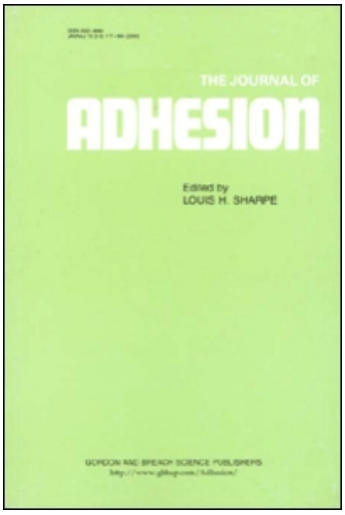

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Investigation on the Adhesion of Polymer Particles to the Surface of a Semiconductor†

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In this work the role of electrostatic forces in the adhesion of particles of dielectrics to a solid surface was studied. The experiment consisted in measuring simultaneously the force of adhesion and the charges of the electric double layer arising upon contact. The measurements were made with specially developed units—a pneumatic adhesiometer and a charge-spectrometer. The objects of study were polymer powders used in electrography, whose adhesion to thin layers of selenium samples were varied by varying the illumination and were estimated by their volume resistance in the dark and in the light. The shift in the Fermi level of the selenium caused by the change in the output work is accompanied by a change in adhesion of the particles. Experiments on the separation of polymer particles and films from selenium surface on illumination revealed spectral dependence of adhesion. In accordance with the electronic theory of adhesion, the effects observed may be attributed to the change in charge density of the electric double layer.

The theoretical and experimental study on the adhesion of polymer films to solid surfaces[1,2] has shown that the work of film separation is determined mainly by the double electric layer formed at the film-solid interface.

Experimental studies on the adhesion of powders[3] have also shown that the part played by the electrostatic forces, controlled by the electric double layer, is very important.

In our earlier study[4] the electrostatic component of the force of adhesion

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was investigated by parallel measurements of adhesion forces of the particles and their charges after separation from the solid surface. The measurements of adhesion were performed by means of an adhesiometer[5] which permits to obtain separation accelerations over the range 10^3 to 10^6 g. The separation of the particles from the surface of the target takes place under the impact of a bullet accelerated by compressed air on the opposite side of the target. Individual particle charges were measured with a charge-spectrometer[6] in the process of particle deposition from a laminar flow in the field of a stepped capacitor. The chamber of the charge spectrometer was also used to deposit on the target the particles with fixed charges of only one sign.

It should be noted that charges of the small particles after separation may serve as a quantitative characteristic of an electric double layer at the interface as, due to the low probability of the development of a gas discharge, the charges are measured under no-loss conditions.[7] To verify this assumption additional adhesion measurements were performed at moderate conditions by means of a special device to the pneumatic adhesiometer. Simultaneously particle charges were measured in vacuum by the method based on comparing particle displacement in gravitational and electric fields inside the capacitor. The order of magnitude of particles charges and the character of the charge *vs.* radius relation are practically not influenced by pressure over the pressure range 10^3 to 1 mm Hg. This should be impossible if the process is controlled by the development of the gas discharge.

Measurements of the charges of some polymer particles before and after separation from the metal surface have shown a hundred fold increase of particle charge after separation, which points to the formation of an electric double layer at the particle—metal interface.

The performed experiments have shown that the force of adhesion increases with the radius of the particle, the relation being close to the quadratic one. As it was shown analitically a dependence like that between the adhesion force and the particle radius may be explained only under the assumption that the electrostatic component of adhesion is prevalent. The fact is that in pneumatic adhesiometer measurements the powder particles are subjected to "pressing-in" acceleration before separation and to an equal separating acceleration after the reversal of the direction of the target acceleration. Calculation of the dependence $F(r)$ was based on the assumption that the separation is counteracted by the electrostatic force due to the electric double layer formed on the contact area—which increase sharply during the pressing—in phase but retained in the separating phase.

The suggested hypothesis on the effect of "pressing-in" was checked by comparing the values of S_c (contact area between the particle and substrate) calculated by the use of the Hertz formula with those calculated from the values of adhesion force (F) and particle charge after separation (q) obtained

experimentally ($F = F_{el} = 2\pi\sigma^2 S_c = 2\pi\sigma^2 q^2/S_c$, where σ—surface electrization density and q—particle charge). This comparison has shown a satisfactory agreement of both values. It should be noted that under similar pressing—in conditions the molecular component of the adhesion force remains proportional to r and does not depend on the degree of pressing.[8]

Calculation of the surface charge density from the experimental values of F and q after separation has shown that within experimental errors, σ does not depend on S and to order of magnitude is equal to 10^3 CGSE, which is compatible with the electronic theory of adhesion.

Thus the results of the experiments confirm the prevailing role of the electrostatic forces due to the electric double layer. However, the problem of separating the molecular and electrostatic components of adhesion may be simpler in an experiment where the change of the electrostatic component is not accompanied by the change of the molecular one. Such an experiment was suggested in the paper[9] on the study of particle adhesion to a semiconductor substrate the electronic properties of which change in illumination.

It should be noted that the possibility of producing an effect on the electric double layer at the interface of two bodies by irradiation was established for the first time in studies published in ref. 1. γ-ray and X-ray irradiation of the boundary of separation of the polymer film from glass established a change of adhesion which is conditioned by ionization of the ambient medium as well as by the effect of irradiation on the formation of a molecular capacitor at the interface. Similar results were obtained in[10] on ultraviolet irradiation of polar polymers in contact with glass fibres, and the possibility of a recharge of the contact zone under illumination was suggested.

In the present study we investigated the adhesion of different polymers to the surface of selenium under illumination. The reason for the selection of selenium as a substrate is the necessity to solve a series of problems of electrophotography where selenium is now widely used. The change of the photoelectric properties on illumination of thin layers of amorphous selenium sublimated in vacuum on a metal substrate was estimated from the measurements of their bulk resistivities. Calculation of the charge carrier concentrations has permitted us to evaluate the shift of the Fermi level on illumination of the semiconductor surface. An example of our results for polysytrene particles under illumination of selenium by light of the wavelength $\lambda =$ 455 nm is given in Tables 1 and 2.

It can be seen that Fermi level shift corresponding to the decrease in the work function of selenium is accompanied by a decrease in particle adhesion on illumination, which is in agreement with the electronic theory of adhesion.

Similar conclusions were made in the paper,[11] in which an analytical expression for the adhesion force component due to the electric double layer is given in terms of electron parameters of contacting bodies (a planar

TABLE 1

Change in adhesion of polystyrene particles with rhodamine to an illuminated selenium surface†

d	Conditions of experiment	Average separation acceleration $\bar{a}$, 10^7 cm/sec^2	$\frac{\bar{a}_d - \bar{a}_l}{\bar{a}_d}$	Experimental error, per cent
10	illumination out illumination on	47.9 35.5	25.8	5.6
20	illumination out illumination on	26.4 16.8	36.4	6.6

TABLE 2

Change in photoelectric parameters of selenium layer illuminated with light of the wavelength $\lambda = 455$ nm

Conditions of experiment	Bulk resistivity (ohm-cm)	Concentration of carriers (1/cm^3)	Shift of Fermi level (ev)
illumination out	2×10^{13}	2.2×10^6	0.16
illumination on	3.2×10^{10}	1.4×10^9	

semiconductor substrate and a spherical metal particle). The use of two types of crystals of the semiconductor CdS, the work function (without illumination) of one of which was higher and of the other lower than that of metal, has allowed to create conditions under which adhesive ability of the semiconductor surface may be lowered or raised as determined by the intensity of illumination.

To specify the mechanism of adhesive interaction between the dielectric particles and solid surface it is of utmost interest to use such a physical modification of the contact zone (for instance by illumination), which by changing the polarity of the electric double layer may result in sign reversal of separated particle charges. Evaluation of the adhesion force at the point of reversal of the charge sign would allow us to determine the quantitative relation between the molecular and electrostatic components of the adhesion force.

It is of interest to note in the investigations on the spectral characteristics of the photoelectromotive force (of amorphous selenium layers) both positive and negative charging of the selenium surface was observed depending on the wavelength. The obtained results were explained on the basis of the band structure of selenium.

It is natural to assume that the changes of selenium surface electronic parameters versus wavelength influences the strength of adhesive interaction.

† The data listed here and onwards relate to the particle diameter 10 μm.

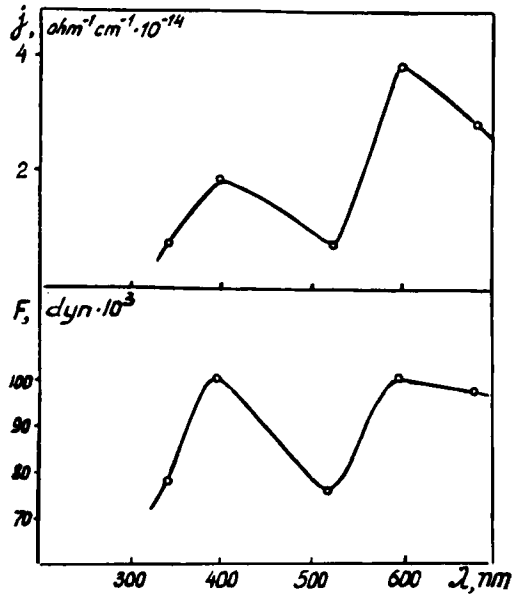

FIGURE 1 Spectral curves of selenium bulk conductivity (j) and adhesive force (F) of polystyrene particles on selenium surface.

Separation of polystyrene particles, containing Rodamin (this is one of the developing compounds used in electrophotography), from the selenium surface was carried out at constant intensity of illumination, monitored by an irradiation thermocell. Experimental results are presented in Fig. 1. This figure shows that the spectral curves of selenium bulk photoconductivity and adhesive force are in agreement (a somewhat unusual appearance of the spectral characteristic in our samples of amorphous selenium was presumably determined by the thermal history of their deposition onto the metal substrate). Figure 2 gives the spectral dependence of the relative variation of the

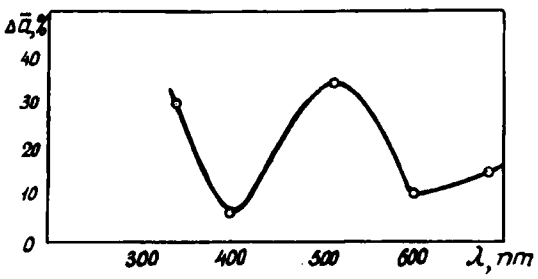

FIGURE 2 Spectral dependence of the relative variation of the mean separating acceleration of polystyrene particles from selenium surface.

mean separating acceleration. As follows from the data the ratio

$$\Delta\bar{a} = \frac{\bar{a}_d - \bar{a}_l}{\bar{a}_d}$$

is at its minimum when the wavelength of illuminating light corresponds to the maximum of bulk photoconductivity. This means that the influence of illumination on the adhesion of particles has its minimum in this range of wavelengths.

Experiments on the separation of transparent cellulose film from selenium surface revealed similar spectral dependence of adhesion (Fig. 3).

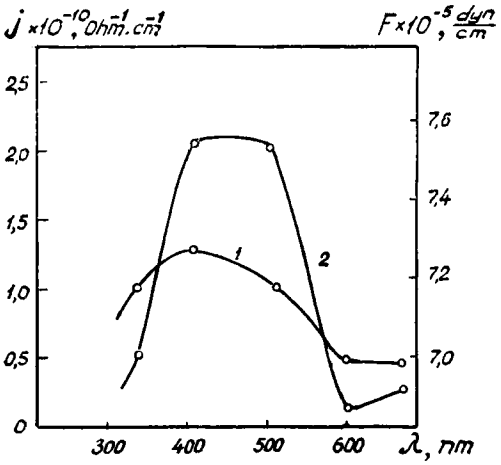

FIGURE 3 Spectral behaviour of the bulk conductivity of the selenium subsrate (2) and the adhesion (1) cellulose film—selenium substrate.

It is known[12] that such character of photoconductivity spectral curves (reductions of effect at smaller λ) is generally attributed to the existence of two competing processes: the rise of absorption coefficient with decreasing λ, leading to reduced thickness of light absorbing layer, and the increase of carrier recombination rate due to their increased concentration in this layer.

It is possible that the same processes are responsible for the changes in the charge density of the electric double layer at the particle-semiconductor interface. These changes induce charge carrier redistribution within the double layer (in the investigated wavelength range). Further research into the spectral characteristics of adhesion will probably make it possible to find out the origin of charge carriers that form the "plates" of the double layer on the interface.

The corollary of the reported experiments is that they underline once again the role of electric double layer in the adhesive interaction of particles with the solid interface.

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