STATIC ELECTRIFICATION
OF TEFLON BY METALS

Anders Wåhlin
Department of Physics
SUMMARY

The electrification of a system consisting of a metal and polytetrafluoroethylene (Teflon) has been investigated under relative motion. First, the electrification charge received by the insulator was measured when velocity, radius of curvature of the metal electrode and normal force were varied. The measurements were performed both in atmospheric pressure and later under vacuum, since electrical breakdown sometimes limited the charge of the insulator.

The results of these investigations indicated that the electrification charge received by the insulator is proportional to the real area of contact. Electrification in the sliding mode might therefore be analysed and interpreted as simply as in lifting experiments.

Electrification experiments were then carried out using several metals, and a linear relation was found between the insulator charge density and the metal work function. This result together with the short charging time observed suggest a charging mechanism, in which electrons from the metal fill empty surface states in the insulator up to a level corresponding to the Fermi level of the metal.
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Definition and practical consequences</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Historical survey</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>2 CHARGING MECHANISMS</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Electronic properties of polymers</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Contact charging mechanisms</td>
<td>10</td>
</tr>
<tr>
<td>2.2.1 Electron transfer</td>
<td>11</td>
</tr>
<tr>
<td>2.2.2 Ion transfer</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Frictional charging mechanisms</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Charge backflow during separation</td>
<td>26</td>
</tr>
<tr>
<td>3 APPARENT AND REAL AREA OF CONTACT</td>
<td>27</td>
</tr>
<tr>
<td>3.1 Theoretical calculations of the contact area</td>
<td>28</td>
</tr>
<tr>
<td>3.2 Experimental determinations of the contact area</td>
<td>30</td>
</tr>
<tr>
<td>4 METHODS FOR MEASURING CHARGE AND WORK FUNCTION</td>
<td>31</td>
</tr>
<tr>
<td>4.1 Methods for measuring static electric charge</td>
<td>31</td>
</tr>
<tr>
<td>4.1.1 Inductive methods</td>
<td>31</td>
</tr>
<tr>
<td>4.1.2 Ponderomotive method</td>
<td>33</td>
</tr>
<tr>
<td>4.1.3 Galvanometric method</td>
<td>34</td>
</tr>
<tr>
<td>4.2 Methods for measuring work function</td>
<td>34</td>
</tr>
<tr>
<td>4.2.1 Thermionic emission</td>
<td>35</td>
</tr>
<tr>
<td>4.2.2 Photoelectric emission</td>
<td>37</td>
</tr>
<tr>
<td>4.2.3 Contact potential</td>
<td>38</td>
</tr>
<tr>
<td>4.2.4 Changes of work function due to adsorbed atoms</td>
<td>41</td>
</tr>
<tr>
<td>5 EXPERIMENTAL TECHNIQUE</td>
<td>43</td>
</tr>
<tr>
<td>5.1 Mechanical arrangement</td>
<td>43</td>
</tr>
<tr>
<td>5.2 Measurements</td>
<td>46</td>
</tr>
<tr>
<td>5.3 Preparation</td>
<td>54</td>
</tr>
<tr>
<td>Chapter</td>
<td>Section</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>6</td>
<td>6.1</td>
</tr>
<tr>
<td>6</td>
<td>6.2</td>
</tr>
<tr>
<td>6</td>
<td>6.3</td>
</tr>
<tr>
<td>6</td>
<td>6.4</td>
</tr>
<tr>
<td>6</td>
<td>6.5</td>
</tr>
<tr>
<td>7</td>
<td>7.1</td>
</tr>
<tr>
<td>7</td>
<td>7.2</td>
</tr>
<tr>
<td>7</td>
<td>7.3</td>
</tr>
<tr>
<td>7</td>
<td>7.4</td>
</tr>
<tr>
<td>7</td>
<td>7.5</td>
</tr>
<tr>
<td>7</td>
<td>7.6</td>
</tr>
<tr>
<td>7</td>
<td>7.7</td>
</tr>
<tr>
<td>8</td>
<td>8.1</td>
</tr>
<tr>
<td>8</td>
<td>8.2</td>
</tr>
<tr>
<td>8</td>
<td>8.3</td>
</tr>
<tr>
<td>8</td>
<td>8.4</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS 87

REFERENCES 88

APPENDIX BIBLIOGRAPHY 93
1 GENERAL INTRODUCTION

1.1 Definition and practical consequences

The conception "static electrification" has in the widest sense been defined by Loeb (1958) to include all processes producing segregation of positive and negative electrical charges by mechanical actions which operate by contact or impact between solid surfaces, between solid and liquid surfaces, or in the rupture or separation of solid or liquid surfaces by gases or otherwise, including also ionized gases. These involve such processes as frictional, contact, or triboelectrification, spray electrification and electrification in dust, snow or in thunderstorms.

Many effects which have their origin in static electrification are familiar to everyone. Anyone who has ever walked across a rug in a dry room and received a shock from a metal doorknob has had a first-hand experience of an electrostatic effect. Another one, on a grander scale, is thunder and lightning. Although static electrification is a thing of everyday occurrence surprisingly little is known about the processes leading to the accumulation of charge on insulating materials.

Electrostatic phenomena have many technological consequences. They are responsible for destructive dust explosions in sugar mills, granaries and in coal handling for instance. Electrostatics is also strongly suspected in several recent disastrous explosions aboard oil tankers. The infrequent disasters, however, are far outnumbered by the nuisance effects. Charge may accumulate on running belts, yarns, plastic films, paper and kindred materials to the point where an industrial process will have to shut down temporarily. Aircraft can also become highly charged from flying through dust, sleet or snow. Their communications equipment can be rendered useless or their control system can be damaged by subsequent discharges. These effects result from uncontrolled static electrification but in cases where one can control the electrification process one can make use of it. Examples of the successful use of static electricity are electrostatic precipitation of particulate industrial wastes, such as fly ash, dust and fumes; electrostatic separation of mixed granular solids, principally minerals; electrostatic coating, both wet and dry, and electrostatic imaging, the best known example of which is the xerographic process. The Van de Graaff generator
used for high-voltage testing and the acceleration of subatomic particles works by electrostatic principles. The history of electrostatics is very long and the simplest effect of this kind was known to the ancient Greeks. A brief historical outline may therefore be of some interest.

1.2 Historical survey

It may have been known in remote antiquity that a piece of amber which has been rubbed, perhaps first accidentally against the skins with which early man clothed himself, attracts to itself the hairs of fur and other light objects. Amber was used by the ancients as a jewel and for ornamentation, and is the fossil resin of pine trees which probably have been extinct for many millions of years. Among the Greeks amber came to be called "electron".

There is no extant written record about the amber effect until the early part of the 4th century B.C. when Plato mentioned it in one of his dialogues. Otherwise Thales of Miletus (6th-century B.C.) is credited with having observed the amber effect. Such credit, however, is based entirely on hearsay, for none of Thales' writings is extant. During the following two thousand years no progress was made except that some other substances were found to possess the same virtue as amber.

In the year 1600, however, Gilbert proved that the "amber effect" is induced by friction in quite a large class of bodies, among which he mentioned glass, sulphur and sealing wax. A force which was manifested by so many different kinds of matter seemed to need a name of its own; accordingly Gilbert gave to it the name "electric", which it has retained ever since. Du Fay discovered in 1733 that there were two kinds of electricity, namely that of transparent solids such as glass and that of resinous bodies such as amber. To the two kinds of electricity, whose existence he demonstrated, du Fay gave the names "vitreous" and "resinous". The notations "positive" and "negative" electricity were introduced by Franklin. This discovery made it possible to arrange different substances in a sequence according to their disposition to acquire a positive or a negative charge. The first person to set up such a sequence, or tribo-electric series as it is called today, was the Swedish scientist, J.C. Wilcke, who made a list of common substances in such a way that any member of the list exhibits a positive charge if rubbed with a substance lower down on the list and a negative charge if rubbed with a substance above it.
The principle of conservation of electric charge was first formulated by Watson in 1746 and independently by Franklin, unaware of Watson's hypothesis in 1747. From their experiments they were able to conclude that electricity was not created by rubbing two substances against each other but existed in all matter in its normal state, and by rubbing a certain amount was transferred from one substance to the other in such a way that the total quantity of electricity in an insulated system is invariable. In 1766 Priestley showed that the force which two electric charges exerts on each other is proportional to the inverse square of the distance between them. This result was not generally accepted until Coulomb in 1785 verified Priestley's findings. By the laws of conservation of electric charge and force between charged bodies electricity was raised to the position of an exact science, and when Henley in 1772 constructed the first electrometer, it also became possible to measure the magnitude of charges. Quantitative measurements were not made until 1834, however, when Péclet carried out the only substantial work done before the beginning of the twentieth century, when sporadic activity commenced.

The chief theoretical ideas advanced before the advent of quantum mechanics stem from those of Volta and Helmholtz. Volta in 1789 postulated that the source of the frictional electrification of two bodies lies in the contact between them, rather than some effects due to friction. Rubbing serves merely to increase the area of contact. Helmholtz in 1879 accepted this picture, in addition postulating that a double layer of charge only a few atoms thick is formed at the region of contact. This Volta-Helmholtz hypothesis, as it is frequently called, has a substantial history of acceptance and rejection by various workers. Another hypothesis was published in 1898 and is called Coehn's law. It states that substances with a high dielectric constant in contact with substances of a lower dielectric constant charge positively in relation to the substance of lower dielectric constant. The law was extended later to the statement that the charge produced is proportional to the difference in dielectric constants. The first theory about the origin of frictional electricity was propounded by Frenkel in 1917. He used the concept "intrinsic potential" for an insulator corresponding to the work function for a metal. Frenkel assumed that electrons were driven from the material with the smaller value of the potential to the material with the larger value of the potential.
Activity in the field of static electrification was rather desultory during the first decades of the twentieth century and died off almost completely in about 1930, at which time it could be fairly said that no clear picture of either the qualitative or quantitative phenomena had emerged. But in the late 1940's, stimulated to a great extent by the demands of the textile and the plastic industries, the problem began to be tackled afresh.

1.3 Introduction

Transfer of charge carriers between solid bodies in contact becomes observable only after separation of the charged surfaces by some means. This separation may be effected by motion perpendicular to the area of contact, that is by lifting or rolling, or by motion tangential to the surface, that is by sliding one body on another. The distinction between these modes of separation is not complete, however, since in practice lifting or rolling certainly involves some sliding, and vice versa. In order to understand the process of static electrification satisfactorily one would have to consider the two main modes of motion separately. The charge remaining on an insulator after a perpendicular separation has already been subject to quantitative investigation, and the surface charge density could be correlated with the work function of the metal electrode, this property being determined by an independent method (Arridge 1967, Davies 1967a, 1969). The magnitude of the surface charge density can, however, still not be predicted from independently measured properties of the solids involved, which would constitute a reasonable aim of the theory.

The mechanism of charge transfer between metals is well understood (Harper 1951), whereas there is much uncertainty about what the relevant properties are where insulators are concerned. There seem therefore to be better chances of success for theoretical and experimental studies of metal-insulator systems than of insulator-insulator systems. In sliding experiments, metals also have the advantage of high thermal conductivity which provides good temperature control in the contact area. The reason for choosing Teflon\(^{x}\) as the insulator in the present investigation was mainly its high electrical resistivity, which simplifies the interpretation of the results, but also its low friction coefficient and its chemical inertness.

\(^{x}\) Teflon is Du Pont's registered trademark for its fluorocarbon resin polytetrafluoroethylene (PTFE)
It also has a low surface energy compared with analogous hydrocarbons so that the surface does not accept impurities extensively. A plane surface was chosen for the insulator and a spherical one for the metal, since this was considered to be a reasonable approximation to any simple sliding situation.
2 CHARGING MECHANISMS

One goal of static electrification experiments has been to arrange various materials into a triboelectric series, and the first one was set up in 1757 by Wilcke as mentioned earlier. The charging of common materials such as glass, metal oxides, furs and fabrics was, however, found to be unpredictable, and the charging of some groups of materials could not be fitted into a linear series at all. More recently Skinner et al (1956), Rose and Ward (1957), Fukada and Fowler (1958) and Henniker (1962), among others, have published tribo-electric series which contain synthetic polymers, and from these it can be noticed that polytetrafluoroethylene, polyethylene and polystyrene are found at the negative end and nylon and polymethylmethacrylate at the positive end.

If the charging of two materials in contact always resulted from the exchange of a single type of charge carrier common to both of them, the direction of transfer being determined by the relative affinities of the surfaces for the carrier, then a unique triboelectric series would exist. This is the case when only metals are involved, the charge carriers being electrons and the direction of transfer depending on the relative position of their Fermi levels. Coehn's law can also be explained on this basis. An ion or electron being equidistant between the surfaces of two dielectrics will be more strongly attracted to the one with the higher dielectric constant if the conditions are the same in other respects.

The inconsistency between the findings of various investigators can partly be explained by the different preparation methods used and by the fact that many of the materials are not well-defined. That a unique tribo-electric series has not been established indicates however that more than one charging mechanism may be involved in electrification processes.

The sliding of one body on another involves some amount of friction, and the role of friction in charging processes has been the subject of much debate. It has been stated that the action of rubbing is merely to increase the area of close contact between two surfaces, thereby increasing the
charge transferred by processes requiring only contact. This statement is exactly the earlier mentioned Volta-Helmholtz hypothesis. Friction will certainly have this effect, but the charging of two identical pieces of material by asymmetric rubbing must be a consequence of the expenditure of energy in friction. Experiments of this kind were first performed by Shaw (1927), and their importance has been emphasized by Henry (1953).

Two similar rods of the same insulating material are rubbed as if one were being sawn by the other, whereby the rods acquire charges of opposite sign, the signs reversing when the manner of rubbing the two rods is interchanged. The only difference that can account for one rod becoming positive and the other negative is the difference in the ways in which the work expended in friction affects the rods. Harper (1967 a) makes a distinction between "smooth" sliding, where points of contact are multiplied, but the sliding is not otherwise significant at the contact and separation of the undulations, and "rough" sliding, in which contact and separation involve the seizure and fracture of material. Truly frictional charging would be a consequence of rough sliding, whereas smooth sliding implies contact charging according to the Volta-Helmholtz hypothesis.

Solid bodies may also receive surface charges by deformation or cleavage. References to works dealing with this kind of charging are found in the bibliography at the end.

Before discussing the various charging mechanisms for systems involving insulators, it is valuable to see to what extent the conventional energy band model for insulators can be applicable to polymers. These materials are more or less crystalline, so the existence of a band structure is not so obvious. The author has used a polymer, Teflon, with a crystallinity of about 60% in the electrification experiments to be described later.

2.1 Electronic properties of polymers

Estimates of the position of energy levels for insulators, based on either theory or experiment, are scarce even for simple substances. Montgomery (1959) outlines a model for fiber-forming polymers proceeding from the electron affinity and the ionization potential of the constituent molecules. Krupp (1971) derives the energy levels for a polymer in a similar way, which is quoted below.
First, we look at the electronic properties of individual molecules in the gas phase.

Second, we condense these molecules into a molecular crystal.

Third, we take the molecular crystal as a model of a polymer. The electronic properties of a polymer are determined primarily by that constituent group in which the electrons are least firmly bound. Thus an electronic model of for instance polytetrafluoroethylene is a molecular crystal of fluorocarbon chains. In this simplified picture different degrees of crystallinity of the polymers are ignored. Using the first and second steps of this procedure we obtain the energy band description of a molecular crystal shown in figure 2.1.

![Energy levels of a molecular crystal derived from the energy states of gas molecules. A = 0.1-1 eV; P = 1.5-2 eV; I = 8-11 eV. A is the electron affinity, P the polarization energy, I the ionization energy. After Krupp (1971).](image)

The energy difference $I-A$ between the negative and the positive molecular ion in the gaseous state is reduced by $2P$ when the solid is formed. This polarization energy is gained by these two ions polarizing their respective environments in the solid. Hence, the corresponding band gap in the solid is

$$E_g = I - A - 2P$$  \hspace{1cm} (2.1)
A second conduction band $E'_c$ is obtained by placing a free electron into the solid so that again a polarization energy $P$ is gained. In this case, the electron is not in an orbital of a constituent molecule. The energy difference between the first ($E_c$) and the second ($E'_c$) band is

$$E'_c - E_c = A$$

(2.2)

This extrapolation from the properties of gas molecules is justified by the fact that a long chain of atoms is connected by primary valence bonds having large penetration of electron charge densities along the chain, whereas transverse to the axis of the fiber there are secondary valence bonds between atoms of different chains, and there is only slight interpenetration of electron charge clouds. Thus the properties of the constituent atoms of a chain are greatly affected by being built into a chain, whereas the properties of the chains themselves are affected little by being built into an aggregate. The intramolecular binding energies are $\geq 3$ eV and the intermolecular ones about 0.1 eV according to Krupp. For the same reason the width of the energy bands $E_v$ and $E_c$ is of the order of 0.1 eV only.

![Figure 2.2 Electronic levels in a polymer. After Bauser et al (1971).](image)

Following Bauser et al (1971), we now take the final step from a molecular crystal to a polymeric insulator, see figure 2.2. Instead of a valence band $E_v$ and a conduction band $E_c$ one has individual energy levels closely spaced with respect to location (intermolecular distance) and energy (fraction of 1 eV). Each level represents a whole molecular unit (e.g. fluorocarbon chain). The energy differences are due to local differences in the overlap integrals...
which, in turn, result from differences in the local molecular environment of each molecular unit.

In order to arrive at a more realistic picture, figure 2.2 has to be modified by introducing surface states and bulk defect states within the energy gap. The complete energy diagram of a polymer is shown in figure 2.3.

Figure 2.3 Energy diagram of a polymer including surface states and bulk defect levels. After Krupp (1971).

Bauser et al (1971) say that these trap levels in the energy gap are due to chemical and mechanical defects, and the surface states are due in addition to specific surface defects such as oxidation products, broken chains and adsorbed molecules.

Because of the small energy differences between the localized conduction and valence levels in a polymer these can as an approximation be represented by a solid line as in conventional energy level diagrams of insulators.

2.2 Contact charging mechanisms

A great deal of empirical evidence has accumulated concerning the charging of insulators, but there is still no great consensus of opinion about the mechanisms involved. Charging mechanisms can be classified according to the type of charge carrier transferred, electrons and ions.
2.2.1 Electron transfer

Several authors, for instance Gonsalves (1953), Vick (1953) and Arthur (1955), have discussed the possibility of electron transfer between crystalline insulators and other materials in terms of the band theory of the solid state, and some detailed calculations have been made by Van Ostenburg and Montgomery (1958) and Harper (1967 b). According to Morris (1970) the most likely relative dispositions of the various electronic energy levels which can arise at a metal-insulator contact are shown in figure 2.4.

In these diagrams the energy levels are shown before contact. $W_m$ is the work function of the metal, $\chi$ is the electron affinity of the insulator and $E_g$ is the width of the energy range which, according to the simple band theory of crystals, is forbidden to electrons in the material. Morris asserts that the value of $W_m$ is usually from 3 to 5 eV, $\chi$ is from 0.5 to 2 eV and $E_g$ is from 5 to 9 eV for a good insulator. The depth of the Fermi
level in the insulator, $W_1$, is conventionally taken as $x + \frac{1}{2} E_g$.

Both Van Ostenburg and Montgomery (1958) and Harper (1967b) calculate the charging that would occur by electron transfer at contact between a metal and an insulator from the premise that when contact equilibrium has been established the Fermi levels of the two materials must be lined up horizontally. That it must be so can be seen from the following thermodynamical argument. Suppose two sets of energy levels, distinguished by the subscripts 1 and 2, are in thermal equilibrium at constant pressure and temperature. This means that the Gibbs thermodynamic potential $G$ of the combined system should be a minimum, i.e., when one electron is transferred from system 1 to system 2, the resulting change $dG = dG_1 + dG_2$ should vanish. Now according to thermodynamics
\[ T \, dS = dE + pdV - \mu dN \]
where $T$ is the temperature, $S$ the entropy, $E$ the total energy, $p$ the pressure, $V$ the volume, $\mu$ the electrochemical potential and $N$ the number of particles. Now $-\mu/T$ is the change in entropy per particle added at constant $E$ and $V$, so that
\[ \mu = -T \frac{\partial S}{\partial N} E, V \]
(2.4)

At constant pressure and temperature, therefore,
\[ dG = d(E - TS + PV) = \mu dN \]
(2.5)

Applying this to the combined systems under consideration and keeping in mind that $dN_1 = -dN_2$, we may write as the condition for equilibrium at constant $p$ and $T$
\[ \mu_1 dN_1 + \mu_2 dN_2 = 0 \]
(2.6)
or
\[ \mu_1 = \mu_2 \]
(2.7)

Equilibrium thus requires that the $\mu$'s of the two systems be the same. But at low temperatures $\mu$ is close to the Fermi energy $E_F$ in value, so that for two sets of electronic levels, the Fermi level must be the same in equilibrium.
For two metals in contact this leads to the establishment of a contact potential between them. Consider as in figure 2.5 two metals with different work functions $W_1$ and $W_2$.

![Energy diagram for two metals](image)

**Figure 2.5** Energy diagram for two metals, (a) before contact, (b) in contact.

When the two metals are brought into contact electrons will pass over from one metal to the other in such a way as to equalize the Fermi levels of the metals. One metal charges positively and the other negatively, which causes a potential difference between them, called the contact potential, equal to $W_2 - W_1$.

Consider now the case when the insulator (b) and the metal in figure 2.4 are brought together, as shown in figure 2.6. The Fermi level in the insulator is lower than that in the metal and must thus be raised to comply with the condition mentioned above. That is, higher levels in the insulator must become more likely to be occupied and lower levels less likely to be empty. This makes the insulator negatively charged since it was electrically neutral before contact was established. The Fermi level in the metal is lowered and the converse is true; it will be positively charged by supporting the electrons which charge the insulator negatively. In metals the layers of charge are of molecular dimensions, but such concentrated layers of charge cannot be accommodated in the levels which are available in insulators, so that the charge layers will be of a considerable thickness.
The charging process superposes an electrostatic potential in the insulator given by Poisson's equation. The charge density appearing in Poisson's equation is equal to the difference between the concentration of positive holes in the valence band and the concentration of electrons in the conduction band multiplied by the electronic charge. These concentrations can be obtained by multiplying the density of states in the valence band and conduction band respectively by the probability of these states being occupied, when the Fermi level has been displaced an amount eV due to the space charge.

For an insulator containing no surface states or impurity levels, according to Harper (1967b), Poisson's equation will then be of the form

\[ \frac{d^2V}{dx^2} = \alpha \sinh \frac{eV}{kT} \]  

(2.8)

where \( \alpha \) is a constant. When the insulator is in equilibrium with the metal, the displaced Fermi level in the insulator must be at the same height as the Fermi level in the metal. This situation is illustrated in figure 2.6b.

![Diagram of electronic energy levels in a metal-insulator system.](image)

**Figure 2.6** Diagram of electronic energy levels in a metal-insulator system. (a) The materials are separated. (b) The materials are in contact and equilibrium has been established.
The condition mentioned above implies that

\[ W_m - x + eV_o = \frac{1}{2} E_g \]  

(2.9)

where \( V_o \) is the value of \( V \) at \( x = 0 \). Thus, the first boundary condition to be satisfied is

\[ eV_o = \frac{1}{2} E_g + x - W_m \]  

(2.10)

The second boundary condition is

\[ \frac{dV}{dx} = 0 \text{ at } x = \infty \]  

(2.11)

From equation (2.8) the charge per unit area of charge layer \( \sigma \) in the insulator can now be found, and appears to be

\[ \sigma = \exp \left( - \frac{W_m - x}{2kT} \right) \]

If one considers the case where the metal and the insulator (a) in figure 2.4 are brought together, it will be found that the insulator charges positively with the charge per unit area given by

\[ \sigma = \exp \left( - \frac{x + E_g - W_m}{2kT} \right) \]

Thus charge transfer, on this theory would be exponentially dependent on the work function of the metal and negligibly small unless \( W_m \) happened to be very close to either \( x \) or \( (x + E_g) \). Furthermore, if one calculates the thickness of the charge layer, it is found to be much larger than the dimensions of insulators used in electrification experiments. However, putting \( \frac{dV}{dx} = 0 \) at \( x = L \) where \( L \) is the thickness of the specimen, instead of at \( x = \infty \), does not in principle alter the preceding results according to Harper (1967 b).

These calculations exclude the presence of localized electron or hole trapping sites in the insulator which have energies in the "forbidden" range. Harper (1967 b) considers the contact between a metal and an insulator containing such traps. He concludes that significant contact charging might arise from the filling up of previously empty electron traps in an
insulator as a result of contact with a metal, but that doubts about this charging mechanism occur as one considers the time scale. In order to find the localized electron levels in which electrons from the metal become captured, these electrons have to diffuse through insulating material in which the resistivity is unaffected by the presence of traps. When this diffusion process is completed, the concentration gradient gives rise to a diffusion transport of electrons which is balanced by the electrical current which flows down the potential gradient. The rate at which equilibrium is set up by diffusion is therefore correlated with the rate at which charge is transported by the electric field when equilibrium has been reached. This can be calculated from the resistivity of the material. If the time constant associated with the charging is $\tau$, then the order of magnitude will be given by the charge divided by the mean current and this is

$$\tau = \frac{2\rho X}{\sigma}$$ (2.12)

where $\rho$ is the resistivity, $X$ is the thickness of the charge layer, $V$ is the potential, which multiplied by $e$ gives the shift of the Fermi level in order to establish thermodynamic equilibrium and $\sigma$ is the charge per unit area of the insulator. There is a relation between the thickness of the layer and the density of traps, $N$, of the form

$$X = N^{-1/2}$$

Harper gives a numerical example with following values: $N = 10^{12} \text{ cm}^{-3}$, for which $X$ becomes $3.3 \times 10^{-3} \text{ cm}$, $V = 1 \text{ V}$, $\sigma = 0.53 \times 10^{-9} \text{ C cm}^{-2}$ and $\rho = 10^{18} \Omega \text{ cm}$. These values give $\tau \sim 41 \text{ days}$. For an insulator to be a good one, the trap density cannot be exceptionally large and with observed values of charge densities the charging process would take too long to be observable in general.

Bauser et al (1971) estimate the charging time from another basis, and they consider polymers. They argue that as long as tunnelling between impurity levels can be neglected, something which must be true of highly insulating polymers, the traps have to be filled via the conduction levels. An upper limit for the current injected into the insulator can be calculated from the Richardson equation for thermionic emission.
\[ j < j_{\text{Rich}} = A T^2 \exp(-W_{\text{eff}}/kT) \]  \hspace{1cm} (2.13)

where \( W_{\text{eff}} = W_m - x \).

For \( W_{\text{eff}} = 1 \text{ eV} \) the time necessary for accumulating a surface charge of \( 10^{-8} \text{ C cm}^{-2} \) will be longer than 3 minutes and if \( W_{\text{eff}} = 2 \text{ eV} \) it will take more than \( 5 \times 10^{14} \) days to achieve this charge density. Actually \( j \) may be much smaller than \( j_{\text{Rich}} \), but even if \( j = j_{\text{Rich}} \), there is no appreciable charge transfer to the polymer within a reasonable time unless \( W_{\text{eff}} < 1 \text{ eV} \).

In order to explain the results obtained from electrification experiments Bauser et al consider the effect of the occurrence of surface states.

Before contact the surface states will be filled to a level corresponding to the Fermi level of the insulator. Band bending in the insulator is ignored. When bringing it into contact with a metal, surface states between this limit and the Fermi level of the metal can be filled or emptied instantaneously, depending on whether the Fermi level of the metal lies above or below that of the insulator.

If the density of surface states is not too large, all the states between the insulator and metal Fermi level will be filled (or emptied), see figure 2.7.
The instantaneous filling of the surface states causes only a small potential difference so that no thermodynamic equilibrium is established by this mechanism only. In a second step equilibrium is established by the formation of a space charge involving bulk levels, but this process will take a very long time.

For a high density of surface states the Fermi level of the insulator will be closely fixed to the surface because enough surface states close to the Fermi level can be filled in order to raise it up to the Fermi level of the metal, i.e. in order to build up the contact potential.

According to Krupp (1971) the charge per unit area of the insulator can be written

$$\sigma = - e D_s \Delta W_i$$

(2.14)

since all charges are in surface states.
$D_s$ is the number of surface states per unit area and unit energy, and is assumed to be constant. $\Delta W_i$ is the shift of the surface Fermi level caused by the surface charge. When the surface states are filled up to the Fermi level of the metal the energy necessary to take an electron from the Fermi level of the metal onto that of the insulator surface is zero, thus

$$W_m + eV = W_i - \Delta W_i$$  \hspace{1cm} (2.15)

$V$ is the potential difference in the gap between the metal and the insulator and is given by

$$V = - \frac{\alpha z}{\varepsilon_0}$$  \hspace{1cm} (2.16)

where $z$ is the width of the gap. If $D_s$ is not too large so that $\frac{\varepsilon^2 z}{\varepsilon_0} D_s << 1$ then

$$\sigma = eD_s (W_m - W_i)$$  \hspace{1cm} (2.17)

for the surface charge density of the insulator. The energy distribution of the surface states is considered to be continuous.

Thus the surface charge $\sigma$ of the insulator after contact with a metal is directly proportional to its surface state density $D_s$ and to work function difference.

Several experiments have been reported on the charging of insulators, mostly polymers, by contact with metals. The linear relationship between $\sigma$ and $W_m$ has been confirmed by for instance Arridge (1967), Davies (1967a, 1969), Inculet and Wituschek (1967), Challande (1971) and Cunningham and Hood (1970). In the experiments of Arridge (1967), threads of nylon were charged statically by light contact with various metals, the contact potentials of which were measured against Au at the same time. Davies (1967a) measured the charge density deposited on polythene and boron aluminosilicate glass by contact with various metals in a vacuum of $10^{-5}$ torr. The contact potentials of the metals used were measured during the experiments. These investigations were later extended to include a number of polymers (Davies 1969). Davies then made use of rolling contact between an earthed contact
wheel, comprising segments of different metals, and polymeric specimens mounted on an earthed drum. The contact time was long to ensure charge saturation. Inulet and Wituschek (1967) studied the charge deposited on borosilicate glass by various metals sliding on the glass in a vacuum of \(3 \times 10^{-7}\) torr. The charge densities obtained were correlated to values of the metal work functions not measured in the same experiment but taken from another investigator. The same is valid for the experiments of Challande (1971), in which he rubbed wires of various metals against sapphire. Cunningham and Hood (1970) altered the work functions of the metals used in the contact charging of X-ray films by manipulating the surfaces.

Hays and Donald (1972) investigated the contact charging between mercury and thin polymer films on a grounded substrate. The effect of an external electric field on mercury-polymer charging was studied by applying a bias voltage between the mercury and the grounded substrate. They found that the variation of the contact charge density with the applied field was approximately linear, and the charge density did not depend on contact time when it exceeded a few seconds. From the latter result they concluded that surface rather than bulk properties of the polymer are the determining factors in charge exchange. Extending the theory of Bause et al (1971) and Krupp (1971) to include external electric fields, the charge density \(\sigma(E_A)\) for an applied field \(E_A\) will be

\[
\sigma(E_A) = eD_S(W_m + eE_AZ - W_i)
\]

The fact that \(\sigma\) varied approximately linearly with \(E_A\), together with the observation of the short charging time, supports this theory.

On the other hand, the charging of \(\frac{5}{32}\) - in spheres of amber, polyethylene, polystyrene, nylon, polymethylmethacrylate, polytetrafluoroethylene and ceresin wax against \(\frac{1}{2}\) - in spheres of steel, chromium and gold was found by Harper (1953, 1967 c) to be below the limit of sensitivity of his apparatus (\(3 \times 10^{-10}\) C cm\(^{-2}\)). These materials were classified as electrophobic, whereas others which charged freely such as quartz, silica, magnesium oxide and glass, were called electrophilic. A variety of cleaning procedures was used, so the lack of charging of the electrophobic insulators was unlikely to be due to contamination. Harper concluded that when electrophobic insulators really do charge it is due to electrophilic contamination.
Furthermore, the charging of electrophilic insulators did not show any correlation with the metal work function. From these findings Harper concludes that electrons cannot be involved in the charging of insulators.

2.2.2 Ion transfer

Electrons are thus ruled out as charge carriers in electrification experiments by Harper, and he suggests a mechanism for ionic transfer as being the most important one in electrification experiments where insulators are involved. This mechanism was first considered by Henry (1957) for two insulators in contact, and works so that adventitious ions from a surface on which they are lightly bound cross to another on which they are somewhat more strongly bound, or that these ions diffuse from a surface on which they are abundant to another on which they are less abundant.

A freshly formed surface will frequently be covered with "dangling bonds" and is not permanently stable. In the course of time it will stabilize itself by attracting stray atoms or ions from the surroundings. A probable way is for it to adsorb oxygen. Since oxygen can accept an electron into a deep level, the surface is likely to become negatively charged. It must then acquire positive ions from the surroundings to become neutral. These positive ions may be lightly bound to the surface. Harper (1967 d) considers a simple situation in which ions of charge e are relatively loosely bound to the surfaces of two materials, there being ions of opposite sign, to compensate the charge, more deeply bound to the surfaces, so that only the first kind of ion can escape from one surface and cross to the other when these come into contact. The potential energy of the ions is given as a function of the position between the surfaces in figure 2.8.
Figure 2.8 Potential energy curves for an ion between two surfaces. After Harper (1967d).

In (a) the surfaces are far apart and the energy wells near the surfaces are quite separate. As the surfaces come together the two wells overlap, (b), and in (c) the surfaces are so close that the ions belong effectively to them both, and there is a single narrow energy well. As the surfaces move apart a hump appears at the bottom of the energy well, and this divides the ions into a group that will subsequently belong to one surface and a group that will belong to the other. Let there be a difference in energy $W$ between an ion at the bottom of one well and at the bottom of the other at the critical gap $b$ for which the redistribution is complete. Let the number of mobile ions before contact be $n_1$ and $n_2$ per unit area of the two surfaces respectively. If $n$ ions per unit area cross from one surface to the other as a result of contact, the final distribution is $n_1 - n$ and $n_2 + n$ on the two surfaces respectively and the surface charge densities $\pm ne$. The energy $W$ refers to a single ion unaffected by the presence of other ions. The charge densities on the surfaces give rise to an electric field in the gap equal to $\frac{ne}{\varepsilon_0}$. The total work required to transfer a single ion, allowing for the other ions that have been transferred, is therefore $\frac{ne^2}{\varepsilon_0} b - W$. The distribution function which applies to ions in the present problem is Boltzmann's function, which gives the ratio
\[
\frac{n_1 - n}{n_2 + n} = \exp\left(-\frac{W - \frac{ne^2}{\varepsilon_0}}{kT}\right)
\]

By taking logarithms and rearranging, one obtains for the charge density

\[
\sigma = ne = \frac{W + kT \ln(n_1 - n)/(n_2 + n)}{be/\varepsilon_0}
\]

If \(n_1 = n_2\) and there are plenty of ions so that \(n \ll n_1 \) and \(n_2\), the formula reduces to

\[
\sigma = ne = \frac{W \varepsilon_0}{be}
\]

This is a simple levelling up. The double layer of positive and negative charge on the two surfaces shifts the energy wells belonging to the two surfaces until they are at the same depth, so that no further transfer of ions occurs. If however \(n_1 \neq n_2\), the initial abundance of ions on the two surfaces being different, then a second term is involved which does not disappear for \(W = 0\). Charging occurs because of diffusion of ions from the surface on which they are more abundant to the surface on which they are less abundant. The diffusion would continue until the abundance on the two surfaces was the same, were it not for the fact that the ions are charged. The charge transferred produces an electric field which discourages further transfer and ultimately terminates it.

The author is however not aware of any case in which such a transfer of ions has clearly been proved to be the charging mechanism.

Many surfaces are covered with a water layer under laboratory conditions, and this water layer, normally several molecules thick, will usually contain dissolved impurities. Such impurities are likely to be ionized and the ions could be a source of electrification. Since it is certain that many insulators can charge when completely dry, this mechanism cannot be all-important as is maintained by some investigators. There are however experiments which can very well be explained on the basis of electrolytic charging. This mechanism can be illustrated by experiments described by Knoblauch (1902). They were performed with powders of varying chemical nature. A small quantity of the powder was placed on a plate and then allowed to slide off. Glass and platinum plates, and plates coated with sulphur or paraffin wax were used.
Irrespective of what powder was used, the sulphur was left negatively and the glass plate positively charged. Acid powders charged the platinum and paraffin plates positively and basic powders negatively. The outstanding fact was the strong correlation between the sign of charging and acidic or basic properties. Knoblauch explains the mechanism in the following way: Some water is always present in the neighbourhood of the contact. \( \text{H}^+ \) and \( \text{OH}^- \) ions, when present, diffuse into the water layer and away from the contact. Being light ions, they diffuse further than sluggish heavy ions and are the ones most likely to be left behind when contact is broken. Thus, acids and bases tend to charge chemically inactive and insoluble plates (platinum and paraffin) positively and negatively respectively. Glass surfaces, however, are slightly soluble and strongly basic in character, and this over-rides the nature of the powder, the glass becoming positive. Sulphur, an acid-forming element, works the opposite way and becomes negative.

More recent experiments of Medley (1953) point even more clearly to electrolytic charging. Basic and acidic resins were found to acquire positive and negative charges respectively when shaken from a filter paper. De-acidite is a strong base and Permutit sulphonated polystyrene is a strong acid and due to electrolytic dissociation in adsorbed water

\[
\text{R. NOH} \rightleftharpoons \text{R.N}^+ + \text{OH}^- \\
\text{R. SO}_3\text{H} \rightleftharpoons \text{R.SO}_3^- + \text{H}^+
\]

De-acidite became positive and Permutit negative presumably owing to the transfer of the hydroxyl and hydrogen ions to the paper because the other ion constitutes a part of the polymer matrix and is not free to move.

2.3 Frictional charging mechanisms

The experiments involving asymmetric rubbing of identical rods performed by Shaw (1927) and Henry (1953) are probably the most striking evidence of true frictional charging. Henry (1957) has put forward a theory concerning asymmetric rubbing in which charging depends upon the temperature gradient across the interface. Where a given spot on one surface is continually brought against fresh unrubbed places on the other, there will be a large
temperature gradient maintained across the interface. This will cause any mobile particles to travel more frequently from the hot to the cold region, a process analogous to the Thomson effect in metals. If the mobile particles are charged and predominantly of one sign, there will be a net transfer of charge from one surface to the other which will continue until the increasing electrostatic field caused by the charge built up balances the thermal effect and stops further transfer. The charge carriers may be electrons or ions, positive or negative, and if mobile ions of both signs are present, the sign of charging will depend on the relative mobilities. Apart from complications, the sign of the significant charge carrier is the same as the sign of the charge on the rubbing surface (that with the extended contact area). One would expect a rise in temperature to release electrons before releasing positive ions, and hence an insulator should give rubber/rubbed negative/positive. Shaw and Hanstock (1930) found this to be true only for silk but not for other materials, and Henry (1957) also stated that the converse is valid for most of the materials he investigated. It would thus seem that it is usually positive ions that move, but not always.

Besides charging due to the formation of hot spots, frictional charging can also result from material transfer. Rough sliding involves some transfer of bulk matter from one surface to the other. The specks of matter transferred will come from asperities, and these asperities may be different electrically from the rest of the surface. In the case of a metal covered with a film of oxide, for instance, the transferred material may be the underlying metal exposed by breaking up the oxide. The metal will have a different contact potential from the oxide, so the specks transferred will carry a charge derived from the potential difference between them. However, little is as yet known about charging by material transfer and its importance.

Friction being high does not however necessarily lead to phenomena which give rise to frictional charging. The work expended in friction acts indirectly, and hence there is no reason to expect a correlation between the work done and the charge generated. Nor has any such correlation been found, with the exception of the investigations of Cunningham (1964). Insulating belts passed over grounded metal rollers, and for small values of the work expended he found a linear relationship between charge and work.
2.4 Charge backflow during separation

It is comparatively easy to measure the charge on one body after it has been separated from another. Owing to charge backflow during the separation of bodies the charge measured may be much less than that which existed when the bodies were in contact. It is important to know whether the mechanism and magnitude of charge backflow are such that the theories of electrification can be tested by measuring the charge after separation. During the initial part of the separation some of the charge may leak back by tunnelling if the carriers are electrons. The charge decreases, as long as the tunnel effect is operative, so as to maintain the contact potential between the surfaces, since the capacitance between them decreases at separation. After the tunnel effect has faded out the remaining charge is retained and the potential difference between them rises above the contact potential. Under the influence of this increasing potential the charge carriers tend to move in such a way as to recombine, except when the separation is effected by lifting; moreover the potential difference may reach breakdown voltage leading to ionization of gas molecules in the gap between the charged surfaces, and charge can be transported back across the gap. To avoid breakdown one can work in a vacuum or in a pressure greater than atmospheric; in both cases breakdown voltage is increased. Another method is to use samples in thin sheet form backed by an earthed conductor. The induced charge on this conductor cancels most of the field due to the charge to be measured. This protective effect does not come into action until the distance between the retreating surfaces is comparable with the thickness of the insulating sample.

Recombination by conduction and electrical breakdown are discussed further in chapter 6.1 and 7.1 respectively in connexion with experiments concerning these factors.

Backflow of charge due to tunnelling is discussed by Krupp (1971) to some extent. He concludes that for a polymer with a density $D_S$ of surface states which is not too large so that equation (2.17) is valid, the charge density $\sigma$ is independent of the distance $z$ between the surfaces, and hence the back tunnelling of surface charge is negligible.
3 APPARENT AND REAL AREA OF CONTACT

It is very difficult to prepare surfaces which are really flat. Even on carefully polished surfaces, hills and valleys are present, which are large compared with the size of a molecule. If two solids are placed in contact, the upper surface will be supported on the summits of the irregularities, and large areas of the surfaces will be separated by a distance which is great compared with the molecular range of action. Most of the surfaces which are characterized as flat have irregularities which are much greater than \( 1 \mu \). Since the range of molecular attraction is only a few Angström, we may expect that the area of intimate contact, i.e. the area over which the surfaces are within molecular range, will even for carefully prepared surfaces be considerably less than the apparent area of contact. Various experimental methods have been developed and applied to the measurement of the size and shape of the irregularities which are present on solids. In one method, a tracer needle passes slowly over the surface and follows its contours. The stylus is usually a conical diamond, which may have a radius of curvature at its tip as small as \( 2 \times 10^{-4} \) cm. The vertical movement of the stylus is amplified electronically and recorded on a moving paper.

One of the Teflon strips used in an electrification experiment has been examined with such a method, and the result is shown in figure 3.1.

![Figure 3.1](image)

**Figure 3.1** The profile of the surface of a Teflon strip used in electrification experiments. Electrification tracks are to be seen at A and B.

The stylus has passed across the surface with two electrification tracks at A and B. It can be seen that there are asperities and valleys the dimensions of which are some \( \mu \).
3.1 Theoretical calculations of the contact area

The calculation of the real area of contact, or even the prediction of how this varies with load, is very difficult. Early attempts to develop a mathematical treatment applied the deformation laws of ideal macroscopic bodies to individual asperities. For example, classical elastic theory, Hertz (1881), was applied to the contact between a spherical asperity and a flat to obtain the relation

\[ A = k_1 M^{2/3} \]  

(3.1)

where \( A \) is the real area of contact, \( M \) is the load and \( k_1 \) is a constant. Alternatively, Meyer's law for the plastic contact between a sphere and a plane, Meyer (1908), was used to support the assumption that the contact area is proportional to the load.

Archard (1957) extended the spherical asperity model by assuming that each asperity is covered with microasperities, and each microasperity with micromicroasperities thus obtaining successively closer approximation to the law

\[ A = k_2 M \]  

(3.2)

as more stages were considered. Archard explained that the essential part of the argument was not the choice of asperity model, but whether an increase in load creates new contact areas or increases the size of existing ones; for physically plausible surfaces any elastic model in which the number of contacts remains constant will give \( A \propto M^{2/3} \), but if the average size remains constant and the number increases the area will be proportional to the load.

More recently Greenwood and Williamson (1966) developed a theory which combines the elastic behaviour of individual asperities with a realistic description of the statistics of the asperity population, and this approach has been extended by Greenwood and Tripp (1967) and (1970-1) to treat the cooperative behaviour of the asperities corresponding to the case of contact between rough curved bodies. First they take as their model surfaces which have asperities closely resembling those found on real surfaces, the levels usually showing a Gaussian distribution. They then consider how these will deform if there is a finite elastic limit. They show that for very smooth contours and modest loads the asperities may still be within the elastic limit of the material. For rougher surfaces or higher loads plastic deforma-
tion gradually takes over. In both situations the area of real contact is very nearly proportional to the load.

For greater loads or rougher surfaces the pressure on the asperities reaches the local plastic yield pressure \( p \), which is very nearly constant and is comparable to the indentation hardness. Under these conditions the area of contact for any one asperity bearing a load \( m_1 \) is \( A_1 = \frac{m_1}{p} \), so that for an assembly of asperities the total area is

\[
A = A_1 + A_2 + \ldots = \frac{m_1}{p} + \frac{m_2}{p} + \ldots = \frac{M}{p} \quad (3.3)
\]

where \( M \) is the total load. The area is thus proportional to the load and independent of the geometry of the surfaces. When the local pressures suffice to cause plastic flow, an approximative value of the total area of true contact may be obtained by dividing the applied load by the flow pressure of the softer material.

In marked contrast to metals, there appears to be little or no junction growth during sliding on a polymer, so that the area of junctions sheared is essentially the same as the area of contact formed under static loading conditions. Evidence of this is provided by careful comparisons of the track width formed during sliding and the diameter of the equivalent static indentation. It is also confirmed by a preliminary study of the deformation properties of "model" junctions made of polymeric materials (Pascoe and Tabor, 1956). Adams (1963) has carried out a detailed study of the contact between a smooth hemisphere of nylon and flat glass surface whilst sliding occurred. Using optical interference, he found that the static area of contact did not change when sliding occurred, indicating that the area of contact is determined primarily by the normal load and that the junction growth during sliding is negligible.

If we approximate the yield pressure during sliding with the static yield pressure or indentation hardness \( P \), then the real area of contact can be expressed as

\[
A = \frac{M}{P} \quad (3.4)
\]

The value of \( P \) found from a hardness measurement cannot of course be assumed to be identical with the mean pressure \( p \) in the sliding process,
since the magnitude and the time of application \( t \) of the load \( M \) are quite different in the two cases. However, according to King and Tabor (1953) the variation of \( P \) with \( M \) and \( t \) is not very rapid; it does not therefore seem unreasonable to use the static yield pressure \( P \) instead of the local yield pressure during sliding \( p \) in order to get an estimation of the real area of contact \( A \).

3.2 Experimental determinations of the contact area

Several investigators, among others Lincoln (1952), Howell and Mazur (1953), have attempted to determine the apparent area of contact between polymeric materials by pressing a specimen of spherical or elliptical shape of the polymer against a hard flat surface, (for instance, glass) and measuring the boundaries of the region of contact by means of optical interference methods or by direct microscope inspection. Pascoe and Tabor (1956) pressed a hard steel sphere on to a flat block of polymer. The size of the indentation formed was measured with a microscope. In some cases a thin soot film was used to facilitate the observations. Common to all these investigators is that they found a relation between the apparent area \( A \) of contact and the load \( M \) of the form

\[
A = k_3 M^n
\]  

(3.5)

where for each polymer \( n \) takes a single value for a wide range of loads, and that value lies between the values for true elastic deformation and plastic deformation, indicating that the deformation is neither plastic nor elastic. Measurements of the area of contact have very marked limitations, however. First, the exact location of the boundary of the contact region is uncertain. Second, the optical area of contact is the same as the real or true area of contact only if the surfaces are molecularly smooth, and for most surfaces this is not the case.
4 METHODS FOR MEASURING CHARGE AND WORK FUNCTION

In electrification experiments, static electric charge must be measured in some convenient way. This chapter therefore starts with a survey of the methods available for that purpose. After that the most important methods for measuring the work function of metals are summarized, since the aim of the final part of the investigations was to test the contact potential theory in which work functions for metals are involved.

4.1 Methods for measuring static electric charge

For qualitative measurements of excess charge on insulators, a technique of value has been the use of "Lichtenberg figures", named after the scientist researcher who discovered them in 1777. In this technique a well-triturated mixture of powdered materials, differing in electrifiability and in colour, is dusted over a charged surface. During the mixing of the two powders, one will charge positively and the other negatively by means of the contact between them. Each of the two powders is then attracted to the areas of the insulator having a charge of opposite sign. Traditionally a mixture of sulphur and red lead has been used.

A charged body induces charge on a conductor and exerts force on it. Quantitative methods of measuring charge are based on either of these effects, or in a few cases involving continuous production of static electric charges, galvanometric methods can be used.

4.1.1 Inductive methods

The method of the Faraday cage gives an absolute value of the total charge of a body and it is useful not only for solid bodies but also for liquids and gases. Figure 4.1 shows a schematic diagram of components necessary for a measurement.
Figure 4.1 Schematic diagram of the experimental arrangement for measurement of charge with the method of the Faraday cage. $C_s$ is a shunt capacitor, $S$ a switch and $E$ an electrometer.

The Faraday cage consists of two electrodes. The inner electrode is electrically connected to the shunt capacitor and electrometer input, and is supported from the outer electrode by high-resistance insulators. The inner electrode is hollow and shaped so that it can contain the specimen to be measured. The outer electrode is electrically grounded and encloses the inner electrode.

To perform the experiments one briefly closes the switch ($S$) and inserts the specimen the charge of which is to be measured into the inner electrode. A charge $Q$ of the same magnitude as that of the specimen but of opposite sign is now induced in the system of capacitances $C$ consisting of the capacitances in parallel of the Faraday cage, the shunt capacitor and the electrometer. The resulting potential $V$ on the inner electrode is read on the electrometer and the relation

$$ Q = CV $$

(4.1)

gives the magnitude of the total charge of the body.
It is not always possible to have the experimental body even approximately surrounded by a conductor, and then the method of the Faraday cage is not applicable, and many times one is interested in the distribution of the charge. In such cases a capacitive probe can be used. The probe, which is a conductor, is connected to an electrometer. It is usually situated in a fixed relationship to the region the charge of which is to be measured, and surrounding bodies, which should be conductors held at a fixed potential. The probe is exposed to the field from the charge to be measured and takes a potential proportional to that charge. Since the induced charge on the electrode is no longer equal to the inducing charge, the necessary induction coefficient, giving the relation between the potential of the probe and inducing charge, is no longer equal to the capacity to earth of the detecting system and is more difficult to determine. Generally this method does not give the absolute values of the charge, but it is very useful for relative measurements. Probe electrodes can however be calibrated in absolute terms by placing the sample in a Faraday cage, if possible, and comparing the readings. With proper geometry, for instance when the sample is flat and the probe electrode is a flat plate parallel to the sample and at a short distance from it compared with its dimensions, and all other bodies are at much greater distances, the coefficient of induction can be determined and then absolute measurements with the charge detecting probe can be made. This type of charge detector can be designed in various ways, see for instance Ieda et al (1968), Davies (1967b, 1969), Foord (1969), Wintle (1970) and van Turnhout (1971).

4.1.2 Ponderomotive method

The fact that a charged object exerts a force on a conductor is a basis of a method for measuring charge. An electrode which covers the charged area is placed on it and the force needed to separate the electrode from the object is measured by some means, Turnhout (1971). With favourable experimental geometry, plane parallel samples and electrodes, this force can be related to the surface charge density of the sample. With inductive methods the mean value of the surface charge density of the region A, over which the electrode is effective, is read,

$$\sigma_i = A^{-1} \int_{A} \sigma \, da$$  \hspace{1cm} (4.2)
Ponderomotive methods give the R.M.S.-value

\[ \sigma_p = \sqrt{A^{-1} \int_0^A \sigma^2 \, da} \quad (4.3) \]

For uniform charge \( \sigma_p = \sigma_1 \), otherwise they differ, so whenever the force of a charge is important, ponderomotive methods should be used.

4.1.3 Galvanometric method

In the cases involving continuous production of static electric charge in a metal-insulator electrification system, galvanometric methods for measuring the charge can be used. By connecting the metal electrode to an electrometer, the separation charge received by the metal will be conducted to the electrometer, which can register the electrification current by measuring voltage drop across a high resistance. A charge corresponding to that which the electrometer has measured but of opposite polarity is deposited on the insulator. The variations of the electrification current have consequently their analogies in the variations of the charge distribution on the insulator. Thus this method gives information concerning the charge distribution as well as the total charge, obtained by integrating the electrification current.

Since the investigations to be described later were intended for the tangential separation mode of an electrification system consisting of a metal and an insulator, the galvanometric method will be the most suitable one, since one can obtain the charge distribution as well as the total charge of the insulator at the same time. The method of the Faraday cage gives only the total charge, whereas the determination of the absolute value of this quantity by a capacitive probe is not as easily carried out.

4.2 Methods for measuring work function

The most important methods for measuring work functions of metals are those of thermionic emission, photoelectric emission and contact potential, and these will be described later. The first two give absolute values of the work functions, whereas the third gives relative values.

Of other methods available the calorimetric one may be mentioned. It also gives absolute values. For a more exhaustive review of methods to determine
4.2.1 Thermionic emission

The emission current density is given by the Richardson-Dushman equation

\[ j = A(1-r) T^2 e^{\frac{W}{kT}} \]  

(4.4)

where \( A \) is a constant, \( r \) is a coefficient taking into account the reflection of electrons against the potential barrier, \( W \) is the work function and \( k \) is the Boltzmann constant. From the form of equation (4.4) one may be inclined to conclude that by simply plotting \( \ln \frac{j}{T^2} \) against \( \frac{1}{T} \), one obtains \( W \) from the slope of the resulting straight line. There are however factors which complicate the measurements. The apparent work function increases if a negative space charge exists in the vicinity of the emitter. The anode potential should therefore be sufficiently positive to prevent space charge build-up, i.e. one should work in the region of saturation-current density. In simple models the metal-vacuum limit is represented by a discontinuity in the potential. Actually the potential changes smoothly because of the image force on the electron. In the presence of an external electric field the existence of the image potential leads to a reduction of the apparent work function by a factor \(-e(\frac{eE}{4\pi\varepsilon_0})^{1/2}\), so that the Dushman equation becomes

\[ j = A(1-r) T^2 e^{\frac{1}{kT} \left[ W - e\left(\frac{eE}{4\pi\varepsilon_0}\right)^{1/2}\right]} \]  

(4.5)

This phenomenon is called the Schottky effect. Thus if one plots the logarithm of the saturation current for a given temperature as a function of the square root of the anode voltage, one expects a straight line (the Schottky line).

The determination of work function is generally effected in the following way: The emission current is measured for a range of values of the external field at a fixed temperature, and is then extrapolated to zero field strength. This procedure is repeated for a range of temperatures, and the values of the current densities \( j_0 \) received in this way are divided by the respective values of \( T^2 \), and the logarithm of this quantity is plotted against \( \frac{1}{T} \). The apparent work function \( W_a \) is now given by the slope of that Richardson plot.
that is

\[ W_a = - k \left( T^2 \frac{dr/dT}{T - r} - \frac{W}{k} + \frac{T}{k} \frac{dW}{dT} \right) \]  

\[ \frac{dr}{dT} \]  is negligible so the true work function can be written

\[ W = W_a + T \frac{dW}{dT} \]  

Thus the apparent work function is equal to the true work function only for \( T = 0 \). Careful measurements of thermionic emission current must be carried out in ultra-high vacuum in order to keep the surface clean, since oxides and small amounts of adsorbed gases may influence the work function strongly. The same is also valid for the other methods of measuring this quantity.

In this derivation it has been assumed that the work function is the same over the whole area of the emitter; this assumption is valid only if the emitter is a single crystal, since \( W \) varies from one crystallographic plane to another. This is because the atoms are arranged differently in different crystal planes and thus exert somewhat varying forces on an electron near the surface. A polycrystalline metal surface exposes several different crystal planes, each with a specific value of the work function. The thermionic current from such a surface is composed of the emission currents characteristic of each patch. Because different patches with different work functions border upon each other, local electric fields exist, which further complicate the situation. When the external field is small compared with the local field, the work function obtained is given by

\[ \bar{W} = \sum_i f_i W_i \]  

where \( f_i \) is the fraction of the area whose work function is \( W_i \).
For external fields much larger than the local fields, when the latter can be neglected, the value of the work function is not given by equation (4.9) but lies somewhere between the highest and lowest values of the work functions of the individual patches.

The calorimetric method of determining the work function is based on the cooling effect of thermionically emitted electrons. This method gives absolute values, and moreover the temperature dependence can be determined, a quantity which is demanded in the thermionic emission method, see equation (4.8).

4.2.2 Photoelectric emission

Light falling on to a metal can excite electrons to higher energy levels, and if the energy of the light quantum is larger than the work function of the metal, the electron can escape. The energy relation can be written

\[ h\nu = E_k + W \]  \hspace{1cm} (4.10)

where \( \nu \) is the frequency of the incoming radiation and \( E_k \) is the maximum kinetic energy of the released electrons. The energy just enough to release the most energetic electrons in the metal is therefore

\[ h\nu_0 = W \]  \hspace{1cm} (4.11)

and the photocurrent is then zero. This is strictly valid only for a cathode temperature of 0 K.

However, Fowler (1931) and later du Bridge (1933) have worked out theories for the variation of the photocurrent for temperatures other than zero. The photocurrent can be written as

\[ j = \alpha A' T^2 e(x) \]  \hspace{1cm} (4.12)

where \( \alpha \) is a constant and \( A' \) is closely related to the universal constant \( A \) appearing in the Richardson-Dushman equation for thermionic emission. \( e(x) \) is a complicated function of \( x \), where \( x \) is given by
By taking logarithms equation (4.12) can be written

$$\ln \frac{j}{T^2} = \ln(\alpha A') + \ln e(x)$$

(4.14)

The logarithm of e(x) is calculated for various x, and these values are plotted as a function of x. J is measured experimentally as a function of ν and in the same diagram the experimental values of ln \( \frac{j}{T^2} \) are plotted as a function of \( \frac{hν}{kT} \) (= x + \( \frac{hν_o}{kT'} \)).

The two curves plotted in this manner are displaced relative to each other, but by a vertical and a horizontal displacement they can be made to coincide.

The theoretical curve has \( \frac{hν}{kT} - \frac{hν_o}{kT} \) as abscissa whereas the experimental one has \( \frac{hν_o}{kT} \). Thus the horizontal displacement is \( \frac{hν_o}{kT} \) which is equal to \( \frac{W}{kT} \) according to equation (4.11), and knowing this displacement the threshold frequency ν₀ and the work function can be determined.

This is the method, generally accepted and used, for determining the photoelectric threshold and thus the work function by photoemission.

A variant of this method is to measure the photocurrent as a function of temperature for a fixed value of the frequency. It has the advantage that the relative intensities of the spectral lines need not be measured. e(x) is now plotted against ln|x| and the observations of the photocurrent are plotted against ln \( \frac{1}{j} \). The horizontal displacement is in this case ln \( \frac{hν-hν_o}{k} \), from which ν₀ and W can be determined.

4.2.3 Contact potential

By measuring the contact potential between two metals one obtains the difference between their work functions as mentioned in chapter 2.2.1. Of the methods available for measuring contact potentials only the Kelvin-Zisman method will be mentioned here.
Figure 4.2 shows a circuit for measuring the contact potential between the two metals (A) and (B).

Figure 4.2 Circuit for measuring contact potentials by the Kelvin method.

Start with (A) and (B) close together and the switch (S) closed. If the potentiometer is in a position so that no external voltage is applied at (A), then, as the plates are connected to each other, they will be charged according to the condition that in equilibrium their Fermi levels must be at the same height. As a result of that charging, a contact potential $V_c$ exists between the metal electrodes. If after opening the switch (S), one of the two electrodes is suddenly removed, a voltage pulse results from the decrease in capacity which is detected by the electrometer (E). If an external potential is applied to (A) by means of the potentiometer when the switch is closed, the levels of metal (A) are raised or lowered relative to those of metal (B). For a particular value of the external voltage, the charges on the plates vanish, and a change in distance between the plates, when (S) is opened, will not yield a voltage pulse. Clearly, the external voltage then just compensates the contact potential and is equal to $V_c$.

Zisman (1932) improved the method by letting one electrode vibrate with respect to the other. Instead of a dc potential being produced as before, an alternating voltage whose frequency is that of the vibration is thus
developed between the electrodes. This ac signal can be amplified and detected in some appropriate way. As before, an adjustable voltage is applied to one electrode, and when this is equal to the contact potential, the signal vanishes. In this way the contact potential can be measured to an accuracy of 1/1000 of a volt.

As pointed out earlier, this method gives the difference between the work functions of two metals, and it is thus suitable for measurements of the variation of the work function of one of the electrodes. The change of work function with temperature can be measured by this method. It has particular advantages for studying a heterogeneous surface, or for studying the effect of adsorbates on a surface. Unlike many other methods, the calculation of the work function does not depend on an estimate of the electron reflection coefficient of the surface. There are, however, several factors which limit the accuracy of this measuring method, among others noise, the effects of stray capacitance, and variations in the work function of the reference surface.

For polycrystalline materials the contact potential measured is

\[
V_c = \frac{W_2 - W_1}{e}
\]  

(4.15)

where the quantity \( W \) is defined in equation (4.9).

Since the aim of the final part of the electrification experiments was to test the contact potential theory of charging, it was sufficient to know the differences in work functions between the metals used. In the electrification experiments, the metal electrode makes contact with the insulator with the outermost part of its end surface (see chapter 5.1). The work function of interest will thus be the mean of that part of the metal surface. In a contact potential measurement with this electrode, the same part of the surface will be of importance because of the spherical form of the end surface. Furthermore, as can be seen from equations (4.15) and (4.9), the value of the contact potential received refers to the weighted arithmetic mean of the work function of the electrode, and it must be the same mean which is effective in the charging process. The other methods described give an average value that is weighted in favour of low work function patches. Therefore the most convenient method in these experiments is that of contact potential measurements.
4.2.4 Changes of work function due to adsorbed atoms

It is well known that monolayers of adsorbed atoms on pure metals have a surprisingly great effect on the work function. The work function of tungsten may be lowered 3 eV by Cs-adsorption, whereas adsorption of oxygen usually increases the work function of metals.

When an atom which has an ionization energy $I$ is brought near a metal surface whose work function $W$ is greater than $I$, there is a tendency for the outer electron belonging to the atom to be captured by the metal since this situation represents a lower energy configuration. This leaves the atom ionized, and when a monolayer of such ions covers the metal surface a charge double layer results, and the field thus produced reduces the work function. The changes in work function due to adsorbed atoms are not always as large as predicted by this simple explanation. In many cases it is very much as though the layer of adsorbed atoms was only partially ionized. When a free atom with ionization energy little less than the work function of the metal is brought in the neighbourhood of the metal surface, an interaction takes place and the discrete energy state occupied by the outermost electron in the free atom becomes broadened into a band of considerable width. If none of the broadened states lies below the top of the Fermi level in the metal when the atom is on the surface, the atomic electron will leave the atom entirely and reside in the metal leaving the atom ionized, thereby establishing a strong double layer and producing an appreciable decrease in the work function. However, if part of the band of states lies below the Fermi level these states can be occupied by an electron part of the time by tunnelling. Under these circumstances the adsorbed atoms will not be completely ionized, and the resulting charge double layer will not be as strong, and the work function of the monolayer will not be so much smaller than that of the metal before adsorption. The work function can also be reduced though $I > W$ because even here some of the states in the broadened band can lie above the Fermi level in the metal, in which case the layer of atoms will still be partially ionized.

Certain atoms, for instance oxygen and chlorine, have an electron affinity as free atoms, and they can exist stably as negative ions. In oxygen the electron affinity $A$ is of the order of 3 eV. When such an atom is brought to the surface, the deep lying energy state occupied by the outermost electron
of the normal atom is broadened only a little and lies much lower than the Fermi level in the metal, so these states remain filled, there being no exchange of electrons between atom and metal. The upper normally unfilled level is greatly broadened, and some of its states will almost certainly lie below the Fermi level. Since all these states are empty to begin with, some of them become occupied by electrons from the metal. This again produces a charge double layer but in this case the adsorbed atoms are negative. This requires the electrons from the metal to do more work in escaping so that the work function is greater than that of the clean metal.
5 EXPERIMENTAL TECHNIQUE

5.1 Mechanical arrangement

The apparatus consists of a grounded carriage with a plane upper surface (A in figures 5.1 and 5.2), guided by two steel rods (B). The insulator strip (C), 27 cm long, 5 cm wide and 0.2 cm thick is clamped onto the carriage by a frame (D). The metal electrode (E) has a spherical end surface, which makes contact with the insulator as it moves. The electrode is insulated with Teflon from its brass holder (F), which derives a vertical force from a phosphor bronze spring (G), this force being adjustable by means of a screw (H). The spring carries a strain gauge, which enables one to record the possible variation of the force. The strain gauge was calibrated in situ.

The carriage may be moved at constant velocity by means of a play-free lead screw (I), passing between the guide rods (B) and rotated by a motor outside the right flange. The aluminium tank (K) may be pushed to the right to close the chamber, providing the necessary electrostatic screening and an optional vacuum.

In order to facilitate the performance of the measurements in vacuum and to make contact potential measurements possible, the apparatus shown in figures 5.1 and 5.2 was modified somewhat, in a way which can be seen from figure 5.3 and also from figure 5.5 page 50.

The Teflon strip (C), which was put directly on the carriage (A) and fastened by the frame (D), is now "glued" onto a dural plate, which is placed on the carriage, thus making the frame unnecessary.

The screw (H) for manual adjusting of the vertical position of the electrode (E) is replaced by a motor-driven unit with the same notation. The vertical adjusting unit is furnished with a position transducer potentiometer, and with this the desired normal force exerted by the metal electrode on the insulator is adjusted. The dural plate with the insulator strip can be moved sideways on the carriage relative to the electrode by means of two step motors (S), one at each end of the carriage.
Electrification apparatus
A, carriage; B, rods; C, insulator strip; D, frame; E, metal electrode; F, electrode holder; G, spring; H, adjusting screw; I, lead screw; K, tank.

Figure 5.1 Electrification apparatus.
Figure 5.2 Photograph of the electrification apparatus, A, carriage; B, guide rods; C, insulator strip; D, frame; E, metal electrode; F, electrode holder; G, spring; H, adjusting screw; K, tank.

Figure 5.3 Photograph of the modified electrification apparatus. A, carriage; B, guide rods; C, dural plate with insulator strip; E, metal electrode; F, electrode holder; G, spring; H, adjusting equipment; K, tank; R, reference electrode; S, step motor.
The dural plate is a few centimeters longer than the insulator strip, and in the part which protrudes there is a hole drilled through the plate and the upper surface of the carriage. The metal electrode (E) can be lowered through this hole towards a reference electrode (R) situated opposite (E) and just below the upper surface of the carriage when the contact potential between these two metal electrodes is to be measured.

Vacuum is produced by a sorption pump (Varian 949-0010) to obtain a clean vacuum, when evacuation to only about $10^{-2}$ torr is necessary. Otherwise, when a better vacuum is desired, an oil diffusion pump (Edwards E02) backed by a mechanical rotation pump (Edwards ES 100) is used. A baffle and a cold trap are inserted between the diffusion pump and the chamber to obtain a clean vacuum. With this equipment it is possible to achieve a working pressure better than $2 \times 10^{-5}$ torr.

5.2 Measurements

When an electrification experiment was carried out in atmospheric pressure the prepared insulator strip was placed onto the carriage and fastened by the frame. The desired velocity and normal force were adjusted. The carriage was then moved as far as possible to the left, i.e. to the starting position, and the tank was pushed so as to close the chamber. Then the carriage was started. The direction of the movement is to the right in order to provide pure sliding. The run was automatically stopped by the action of a micro-switch. After the run was finished, the metal electrode was lifted up from the insulator by means of the adjusting screw. The carriage was moved to the starting position again, and at the same time the insulator was discharged by a method described in chapter 5.3. The electrode was then moved sideways in relation to the insulator by manually pushing the electrode holder. The process described above for performing an experiment was then repeated, and a new run could be carried out on a fresh part of the insulator.

The velocity was obtained from the figure for the path length and the time for a run which were both measured manually. The normal force was measured by a spring dynamometer. Light was thrown upon the region of contact thus facilitating observation of the moment when the metal electrode was just lifted up from the insulator surface by the action of the dynamometer. The dynamometer then indicated the magnitude of the force derived from the phosphor bronze spring. The strain gauge on the spring was calibrated
in the same way. When the lifting force of the dynamometer was just equal to the normal force from the spring, the strain meter needle jumped, and the scale reading for that movement could be transferred to force by comparing with the dynamometer indication.

The preliminaries for measurements carried out in vacuum are the same as those described above. After the chamber is closed, it is evacuated and the run is performed. When the microswitch has stopped the run, the metal electrode is lifted up from the insulator by the motor-driven adjusting apparatus, and the carriage is brought back to the starting position. The insulator is moved sideways a few millimeters by the action of the stepmotors, and the electrode is then moved down towards the insulator surface. With the aid of the position potentiometer, calibrated by a spring dynamometer, the desired normal force is adjusted, and a new run can be made without breaking the vacuum. The previous charge track has not been discharged, but it influences the electrification current only slightly, and the total charge not at all.

As the Teflon strip moves in relation to the metal electrode, charge will be continuously transferred from the metal to the insulator. The metal will then acquire an ever-increasing potential, unless it is connected to ground, in which case the charge passing to ground equals the charge received by the metal. Approximate grounding of the electrode (< 50 mV) is achieved in this experiment by connecting an electrometer (Keithley 610 B) from the metal electrode to ground, the electrometer then showing the electrification current after passing through a short transient stage. The output of the electrometer is connected directly to a recorder, and via an integrator to a digital voltmeter. The current and the charge are thus continuously recorded along the track.

Charges passing through the electrometer causing the electrification current give rise to image charges on the surface of the grounded carriage. Image charge will also be found on the metal electrode, and it is important to know to what extent the increase of this latter image charge during a run will affect the electrification current. This can be estimated if the charge track on the insulator is approximated by a line charge and the metal electrode by a sphere placed so that one diameter coincides with the extension of the line charge. For the sake of simplicity the thickness of
the insulator is assumed to be much greater than the length of the charge track. The situation is illustrated in figure 5.4.

![Diagram](image)

**Figure 5.4** Approximation of the experimental situation for calculating the image charge on the metal electrode.

The radius of the sphere is a, and the charge density of the line charge, of length L, is \( \lambda \).

According to Reitz and Milford (1960), the situation of a point charge situated outside a conducting sphere can be replaced by that of the point charge and an image charge. If the point charge \( q \) is situated a distance \( r \) from the center of the conducting sphere of radius \( a \), then an image charge equal to \(-\frac{a}{r} q\) situated a distance \( \frac{a^2}{r} \) from the center of the sphere will, together with the point charge, produce a spherical equipotential surface of radius \( a \), concentric with the conducting sphere. Now let the point charge be represented by the charge from an infinitesimal element \( dr \) of the line charge, \( dq = \frac{2}{K+T} \lambda \, dr \). The factor \( \frac{2}{K+T} \) is due to polarization of the insulator. The image charge \( dq_i \) then becomes

\[
dq_i = -\frac{a}{r} \frac{2}{K+T} \lambda \, dr
\]  

(5.1)

The total image charge from a line charge running from \( r=a \) to \( r=a+L \) is then

\[
q_i = \int_{a}^{a+L} -\frac{a}{r} \frac{2}{K+T} \lambda \, dr = -\lambda a \frac{2}{K+T} \ln \left(1 + \frac{L}{a}\right)
\]  

(5.2)
Thus, whereas the charge on the insulator increases in direct proportion to the length of the track, the image charge on the electrode increases by the logarithm of the length, further reduced by a polarization factor, so for the radius $a = 0.15$ cm and the track length $L \approx 20$ cm, the influence of the image charge is of little importance. Moreover, when the length of the charge track is much larger than the thickness of the insulator ($0.2$ cm), the image charge will be found mainly on the surface of the grounded carriage, and the contribution to the image charge on the electrode from that part of the charge track will be negligible. Thus, the influence on the electrification current from the image charge on the metal electrode need not be taken into consideration.

Experiments involving contact potential measurements are carried out in the following way. For reasons given in chapter 8.2, contact potential measurements are carried out only before and not after the electrification experiments. The carriage is moved to the right with the electrode (E) lifted above the insulator strip until the holes drilled in the dural plate and in the carriage (these two holes are always concentric) are directly below the electrode (E) and directly above the reference electrode (R). These two electrodes are always situated immediately opposite each other. This is shown in figure 5.3, and figure 5.5 gives an intersection of the experimental arrangement for measuring contact potentials.
Figure 5.5  Modified electrification apparatus. A, carriage; B, guide rods; C, dural plate with insulator strip; E, metal electrode; F, electrode holder; G, spring; H, adjusting equipment; K, tank; L, permanent magnet; M, coil; N, vibrator holder; O, membrane; P, rod; R, reference electrode. Drawn to scale.
The reference electrode is fixed to a vibrating unit shown in figure 5.6.

![Diagram](image)

**Figure 5.6 Vibrator.** L, permanent magnet; M, coil; O, membrane; P, rod; R, reference electrode.

It consists of a magnet with cylindrical geometry the intersection of which can be seen in figure 5.5. A rod (P), on the top of which is fastened the reference electrode (R), runs through the center of the magnet and is free to move vertically. Fixed on to this rod are also a coil (M), which is located in the gap of the magnet, and a thin brass membrane (O) providing a restoring force on the coil (M).

An alternating current is now sent through the coil (M), and the interaction between the magnetic fields of the current-carrying coil and the permanent magnet (L) causes the rod (P) with the electrode (R) to vibrate with the frequency of the current. The electrical connexion from (E) is switched over from the electrometer to the circuit shown in figures 5.7 and 5.8.
Figure 5.7 Block diagram of the circuit for contact potential measurements.
Figure 5.8 Circuit for contact potential measurements.
The electrode (E) is then lowered towards the vibrating reference electrode (R) and the distance between them is adjusted to obtain the greatest possible signal. Figure 5.7 is a block scheme of the circuit used for the measuring of the contact potential between the metal electrodes (E) and (R) by the Zisman method described in chapter 4.2.3. Figure 5.8 shows the circuit in detail. (E) and (R) constitute together a capacitor with varying capacitance. Since they are in contact with each other via the external circuit, a contact potential exists between them. The periodic change of the capacitance causes a periodic change of charge on the electrodes which appears as an alternating current at the input of the amplifier. The amplified signal is fed to a selective amplifier and is then studied on an oscilloscope. By applying a potential from the potentiometer unit equal in magnitude to the contact potential but of opposite polarity, the initial charge on the electrodes will be neutralized, and the signal on the oscilloscope vanishes. By means of a switch the electrodes can be made to change places in the circuit and the correctness of the measurements can thereby be ascertained. The contact potential could be measured with an accuracy of 0.02 V, which is quite sufficient for the purpose.

After the contact potential is measured, the electrode (E) is lifted up so that the insulator strip can move freely beneath it. The carriage is then moved to the left to the starting position, and the electrification experiment can be performed in the way described earlier in this chapter. All this can be done with the tank evacuated.

5.3 Preparation

The Teflon batches were produced by Habia K B, Knivsta, Sweden, and have a crystallinity of about 60%; the size of the grains comprising the batches was about 20-30 μ.

The Teflon surfaces were prepared by grinding with emery cloth, using gradually finer grain, followed by wet grinding and washing with distilled water. In the first series of experiments, the samples were finally washed with an organic solvent, such as benzine, but since the washing did not seem to have any bearing whatsoever on the results, this last phase in the preparation was later abandoned.
The insulator was found to be charged after the preparation, and it was found that this spurious charge influenced the results. The mechanical preparation was therefore always followed by brief irradiation, using the $\beta$-rays of a $^{85}$Kr source, with a strength of 1 mC. The result of this treatment could be examined with the present apparatus, which permits measurements to be taken with the metal electrode lifted slightly (0.5 mm) above the surface of the insulator. As the carriage moves, the electrometer then registers the time derivative of the image charge on the electrode, the latter charge being proportional to the density of spurious charge. It was found that the irradiation reduced the spurious charge to less than $10^{-3}$ of the original charge density.

The purity of the polycrystalline metals used was better than 99.95% with the exception of the copper electrode used in the investigations concerning the role of friction in the electrification experiments, in which case it was about 99.8%.

The metal end surfaces were ground and polished using normal workshop procedures, and the spherical shape was inspected and the radius measured by observation of the silhouette under a microscope.
6 RESULTS FROM ATMOSPHERIC MEASUREMENTS

The electrification experiments were first performed in atmospheric pressure in order to obtain as soon as possible an indication of how the parameters—velocity, radius of curvature and normal force, characterizing the friction involved, influence the charging of Teflon. On the basis of these first-hand data, the directions of following work and the final design of the apparatus could then be determined.

6.1 Recombination by conduction

In order to arrive at the primary charge of electrification, one must take into account besides the influence of the image charge which was discussed in chapter 5.2, also the conduction current back to the metal from charges already deposited on the insulator. Knowing the conduction properties of the insulator, one could in principle calculate the current back to the electrode, but reasonably complete knowledge of the surface and volume conductivities, including non-linear effects, are not available to accomplish such a calculation.

Information regarding the magnitude of the conduction current may be obtained in a direct manner in the experimental arrangement. The carriage may be stopped suddenly during the electrification process, in which case the electrometer proceeds to measure only the conductivity current, which has the opposite sign. Figure 6.1 illustrates such a measurement. Recordings of the electrometer display when the metal electrode stands on an uncharged Teflon surface are shown in figure 6.1a and immediately after the carriage has been stopped during an electrification process in figure 6.1b. The currents measured in these experiments are a factor of about 0.01 times the smallest ones obtained in electrification experiments.
Figure 6.1a Electrometer current when the metal electrode stands on an uncharged part of a Teflon plate.

Figure 6.1b Electrometer current immediately after the carriage has been stopped in an electrification experiment.
If there was an appreciable back flow of charge, the electrometer would have shown a negative or at least a less positive current at first, but no such reduction of current can be seen in (b) compared with (a). Due to the finite response time of the electrometer (1 sec) the possibility of conductive recombination may not be completely ruled out on the basis of these tests. It can be concluded however, that 1 second after the carriage has been stopped, there is no detectable conduction current. That means that during a run with the velocity \( v \) mm s\(^{-1}\) there is no back flow of charges from that part of the charge track which is situated further away from the metal electrode than \( v \) mm. This conclusion can be drawn only for velocities giving rise to electrification currents much larger than the grid current of the electrometer, since otherwise one cannot rule out the occurrence of a long range conductivity current of importance. On basis of the values of velocities used and of electrification currents measured, one can say that long range conductivity (> 0.01 mm) had a negligible influence in the electrification experiments on Teflon.

Since the metal electrode moves away from each charged region, the conduction current would depend on the velocity of the electrode. Charges from the depletion region would have more time to flow back for a low sliding velocity than for a high. The total back flow of charge would then be more complete from the depletion region if the velocity is low. Table 7.1 (page 71) shows, however, that the electrification charge received from the experiments does not decrease with decreasing velocity but is constant, indicating that recombination by conduction is of no importance in the experiments.
Figure 6.2 (a) The electrification current from an experiment. (b) The time derivative of the charge deposited on the insulator immediately after the electrification experiment. (c) The time derivative 14 days later.
Information on the long-range conductivity was also obtained by observing charged tracks after electrification. The charge along the track was investigated repeatedly in the same manner as in chapter 5.3. To avoid that the charge track collected ions of opposite sign from the atmosphere this experiment was performed in a vacuum of about \(10^{-6}\) torr. It was found that the charge density was reduced to 90\% of its original value after 24 hours and to 70\% after 14 days. A corresponding investigation performed in air gave the result that the charge diminished to half the original value after 60 hours. The charge density structure remained virtually the same, as can be seen from figure 6.2, which indicates that the charges had not distributed themselves on the surface but had proceeded across the strip to ground. A flow of charges once deposited on the insulator surface directed elsewhere than towards the metal electrode does not affect the primary charge measured. Under all circumstances, however, it may be estimated from these data that the contribution to the electrification current due to long-range recombination would be less than \(10^{-3}\).

6.2 Reproducibility

An investigation of the reproducibility for the system copper-Teflon was carried out. A number of Teflon strips cut from a larger batch were used in the investigation. A few runs were made on each strip, and in all 40 runs were performed. The velocity was 2.0 mm s\(^{-1}\), the radius of curvature of the copper electrode was 1.5 mm and the normal force was 0.50 N.

Teflon proved to charge negatively with a mean value of the linear charge density of \(2.6 \times 10^{-10}\) C cm\(^{-1}\) for the values of the parameters above. The standard deviation was 8\%. Figure 6.3 shows the frequency of occurrence for the different values of the linear charge density obtained.
A similar investigation was performed for another batch of Teflon. The two batches were observed to yield 6% difference in the mean value.

Of other investigators of metal-insulator electrification involving sliding or rolling friction, Wagner (1956) obtained a reproducibility of 20% when quartz spheres were rolling on a metal in high vacuum. For spheres of ionic crystals the reproducibility was found to be within a factor of two only. In rubbing a filament of nylon on a filament of tantalum, Cunningham and Montgomery (1958) obtained values from sample-to-sample and day-to-day runs lying within $\pm$ 20% of the mean. The reproducibility of similar experiments carried out by Montgomery et al (1961) was found to be of the same magnitude. Challande (1967) rubbed metal wires on crystals of NaCl and Al$_2$O$_3$ and his results were determined with a variation of less than 5% making about 100 measurements on each sample.
6.3 Velocity dependence

Twenty measurements were made at each of the velocities 0.20, 2.0 and 20 mm s\(^{-1}\), each time using a fresh part of the Teflon plate. The radius of curvature of the metal electrode was \(r = 1.5\) mm and the perpendicular load \(F = 0.50\) N throughout this series of experiments. The results are summarized in table 6.1. It is evident that the linear charge density is independent of the velocity.

Table 6.1

<table>
<thead>
<tr>
<th>Velocity (mm s(^{-1}))</th>
<th>0.20</th>
<th>2.0</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density (10(^{-10}) C cm(^{-1}))</td>
<td>2.6</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Standard deviation (%)</td>
<td>12</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

6.4 Radius of curvature dependence

The radius of the copper electrode was varied, while the load was kept constant at 0.50 N and the velocity at 2.0 mm s\(^{-1}\). Twenty measurements were carried out for each value of the radius. The results are given in table 6.2.

Table 6.2

<table>
<thead>
<tr>
<th>Radius of curvature (mm)</th>
<th>0.3</th>
<th>0.6</th>
<th>1.1</th>
<th>1.5</th>
<th>3.2</th>
<th>4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density (10(^{-10}) C cm(^{-1}))</td>
<td>2.3</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Standard deviation (%)</td>
<td>9</td>
<td>9</td>
<td>8</td>
<td>11</td>
<td>12</td>
<td>13</td>
</tr>
</tbody>
</table>

In addition, the width of the area of contact was measured as a function of the radius of curvature. An aluminium layer 10 µm thick was evaporated onto a Teflon plate, which was then fixed to the carriage in the apparatus, and the width of the track left by the copper electrode was measured by means of a workshop microscope. The result of these measurements was that the track width increased by a factor of 1.6 with increasing radius over the interval of radii given in table 6.2 while the linear charge density increased only by a factor of 1.1.
Figure 6.4 Photograph of the tracks left on an aluminized Teflon surface by metal electrodes with radii of curvature equal to 0.3 mm (at the top), 1.5 mm (in the middle) and 3.2 mm (at the bottom). The normal force was 0.50 N. Magnification: 20 times.

Figure 6.4 shows a photograph of the tracks left on an aluminized Teflon surface by a copper electrode for various radii of curvature. From this figure it can be seen that within the general area scraped by the slider there appear to be untouched areas, and that the fraction of untouched area is larger for larger radii than for smaller. The track width thus over-estimates the real contact area particularly for large radii of curvature and is consequently not a good measure of the real contact area.

6.5 Force dependence

The charge density was also investigated as a function of the normal force (F) between the metal and the insulator. Twenty measurements were carried out for each value chosen between the limits 0.05 N and 3.0 N. The variation of the force during a run and from run to run was less than 6% for the smallest force, and less than 1% for the largest one. The radius of curvatur
was constant at 1.5 mm and the velocity at 2.0 mm s\(^{-1}\) during this series.

The charge per cm \( (\lambda) \) was found to fit well to the formula
\[
\lambda = F^{0.42}
\]  
(see figure 6.5)

![Graph showing \( \lambda \) (C cm\(^{-1}\)) versus \( F^{0.42} \) with data points and error bars.](image)

**Figure 6.5** Plot of the charge per cm \( \lambda \) versus \( F^{0.42} \), where \( F \) is the normal force. The standard deviations are marked.

The track width \( (d) \) was measured as in section 6.4, and it was found that excellent fit was obtained by means of the functional relation \( d = F^{0.43} \) as illustrated by figure 6.6. The exponent obtained is in reasonable agreement with the results of Pascoe and Tabor (1956), who report a value of 0.40 for this exponent.
Figure 6.6 Plot of the track width $d$ versus $F^{0.43}$, where $F$ is the normal force.
Figure 6.7 Photograph of the tracks left on an aluminized Teflon surface by a metal electrode. The normal force in each case was from the top to the bottom of the figure 0.10 N, 0.50 N, 1.2 N and 3.0 N. The radius of curvature was 1.5 mm. Magnification: 20 times.

Figure 6.7 shows a photograph of the tracks on an aluminized Teflon surface for various normal forces exerted by the slider. From this figure it can be seen that the fraction of untouched area within the general area of contact is larger for small normal forces than for large ones.
7.1 Pressure dependence

Measurements of the electrification charge were made for various pressures from 760 torr to $2 \times 10^{-5}$ torr. The velocity was $2.0 \text{ mm s}^{-1}$, the radius of curvature 1.5 mm and the normal force 0.50 N. To avoid the risk of differences between various Teflon specimens influencing the results, the experiments were carried out in such a way that on each Teflon specimen one measurement for each of the pressures was made. Five measurements for each pressure were sufficient to establish the charge-pressure dependence shown in figure 7.1.

Figure 7.1 Plot of the charge per cm $\lambda$ against the pressure $p$.

From the figure it can be seen that the linear charge density decreases with the pressure down to about 10 torr, where it is approximately zero. For further decrease in pressure the charge density now increases, but for pressures of 0.1 torr and below, the charge density takes a constant value about 20% higher than that for 760 torr.
Figure 7.2 Electrification current from experiments performed in 0.01 torr (a) and 760 torr (b) on the same Teflon plate.
For those Teflon specimens acquiring low charge density the magnitude of this quantity was about the same for 760 torr as for pressures below 0.1 torr. For those Teflon specimens acquiring high charge density, however, for low pressures one could obtain a charge exceeding that received for 760 torr by far more than 20%. Such a case is illustrated in figure 7.2 showing the electrification current from a run at the pressures 0.01 torr and 760 torr respectively. The runs were made on the same Teflon strip. In the current curve from the atmospheric experiment there are several jerks downward. It is highly probable that these are due to electrical breakdown, which limits the charge density in atmospheric pressure. It was not possible to manifest the breakdown by seeing or hearing sparks. However, in an experiment carried out in atmospheric pressure an electrified region of a Teflon plate was made to pass just beneath the metal electrode. The electrometer in this case shows the variations of the charge induced in the metal electrode, and the recorded curve exhibits the same type of jerks. In this latter case breakdown could be detected both by seeing and hearing. It therefore seems very probable that breakdown causes the jerks in the electrification current curves.

The conditions for breakdown can in certain cases be found from the so-called Paschen curves. These are graphs of the dependence of the sparking potential $V_s$ on the product $pd_s$, where $p$ is the pressure and $d_s$ is the sparking or breakdown distance. It has namely been found experimentally that the sparking potential is a function of the product of the pressure and the sparking distance, i.e.

$$V_s = f(pd_s)$$  \hspace{1cm} (7.1)

and this has been proved theoretically correct. This relation is called Paschen’s law. It holds true for uniform fields or non-uniform fields caused by gap geometry. The general shape of the Paschen curves may be deduced from elementary considerations. At very low pressures the collision frequency is low, so that sufficient ionization is maintained only by increasing the probability of ionization at each collision; consequently the electron velocity, and thus the electric field, must be high. Hence $V_s$ must increase as $p$ diminishes when $p$ is very low. On the other hand, at higher pressures, the collision frequency is high, and the rate of energy loss correspondingly high, while the energy gained per free path is low unless the field is correspondingly high. Thus, the field must be increased when $p$ is increased at high pressures for a given $d_s$, and the curve must show a
minimum value of $V_s$ for a certain value of the product $p d_s$. This minimum occurs when $p d_s$ is of the order of 1-10 torr cm. Paschen's law holds strictly true only if the form of the field does not change when $p d_s$ is changed.

In the experimental arrangement used in these investigations that condition can hardly be fulfilled, since sparking may occur from different regions of the charge track for different pressures. However, it seems reasonable according to the shape of the Paschen curves to assume that for each pressure $p$ there exists a region a distance $d_s$ (which can have different values for different pressures) from the metal electrode for which the conditions for sparking are especially favorable. The geometrical arrangements of the experiments would then favor sparking at pressures of about 10 torr. For low pressures, the value of the sparking potential is never reached and therefore sparking does not occur.

Variations of the electrification charge with the pressure similar to those found in this investigation were discovered by Debeau (1944) in experiments where insulating particles slid down a metal. The charge had a minimum value at 1 torr. Debeau explained the results as being due to adsorbed layers of gas. Gill (1948) suggested, however, that breakdown is the factor which limited the charge in Debeau's experiments and pointed out the resemblance between the curve charge against pressure and the curve of sparking potential against pressure. Medley (1954) rubbed films of nylon and alkanthene against a platinum wire at various pressures. When he decreased the pressure from 760 torr, the charge density first decreased and had a minimum value of about zero for pressures around some 20 or 30 torr. For still decreasing pressure the charge now increased and finally reached a value about twice that obtained at 760 torr. This result agrees very well with my findings. Peterson (1954a, b) also found a minimum in the curve charge against pressure when a borosilicate glass sphere was rolling in a nickel cylinder. Like Debeau, he found that the minimum value of charge occurred at 1 torr. The charge on the glass sphere was measured by means of a probe placed above the sphere, and Peterson observed that for pressures below 10 torr all discharges went to the probe and above 40 torr all discharges occurred to the nickel cylinder. Peterson explained this observation thus: for higher pressures the most favorable distance for sparking becomes less than that from the sphere to the probe, and discharges occur to the cylinder. For lower pressures the conditions for discharges to the probe
are more favorable. This explanation is based on Paschen's law. It is striking that the minimum values of charge for various investigators all occur at pressures of the order of 1-10 torr although the experimental arrangements differ.

The most important conclusion that can be drawn from the measurements described in this chapter is, however, that in some of the experiments carried out under atmospheric conditions, breakdown has been the factor which determined the value of the electrification charge received, and not solely the parameters in regard to which the measurements were made. No conclusions should therefore be drawn from the measurements in atmospheric pressure only, because the results could be misleading. These measurements had to be repeated in vacuum, and from figure 7.1 it can be seen that it is sufficient to work in vacuum better than 0.1 torr. Thus, experiments were carried out in a pressure of 0.01 torr in which velocity, radius of curvature and normal force were varied.

### 7.2 Velocity dependence

The linear charge density was measured for the velocities 2.0, 0.20 and 0.02 mm s\(^{-1}\). This investigation, as well as those of radius and force dependence, were carried out in the same way as corresponding ones in atmospheric pressure. The results are summarized in table 7.1. It is evident that the linear charge density is independent of the velocity even when measured in vacuum.

<table>
<thead>
<tr>
<th>Velocity (mm s(^{-1}))</th>
<th>0.02</th>
<th>0.20</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density (10(^{-10}) C cm(^{-1}))</td>
<td>2.9</td>
<td>3.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

### 7.3 Radius of curvature dependence

The measurements were carried out for the smallest, an intermediate and the largest value of the radii of curvature used in the measurements under atmospheric conditions. The results are given in table 7.2.
Table 7.2

<table>
<thead>
<tr>
<th>Radius of curvature (mm)</th>
<th>0.3</th>
<th>1.1</th>
<th>4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density (10^{-10}\text{ C cm}^{-1})</td>
<td>3.0</td>
<td>3.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

7.4 Force dependence

The results of these measurements are shown in figure 7.3, where it can be seen that the charge per cm (\(\lambda\)) fits well to the formula \(\lambda \sim F^{0.50}\).

As a comparison the linear charge densities obtained in the measurements in atmospheric pressure are plotted in the same diagram versus \(F^{0.50}\) instead of \(F^{0.42}\) as in figure 6.5.

Figure 7.3 Plot of the charge per cm \(\lambda\) versus \(F^{0.50}\), where \(F\) is the normal force.
7.5 Charging by an electrode with ellipsoidal end surface

Measurements were made in vacuum of the electrification charge generated by an electrode with approximately ellipsoidal end surface. The radii of curvature of this end surface at the region where contact was made were 0.5 mm and 2.5 mm. The area swept out on the insulator could thus be changed by orienting the ellipsoid in different directions with respect to the velocity. The ratio between the charges acquired when maximum area and minimum area was swept out was found to be 1.7, whereas the ratio between corresponding track widths was 1.8.

7.6 Comparisons between vacuum and atmospheric measurements

Concerning velocity and radius of curvature the trend is the same for the results from the measurements in air and in vacuum. Experiments performed in vacuum gave a higher value of the charge densities quite in agreement with the results from the investigation of the linear charge density as a function of the ambient pressure presented in section 7.1.

The variation of the linear charge density $\lambda$ with the normal force $F$ differs, however, in the two cases. It is evident from figure 6.5 page 64, that the charge per cm received from measurements in air fits well to the formula $\lambda = F^{-0.42}$. Figure 7.3 on the other hand shows a relationship of the form $\lambda = F^{-0.50}$ for vacuum measurements when the normal force does not exceed 1.5 N. For forces larger than this $\lambda$ increases still more rapidly. Possible reasons for this are given later in this section. This figure also shows that there is a linear relationship between charge and force up to $F = 1.2$ N, when the values of the charge from the atmospheric measurements are plotted against the square root of the force. The slope of this line is however different, namely 0.7 times that for the line corresponding to the vacuum measurements. This is in agreement with previously found quota between the charge densities received in air and vacuum respectively. For forces greater than 1.2 N, $\lambda$ diverges from the straight line. A plausible explanation is that according to the results of the vacuum measurements in figure 7.3 the charge density increases more rapidly for large normal forces than for small ones, leading to greater probability of breakdown with accompanying decrease of the charge on the insulator as a consequence when measuring in air. The fact that the linear charge density in air for large normal forces as a result of breakdown increases more slowly than
for small ones means that all values measured could be fitted to the relation \( \lambda \propto F^{0.42} \) as in figure 6.5.

In order to see if the large charge density acquired in vacuum measurements for the force 3.0 N could be explained by the influence of frictional heating, a thermocouple was placed in a hole drilled into the metal electrode, so that it was situated just at the contact region when a run was carried through. The temperature rise of the metal in the contact region was however less than 0.1 degree, so an additional charging due to frictional heating could be excluded.

An experiment was also carried out in which an electrification run was first made with a normal force of 0.8 N. Then a new run was made with a normal force of 0.2 N in the charge track made in the previous run without first discharging it. The charge now deposited on the already charged insulator was not zero, however, but a factor of 0.3 of what was acquired when performing a run with the force 0.2 N on a fresh part of the same insulator strip. If one anticipates the results of experiments being described later and assumes that the charging mechanism consists of electrons from the metal being drawn into traps in the insulator, the following factors may contribute to this charging. First, during the time between the two runs, electrons may have diffused from traps near the surface into deeper-lying ones, thus leaving empty ones at the surface which can readily be filled again. Experiments concerning the decay of a charge track indicate, however, that the rate of such a process is too slow to account for the magnitude of charging. Second, although the normal force in the second run is less than in the first, owing to irregularities on the metal electrode and on the insulator surface, the metal may have been in contact with fresh areas within the charged track of the insulator, and third, the metal electrode may have created new traps during the first run as a consequence of the force exerted by it. For a large normal force a large area of the metal electrode is in contact with the insulator thus increasing the possibility for the two last mechanisms mentioned above to give the insulator an extra amount of charge.

7.7 Conclusions and discussion

We have seen that the linear charge density is independent of the relative velocity, that it is independent of the radius of curvature and that its
variation with the force could be expressed by a simple power law $\lambda \propto F^{0.50}$ for forces less than 1.5 N.

Figure 6.7 page 66 indicates that the fraction of untouched area within the general area of contact is larger for small normal forces than for large ones, and thus that the real area of contact would increase more rapidly with force than the apparent area, where the latter is given by the product of the length and the track width. It must be noted, however, that the track width varies more slowly with applied normal force ($\propto F^{0.43}$) than is predicted by Meyer (1908), Archard (1957) and Greenwood and Tripp (1970-1) ($\propto F^{0.50}$, corresponding to direct proportionality between contact area and force in the case of static indentation). This depends on the fact that for the constant length of the track, the width of it constitutes a measure of the apparent area of contact, while the theoretical predictions are valid for the real area of contact. The relation found by most investigators $A \propto F^n$ where $n$ takes a value between the theoretical expectation for elastic deformation (0.33) and for plastic deformation (0.50) is valid for the apparent area.

Thus, the real contact area varies with the applied normal force with an exponent larger than 0.43. It seems therefore plausible to assume that the value of this exponent is 0.50. The charge deposited on the insulator would consequently be proportional to the real area of contact within the range of the parameter values, for which the above summing-up is valid. The results from the measurements with the electrode with ellipsoidal end surface support the hypothesis of proportionality between charge and area.

Lacking knowledge of the way in which the Teflon surface deforms, one does not know the real area of contact. Therefore one must express the charge density as the charge per unit apparent area. The apparent area used is what which is observed for the normal force 0.50 N, which is an intermediate value. From the experiments performed, one can thus conclude that Teflon acquires a charge of $-2.4 \times 10^{-8}$ C cm$^{-2}$ when sliding against copper.

Velocity dependence of the charging of nylon monofils rubbed with a Ta wire is reported by Cunningham and Montgomery (1958). They find a charge which is approximately proportional to velocity up to about 20 mm s$^{-1}$, tending to a constant value at higher velocities. I find a constant value throughout
their proportionality region, and I believe that the difference arises from conductive recombination in nylon. The effect of varying force is given by Medley (1954) for Pt and keratin fiber. The dependence is in qualitative agreement with the present results. The dependence of charge on normal force and filament diameter for nylon monofils rubbed on a Ta wire has been investigated by Montgomery et al (1961). Their data suggest a relation \( q = F^{0.5} \), which with a dependence on the filament diameter for the geometry of their arrangements lead to the conclusion that the charge is proportional to the true or real area of contact. Sasaki (1969) also concluded that the charge generated on a polypropylene sample is proportional to the real area of contact when it is rubbed against both metals and insulators. The charge was approximately independent of the rub velocity in the interval 1-11 mm s\(^{-1}\) for the electrification system polypropylene-Pt.

Investigations of the relationship between charge and normal force for NaCl and Al\(_2\)O\(_3\) rubbed against a Ta wire have been made by Challande et al (1967). They find a linear relationship for the perfect crystal of Al\(_2\)O\(_3\) and an exponential relationship for NaCl owing to lattice defects present. Challande used insulating materials quite different from polymers and the charging mechanism for the crystals used may be different from that for polymers, which perhaps can be the reason for the discrepancy between his results and mine.

Cunningham (1964) found a linear relationship between charge per unit area and work per unit area of an insulating belt passing over grounded metal rollers for small values of work. For large values of work Cunningham (1966) found that the charge approached a limiting value. If Amonton's law of friction (frictional force is proportional to normal force) holds true in that case, then the charge generated is directly proportional to the normal force for low values of this quantity and independent of the normal force for high values of the force. These results are not consistent with those presented in this paper, but the two investigations are not directly comparable since Cunningham relates the charge to the work done and not to the normal force.

The proportionality found between charge and area in my investigations is, of course, compatible with the contact potential theory, but the same is
true of other theories which have been advanced. My results indicate that electrification in the sliding mode may be analysed and interpreted as simply as the lifting mode experiments, and that it can be used for investigation of the fundamental mechanism of charge transfer.
8 MEASUREMENTS WITH ELECTRODES OF DIFFERENT METALS

8.1 Experimental arrangement

In order to investigate the influence of the metal work function on the charging of Teflon electrification experiments were carried out with electrodes of Al, Au, Cu, Mg, Ni, Pt and Dural. Ten measurements were made with each of the metal electrodes in a vacuum better than \(2 \times 10^{-5}\) torr. In order to avoid, as far as possible, the risk that inhomogeneities in the Teflon batch from which the experimental specimens were taken would influence the electrification experiments, on each Teflon specimen used an equal number of runs with each metal electrode was made. Successive runs with the same electrode could be made without breaking the vacuum, and when changing metal electrode the Teflon specimen was discharged. The contact potential between the metal electrode to be used in the electrification experiment and the Pt reference electrode was measured in a vacuum better than \(2 \times 10^{-5}\) torr immediately before the electrification run; the latter could then be performed without breaking the vacuum as described in chapter 5.2.

In order not to contaminate the metal, no polish was used in the preparation of the spherical end surfaces of the electrodes. These were prepared twice during the experiment series to avoid too much abrasion.

The radius of curvature of the electrodes used was 1.5 mm, the normal force 0.50 N and the velocity \(0.8 \text{ mm s}^{-1}\).

8.2 Contact potential measurements

The contact potentials between the metal electrodes used and the Pt reference electrode were measured in connexion with the electrification experiments as described in chapter 5.2. The measurements were made only immediately before and not after the electrification runs, because the values obtained after the runs were inconsistent. Sometimes the values were the same as measured before the run, but otherwise large negative values were obtained, and these were also time-dependent. The reason for this discrepancy is probably that small, negatively-charged pieces of Teflon have attached themselves to the metal electrode, so in these cases it is not the real contact potential which is measured.
The values of the contact potentials between the metals used and the reference metal Pt are given in table 8.1 together with the standard deviations.

Table 8.1

<table>
<thead>
<tr>
<th>Metal</th>
<th>Contact potential versus Pt (V)</th>
<th>Standard deviation (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>+ 0.96</td>
<td>0.19</td>
</tr>
<tr>
<td>Al</td>
<td>+ 0.61</td>
<td>0.17</td>
</tr>
<tr>
<td>Dural</td>
<td>+ 0.35</td>
<td>0.07</td>
</tr>
<tr>
<td>Pt</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>- 0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>Cu</td>
<td>- 0.18</td>
<td>0.08</td>
</tr>
<tr>
<td>Au</td>
<td>- 0.23</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The value obtained for Cu indicates a remarkably high work function compared with the sparse values found in reference sources. A possible reason for this may be that the metals are prepared in atmospheric pressure and no cleaning procedure is applied in vacuum, and therefore the values in table 8.1 may be more or less affected by oxide layers and adsorbed atoms. Rivière (1957) measured the contact potential between clean metal surfaces in ultra high vacuum using the vibrating condenser method, and his results show that the work function of Cu is lower than that obtained from table 8.1 when comparing the contact potentials of Cu, Au, Ni and Al versus a reference metal.

To see if the crystallinity of the Cu electrode would have a noticeable influence on the contact potential and thus explain the value in table 8.1, a Cu electrode formed as a plate was made. This plate was heated, a process which caused the plate to recrystallize. After cooling the plate was bent sharply and then straightened in the middle, thus destroying the crystallinity in that region. The contact potential of different regions of different degrees of crystallinity could then be measured, but no significant differences could be observed.

For the other metals, however, there is reasonable agreement between the values measured and those found in reference sources. Thus it might
probably be said that the contact potentials measured are representative of the work functions of the clean metals.

The variation with the pressure of the contact potentials was also studied to see if it had any significance in the pressure region in which the measurements were made. The results are shown in figure 8.1, from which it can be seen that for each of the metals the contact potential decreases with decreasing pressure in the region from 760 torr to \(10^{-1}\) torr. Except for Mg, the contact potential is constant for lower pressures, so the dependence on the pressure is not critical for the measurements. Furthermore, it seems unlikely that an improvement of the vacuum to \(10^{-6}\) torr, which is the ultimate pressure with the pump equipment, would drastically alter the conditions present at the working pressure \(2 \times 10^{-5}\) torr. The trend is the same for decreasing and increasing pressure, and the variation is probably due to the release and adsorption of atoms.
Figure 8.1 Variation of the contact potentials with the pressure.
8.3 Work function dependence of charge

The results from the electrification experiments with electrodes of different metals are shown in figure 8.2, where the linear charge density deposited on the Teflon surface by a certain metal electrode is plotted against the measured contact potential of this metal relative Pt.

![Graph showing charge density versus contact potential for different metals](image)

Figure 8.2 Plot of the charge per cm \( \lambda \) against the contact potential measured relative Pt. Standard deviations are marked.
Disregarding Cu, for which the value is marked by a circle as distinct from the other values plotted, the linear dependence is quite evident. The charge density obtained from Cu is too great in relation to the contact potential measured to fit the linear relation. However, as mentioned before, the contact potential value for Cu indicates a remarkably large work function. The metal surfaces are not clean at the beginning of the electrification experiments, but during the run they are scraped, and this can be seen after the run, so it seems reasonable to suppose that the contact is between the insulator and the clean metal. Since the vacuum is not better than $10^{-5}$ torr, the metal end surface will be covered by adsorbed gas atoms within a few tenths of a second. This layer may affect the work function of the metals in some of the ways described in chapter 4.2.4. If one assumes that for some reason electronegative atoms are adsorbed more readily on Cu than on the other metals used, thus increasing the work function, then the contact potential relative Pt measured before or after the electrification experiment represents a larger work function than that which is effective during an electrification experiment. As a consequence of this the circle representing Cu should be moved to the right in figure 8.2 and it would then fit the linear relation better.

8.4 Conclusions and discussion

A linear relation was found between the linear charge density and the contact potential. As the radius of curvature and the normal force were the same for each metal electrode, and the apparent contact area was found to be the same, one can state that the real area of contact also was the same for all metals used. As contact potentials give relative values of work functions, the obtained results can be expressed by saying that the charge per unit area deposited on Teflon by a metal is directly proportional to the work function of the metal. The charge per unit area of apparent contact is given in table 8.2.

Table 8.2

<table>
<thead>
<tr>
<th>Metal</th>
<th>Charge density on Teflon ($10^{-8}$ C cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>- 2.6</td>
</tr>
<tr>
<td>Al</td>
<td>- 2.2</td>
</tr>
<tr>
<td>Dural</td>
<td>- 2.0</td>
</tr>
</tbody>
</table>
Consider now the time it takes the charging process to occur. Table 7.2 in chapter 7.3 gives a linear charge density of $3.0 \times 10^{-10} \text{ C cm}^{-1}$ for a Cu-electrode with radius of curvature equal to 0.3 mm sliding over the insulator with a velocity of 2 mm s$^{-1}$. The track width for the normal force used was found to be 0.1 mm, and this is also the diameter of the instantaneous contact region. With the velocity used, no point on the insulator will be in contact with the metal for more than 0.05 seconds. During this time that part of the Teflon surface which is in contact with the metal acquires the charge density $2.7 \times 10^{-8} \text{ C cm}^{-2}$. Using the velocity 0.02 mm s$^{-1}$ and the radius 1.5 mm, contact is extended to 7 seconds, a factor 140 larger than the time obtained above. Table 7.1 in chapter 7.2 gives a linear charge density of $2.9 \times 10^{-10} \text{ C cm}^{-1}$, i.e. approximately the same as in the previous example. The charging can thus be considered to be instantaneous, since after the first few hundredths of a second, no further charging of noticeable magnitude takes place.

The experimental findings of this investigation, a linear relationship between the polymer charge density and the metal work function and an effective charging time of less than one tenth of a second, support the theory of Bauser et al (1971) and Krupp (1971). This theory, which is described in chapter 2.2.1, can be summarized by saying that a polymer in contact with a metal is instantaneously charged by means of electrons from the metal filling empty surface states up to a level corresponding to the Fermi level of the metal. Equation (2.17) gives the charge density obtained from this theory:

$$\sigma = e D_s (W_m - W_f)$$  \hspace{1cm} (2.17)

As can be seen from this equation, the charge density is directly proportional to the metal work function when the energy distribution of the surface states ($D_s$) is continuous. The linearity found between these parameters thus indicates that the number of surface states per unit energy and unit area is constant and can be calculated from the slope of the line in figure 8.2 by converting linear charge density to charge per unit area, and contact
potentials to relative values of work functions. One finds that
\[ D_s = 7 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}. \]
This value fulfills the condition
\[ \frac{e^2}{\varepsilon_0} z D_s \ll 1, \]
even when taking into account the fact that the charge per
unit area of real contact is larger thus giving a greater value of \( D_s \) than
that mentioned above, which it had to do in order that equation (2.17)
should be valid. \( z \) is the distance between the bodies in contact and is
about 4 Å. \( \sigma \) does not depend on \( z \), for which reason there will be no back
tunnelling of charge, so the values in table 8.2 are representative of the
charging due to contact between these metals and Teflon.

Hays and Donald (1972) also suggest this charging mechanism for explaining
their experimental findings described in chapter 2.2.1.

The linear relationship between \( \sigma \) and \( W_m \) for metal-insulator systems has been
confirmed by among others Arridge (1967), Davies (1967a, 1969), Cunningham
and Hood (1970), as mentioned in chapter 2.2.1. Of these investigators, only
Davies (1969) studied the charging of PTFE. The only fact mentioned about
the preparation of the polymers in his experiments is that they are washed
with isopropanol. Davies found, however (and this is quite remarkable), that
PTFE acquired a positive charge from contact with Pt and Au, that is, the
work function of PTFE would be smaller than that of these two metals. Extrapolating the line in figure 8.2 gives a work function for Teflon which is
about 1.5 and 1.3 eV larger than those of Pt and Au respectively. These values
are in reasonable agreement with the value of the work function for Teflon
found by Strelia (not published) and which is mentioned by Seanor (1972).
According to Strelia the work function for Teflon is about 1 eV larger than
that of Au. Kittaka (1959) also found the work function of Teflon to be
larger than that of Pt from the fact that Teflon charged negatively against
Pt.

On the other hand the charging of a \( \frac{5}{32} \) - in sphere of Teflon against \( \frac{1}{2} \) -
in spheres of steel, chromium and gold was found by Harper (1953) to be below
the limit of sensitivity of his apparatus (3 \( \times \) \( 10^{-10} \) C cm\(^{-2}\)). Harper prepared
the Teflon spheres mechanically by using a microtome. The lack of charging
of Teflon in contact with metals is in disagreement with the results of the
present investigation (and of all others concerning Teflon as far as the
author is aware).
According to equation (2.17), the charge density is proportional to the surface state density. A possible explanation of the disagreement between the findings of Harper (1953) and the results from this investigation may be that the different mechanical preparation methods used have created different densities of surface states leading to different degrees of charging.

In conclusion one can say that although the results from these investigations support the theory for charging of a metal-polymer system worked out by Bauser et al (1971) and Krupp (1971), equation (2.17) has not been experimentally verified in a satisfactory way, since no independent measurement has been made either of the surface state density for the Teflon specimens used, or of the work function difference between Teflon and Pt.
ACKNOWLEDGEMENTS

I wish first to express my sincere gratitude to Professor Gunnar Bäckström for his inspiring interest, valuable criticism and never-failing support throughout my work.

I am also most indebted to Mr Martin Forsgren for his ingenuity and skill devoted to building the equipment, and to Mr Frank Nordhage for many intelligent ideas and valuable discussions.

Thanks are also due to Miss Margaretha Schörling for the many hours of conscientious work she has devoted to typing the manuscript.
REFERENCES

Adams, N. 1963, J. Appl. Polymer Sci. 7, 2075
Archard, J.A. 1957, Proc. R. Soc. A 243, 190
Bauser, H. 1971, Advances in Static Electricity, vol. 1 (Brussels: Auxilia), pp 2-9
Klöpffer, W. Rabenhorst, H.
Montgomery, D.J.
1958, Text. Res. J. 28, 971
1964, J. Appl. Phys. 35, 2332
1966, J. Appl. Phys. 37, 1734
1970, J. Colloid Interface Sci. 32, 373
1971, Advances in Static Electricity, vol. 1 (Brussels: Auxilia), pp 156-63
1944, Phys. Rev. 66, 9
Du Bridge, L.A. 1933, Phys. Rev. 43, 727
Fowler, R.H. 1931, Phys. Rev. 38, 45
Fukada, E. 1958, Nature 181, 693
Fowler, J.F.
Gill, E.W.B. 1948, Phys. Rev. 74, 842
Greenwood, J.A.
Tripp, J.H.
Tripp, J.H.
Hays, D.A. 1972, Annual Report, Conference on Electrical
Insulation and Dielectric Phenomena. National
Academy of Science, Washington, D.C. pp 74-82

Donald, D.K.

Henniker, J. 1962, Nature 196, 474

Henry, P.S.H. 1953, Brit. J. Appl. Phys. (Suppl. 2) 4, S31


Herrmann, G. 1951, The Oxide Coated Cathode
Wagener, S.

(London: Chapman and Hall), chapter 2

Hertz, H. 1881, J. reine angew. Math. 92, 156


Mazur, J.

Ieda, M. 1968, Elec. Eng. in Japan 88, 67

Sawa, G.

Shinohara, U.

Incuilet, I.I. 1967, Proc. 2nd Conf. on Static Electrification:
Wituschek, E.P.


Tabor, D.


Knoblauch, O. 1902, Z. phys. Chem. 39, 225

Krupp, H. 1971, Proc. 3rd Conf. on Static Electrification:


Loeb, L.B. 1958, Static electrification (Berlin: Springer), p 1
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Year &amp; Publication Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medley, J.A.</td>
<td>1953, Nature 171, 1077</td>
</tr>
<tr>
<td>Medley, J.A.</td>
<td>1954, J. Text. Inst. 45, T123</td>
</tr>
<tr>
<td>Meyer, E.</td>
<td>1908, Z. Ver. dt. Ing. 52, 645</td>
</tr>
<tr>
<td>Montgomery, D.J.</td>
<td>1959, Solid State Physics, vol 9</td>
</tr>
<tr>
<td></td>
<td>(New York: Academic Press), pp 139-97</td>
</tr>
<tr>
<td>Smith, A.E.</td>
<td></td>
</tr>
<tr>
<td>Wintermute, E.H.</td>
<td></td>
</tr>
<tr>
<td>Morris, W.T.</td>
<td>1970, Plastics and Polymers 38, 41</td>
</tr>
<tr>
<td>Tabor, D.</td>
<td></td>
</tr>
<tr>
<td>Reitz, J.R.</td>
<td>1960, Foundations of Electromagnetic Theory</td>
</tr>
<tr>
<td>Milford, F.J.</td>
<td>(Reading: Addison-Wesley) pp 59-61</td>
</tr>
<tr>
<td>Rose, G.S.</td>
<td>1957, Brit. J. Appl. Phys. 8, 121</td>
</tr>
<tr>
<td>Ward, S.G.</td>
<td></td>
</tr>
<tr>
<td>Sasaki, K.</td>
<td>1969, Kobunski Kagaku 26, 21</td>
</tr>
<tr>
<td>Seanor, D.A.</td>
<td>1972, Polymer Science, vol 2</td>
</tr>
<tr>
<td></td>
<td>(London: North Holland), p 1267</td>
</tr>
<tr>
<td>Shashoua, V.E.</td>
<td>1958, J. Polymer Sci. 33, 65</td>
</tr>
</tbody>
</table>
Shaw, P.E.  1930, Proc. R. Soc. A 128, 480
Hanstock, R.F.

Skinner, S.M.  1956, Mod. Plast. (febr. 1956), 127
Gaynor, J.
Sohl, G.W.

Montgomery, D.J.

Van Turnhout, J.  1971, Advances in Static Electricity, vol. 1
(Brussels: Auxilia), pp 56-81

Vick, F.A.  1953, Brit. J. Appl. Phys. (Suppl. 2) 4, S1

Wagner, P.E.  1956, J. Appl. Phys. 27, 1300


APPENDIX BIBLIOGRAPHY

The bibliography will comprise theoretical and experimental works of importance in the field of "static electrification of solids". The majority of the works treat systems of which at least one insulator is an integral part, and in a few works semiconductors are involved. Metal-metal systems will not be mentioned. A distinction is made between perpendicular and tangential separation mode. Those experiments in which the investigations concern parameters characteristic of the tangential separation mode, such as velocity, normal force and rub length, are collected under the heading of "frictional electrification". This is the current notation even if the friction involved does not play an important part. Otherwise the two separation modes are not distinguished, but the works are divided according to the parameters whose effects are investigated. Special charging mechanisms, such as electrification by cleavage and deformation, will also constitute separate groups. The works are classified under the following headings:

General (monographs, reviews, conference works)
Measuring methods
Electron energy levels (in polymers and amorphous insulators)
Theories of electronic charging
Ionic charging (theory and experiment)
Electrification by cleavage and deformation
Triboelectric series
Frictional electrification (velocity, force, rub length, radius of curvature etc)
Ambient conditions (pressure, relative humidity etc)
Electric field
Irradiation
Metallic work function
Resistivity
Temperature
Time
Semiconductors
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Publication Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various contributions</td>
<td>Proc. 1st Conf. on Static Electrification; Brit. J. Appl. Phys. (Suppl. 2) 4, (1953).</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Measuring methods</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shikhov, V.N.</td>
<td>&quot;Instruments for Measuring Static Electricity Charges&quot;</td>
</tr>
<tr>
<td>Shikhov, V.N.</td>
<td>&quot;On measuring the charge of Static Electricity&quot; Elektrichesvo, 10, 83-4 (1968).</td>
</tr>
<tr>
<td>Tkachev, V.V.</td>
<td></td>
</tr>
<tr>
<td>Medvedev, G.V.</td>
<td></td>
</tr>
<tr>
<td>Shikhova, N.V.</td>
<td></td>
</tr>
<tr>
<td>Sawa, G.</td>
<td></td>
</tr>
<tr>
<td>Shinohara, U.</td>
<td></td>
</tr>
</tbody>
</table>
Anon.  "Standard Method of Test for Electrostatic Charge"

Hood, H.P.  Cunningham, R.G.
"A New Method of Measuring Contact Electrification
Characteristics of Materials"

Wintle, H.J.
"Theory of the Potential Probe Used in Static Electrification Measurements on Insulators"

Sessler, G.M.  West, J.E.
"Method for Measurement of Surface Charge Densities
on Electrets"

Van Turnhout, J.
"Methods for Measuring Static Charges"
Advances in Static Electricity, vol. 1
(Auxilia, Brussels), 56-81 (1971).

Benninghoff, U.  Fuhrmann, J.  Rehage, G.
"Measurements of Electrostatic Charging and Discharging of Polystyrene"
Advances in Static Electricity, vol. 1
(Auxilia, Brussels), 96-104 (1971).

Czeija, E.
"Measurement and Calculation of Electrostatic Charging in Theory and Practice"
Advances in Static Electricity, vol. 1
Electron energy levels

Fowler, R.H. "Notes on Some Electronic Properties of Conductors and Insulators"

Simpson, J.H. "The Time Delay in Conduction and Breakdown Processes in Amorphous Solids"

Fowler, J.F. "X-ray Induced Conductivity in Insulating Materials"

Montgomery, D.J. "Static Electrification of Solids"
Solid State Physics, vol 9

Partridge, R.H. "Electron Traps in Polyethylene"

Seanor, D.A. "Charge Transfer in Polymers"

Pohl, H.A. "Theories of Electronic Behavior in Macromolecular Solids"

Goodman, A.M. "Electron Energy-Band Diagrams of Insulators Determined from Internal Photoemission Measurements"
Proc. 3rd Int. Conf. on Photoconductivity.

Morris, W.T. "Static Electrification of Polymers: a Review"

Bausen, H.
Klöpffer, W.
Rabenhorst, H.

"On the Charging Mechanism of Insulating Solids"
Advances in Static Electricity, vol 1

Krupp, H.

"Physical Models of the Static Electrification of Solids"
Proc. 3rd Conf. on Static Electrification;
Theories of electronic charging

Mott, N.F.  "Electronic Processes in Ionic Crystals"

Gonsalves, V.E.  "Some Fundamental Questions Concerning the Static Electrification of Textile Yarns: Part I"

Vick, F.A.  "Theory of Contact Electrification"
Brit. J. Appl. Phys. (Suppl. 2) 4, S1-5 (1953).


Arthur, D.F.  "A Review of Static Electrification"

Hersh, S.P.  "Static Electrification of Filaments: Theoretical Aspects"
Montgomery, D.J.

Van Ostenburg, D.O.  "Charge Transfer upon Contact between Metals and Insulators"
Montgomery, D.J.

Lyons, L.E.  "Electron Transfer across the Boundaries of Organic Solids"

Timan, B.L.  "Theory of Dielectric-Metal Contacts"

Harper, W.R.  "Contact and Frictional Electrification"
Simmons, J.G.  "Theory of Metallic Contacts on High Resistivity Solids - I Shallow Traps"

Bauser, H.  "On the Charging Mechanism of Insulating Solids"
Klöpffer, W.  Advances in Static Electricity, vol. 1

Krupp, H.  "Physical Models of the Static Electrification of Solids"
Proc. 3rd Conf. on Static Electrification;
Ionic charging


Electrification by cleavage and deformation

Peterson, J.W. "Influence of Piezo-Electrification on Tribo-Electrification"

Harper, W.R. "Adhesion and Charging at Quartz Surfaces"

Coolidge, J.E. Schulz, G. "Note on Static Electrification of Dust Particles on Dispersion into a Cloud"

Kunkel, W.B. "Comment on Static Electrification of Dust Particles on Dispersion into a Cloud"

Metsik, M.S. "Electrification of Mica Crystals on Splitting"

Szaynok, A. "Influence of X-rays on the Electrification of NaCl Crystals"

Szaynok, A. "Influence of Irradiation with $\gamma$-rays on the Electrification of KCl Crystals"

Deryagin, D.V. Metsik, M.S. "The Role of Electrical Forces in the Process of Cleaving of Mica"

Jakubiszyn, S. Nikliborc, J. Wolniewicz, H. Szaynok, A. "Electrification of the Dust of NaCl and KCl Whiskers"


Triboelectric series

Henry, P.S.H.  "The Role of Asymmetric Rubbing in the Generation of Static Electricity"
Brit. J. Appl. Phys. (Suppl. 2) 4, S31-6 (1953).

Ballou, J.W.  "Static Electricity on Textiles"

Hersh, S.P.
Montgomery, D.J.  "Static Electrification of Filaments - Experimental Techniques and Results"

Skinner, S.M.
Gaynor, J.
Sohl, G.W.  "Electrostatic Charges in Plastics"

Rose, G.S.
Ward, S.G.  "Contact Electrification across Metal-Dielectric and Dielectric-Dielectric Interfaces"

Fukada, E.
Fowler, J.F.  "Triboelectricity and Electron Traps in Insulating Materials: Some Correlations"

Henniker, J.  "Triboelectricity in Polymers"

Webers, V.J.  "Measurement of Triboelectric Position (of Polymer Films)"

Shashoua, V.E.  "Static Electricity in Polymers I. Theory and Measurement"

Challande, R.F.  "Transfert de charges par frottement entre des halogènures alcalins et des isolants organiques"
Frictional electrification

Gonsalves, V.E.  "Some Fundamental Questions Concerning the Static
van Dongeren, B.J.  Electrification of Textile Yarns: Part II"

Peterson, J.W.  "Contact Charging between a Borosilicate Glass and
  Nickel"

Peterson, J.W.  "Contact Charging between Nonconductors and Metal"

Medley, J.A.  "The Discharge of Electrified Textiles"

Hersh, S.P.  "Static Electrification of Filaments Experimental
  Montgomery, D.J.  Techniques and Results"

Cooke, B.A.  "Charge Acquired by Powdered Salts on Moving over
  Metal Surfaces"

Wagner, P.E.  "Electrostatic Charge Separation at Metal-Insulator
  Contacts"
  J. Appl. Phys. 27, 1300-10 (1956).

Levy, J.B.  "Static Electrification of Filaments"

Levy, J.B.  "Relation of Charge to Frictional Work in the Static
  Wakelin, J.H.  Electrification of Filaments"
  Kauzmann, W.J.  Text. Res. J. 28, 897-911 (Nov. 1958)
  Dillon, J.H.

Cunningham, R.G.  "Studies on the Static Electrification of Filaments"


**Ambient conditions**

Debeau, D.E.  "The Effect of Adsorbed Gases on Contact Electrification"  

Gill, E.W.B.  "Frictional Electricity"  
Phys. Rev. 74, 842-3 (1948).

Medley, J.A.  "Frictional Electrification and Gaseous Discharge"  

Ballou, J.W.  "Static Electricity on Textiles"  

Medley, J.A.  "Discharge of Electrified Textiles"  

Peterson, J.W.  "Contact Charging between a Borosilicate Glass and Nickel"  

Peterson, J.W.  "Contact Charging between Nonconductors and Metal"  

Boyd, J.  Bulgin, D.  "The Reduction of Static Electrification by Incorporating Viscose Rayon containing Carbon"  

Kittaka, S.  "Generation of Static Charge on High Polymer"  

Arridge, R.G.C.  "Contact Electrification and Polarization of Nylon Threads"  

Shashoua, V.E.  "Static Electricity in Polymers. II. Chemical Structure and Antistatic Behavior"  
Sereda, P.J.  
Feldman, R.F.  

"Electrostatic Charging on Fabrics at Various Humidities"  

Cleves, A.C.  
Sumner, J.F.  
Wyatt, R.M.H.  

"The Effect of Temperature and Relative Humidity on the Accumulation of Electrostatic Charges on Fabrics and Primary Explosives"  
Electric field

Gill, E.W.B. "Frictional Electrification"

Medley, J.A. "Static Electrification in an Externally Applied Field"
Research (supplement) 7, 6, S33-4 (1954).

Cho, A.Y.H. "Contact Charging of Micro-Sized Particles in Intense Electric Fields"

Latham, J. "Charge Transfer between Model Ice Crystals Separated in an Electric Field"

Pauthenier, M. "A propos de la charge des particules diélectriques par un champ ionisé: Une difficulté théorique"

Dupuy, J. "Electrisation du polyéthylène et du polystyrène après irradiation γ"

Asch, M.G. "The Influence of Electrical Fields on Triboelectrification Phenomena"

Lavagnino, B. "Influence of Electric Fields on Friction Electrification between Metals and Borosilicate Glass"
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Publication Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whitmore, T.C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Greason, W.D.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Donald, D.K.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Irradiation

Sippel, A.  "Über die elektrostatische Aufladung von hochpolymeren Stoffen"

Ruppel, W.  Schlaile, H.G.  "Zur Aufladung belichteter CdS-Kristalle bei verschiedenen Kontakten"

Weingärtner, G.  "Elektrische Aufladung von KCl-Einkristallen im Kontakt mit Metallen"

Ruppel, W.

Schnabel, W.  "Electrostatic Double Layer Adhesion"
Metallic work function

Harper, W.R.  "Surfaces Showing No Electrification After Light Contact with Metals"

Hersh, S.P.  "Static Electrification of Filaments, Experimental Techniques and Results"

Montgomery, D.J.  "Electrostatic Charge Separation at Metal-Insulator Contacts"
J. Appl. Phys. 27, 1300-10 (1956).

Wagner, P.E.  "The Generation of Static Charge on High Polymer"  

Kittaka, S.  "Static Electrification of Nylon 66"

Arridge, R.G.C.  "The Generation and Dissipation of Static Charge on Dielectrics in a Vacuum"

Davies, D.K.  "Electrification by Friction in a 3 x 10^-7 torr Vacuum"
Proc. 2nd Conf. on Static Electrification; Inst. Phys. Conf. Ser. No. 4, 37-43

Inculet, I.I.  "Charge Generation on Dielectric Surfaces"

Wituschek, E.P.  "The Electronic Behavior of Polymer Surfaces"
<table>
<thead>
<tr>
<th>Author</th>
<th>Title</th>
<th>Journal</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soo, S.L.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hood, H.P.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coffee, R.A.</td>
<td>&quot;Electrostatic Charging of Insulators after Contact with Metals&quot;</td>
<td>Japan J. Appl. Phys. 11, 1391-2 (1972)</td>
<td></td>
</tr>
</tbody>
</table>
Resistivity

Medley, J.A.  "The Dissipation of Electrical Charges Generated by Rollers"

Rose, G.S.  "Contact Electrification across Metal-Dielectric and Dielectric-Dielectric Interfaces"

Ward, S.G.

Shashoua, V.E.  "Static Electricity in Polymers. I. Theory and Measurement"

Henry, P.S.H.  "A Test for Liability to Electrostatic Charging"

Livesey, R.G.

Wood, A.M.

Ramer, E.M.  "Correlation of the Electrical Resistivities of Fabrics with Their Ability to Develop and Hold Electrostatic Charges"

Richards, H.R.

Cunningham, R.G.  "Electrification of Insulating Belts Passing over Grounded Rollers"

Ramer, E.M.

Gabel, M.

Schön, G.  "Elektrostatische Aufladung von Papier beim Rotationstiefdruck"
Advances in Static Electricity, vol. 1 (Auxilia, Brussels), 82-95 (1971).
<table>
<thead>
<tr>
<th>Authors</th>
<th>Title</th>
<th>Journal</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author</td>
<td>Title</td>
<td>Journal</td>
<td>Volume</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------------------------------------------------------------</td>
<td>--------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Philp, S.F.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tödheide-Haupt, U.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ruppel, W.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cunningham, R.G.</td>
<td>&quot;Electrification of Insulating Belts Passing over Grounded Rollers&quot;</td>
<td>J. Colloid. Interface Sci.</td>
<td>32</td>
</tr>
<tr>
<td>Latham, J.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kamra, A.K.</td>
<td>&quot;Experimental Study of the Electrification Produced by Dispersion of Dust into the Air&quot;</td>
<td>J. Appl. Phys.</td>
<td>44</td>
</tr>
</tbody>
</table>
Semiconductors


