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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text****PHYSICAL CHEMISTRY**

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**INVESTIGATION OF THE INTENSITY OF
MECHANO-ELECTRON EMISSION DURING
DETACHMENT AND DEFORMATION OF
POLYMER FILMS***(Presented by Academician A. N. Frumkin, March 5, 1963)*

As is known, there are various types of emission from the surface of a solid: thermionic emission, photoemission, autoelectronic emission. Recently, much interest has been aroused by the phenomenon of so-called exoelectronic emission (the Kramer effect), observed under the most varied conditions, for example: during mechanical treatment of a surface, its treatment in a glow discharge, as a result of the occurrence of surface chemical reactions, etc. A distinguishing feature of exoelectronic emission is the need for preliminary treatment of materials in order to create centers that cause emission under subsequent physical action. Thus, for example, heating certain minerals gives an electron-emission effect only after preliminary irradiation of the specimen (¹⁻⁶). The same may be said with regard to the emission of certain minerals in a pulverized state (^{7,8}). Exoelectronic emission is observed in metals, semiconductors, and dielectrics, and the velocity of the emitted electrons corresponds to units or fractions of an electron-volt (^{9,10}).

Fig. 1. Vacuum adhesionmeter for studying mechanoemission. 1 –glass bell jar, 2 –cassette with film, 3 –starting mechanism, 4 –lever for detaching the cassette, 5 –prism for dropping the load, 6 –damper, 7 –specimen, 8 –plate with strain gauges.

In previous works of our laboratory (¹¹⁻¹⁷), carried out under high-vacuum conditions, the phenomenon of emission of high-energy electrons, reaching hundreds of keV, was discovered. This phenomenon is observed during mechanical destruction of crystals and detachment of polymer films from a substrate. Evidently, its nature is fundamentally different from the Kramer effect. Therefore, to designate the emission of fast electrons observed under mechanical actions in

Fig. 2. Block diagram of the setup.

Figure 2: Fig. 2. Block diagram of the setup.

high-vacuum conditions, it is reasonable to introduce the term “mechanoemission.”

Studies of mechanoemission during the detachment of polymer films were carried out by us in connection with general work in the field of adhesion. In works (¹⁴, ¹⁵) it was found that the velocities of the emitted electrons correlate with the mechanical adhesive strength. This is in good agreement with the electrical theory of adhesion (¹³). By means of fast electrons emitted by the surface of a dielectric, the distribution of emission centers on a freshly formed surface (a detached polymer film

Fig. 2. Block diagram of the setup. 1—roller with the film being detached, 2—clamps with the film for the case of deformation, 3—plate with strain gauges, 4—amplifier, 5—loop oscillograph (H-700), 6—secondary electron multiplier, 7—microammeter, 8—separating capacitor, 9—voltage stabilizer (“Orekh”), 10—counting device (PS-10000 “Floks”), 11—count-rate meter (ISS, “Tyulpan”), 12—electronic self-recording potentiometer (ÉPP-09)

or the cleavage surface of a crystal) was also obtained (¹⁵⁻¹⁷). These works made it possible to characterize qualitatively the phenomenon of mechanoemission. The tasks now set by us are aimed at a systematic investigation of mechanoemission, mainly its intensity (emission current), the velocities of the emitted electrons, and the conditions of its occurrence in connection with the peculiarities of the chemical structure of the materials under study. To carry out these studies, a complex vacuum apparatus was constructed that makes it possible simultaneously to determine the mechanical characteristics of adhesion and the parameters of the emission arising upon disruption of the adhesive bond, mechanical fracture, and deformation of solids.

Figure 1 shows one version of the apparatus intended for studying mechanoemission during the instantaneous rupture of bonded specimens, as well as during the fracture of crystalline and polymeric materials. The emitted electrons are recorded by a sensitive X-ray film placed in a cylindrical cassette (2). The starting mechanism (3) is designed so that first, with the aid of a lever (4), the cassette is opened, and then a conical prism (5) releases a load producing detachment. The shock wave arising under the instantaneous action of the force is damped by a special damper (6) (¹⁸). The detachment (rupture) force is recorded by a system of strain gauges assembled in a bridge circuit; the signal from them is fed to a special amplifier of type UD-3 (Fig. 2, 4) and recorded on an H-700 loop oscillograph (Fig. 2, 5). The apparatus also permits installation of a flat cassette for the film and a set of diaphragms for cutting out a narrow beam of electrons. In this case, a constant magnetic field can be produced between the diaphragm system and the cassette and, from the magnitude of the

Fig. 3. Recording of post-emission during detachment of a β -gutta-percha film from glass. The experimental scheme is shown in the upper right corner. 1—emission as a freshly detached film passes in front of the multiplier entrance; 2—decline of emission from the detached film after detachment is completed

Figure 3: Fig. 3. Recording of post-emission during detachment of a β -gutta-percha film from glass. The experimental scheme is shown in the upper right corner. 1—emission as a freshly detached film passes in front of the multiplier entrance; 2—decline of emission from the detached film after detachment is completed

beam deflection, the mean electron energies can be determined. However, when film is used for recording the electrons, it is impossible to determine the intensity of the electron emission and its change during the course of the experiment; there is no possibility of establishing the time dependence of the emission from the freshly formed surface;

Finally, the low sensitivity of films does not allow electrons of low energies to be recorded. For these reasons, to record electron emission we used special secondary-electron multipliers (SEM), designed at the State Optical Institute (^{19–21}). These open-type multipliers have a large amplification factor (10^8 — 10^9), possess good operating stability, and are only slightly sensitive to the admission of air after the experiment is completed. With these multipliers it is possible to record electrons over a broad energy range (from several eV to hundreds of keV).

Figure 2 shows a block diagram of the apparatus intended for recording electron emission observed during the adhesive detachment of polymer films from a glass or metal roller. The mechanical characteristics of adhesion were recorded with the aid of the described circuit. The emission intensity was measured by an electron multiplier with a uniform voltage divider. The multiplier cathode was grounded, and a positive voltage (up to 5 kV) from the “Orekh” voltage stabilizer was applied to the anode. A microammeter could be included in the anode circuit, with which the primary emission current was estimated (for the case β -gutta-percha–glass, the current during detachment of the film was of the order of 10^{-14} A). When the multiplier was operated in the pulse-counting mode, signals from it were fed to electronic counting equipment. The total number of pulses during the entire detachment was counted by a PS-10 000 (“Floks”) counting device. The intensity of electron emission during detachment, its changes with time, and also the course of the emission observed from a freshly detached polymer film were recorded by the ISK “Tulpan” counting-rate meter (Fig. 2, 11) and recorded with an EPP-09 electronic potentiometer with a carriage travel time of 1 sec (Fig. 2, 12). The experiments were carried out in a vacuum of 10^{-5} mm Hg. The vacuum part of the apparatus is outlined by a dashed line in Fig. 2.

Fig. 3. Recording of post-emission during detachment of a β -gutta-percha film

Fig. 4

Figure 4: Fig. 4

from glass. The experimental scheme is shown in the upper right corner. 1—emission as a freshly detached film passes in front of the multiplier entrance; 2—decline of emission from the detached film after detachment is completed.

Figure 3 gives a typical curve for recording electron emission from a freshly formed β -gutta-percha film. In these experiments the gap between the separating surfaces was specially shielded so that electrons emitted at the moment of detachment did not enter the multiplier input (the experimental scheme is shown in the upper right corner of Fig. 3). It is seen from the figure that the greatest intensity of post-emission is observed when the freshly detached film passes in front of the multiplier input, several seconds having elapsed since its detachment (1). After detachment is completed, a freshly formed section of film remains in front of the multiplier. The intensity of its post-emission falls rather rapidly (2). But even after 1-1.5 hours the emission still retains a substantial value, ~ 100 pulses/sec. It is interesting to note that the emission intensity increases noticeably under additional illu-

the film was illuminated with visible light. It may be assumed that free radicals formed upon the rupture of adhesive bonds play a substantial role in these phenomena. Of particular interest are experiments on deformation and fracture of polymer films carried out in the following manner. Instead of the roller, clamps with a film were placed in front of the VEI input (Fig. 2, 2); at definite time intervals the film was stretched by 10% of its original length. Figure 4 shows a record of the electron emission observed during deformation of a specimen of β -gutta-percha (specimen dimensions: $7 \times 5 \times 0.5$ mm). During stretching in the elastic region (the acts

Fig. 4. Electron emission during periodic deformation of a β -gutta-percha film. The arrows indicate the stretching acts.

1 —region of elastic deformation, 2 —region of plastic deformation, 3 —region of strain hardening

of stretching are indicated by arrows), the deformation was not accompanied by electron emission. The first emission peak was associated with the appearance of a shear band on the specimen. With further deformation (2), this band propagated along the specimen, and strong emission peaks were observed at each stretching act. In the region of mechanical hardening (3), corresponding to propagation of the shear band over the entire specimen, the emission disappears. Subsequent stretching, even with an increase in the degree of deformation up to rupture of the specimen, does not produce noticeable emission. It is interesting to note that, in contrast to emission during rupture of an adhesive bond, the emission intensity during deformation of polymers rapidly decreases with time.

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