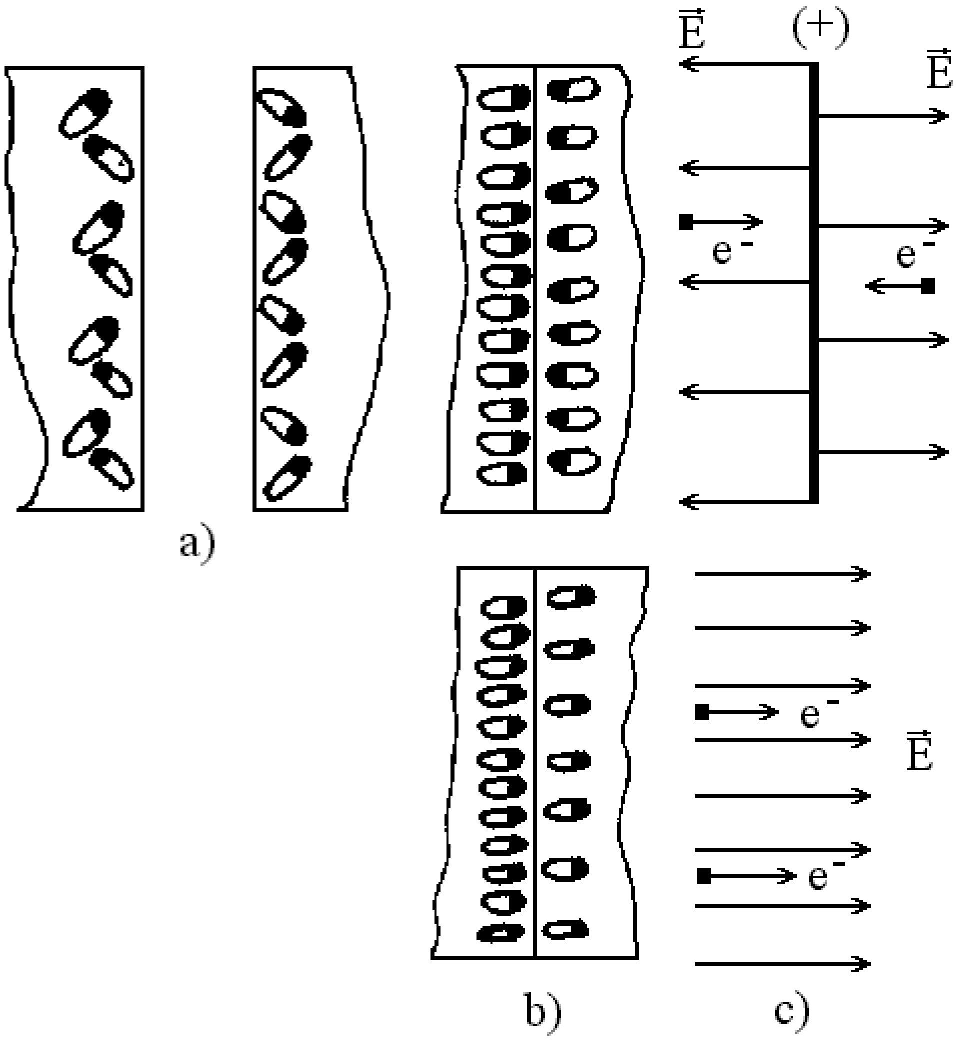


Fig.37

The scheme of electrization due to contact orientation (see text).

In order to understand it, I considered the idea of segnetoelectricity. In the case of certain polymers, when they are placed in a strong electric field, the orientation of the electric dipoles take place, thus leading to the after cooling to the freeze of the permanent electric field [1]. In this case the first step is the outer electric field an the second step is orientation of the molecules (or parts of the molecules, not just polar groups of the molecules). If the first step is orientation of the molecules by some molecular forces, so that the dipoles are oriented, then the electric field appears as the result of this orientation. If that field is strong enough, all the defects in the vicinity of say 100 Å with low ionization potential (including, for example, mechanochemically generated radicals and the radicals, generated by other methods) are ionized, thus leading to the charge separation.

This is presented schematically in Fig.37. At the first moment (a in Fig.37) two different materials have an inherent orientation of the dipoles and no permanent electric field is possible. At contact the orientation or even position of the molecules in near surface layer changes (it might be even generation of a new phase). In some cases (more or less in any case) because of the outer energy (mechanical energy) the dipoles are oriented by some molecular forces (if this process is most profitable from the point of view of the crystal lattice or quasicrystal lattice in the solid state) and thus the orientation is so (Fig.37 b upper or lower scheme) that it is equivalent to the presence of the electric charge (positive one in the upper scheme in Fig.37 c) or to the permanent electric field (lower scheme in Fig.37 c). In both cases, if the field is strong enough, the electron leaves the defects, trying to compensate the permanent field, and the charge separation, profitable in the present case because of the thermodynamic reasons, takes place. After the separation of the initial compounds the dipoles are back, but the transferred charge remains.

I called this mechanism due to the phase transition since in this case the rearrangement of the molecules in the place of the contact takes place (like in a real phase transition), thus leading to electrization.

It is necessary to emphasize, that unlike segnetoelectricity (another mechanism, that induces the electric field) the charge separation is a different mechanism. In the case of the segnetoelectricity the ions exhibit displacements from their permanent positions due to the action of the external stress and the permanent electric field appears (like an orientation of the dipoles). But the charge is not transferred, unless the defects are ionized. Exactly the same mechanism is responsible for mechanoelectrets, when certain polymer is influenced by a strong pressure, sometimes combined with shearing deformation. For example, in [89] investigation of the electric charge appearance at deformation of the polymers is described. Some polymers, consisted from the polar monomers (polymethylmethacrylate and polycarbonate) give mechanoelectrets at pressing. The electric field appears because of the mechanically induced orientation of the polar groups, the field is hold for something like 1 year at 20 ^{o}C. Activation energy of backward process is 9-21 kJ/mol. Here is the difference between the electrization induced by the phase transition and the mechanoelectrets – in the case of the electrization the charge decayed for something like minutes or even seconds.

The mechanoelectrets are possible to generate just in very polar polymers. Probably for polymers like paraffin this is impossible. And the mechanism of the charge transfer due to the phase transition, outlined in Fig.37 is probably also possible just for the case of very polar compounds. The problem is as follows. As a rule of thumb it is accepted, that the longest possible distance of the electron tunneling in the solids is around 100Å . The electron tunneling is the only possibility to conduct charge transfer according to Fig.37. Therefore, the electric field, induced by polar groups should be stronger then E>I/2, where I is the ionization potential. Even for distorted molecules or radicals in the solid state it is no less then 3-4 eV and as the result $E>3 \div 4 \cdot 10^8$ V/m – very high intensity. I estimated this value in real compounds in the following way. Polarization is equal to [1]:

$$\underline{P}=\sum N\mu \quad (109)$$

here N – amount of the molecules in the unit volume, μ - electric dipole moment of the molecule.

The electric field inside the uniformly polarized ball is equal to [1]:

$$\underline{E}= - (4\pi /3)\underline{P}\cdot 1/(4\pi \varepsilon_o)=[1/(3\varepsilon_o)]N\mu \qquad (110)$$

(it is necessary to remember that 1 D= $1/3\cdot 10^{-29}$ C·m). The calculated electric fields are summarized in Table 13.

Table 13.

The electric field inside the ball of the fully oriented polar molecules.

Compound	μ , D	E, V/m
Methylmethacrylate CH_2=CH-C(O)-O-CH_3	2	$4,2\cdot 10^8$
Polyethylene	0,08	$1,68\cdot 10^7$
Keratin	0,6-1,6	$\sim 3\cdot 10^8$

As it is possible to see, may be, just for very polar dielectrics this is possible.

But this mechanism should easily work for the conducting polymers or low-molecular weight organic compounds (an ionic conductivity, in the case of electronic conductivity Fermi-level appears and band theory is applicable). In this case the energy I ~ 0 and even very weak electric field induces charge transfer.

I considered water. The mechanism of water charging is a well known one and it is described, for example, in [90]. For the drop of the water the structure is as follows – the polar molecules in the near-surface layer of the drop are oriented in such a way, that the positively charged parts of the molecules are oriented inside and the negative one –

outside, that’s why near the surface of the water the double electric layer is formed. Inside the layer the field is pointed outside, outside the layer the field is absent. The potential inside the drop is higher, then in a surrounding media for $\Delta \varphi = 0{,}26$ V. Inside the drop H^+ and OH^- ions are present (because of the high dissociation ability of water) and as the result, the drop gives H+ (actually H_3O^+ or $H_5O_2^+$), thus obtaining negative charge. This process lasts before the end of the potential difference $\Delta \varphi$ between the near-surface layer and the bulk of the liquid, as it is demonstrated by the thermodynamic equilibrium conditions. The number of the positive charges is equal to $N=4\pi \varepsilon_{o\Delta \varphi} \cdot r/e$, here r- the radius of a drop. At $r=10^{-4}$ cm N~200 [90].

I tried to calculate starting from 1 till macroscopic N number (here N – number of molecules in a drop) the change of energy what is necessary for the charge separation in a water molecule. The calculations were performed with the help of the semiempirical methods AM1, MINDO3, MNDO, PM3 with the help of GAUSSIAN program [34]. The reactions were considered:

$$(H_2O)_N \rightarrow H_5O_2^+ + H_{2N-5}O_{N-2} \text{ (cluster)} \qquad (111)$$

The data obtained are reflected in Fig.38 as a curve 1 (upper part of a curve). Unfortunately, the calculations were possible to conduct just for a small number of the molecules N in the cluster). Assuming that the energy of the dissociation of the water molecule in the macroscopic drop onto H+ and OH- is negligibly small, I neglected it and I considered just the energy of the electrostatic ions separation:

$$\Delta H + CU^2/2=[1/(4\pi \varepsilon_o)]e^2/R \qquad (112)$$

here ΔH – the energy, necessary for the ions separation ($H_5O_2^+$ and the negatively charged drop into the infinity), R – the diameter of the drop, C – capacitance of the double layer of the water drop, $C=4\pi \varepsilon_o R$, $U=\Delta \varphi$ - potential of the double electric layer.

$$\Delta H + 4\pi \varepsilon_o R(\Delta \varphi)^2/2=[1/(4\pi \varepsilon_o)]e^2/R \ (113)$$

Therefore:

$$\Delta H=[1/(4\pi \varepsilon_o)]e^2/R-2\pi \varepsilon_o R(\Delta \varphi)^2 \ (114)$$

Since for a spherical drop:

$$(4\pi /3)R^3=(1/\rho)(N/N_a)M \ (115)$$

where R – the radius, ρ - density, M – molecular weight, $N_a=6{,}02 \cdot 10^{23}$.

I obtained:

$$\Delta H=721{,}2/(N)^{1/3} - 0{,}4357(N)^{1/3} \text{ (kJ/mol)} \ (116)$$

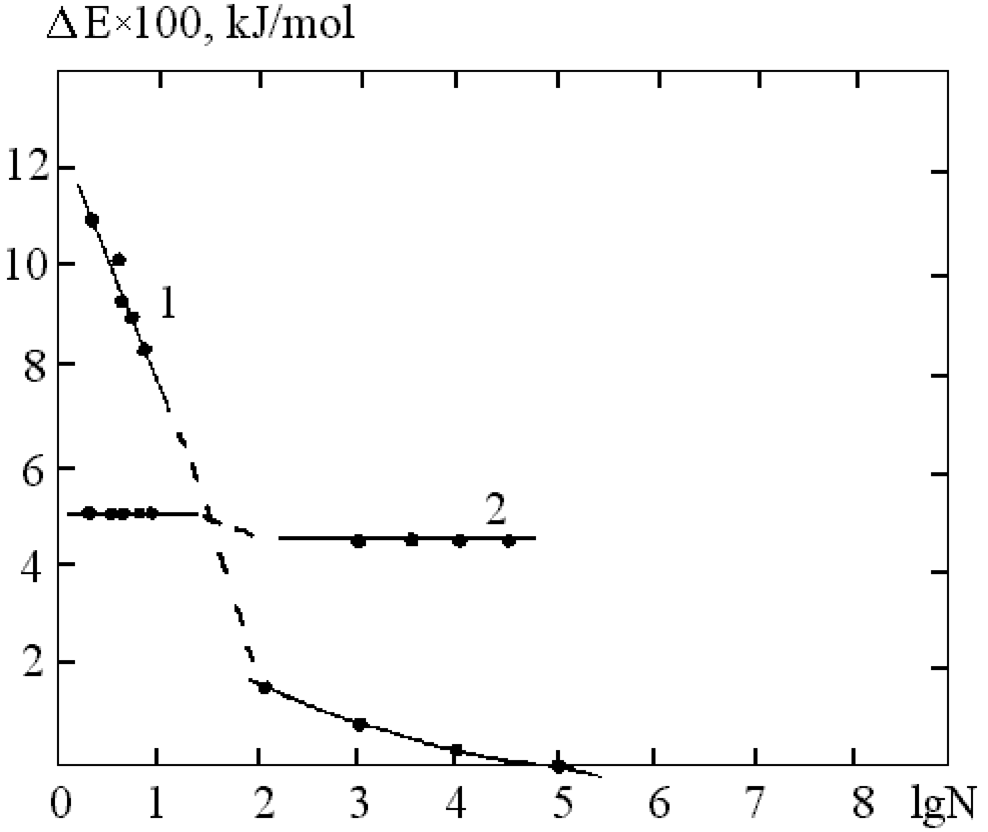


Fig.38

Energy dependence of the ionic bond rupture (1) and the radical bond rupture (2) in water.

This is shown as a lower part of the curve 1 in Fig.38. The higher and the lower parts of the curve 1 are connected by a dashed line, demonstrating schematically how it looks like in the intermediate region. From the upper part of the curve 1 it is possible to see, that even for a very small cluster the energy of dissociation drops very quickly as the value N increases and for very large number N the collective phenomenon of the dipole interaction makes charging of the water almost inevitable.

The curve 2 in Fig.38 demonstrates the theoretical calculations of the disruption of the water molecule onto a couple of the free radicals:

$$(H_2O)_N \rightarrow R_1^{\cdot} + R_2^{\cdot} \quad (117)$$

From the curve 2 it is possible to see, that this process almost does not depend upon the number of the molecules in the drop. Despite the energy of the free radicals production is much smaller for small N then the energy of the separation onto the ions, it does not depend strongly on N and therefore, the process, similar to the mechanochemical one (the next step – the electron transfer between the radicals) for the water is impossible. But the process (117) might be responsible for the free radicals generation in a water, since it is known, that at moving of the water through the thing capillaries [91] the generation of H_2O_2 takes place.

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