Electric phenomena on the rupturing of adhesive contact and failure of solids: development stages from gas discharge to cold nuclear fusion

Yu.A. Khrustalev

Institute of Physical Chemistry of the Russian Academy of Sciences, Leninsky prospect 31, Moscow 117915, Russian Federation

Abstract

A brief review is presented of the development of work carried out mainly by Derjaguin and co-workers since the end of the 1940s concerning electrophysical phenomena accompanying the rupture of the adhesive bond and the failure of solids under mechanical loads (e.g. the electrical charging of fresh surfaces and gas discharge processes due to the excess charges, and the emission of electrons and X-rays, as well as cold nuclear fusion). A correlation between the electron emission phenomenon and mechano-chemical processes in solids is noted.

Keywords: Adhesive contact rupture; cold nuclear fusion; electrical phenomena; failure of solids; gas discharge.

Boris Vladimirovich Derjaguin is the originator of a new direction in the study of the surfaces of solids. Together with N.A. Krotova and V.V. Karasev, he discovered in 1952 the phenomenon of the emission of high energy electrons (EHEEs) from mechanically formed fresh surfaces of solids on rupturing of the adhesive contact or the failure of the solids in a vacuum. Thus Derjaguin's scientific school was born and has gained strength.

Experimental and theoretical studies, carried out over about half a century, of the formation of an electric double layer (EDL) on the adhesive contact interface and the consequences of its failure enabled an electronic concept concerning the strength of an adhesive joint to be formulated. The theory developed by Derjaguin and Smilga has become a fundamental theory for examining adhesion and especially electroadhesive phenomena.

When the adhesive contact is broken, and solids undergo failure under a mechanical load, X-ray emission and cold nuclear fusion were found to occur. A correlation between the EHEEs and mechanical transformations was established. The theses of tens of candidates and a number of doctoral dissertations have been concerned with the detailed examination of separate problems in that field of surface phenomena. Since 1968, symposia on mechano-emission and the mechano-chemistry of solids have been held regularly, with the participation of foreign scientists and specialists.

The present paper is a brief review of the origin and the development by Derjaguin and scientists of his school of investigations of electrophysical phenomena in adhesion and the failure of solids, which have been carried out mainly at the Institute of Physical Chemistry of the USSR Academy of Sciences. Many investigations have been performed, based on the ideas of Derjaguin, and with his support and advice.

In the 1940s, Derjaguin and Krotova carried out the first studies of electrical phenomena observed

during the tearing off of a polymer film from a substrate. They detected the electrical charging of surfaces after the tearing-off of a number of polymeric films from metal and glass [1]. The high values of the work of adhesion (A) (up to 10^5 erg cm^{-2}) obtained in the experiments proved to be higher by two orders of magnitude than the energy of a chemical bond. It was shown that the values of A calculated for the polymer peeling from the substrate mainly correspond to the true work of tear-off, and a correction for the work of deformation is not essential. The authors suggested the concept of an electric component of adhesion [1] in accordance with which, on the tearing-off of the films, the new surfaces are electrified by opposite charges as a result of the separation of the plates of a molecular EDL. After the tear-off the charge density σ increases with the tearing-off velocity v. At high values of v there is an observed glow visible in darkness accompanied by a sound effect (a so-called crackling) which is characteristic of a discharge. Applying the model of the plane capacitor discharge and assuming that σ does not have enough time to decrease greatly owing to its conductivity, it is possible to represent the specific work A_0 due to the tearing-off of the polymer film, by the following expression:

$$A_0 = \frac{2\pi\sigma_0^2}{D}h = \frac{\sigma_0 V}{2} \qquad \text{erg cm}^{-2} \qquad (1)$$

where σ_0 is the initial electric charge density, h is the distance (cm) at which (on average) a discharge occurs, D is the dielectric permittivity of the medium (for air, $D=1$), and V is the discharge potential

$$(V/h = 4\pi\sigma \text{ is the potential gradient}). \qquad (2)$$

The experiments confirmed the significance of electrical forces in adhesion. It was found that the well-known law of similarity for the Paschen gas discharge is applicable also in the case of the tearing-off of the polymer film from the substrate, i.e. there exists a dependence of the work of tearing-off on the pressure of the ambient medium.

Two main conclusions follow from the concept of the electric component of adhesion.

(1) The electric component of the adhesion of solid films is due to the electrostatic attraction of EDL charges (of a microcapacitor) formed on the film–support interface.

(2) The tearing-off of the film from the substrate in the range of high tearing-off velocities ($v = 1$ cm s^{-1}) represents a drawing apart of the microcapacitor plates until a gas discharge occurs; the process follows the Paschen law (i.e. the dependence of the discharge potential V on the product of the pressure of the gas medium p and the value of the discharge interval h):

$$V = ph \qquad (3)$$

The results of the first experiments relating to the study of electroadhesive phenomena were generalized both in Krotova's doctoral dissertation [2] and in a review [3].

In the 1950s, further investigations of electroadhesive phenomena and, in particular, the properties of the EDL were given impetus by the discovery by Karasev et al. [4] of the emission of electrons during the tearing-off of a polymer film from a glass substrate in a vacuum. The detection of the electron emission thoroughly confirmed the electrical concept of adhesion.

A photographic plate was used for recording the electron emission. If a permanent magnet was placed in the path of electrons behind a slit in a diaphragm, the slit image was blurred on the photographic plate. The radiation was only completely screened by a glass plate 165 μm thick; however, it was partly retained by a thin mica screen (about 2–5 μm thick). On the basis of these experiments, the workers had supposed that electrons were emitted on the tearing-off of the polymer film from the glass substrate. The electrons were able to cause the glass to fluoresce on bombarding it. In accordance with the workers' assessment [5], the energy of the electrons was about 10^3–10^4 eV. It was established that the electrons are emitted not by the whole surface of the torn-

off polymer film but by separate areas of the surface [5] — the so-called emission centres.

They also detected electron emission on cleaving crystals of quartz, Seignette salt, sugar, and on laminating samples of mica and gypsum [6]. In this case, the energy of the electrons amounted to scores of kilo-electron volts, while that for quartz was about 120 keV [6]. In the case of mica, a mosaic pattern of the charging of the new or fresh surface had been observed.

Morozova and Krotova [7] examined the formation of the adhesive bond between two polymers with a view to elucidating the relative role of the electrical and diffusion processes in adhesion. In the case of the interdiffusion of polymers, no influence was noted of the tearing-off velocity v on the adhesion value. If electrical processes taking place on the interface prevail, then the adhesiogram (the dependence of the work of tearing-off (A), the adhesive bond strength, on the velocity, i.e. $\log A = \varphi(\log v)$) exhibits three characteristic areas. Electroadhesion phenomena (e.g. gas discharge, electron emission) are observed at $v \geqslant 0.1$ cm s^{-1}, when charge relaxation on the freshly torn-off surface does not play a noticeable role because of the surface conductivity. In contrast, if $v \leqslant 0.1$ cm s^{-1}, then the charge does practically leak off, and electrical phenomena are not recorded.

The electrons are emitted by the negatively charged surface of the torn-off polymer film. Yet the positively charged substrate (e.g. glass, metal) does not exhibit any emission. In the case of the cohesive type of tearing off, when the cohesive work is smaller than that of adhesion, no emission was recorded, nor was there a residual charge on the surfaces that had been drawn apart [7].

Morozova and Krotova [7] also noted the influence of the nature of fillers in rubber on the electrical phenomena when the polymer film was torn off from the rubber: if carbon black was used as a filler, then the surfaces that had been drawn apart showed no emission or charge. However, if kaolin was used as a filler, the electrical phenomena were observed to a considerable degree.

The electron emission continued for some time after the polymer film had been torn off from the glass or metal substrate. The mechanical treatment of the metal enhanced the adhesion of the polymer and the emission intensity [8].

By the end of the 1950s, Smilga and Derjaguin had developed the concept of the electrostatic component of adhesion [9–13]. In the formation of an EDL on model systems, one of the contacting bodies is an electron donor, while another is an electron acceptor. The authors had a problem in clarifying the general qualitative characteristics and evaluating the possible role of the EDL in the adhesion phenomenon. It was shown that the charge density and the electrostatic component of the adhesive force can attain very large values and can play a determining part in the phenomenon of adhesion of solids. Thus the electrostatic component of the adhesion force was calculated for semiconductors with any zone structure and an arbitrary spectrum of surface states [12,13]. The role of the surface properties in the formation of an EDL in adhesion was determined and the donor–acceptor chemical bond was phenomenologically considered while taking into account the influence of the functional chemical groups — electron donors and acceptors [11–13]. The role of the tunnel effect was assessed in the destruction of the EDL on the tearing-off of the polymer film from the substrate [13].

Theoretical developments by Smilga and Derjaguin indicated a novel method for developing the examination of electroadhesive phenomena, first for the experimental substantiation of the main statements following from the concept of the electrostatic component of the adhesive force. In particular, it was necessary to substantiate the essential possibility of controlling the adhesive strength of different contacting bodies by selecting corresponding surface functional groups (donors and acceptors) for the polymer and the substrate, including a method of chemical modification of the surfaces. The formation of an EDL is due to the redistribution of the electron density, and hence of the charge between the contacting surfaces. In fact, the more distinct is the donor–acceptor char-

acter of the adhesive bond, the stronger on the macroscopic scale must appear the electrostatic component of the adhesive interaction of solids. However, if the chemical bond is almost homopolar or covalent, then the electrostatic component is of small significance [13].

Here, it would be appropriate to emphasize that if interdiffusion of contacting polymers occurs then the interface is blurred. In this case, there is no sense in referring to adhesion as being a result of the intermolecular interactions of surfaces of different natures; electrical phenomena occurring on the separation of components having a blurred interface are not recorded at all [14].

The following important fact should be noted: Morozova [15] assessed the chemical activities of the freshly torn-off surfaces according to their ability to cause the grafted polymerization of a gaseous polymer (acrylonitrile). Infrared spectra demonstrated that such an activity is proportional to the emission from the fresh surface.

At the beginning of the 1960s, work in the field of electroadhesive phenomena mainly concerned experimental confirmation of the theoretical concepts of Smilga and Derjaguin. The work [14,16] examined adhesive couples of the types metal semiconductor, polymer–semiconductor, polymer–glass and polymer–polymer. A universal AZS-1 grade adhesiometer was designed; the instrument enabled one to determine the work of tear-off at a preset tearing velocity, the specific tear-off stress, and the mechanical properties of the materials being joined. It was established that the number of surface states of a semiconductor, which are characterized by the lifetime of the carriers, plays an important role in the adhesive interaction of a metal–semiconductor couple. For a polymer–glass system, the formation of an adhesive bond is due to the existence of hydrogen bonds between the hydroxyl groups of the glass skeleton and the functional polymer groups. The breaking of the hydrogen bonds leads to the electrical charging of the failure surfaces, the polymer having a negative charge while the glass has a positive charge.

One of the problems arising from the theory of

the electrostatic component of adhesion resides in the direct proof of the formation of an EDL on the polymer film–substrate interface. For this purpose, the choice of the field-effect method proved to be advantageous, this effect being applied for the first time by Sokolina et al. to the treatment of the polymer–semiconductor system [17]. The method essentially consists of recording a change in the surface conductivity of a semiconductor as a result of the adsorption of gases, vapours and solutions when a transverse electric field with an intensity of about 10^5–10^6 V cm^{-1} is superimposed on a sample. The contact between the semiconductor and the polymer (a film from the solution) may be considered to be the origin of a defect on the substrate surface, leading to alterations of the semiconductor surface states.

Also examined was the influence of the nature and concentration of the functional groups of a polymer contacting with the surface of a germanium single crystal on the electrophysical characteristics of the semiconductor, the latter being determined by applying the field-effect method [13,16,17]. The experimental results showed that on applying the films (from solutions), depending on the nature of the functional groups of the polymer, the charge as entrapped by the surface states of germanium (Q_0) changes (in the control sample, $Q_0 = -2.5 \cdot 10^{-9}$ C cm^{-2}; in the sample with a polystyrene film, $Q_0 = -0.6 \cdot 10^{-9}$ C cm^{-2}; in the sample with a perchlorovinyl film, $Q_0 = +3.8 \cdot 10^{-9}$ C cm^{-2}).

A change in Q_0 after the application of a polymer film on the germanium surface is evidence of the appearance of new levels, changing the conductivity of the semiconductor. Comparing the data on the charging of the surface for a control sample with that for the surface coated with a polymer film, it is possible to state whether the polymer is an electron donor or an electron acceptor. In other words, an EDL charge is formed on the interface already in the process of providing an adhesive bond of the polymer with the substrate (semiconductor). The destruction of an EDL leads to the charging of the fresh surfaces on the violation of

the adhesive bond, a change in the germanium conductivity, and the appearance of electron emission during the peeling-off of the polymer film [13].

Reference [18] indicates the primary significance of the rate of loading of an adhesive joint: it predetermines the character of failure (either on the interface or inside the polymer) and, consequently, the adhesive strength and the electrical phenomena.

A new stage in the development of systematic and thorough investigations of the emission phenomena had begun when Polyakov and Krotova had applied, as an electron detector, a secondary electron multiplier (SEM) of the open type [19] instead of the earlier photosensitive plates (or films) or fluorescent screens which allowed only the fixing of the electron emission. There now arose the possibility of obtaining quantitative characteristics of the electrons emitted on the failure of the adhesive joints and the solids themselves. The principle of operation of the SEM is based on the phenomenon of secondary electron emission. The SEM can be used in the regime of counting separate pulses with a high amplification coefficient (up to 10^8). Such multipliers are distinguished by good stability under vacuum and a weak dark current; they are also small in size and are convenient for use as electron detectors.

Electron emission of intensity $J \approx 2.5 \cdot 10^4$ pulses s^{-1} and with a time of decay to the background count of about 10 min was recorded by Polyakov and Krotova on the peeling-off of a gutta-percha film from glass. Deformation of the same film in the plastic deformation region is also accompanied by electron emission ($J \leqslant 5 \cdot 10^3$ pulses s^{-1}) which rapidly decays with time t. An extension of a gutta-percha sample to the elastic range is not accompanied by any emission [19].

The regularities of the emission intensity decay obey the exponential equation

$$J = A t^{-b} \tag{4}$$

where the constant A is characteristic of the initial emission intensity (at $t = 0$), while the constant b

determines its decay rate, the constant being associated with the conductivity of an adhesive couple.

Derjaguin et al. [20] had put forward a supposition that the electron emission is a consequence of a gas discharge due to a difference in the potentials applied to the surfaces being drawn apart, taking into account the evolution of gaseous products on the peeling-off of the films from the substrates [21].

These workers [20] showed experimentally that the phenomenon of electron emission is associated with the conductivity of filled rubber peeled off from glass and metal. A high conductivity of the rubber interferes with the achievement of discharge values for the potential difference between the surfaces being separated. The emission in Ref. [20] was recorded by use of the method of exposure to light of a photographic plate, and therefore the emission was only fixed (or was completely absent). The rubber conductivity values were not known either.

A little later, Khrustalev et al. [22] proved the quantitative interrelation of electron emission parameters with the conductivity of filled rubber, from which a polymer film had been peeled off. The conductivity of the rubber was altered by 15 orders of magnitude by adding fillers of different types and properties. It was established that in all the cases the peeling-off of a nairite film from the rubber substrate was accompanied by electron emission. The energy of the electrons was about 40–50 keV. The higher the conductivity of the substrate, the smaller the value of the emission recorded, and the faster it decayed. After-emission was observed for a specific bulk resistance of rubber of 10^{10} Ω cm (up to $4.4 \cdot 10^{15}$ Ω cm). Knowing the value of the work of adhesion ($A = 2.5 \cdot 10^5$ erg cm^{-2}) and the electron velocity (energy) it is possible to evaluate the EDL charge density using Eqn (1): $\sigma = 2A/V = 4 \cdot 10^3$ CGSE. This value is in agreement with that of the theoretical calculation performed by Smilga and Derjaguin [12,13].

The influence of the functional groups of polymers (their donor–acceptor properties) on the provision of an EDL and the density of its charge in the zone of contact with the glass substrate was

investigated by Polyakov and Krotova [23] using a complex adhesiometer within the velocity range 10^{-5}–10^{-2} m s^{-1}. The adhesiometer enabled one to determine simultaneously the strength of an adhesive joint and the parameters of electron emission on the peeling-off of the polymer film from glass at different velocities. A correlation was established between the work of adhesion and the intensity of electron emission on the peeling-off of a polymer film from glass [23] and a semiconductor [24].

The workers [23] supposed that the electron emission is a modification of the autoelectron emission: electrons are emitted from the polymer surface under the effect of the field due to the charge on the fresh surfaces after the destruction of the EDL, distorting the potential barrier and contributing to the appearance of the tunnel effect. In the same field, just the free electrons are accelerated to high energies.

Electroadhesive phenomena are essential not only to the violated extended contacts of solids, but also in the failure of microcontacts, such as, for example, between powder particles and the substrate [25–29]. Thus, the electrostatic character of the adhesive forces and the mechanism of contact charging of particles ($5 \leqslant d \leqslant 30$ μm, where d is the particle size) of electrographic developing polymer powders with fillers and dye-stuffs, after the breaking of their contact with a semiconductor (the failure of the EDL), depend on the parameters of the donor–acceptor interactions of the particles with the substrate [28,29]. The quality of an electrographic image is to a considerable extent determined by the electroadhesive properties of the powder particles. Methods [29] have been suggested for controlling these properties by altering the nature (chemical structure) of and modifying the contact surfaces.

Anisimova [30] continued the investigation of electrical phenomena occurring on the formation and violation of the adhesive contact in the polymer–germanium system, the investigation having been begun by Sokolina et al. [17]. A change in the chemistry of the semiconductor surface through

interaction with alkylchlorosilane vapour was suggested [30] to evaluate the character of the tearing-off in terms of the surface conductivity of germanium–an adhesive (on the interface) or a mixed one (partly throughout the polymer bulk).

The results of the work carried out by Polyakov [24], Anisimova [30] and Sokolina [31] are presented in their respective dissertations.

Polyakov [24] detected a penetrating radiation on the tearing-off of the polymer film from the substrate.

Evdokimov [32], using general ideas on the electrostatic concept of adhesion, suggested a method for the creation and breaking of an adhesive point contact of polymers with dielectrics and metals through the effect of an external electric field. The strength of such an adhesive interaction (the work of adhesion) amounts to about 10^5 erg cm^{-2} and depends on the value of the potential applied, the spacing between the electrodes and the system, the properties of the contacting materials, the state of their surface, time, etc. The adhesive contact is still retained after the removal of an external electric field. The adhesive contact may also be destroyed through an external electric field.

Tyurikova et al. [33] established that radiofrequency radiation occurred on the tearing-off of polymer films from solid substrates as a result of a gas discharge.

Mambetov and Musuraliev [34,35] established a dependence of the intensity of gas-discharge radiation (which is dependent on the nature of the ambient gaseous medium and the pressure of the gas) on the work of adhesion. Mambetov and Knyazeva [36] derived the same dependence in the case of the friction and breaking of the adhesion of modified poly(tetrafluoroethylene) films.

Simakov and Baramboim [37] effected the polymerization of frozen acrylic acid via an electron flux arising from the vibrodispersion of polymers. In this case, any contact between the emitting surface of the polymer particles and the monomers was eliminated. Later, Kapitanchuk [38] calculated theoretically the possibility of a radiation

effect of high energy electrons (HEEs) generated by the destruction of the polymers and the breaking of an adhesive contact between the solids.

The end of the 1960s was significant because in 1968 the First All-Union Symposium on Mechano-emission and Mechano-chemistry of Solids was held with the participation of foreign scientists, the symposium taking place at the time of the Anniversary Colloidal Conference (in Voronezh). This symposium has given rise to the tradition of organizing regular meetings of scientists and experts in the field during almost 25 years. From the very beginning, electrophysical phenomena and chemical transformations during the mechanical treatment of solids have been considered simultaneously. Derjaguin has supervised the organization committees of all the symposia from the first. In the following year (1969), the second symposium was held in Frunze (Kirghizia) with the participation of experts from the German Democratic Republic, Czechoslovakia and Poland. The symposia have attracted the attention of specialists from different research institutes, high schools, and other scientific and industrial collectives — physicists, chemists, mechanical engineers, etc. — to the investigation of electrophysical phenomena and chemical reactions taking place when solids undergo mechanical treatment.

In the 1970s, a major event in the development of the research direction was the publication in 1973 of a book entitled "*Adhesion of Solids*", in which Derjaguin, Krotova and Smilga generalized and analysed work on electroadhesion phenomena in solids [13]. The book was translated into English and published in the USA [39]. It has attracted new research workers to the study of mechano-emission and mechano-chemical processes both in our country and abroad.

In a report presented at the Praesidium of the USSR Academy of Sciences, Derjaguin [40] summarized the results of work performed in the field of electroadhesive phenomena, which underlined the essential difference between the processes of establishing the adhesive contact and the breaking of the contact. A contact is established in a thermo-

dynamically equilibrium manner, yet its breaking is in most cases accompanied by a considerable irreversible dissipation of energy. Of special significance is the investigation of the mechanism of the provision of an EDL on the contacting of different materials including semiconductors and metals, dielectrics and polymers. High values of the surface charges are attributable to a redistribution of the electron density between the contacting donor and acceptor functional groups of both materials. Essentially, the surface groups enter into a hetero-polar chemical bond. Consequently, in Derjaguin's opinion, there is no sense in contrasting chemical mechanisms of adhesion with electrical mechanisms.

In the case of the peeling-off of a non-conducting band, the drawing apart of the EDL plates occurs first at a permanent charge owing to the slowness of its leakage. In this case, the difference between the potentials of the EDL plates increases to some critical value, at which there occurs a gas discharge across the gap formed [40].

Calculations showed that the critical differences in the potentials may amount to thousands of volts, and in a vacuum to tens of thousands of volts. The electroadhesive phenomena enable one to elucidate the dependence of the work of peeling off on the pressure and the type of ambient gas.

Further evidence of the role of electrosurface forces is shown in the HEE phenomenon on the breaking of an adhesive contact in a vacuum. Results of measurements of the maximum energies of the emitted electrons allowed the calculation of the EDL charge density, which coincided with earlier estimates of the charge density obtained by another method (of the order of 10^3 esu cm^{-2} or more) [40].

The emission of high energy electrons (of the order of 10^4 eV) leads to the emission of brake X-rays [41,42]. Kluev and co-workers [43–45] investigated in detail the characteristics of X-rays emitted on the breaking-up of the adhesive contact of diverse systems.

Data were obtained on the energy distribution of HEEs on the breaking-up of adhesion [44,46]

and the failure of solids [47]. Thus the energy of the electrons emitted from a polymer film just torn off from the substrate is close to the electron energy near the monoenergy value. The energy values decrease with time simultaneously with a decrease in the electron flux from 10^4 to $5 \cdot 10^2$ eV, which is explained by a change in the intensity of the electric field of the surface charge on the torn-off polymer film. On the failure of lithium fluoride crystals, for example, the maximum energy of the emitted electrons was about $8.5 \cdot 10^4$ eV [47].

An autoelectron (field) mechanism was suggested for the emission of HEEs [44,48,49] from surface states under the effect of the charge field on a failure surface that had been freshly formed by mechanical means. Here, it is important to emphasize that for the breaking of an adhesive contact and for the failure of solids the HEE parameters (e.g. the flux magnitude, regularities of its decay, the energy, the influence of conductivity etc.) practically coincide [49,49(a)], which is strong evidence for the same nature of the emission.

It should be noted that the electrostatic component of adhesion also appears on the tearing-off of a polymer from a poly(tetrafluoroethylene) surface modified by different functional groups. The existence of an EDL on the interface is substantiated by the emission of HEEs during the failure of such systems [50,51]. Calculated data on the work of adhesion and the EDL charge density are in good agreement with experimental results obtained by Vilensky [50].

Khrustalev et al. [52] detected a long-range action of the EDL when the cohesive failure of one component of a glue–rubber adhesive couple near the interface (up to 100 μm) also led to the emission of HEEs. The cohesive failure of the same materials separately under similar experimental conditions did not lead to electron emission. (Earlier, the emission of HEEs on the cohesive failure of an adhesive joint was not recorded.) The long-range action of the EDL was also noted in Ref. [53].

An EDL usually arises on the contact interface of solids also in the friction process. Derjaguin and Smilga [54] considered this possibility theoreti-

cally, and the role of the electrostatic component of rolling friction was later substantiated experimentally. Gas-discharge and emission phenomena were detected in the friction of dielectrics in a vacuum i.e. glow [55], and the emission of HEEs [56,57] and of X-rays [58].

The emission of HEEs was established in studies on the failure of a series of new substances and materials such as cellulose [59,60], three-dimensional polyesters [61] and multilayer polymer films [62], crystals of alkaline halides [47,63], metal oxides [64], slate [65], polymer composites [66,67], and in the course of crushing coal [68]. The radiation–chemical effect of the emission of HEEs and the correlation between the emission intensity and the mechano-chemical transformations were substantiated experimentally [64,65,69–74].

During this decade, five symposia on mechano-emission and mechano-chemistry of solids were held, namely, the third (in 1971) and the sixth (1977) in Berlin, the fourth in Irkutsk (1973), the fifth in Tallin (1975), and the seventh in Tashkent (1979). Derjaguin actively contributed to the organization and the proceedings of the symposia on a high scientific level; a large number of participants were from former Soviet and foreign organizations and scientific institutions.

In the 1980s, attention was mainly focused on the investigation of the X-rays that were observed to be emitted on the breaking-up of an adhesive contact and the failure of solids. Workers [75] established by using an electron-probe microanalyser that the energy of the X-ray photons may amount to about 70 keV on the peeling-off of a polymer film from an aluminium substrate and the lamination of mica, the maximum on the distribution curve being located at 10 keV. This result proves that in the zone of a developing crack there exists an electron flux having a wide range of energies (up to 100 keV), with their maximum possessing an energy of the order of 10 keV. In accordance with the X-ray yield, the magnitude of the primary electron flux in a growing crack was estimated to be about 10^{12} pulses s^{-1}. This exceeds

by 7–8 orders of magnitude the value of the electron flux recorded in the experiment on the breaking process of an adhesive bond [75]. Theoretical calculations carried out by Molotsky [76] resulted in values of about 10^{21} electrons $s^{-1} cm^{-2}$ for the electron flux in a crack for ionic crystals. (The after-emission from the fresh failure surface corresponds to the true electron flux without the emission of secondary radiation [44].)

Later [77], the following mechanism was suggested for the emission of X-rays on the breaking-up of an adhesive bond when the fresh surfaces are oppositely charged. Microsectors with positive and negative surface charges occur, and high values of the intensity of the electric fields in those sectors are obtained. The electrons emitted by the negatively charged surface areas are accelerated by those fields and are braked by the substrate material, thereby generating X-rays that are similar to the radiation of an X-ray tube. As a result of vacuum breakdown, however, a small portion of the atoms of the substrate material can evaporate from the surface, creating local plasma formations near the surface, in which processes similar to those occurring in a vacuum spark are possible, including X-ray production.

Lipson et al. [78] developed a non-destructive method for the investigation of the EDL parameters; the method permitted one to estimate correctly the contribution of the electrostatic forces to the adhesive strength of the metal–polymer system. It was established that the contribution of the electrostatic component becomes predominant at high concentrations of functional groups. For the case of high adhesion, the EDL charge field was about $2 \cdot 10^7$ V cm^{-1}, which agrees with theoretical data [13]. In accordance with the authors' estimation [78], the effective thickness of the EDL changes within the range 10^{-6}–10^{-7} cm.

The influence of colour centres in alkaline halides after the exposure of samples to ionizing radiation on the parameters of the HEE emission on their failure was studied in Refs [79,80]. It was established that there is no correlation between the concentration of colour centres (F centres), which

depends linearly upon the radiation dose, and the emitted HEE flux. The emission intensity is determined by the character of the failure of the irradiated crystals, while the parameters of the HEE emission (the magnitudes of the flux and the energy) depend on the fine structure of the cleavage surface and the distribution of charge on this surface. In particular, on the cleavage surface not only were the {100} cleavage planes observed but also other planes having a predominant direction ⟨100⟩ when the lattice ions are distinctly separated on the NaCl cleavage plane, while the intensity of the charge field reaches its maximum value. As was found, the parameters of the HEE emission depend on the structural peculiarities of the solid being broken [81,82] and on the presence of internal electric fields, in particular, in a ferroelectric [82].

The emission of HEE has been found to occur on the destruction of hard polycrystalline rocks [83]. Electrophysical phenomena may show up in rocks, leading to the prediction of earthquakes [84–89].

Electrophysical phenomena are also observed on the failure of organic molecular crystals [90,91].

The emission of HEEs may be used as an indicator of the interaction of a polymer with a filler [92].

The emission of electrons from the failure surface of solids gives rise to gas formation. A mass spectroscopic method permitted the evolution of hydrogen to be detected on the failure of diverse solids, such as inorganic crystals, metals and polymers [93,94], as well as in the wear and friction of structural materials [95]. In addition to gas evolution from the bulk on formation of a fresh surface during the mechanical treatment of a solid, for example, the evolution of hydrogen, it is the mechanism of dissociative ionization of water molecules under the effect of the flux of the emitted electrons which plays the determining role [93]. The evolution of hydrogen may lead to undesirable consequences, e.g. hydrogenation and the hydrogen brittleness of steel [94,95].

A further discovery, namely neutron radiation, followed from the electrophysical phenomena

occurring on the failure of solids, in particular, deuterated solids. Neutron radiation had been detected by Derjaguin, Kluev, Lipson, Toporov [96,97] 3 years before publication of the study by Fleischmann and Pons [98] and Jones et al. [89(a)] of cold nuclear fusion, which has so agitated scientific circles all over the world.

A weak emission of electrons was detected on the pulse failure of crystals of lithium deuteride and heavy ice [96,97,99]. The mechanism of cold nuclear fusion or simply cold fusion (CF) was formulated at that time. It consists of the possibility of accelerating free deuterons desorbing from the crystal lattice under the effect of powerful electric fields, induced in cracks, followed by the interaction of the desorbed deuterons with the deuterons that are located in the lattice. At present, the above mechanism is widely used for interpreting the results on CF in different laboratories. At a later date, the group headed by Derjaguin detected the emission of neutrons and traces of tritium during the mechano-chemical synthesis of deuterides of some transition metals such as Ti, Zr, $LaNi_5$ etc. [100,101].

The possibility of initiating nuclear fusion reactions by cavitational action on deuterium-containing media in the presence of a titanium vibrator was investigated in 1990 [102]. Finally, quite recently results have been obtained proving the possibility of CF occurring in high temperature superconductors [103]. This indicates a connection between CF phenomena and high temperature superconductivity.

Lipson et al. [104] studied the occurrence of CF in crystals as a consequence of the transformation of mechanical (elastic) energy concentrated at separate points into nuclear energy.

The present brief review of electrical phenomena occurring during the mechanical loading of solids does not of course comprise the majority of the work carried out by Derjaguin and his co-workers.

I cannot help noting that a series of ideas formulated by Derjaguin, his colleagues and co-workers on electrical phenomena occurring on the adhesive and cohesive failure of solids are scienti-

fically novel, this is substantiated by USSR inventor's certificates. Thus, utilizing electroadhesive phenomena, methods for the hydrophobization of glass [105], for polishing the surface of dielectrics [106] and for protecting the latter against static electricity [107] have been suggested. The non-destructive method for testing the strength of workpieces [108] is based on the recording of the electron emission occurring on the formation of the very first initiating microcracks on mechanical treatment of the solids. Also suggested were methods for recording the deformation of solids [109], for determining EDL charges [110], and for the non-destructive control of the adhesive strength of joints [111], as well as a new X-ray generator [112]. Inventions have been proposed based on the interaction of the emission power with the mechano-chemical processes, in particular [113,114] methods of preparing graft copolymers.

As has already been indicated, sufficiently strong adhesive joints can be obtained by applying an external electric field. The application of that principle to robot engineering in designing gripping and fixing devices can be given as an example [115]. Unfortunately, as far as we know, other interesting and important ideas concerning the mechano-emission and mechano-chemistry of solids have not yet been used to advantage by our industry.

Thus we have tried to show the initiation and the deepening interest in, and the development of the radiation properties of the failure surfaces of solids. We emphasize once more that the fresh or juvenile surface of a solid, which has just been formed under mechanical action, exhibits an unbalanced electrical charge. When conductivity does not play a major role, electrophysical phenomena due to the presence of the charge field have to be taken into account in examining the surface phenomena, especially chemical transformations.

There is no doubt that these aspects of surface phenomena have not been exhausted by far. Boris Vladimirovich Derjaguin and Nataliya Aleksandrovna Krotova are quite rightly considered as being the true parents of the mechano-

emission phenomena. I am sure that in future, when examining the physicochemical properties of the non-equilibrium surfaces of solids as formed by mechanical action, research workers will detect new effects and make new discoveries.

References

1 B.V. Derjaguin and N.A. Krotova, Adhesion. Investigations in the Field of Adhesion and Gluing Action. M.-L., USSR Acad. Sci., Moscow, 1949, p. 244 (in Russian).

2 N.A. Krotova, Doctor of Chemical Sciences Dissertation Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1950, p. 368.

3 B.V. Derjaguin and N.A. Krotova, Usp. Fiz. Nauk, 36 (1948) 387–406.

4 V.V. Karasev, N.A. Krotova and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 88(5), (1953) 777–780.

5 V.V. Karasev and N.A. Krotova, Dokl. Akad. Nauk SSSR, 99(5) (1954) 715–718.

6 N.A. Krotova and V.V. Karasev, Dokl. Akad. Nauk SSSR, 92(3) (1953) 607–610.

7 L.P. Morozova and N.A. Krotova, Dokl. Akad. Nauk SSSR, 115(4) (1957) 747–750.

8 L.P. Morozova and N.A. Krotova, Kolloidn. Zh., 20(1) (1958) 59.

9 B.V. Derjaguin and V.P. Smilga, Dokl. Akad. Nauk SSSR, 121(5) (1958) 877–880.

10 V.P. Smilga and B.V. Derjaguin, Glues and Gluing Technology, Collected Papers, Moscow, 1960, pp. 7–15.

11 V.P. Smilga, Dokl. Akad. Nauk USSR, 138(5) (1961) 1147–1150.

12 V.P. Smilga, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1961, p. 103.

13 B.V. Derjaguin, N.A. Krotova and V.P. Smilga, Adhesion of Solids, Nauka, Moscow, 1973, p. 280 (in Russian).

14 N.A. Krotova, L.P. Morozova and G.A. Sokolina, Phys. Solids., 3(7) (1961) 1999–2009.

15 L.P. Morozova, Chemical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1958, p. 139.

16 N.A. Krotova, L.P. Morozova and G.A. Sokolina, Dokl. Akad. Nauk SSSR, 127(2) (1959) 302–305.

17 G.A. Sokolina, N.A. Krotova and Yu.A. Khrustalev, Dokl. Akad. Nauk SSSR, 147 (1962) 1403–1412.

18 N.A. Krotova and Yu.P. Toporov, Investigations in the Field of Surface Forces, Collected Papers, Nauka, Moscow, 1964, pp. 338–349 (in Russian).

19 A.M. Polyakov and N.A. Krotova, Dokl. Akad. Nauk SSSR, 151(1) (1963) 130–133.

20 B.V. Derjaguin, V.V. Karasev, A.M. Medvedeva and S.K. Zherebkov, Kolloidn. Zh., 27(1) (1965) 35–41.

21 V.V. Karasev, Zh. Eksp. Teor. Fiz., 34 (1958) 1330–1331.

22 Yu.A. Khrustalev, V.M. Ustinova and N.A. Krotova, Dokl. Akad. Nauk SSSR, 186(2) (1969) 381–384.

23 A.M. Polyakov and N.A. Krotova, Researches in the Field of Surface Forces, Collected Papers, Nauka, Moscow, 1967, pp. 461–467 (in Russian).

24 A.M. Polyakov, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1967, p. 132.

26 I.N. Aleinikova, A.V. Kitaev and B.P. Filipenko, Kolloidn. Zh., 28 (1966) 625–630.

27 I.N. Aleinikova, B.V. Derjaguin and Yu.P. Toporov, Kolloidn. Zh., 30(2) (1968) 177–182.

28 B.V. Derjaguin, L.N. Burta-Gapanovich, Yu.N. Toporov and I.N. Aleinikova, Structure and Properties of the Surface Layers of Polymers, Naukova Dumka, Kiev, 1972, pp. 269–274.

29 L.N. Burta-Gapanovich, Chemical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1973, p. 193.

30 V.I. Anisimova, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1967, p. 121.

31 G.A. Sokolina, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1966, p. 148.

32 Yu.M. Evdokimov, Abstr., Chemical Sciences Thesis, MTILP, Moscow, 1968, p. 24.

33 L.A. Tyurikova, Yu.M. Evdokimov, N.I. Moskvitin and N.A. Krotova, Dokl. Akad. Nauk SSSR., 184(3) (1969) 658–660.

34 D.M. Mambetov and T. Musuraliev, Dokl. Akad. Nauk SSSR, 180 (1968) 589.

35 D.M. Mambetov and T. Musuraliev, Dokl. Akad. Nauk SSSR, 185(1) (1969) 122–124.

36 D.M. Mambetov and N.P. Knyazeva, Dokl. Akad. Nauk SSSR, 191(2) (1970) 326–329.

37 Yu.S. Simakov and N.K. Baramboim, Visokomolekyl Soedinenija, B9 (69) (1967) 567 568.

38 V.A. Kapitanchuk, Collect. Rep., 2nd All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Frunze, 1969, Ilim, Frunze, 1974, pp. 28–33.

39 B.V. Derjaguin, N.A. Krotova and V.P. Smilga, Adhesion of Solids, Consultants Bureau, New York, 1978, p. 457.

40 B.V. Derjaguin, Vestn. Akad. Nauk SSSR, (1) (1974) 9–14.

41 N.P. Knyazeva, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1972, p. 175.

42 B.V. Derjaguin, N.A. Krotova and N.P. Knyazeva, Dokl. Akad. Nauk SSSR, 215(5) (1974) 1078–1081.

43 V.I. Anisimova, B.V. Derjaguin, V.A. Kluev and T.N. Vladykina, 5th All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Tallin, 1975, Part 1, Tallin, 1977, pp. 98–103.

44 V.A. Kluev, Physico-Mathematical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1982, p. 167.

45 V.I. Anisimova, V.A. Kluev, T.N. Vladykina, N.A. Krotova, Yu.P. Toporov and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 233(1) (1977) 140–143.

46 B.V. Derjaguin, V.I. Anisimova, V.A. Kluev and N.A. Krotova, Dokl. Akad. Nauk. USSR, 222(3) (1975) 644–646.

47 I. Vollbrandt, Yu.A. Khrustalev, E. Linke, N.A. Krotova and B.V. Derjaguin, Dokl. Acad. Nauk SSSR, 225(2) (1975) 342–344.

48 V.A. Kluev, V.I. Anisimova, Yu.P. Toporov, N.A. Krotova and B.V. Derjaguin, Kolloidn. Zh., 40(2) (1978) 244–251.

49   Yu.A. Khrustalev, Chem. Sci. Thesis, Inst. Phys. Chem., USSR Acad. Sci., Moscow, 1978, p. 196.

49(a) Yu.A. Chrustalev and N.A. Krotova, Krist. Tech., 13(9) (1978) 1077–81.

50   A.I. Vilensky, Chemical Sciences Thesis, Inst. Phys. Chem. USSR Acad. Sci., Moscow, 1972, p. 162.

51   N.A. Krotova, N.N. Stefanovich, A.I. Vilensky and Yu.A. Chrustalev, J. Adhes., 3 (1972) 325–331.

52   Yu.A. Khrustalev, T.A. Moskalets, Yu.P. Toporov and N.K. Baramboim, Kolloidn. Zh., 43(2) (1981) 398–399.

53   Yu.P. Toporov and Yu.A. Khrustalev, Compositional Polymer Materials, No. 23, Naukova Dumka, Kiev, 1984, pp. 34–35.

54   B.V. Derjaguin and V.P. Smilga, Wear, 7 (1964) 270–281.

55   V.I. Anisimova, T.N. Vladykina and B.V. Derjaguin, Abstr. Rep. 8th All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Tallin, 1981, Moskovskii Lesotechnischeskij Institute, 1981, p. 13 (in Russian).

56   V.A. Kluev, T.N. Vladikina, Yu.P. Toporov, V.I. Anisimova and B.V. Derjaguin, IEEE Trans. Ind. Appl., 1A–14(6) (1978) 544.

57   T.N. Vladikina, B.V. Derjaguin, V.A. Kluev, Yu.P. Toporov and Yu.A. Khrustalev, J. Lubr. Technol., 102(4) (1980) 552.

58   Yu.P. Toporov, E.S. Revina and V.A. Kluev, Abstr. Rep. 8th All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Tallin, 1981, Moskovskii Lesotechnischeskij Institute, 1981, pp. 13–14.

59   M.V. Frolov, Yu.F. Barbolin, Yu.A. Khrustalev, V.A. Kluev and Yu.P. Toporov, Proc. Central Res. Inst. of Paper, No. 12, Moscow, 1976, pp. 22–24.

60   Yu.F. Barbolin, M.V. Frolov, N.A. Kalinina and Yu.A. Khrustalev, Proc. Central Res. Inst. of Paper, No. 13, Moscow, 1977, pp. 19–24.

61   Yu.A. Khrustalev, I.I. Nikitina and N.K. Baramboim, Rep. Abstr., 4th All-union Symp. Mechanoemission and Mechanochemistry of Solids, Irkutsk, Nauka, Moscow, 1973, pp. 80–82 (in Russian).

62   Yu.A. Khrustalev, L.I. Prokhorova, N.K. Baramboim, Yu.F. Kurdubov and N.A. Krotova, Kolloidn. Zh., 38(4) (1976) 814–815.

63   N.A. Krotova, E. Linke, Yu.A. Khrustalev, J. Vollbrandt and V.I. Shipovsky, Dokl. Akad. Nauk SSSR, 208(4) (1973) 138–142.

64   L.A. Antonova, Yu.A. Khrustalev, N.K. Baramboim and N.A. Krotova, Kolloidn. Zh., 38(3) (1976) 535–537.

65   G. Heinicke, L.P. Janova, Yu.A. Khrustalev and N.A. Krotova, Z. Chem., 19(3) (1979) 118–119.

66   L.S. Zarkhin, V.A. Kluev, Yu.A. Khrustalev, A.M. Kuperman, E.V. Prut, Yu.P. Toporov and N.A. Krotova, 5th All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Tallin, 1975, Vol. 1, Tallin, 1977, pp. 104–107.

67   Yu.A. Khrustalev, A.Je. Tschalych and N.A. Krotova, Plast. Kautsch., 26(5) (1979) 254–255.

68   Yu.A. Khrustalev, T.M. Khrenkova, V.V. Lebedev, Yu.P. Toporov and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 257(2) (1981) 418–422.

69   A.I. Vilensky, T.N. Vladykina, N.A. Krotova, Yu.A. Khrustalev and N.N. Stefanovich, Abstr. Rep. 4th All-Union Symp. on Mechanoemission and Mechanochemistry of Solids, Irkutsk, 1973, Nauka, Moscow, 1973, pp. 25–26 (in Russian).

70   Yu.A. Khrustalev, Yu.P. Toporov, N.A. Krotova and B.V. Derjaguin, in A.A. Polyakov and Yu.S. Simakov (Eds), Investigation of Hydrogen Wear, Nauka, Moscow, 1977, pp. 34–39 (in Russian).

71   Yu.S. Simakov, Yu.A. Khrustalev and Yu.P. Toporov, Abstr. Rep. Republican Scientific–Engineering Conf. Nikolaev, 1978, No. 1, Kiev, 1978, pp. 6–7.

72   Yu.A. Khrustalev, Yu.P. Toporov and N.A. Krotova, Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 3 (1979) 3–5.

73   Yu.A. Khrustalev, N.K. Baramboim, Yu.F. Kurdubov, Yu.P. Toporov and Yu.S. Simakov, in G.B. Manelis and P.Yu. Butjaguin (Eds), Kinetics and the Mechanism of Chemical Reactions in a Solid, Chernogolovka, 1981, pp. 175–181.

74   Yu.A. Khrustalev, T.M. Khrenkova, V.V. Lebedev and Yu.P. Toporov, Chimia Tverdogo Topliwa, (4) (1983) 64–70 (in Russian).

75   V.A. Kluev, A.G. Lipson, Yu.P. Toporov, A.D. Aliev and A.E. Chalykh, J. Theor. Phys., 10 (18) (1984) 1135–1139 (in Russian).

76   M.I. Molotsky, Phys. Solids, 19(2) (1977) 642–644 (in Russian).

77   V.I. Berkov, A.G. Lipson, V.A. Kluev, Yu.P. Toporov and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 294(1) (1987) 80–83.

78   A.G. Lipson, E.V. Kuznetsova, D.M. Sakov, N.I. Morozova and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 310(6) (1990) 1398–1403.

79   Yu.A. Khrustalev, O.I. Serdyuk, V.I. Savenko, I.I. Bardyshev and B.V. Derjaguin, Kolloidn. Zh., 48(3) (1986) 520–527.

80   Yu.A. Khrustalev, V.I. Savenko, I.I. Bardyshev, Interinstitute Collection of Scientific Proceedings. Radiation-stimulated Phenomena in Solids, UPI, Sverdlovsk, 1989, pp. 59–66 (in Russian).

81   Yu.A. Khrustalev, Rep. 8th All-Union Symp. Mechanoemission and Mechanochemistry of Solids, Tallin, 1981, Vol. 1, Valgus, Tallin, 1986, pp. 36–41.

82   E.V. Minakova, N.A. Tikhomirova and Yu.A. Khrustalev, Poverchnost: Fisika, Chimia, Mechanika, 1986, Vol. 7, pp. 135–136 (in Russian).

83   V.V. Bykova, I.R. Stakhovsky, T.S. Fedorova, Yu.A. Khrustalev, B.V. Derjaguin and Yu.P. Toporov, Izv. Akad. Nauk SSSR, Fiz. Zemli, 8 (1987) 87–91.

84   G.A. Sobolev and V.M. Demin, Mechanoelectrical Phenomena in the Earth, Nauka, Moscow, 1980, p. 215 (in Russian).

85   M.A. Sadovsky (Ed.), Electromagnetic Precursors of Earthquakes, Nauka, Moscow, 1982, p. 88 (in Russian).

86   M.B. Gokhberg, I.L. Gufeld and V.A. Liperovsky, Vestn. Akad. Nauk SSSR, 3 (1987) 43–53.

87   A.I. Grigor'ev, N.I. Gershenzon and M.B. Gokhberg, Dokl. Akad. Nauk SSSR, 300(5) (1988) 1087–1090.

88 A.N. Sulkhankhodzhaev and S.S. Khusamiddinov, Dokl. Akad. Nauk SSSR, 301(5) (1988) 1087.

89 M.A. Yaroslavsky and N.K. Kapustyan, Dokl. Akad. Nauk SSSR, 315(2) (1990) 352.

89 (a)S.E. Jones, E.P. Palmer, J.B. Czirr, D.L. Decker, G.L. Jensen, J.M. Thorne, S.F. Taylor and J. Rafelski, Nature, 338 (1989) 737.

90 E.A. Varentsov, Yu.A. Khrustalev and V.M. Khrapal', Zh. Fiz. Khim., 63(4) (1989) 1085–1086.

91 E.A. Varentsov, Yu.A. Khrustalev and V.M. Khrapel', Zh. Fiz. Khim., 62(8) (1988) 2197–2204.

92 Yu.S. Simakov, S.I. Nechaeva and Yu.A. Khrustalev, Kolloidn. Zh., 49(4) (1987) 806–808.

93 A.P. Gai, M.P. Glazunov, L.T. Zhuravlev, Yu.A. Khrustalev and K.Ya. Shengeliya, Dokl. Akad. Nauk SSSR, 277(2) (1984) 388–390.

94 Yu.A. Khrustalev, Yu.S. Simakov, M.P. Glazunov and V.V. Gubin, Zh. Fiz. Khim., 63(5) (1989) 1355–1357.

95 Yu.S. Simakov, B.M. Kogan, B.F. Lyakhov, M.M. Tenenbaum, Yu.A. Khrustalev and S.M. Kaufman, Frict. Wear, 10(4) (1989) 749–750.

96 B.V. Derjaguin, V.A. Kluev, A.G. Lipson and Yu.P. Toporov, Kolloidn. Zh., 48(1) (1986) 12–14.

97 V.A. Kluev, A.G. Lipson, Yu.P. Toporov, B.V. Derjaguin, V.I. Lushchikov, A.V. Strelkov and E.P. Shabalin, J. Theor. Phys., 12(21) (1986) 1333–1337 (in Russian).

98 M. Fleischmann and S. Pons, J. Electroanal. Chem., 263 (1989) 301–308.

99 B.V. Derjaguin, V.A. Kluev, A.G. Lipson and Yu.P. Toporov, Physica B, 167 (1990) 189–193.

100 A.G. Lipson, V.A. Kluev, Yu.P. Toporov, B.V. Derjaguin and D.M. Sakov, J. Electroanal. Chem., 16(17) (1990) 54–57.

101 B.V. Derjaguin, A.G. Lipson, V.A. Kluev, D.M. Sakov and Yu.A. Toporov, Nature, 341 (1989) 492.

102 A.G. Lipson, V.A. Kluev, B.V. Derjaguin, Yu.P. Toporov, M.G. Sirotyuk, O.B. Khavroshkin and D.M. Sakov, J. Theor. Phys., 16(19) (1990) 89–93 (in Russian).

103 A.G. Lipson, D.M. Sakov, Yu.P. Toporov, V.V. Gromov and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 321(5) (1991) 958–962.

104 A.G. Lipson, V.A. Kuznetsov and B.V. Derjaguin, Dokl. Akad. Nauk SSSR, 318(3) (1991) 636–639.

105 USSR Inventor's Certificate 595 264, Bull. Invent., 8, 1978.

106 USSR Inventor's Certificate 643 302, Bull. Invent., 3, 1979.

107 USSR Inventor's Certificate 646 473, Bull. Invent., 5, 1979.

108 USSR Inventor's Certificate 532 781, Bull. Invent., 39, 1976.

109 USSR Inventor's Certificate 970 082, Bull. Invent., 40, 1982.

110 USSR Inventor's Certificate 1 420 505, Bull. Invent., 32, 1988.

111 USSR Inventor's Certificate 1 693 476, Bull. Invent., 43, 1991.

112 USSR Inventor's Certificate 1 149 331, Bull. Invent., 13, 1985.

113 USSR Inventor's Certificate 854 940, Bull. Invent., 30, 1981.

114 USSR Inventor's Certificate 994 473, Bull. Invent., 5, 1983.

115 V.N. Abrarov, M.V. Sobolevsky and E.M. Kondrat'ev, Plastics, 7 (1984) 41–43 (in Russian).