TRIBOELECTRICITY

Triboelectricity, the exchange of charge between dissimilar materials, is a pervasive phenomenon, and its manifestations are familiar to everyone. For example, after walking across a rug under low relative humidity conditions, many people experience a shock upon touching a grounded surface. The shock is due to current flow needed to capacitively compensate for accumulated charge on the bottom of rubber-soled shoes that results from the exchange of charge between the shoes and the rug. Supertanker and flour mill explosions are dramatic examples of disasters whose source is a spark that may be generated by triboelectricity. In addition, every time a copy is made using electrophotographic (also called xerographic) technology or a print is made using a laser printer, triboelectric effects are utilized that are essential to the underlying process.

The phenomenon of triboelectricity is known to have been observed by the early Greeks as far back as 600 B.C., when it was noticed that rubbed amber would attract particles. During the early part of the twentieth century, it was established that materials could be arranged in a triboelectric series, which is a list of materials arranged such that if a material is above another, it always charges positive when contact is made between the two materials. Several scientific rationales were suggested but were never proven for this observation. In the modern world, eliminating the charging due to triboelectricity is often important because (1) highly insulating industrial materials, such as synthetic polymers, which allow substantial charges to build up as the number of contacts increases, are increasingly being used; and (2) charges on surfaces create electric fields in air that can only withstand a finite electric field (about 3 MV/m at large air gaps) before the air breaks down (i.e., a conductive path is formed, leading to a spark). Some applications make use of the charging. For example, the ability to control the triboelectric charging of small 10 μm diameter polymer particles, called toner, is essential to the electrophotographic copying and printing process. Today this is a $100 billion industry. Powder coating and electrostatic separation of materials are other examples of the industrial use of triboelectricity.

To eliminate the charging due to triboelectricity, a fundamental understanding is not necessary—one merely must ensure that charge does not accumulate. This can be accomplished by the use of appropriate grounding schemes and antistatic agents. The control of the magnitude of the charge for those applications where charge is important is much more challenging. While its measurement is relatively easy, the prediction of the charge exchange, its sign, magnitude, and distribution remains beyond the current state of science because the mechanism(s) of the charge exchange, and therefore the essential materials parameters, have not been identified except in the case of metal-metal contacts. Recently, experiments with insulating materials unique to electrophotography have led to new insights into the mechanisms of insulator triboelectricity. As will be seen, this is a welcome advance in a scientific and technological area that has thwarted all attempts to provide a microscopic understanding. The difficulties in this field of electrostatics should not be underestimated and are well documented in prior reviews and books (1,2). When the surfaces of two materials are brought into contact and separated, the actual area that made contact is difficult to measure. Whether friction plays a role beyond increasing the actual area of contact has not been determined. In fact, the terms *contact electrification* and *triboelectrification* (i.e., frictional electrification) are often used interchangeably. The precise nature of the surfaces is usually not well defined: Dust particles, surface contaminants, and even water layers may be the "surface." Even for "clean" surfaces the nature of intrinsic and extrinsic surface states on insulators is not well understood. The magnitude of return currents during separation remains controversial. Finally, the number of surface molecules involved in the charging process is extremely small, on the order of one molecule in 10^4 or 10^5 molecules. The determination of the nature of the charging sites by surface science tools remains an unsolved solid-state physics problem.

This article discusses the following aspects of triboelectricity: (1) charging methods, (2) applications, (3) nuisances and hazards, (4) the measurement of charge, and (5) the status of our understanding of the mechanism(s) of triboelectrification.

CHARGING METHODS

All materials consist of positive (+) and negative (−) electrically charged particles, which in their neutral state are mutually bound together in atoms and molecules in an equilibrium condition. To produce a net charge, energy must be expended to separate the charges. These separated charges have two main properties: (1) Charge, when exposed to an electric field, will experience a force, and (2) accumulated charge will have a stored amount of electrostatic energy. These two properties manifest themselves in a number of practical ways, but in general the former lends itself to useful application and the latter results in nuisances or hazards.

Tribo (or contact) electrification, which is discussed here, is but one of a number of processes that result in electrostatic

J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*.

charge separation. Other processes include corona charging and induction charging. These will not be discussed in detail but are briefly described since they are found in practical applications often in combination with triboelectrification. The principles and characteristics of each of these charging methods are as follows.

Triboelectrification or Contact Electrification

Whenever any two dissimilar surfaces come into contact, charges are exchanged between them. If contact is broken, a net charge of opposite sign may subsequently remain on each of the surfaces. This is true for both solids and liquids and for materials that are conductors, semiconductors, or insulators. For reasons that will be discussed later, in practice, it is only in situations where one or both of the contacting surfaces is an insulator that a significant net charge will remain after separation.

Corona Charging

A corona discharge results when air is exposed to a localized high-intensity nonuniform electric field. Such a field can be found near fine wires or sharp points connected to a high-voltage source. If the electric field strength is great enough, localized air breakdown results, liberating free electrons and positive ions. In most gases these electrons will quickly combine with neutral molecules to form negative ions. Depending on the polarity of the nonuniform electric field and the geometric arrangement of the electrodes, it is possible to produce a unipolar cloud of either positive or negative ions that may be used to charge neutral materials. Corona charging offers a versatile method for charging because it may be used to charge both liquids and solids, which may be either insulators or conductors. Corona charging is commonly used in electrophotography to charge the photoconductor (see ELECTROPHOTOGRAPHY) and electrostatic precipitators (see ELECTROSTATIC PRECIPITATORS).

Induction Charging

Induction charging (in some configurations also referred to as conduction charging) results when a conductive material, which is connected to ground, is exposed to an electric field and then, in the presence of this field, is disconnected from the ground. This results in the charge that was induced on the surface of the conductor by the external field being trapped on the material, producing a net charge opposite in sign to the polarity of the inducing field. The energy necessary to produce this charge separation usually comes not from the electric field but from the mechanical energy required to remove the material from the electric field. This method of charging may be used with liquids or solids but is restricted to conductors or semiconductors and cannot be used with insulators. Induction charging is used in liquid spray painting and in one form of ink jet printing.

APPLICATIONS

A charged object in the presence of an electric field E will experience a force F_c given by Coulomb's law as

$$F_c = QE$$

where Q is the electric charge on the object. Equating this force to Newton's force $F = Ma$, where M is the mass and a is the resulting acceleration, gives a value for $a = (Q/M)E$. Therefore, for a fixed electric field, the ratio Q/M, known as the charge to mass ratio, will indicate the relative effectiveness of the electrostatic field and can be used to compare the force with accelerations due to other competing forces that may exist, such as gravity, drag, and magnetism. Assuming the object is spherical and recognizing that electrostatic charge is proportional to surface area and mass is proportional to volume, it can be seen that Q/M is inversely proportional to particle radius r. In practice, this means that electrostatic force effects are most important for small particles and electric fields can be used effectively to move, direct, and bond such particles in an energy-efficient manner. In particular, it is generally found that for values of a radii of less than 100 μm, electrostatic forces are larger than gravity and drag forces. In special cases it is possible to use electrostatic forces successfully with particle sizes up to an order of magnitude larger. In the following sections some examples of particular applications that utilize electrostatic forces where the charge is derived from triboelectrification are described (see Refs. 3 and 4 for more complete discussions).

Electrophotography

Electrophotography (see ELECTROPHOTOGRAPHY) is the name given to the process of making copies by using a light image to create a latent image made up of electrostatic charges. The most common way to form these latent charge images is through the use of a photoconductive material that acts as an insulator in the dark and a conductor in the light. If this material is initially uniformly charged on its surface in the dark (normally by means of corona charging) and then exposed to a light image either from light reflected from a document or by a modulated laser beam, charges will remain only in the dark regions, thus producing the electrostatic latent image. This electrostatic latent image produces an electric field that will attract charged colored polymer particles (known as toner) onto the surface to develop the image and make it visible. These toner particles are usually insulating powders approximately 10 μm in diameter that are charged by triboelectrification. Once developed in this form, the toner may then be transferred onto a piece of paper or other material and fused in place to produce hard copy. These principles form the basic technology in the ubiquitous photocopiers and laser printers that have revolutionized the modern home and business office. In fact, these products represent the largest single application of triboelectrification and account for hundreds of billions of dollars of sales worldwide every year.

The most critical part of the electrophotographic process that most determines the copy quality is the development step. This step relies on toner, which must have consistent chemical, mechanical, and electrical properties. Ideally, the toner particles should have one polarity of charge and as uniform a charge among the toner particles as possible. Two principal methods are used to charge the toner triboelectrically. Dual-component development systems mix the toner particles with larger particles called the carrier. The carrier particles are normally 80 to 200 μm in diameter and are made from a magnetically soft material covered with a thin surface coating specially selected for its charging characteristics. When mixed together, the toner charges on contact with the carrier and adheres to its surface by electrostatic attraction. In this electrostatically neutral form, this mixture of toner and carrier can be brought into close proximity with the latent image (using magnetic forces that act on the magnetic carrier), where the toner experiences a Coulomb force of sufficient magnitude to be stripped off the carrier onto the image, resulting in development. As development proceeds, additional toner must be replenished periodically. A second method of triboelectrically charging the toner is found in monocomponent development systems and involves feeding the toner from a hopper and contacting it with a rotating roller, which passes under a rigid blade. This blade ensures good contact of the toner to the roller, producing both triboelectric charging and a thin layer of toner, which can then be exposed to the latent image, either in close proximity or in direct contact, where once again Coulomb forces attract the toner to the latent image, resulting in development. To ensure consistent charging of the toners in both of these methods, special chemical additives known as charge control agents are used that have the property of enhancing the triboelectric charging properties of the toner.

Powder Coating

Electrostatic forces have been widely used in liquid spray painting to improve the transfer efficiency and paint film uniformity. In these applications the paint is normally electrically charged either by corona or conduction and sprayed toward the object to be painted, which is electrically grounded. The resulting electrical force attracts the paint droplets toward the grounded object, leading to improved deposition thus providing an enhancement to the normal mechanical coating and less wasted paint. This process has been used with great success with organic-based solvent paints and to some extent with water-based (latex) paints. However, by using electrostatic forces it is possible to eliminate the solvent completely and spray paint powder directly, thus further reducing the environmental impact of the process. Here the electrostatic force is used to both deposit and temporarily bond the paint to the surface. This is referred to as powder coating.

Powders used in this application usually consist of a mixture of resin, pigments, flow agents, etc. and are ground to an average size on the order of 45 μm. They can be charged either by corona or by contact electrification. Corona charging has the disadvantage that it produces an excess of free ions, which can cause surface imperfections due to micro discharges through the powder layer. Also, difficulties arise in producing uniform coating in depressions, corners, and on edges. Contact charging offers a significant advantage in overcoming both of these problems. In one version of this process, the powder is pneumatically conveyed through the inside of a number of spiraled tubes, typically made of an insulating material such as Teflon made by Du Pont. This produces repetitive contact with the interior of the tubing, resulting in a net charge of one sign on the powder (normally positive polarity) leaving behind an equivalent negative charge on the Teflon. This remaining charge then leaks to ground, forming a continuous current flow. The charged powder is injected into the vicinity of the grounded object to be coated, where it forms a space charge field and creates a deposition force, causing the powder to coat the surface. A particular advantage of this process is the way in which “wrap-around” coverage can occur due to the electric field component, which converges on the back of the object out of the direct line of sight. The powder, which must be a good insulator, retains its charge temporarily and is bonded to the object by an electrical image force. The work piece is then conveyed to an oven, where the powder is fused to form a continuous film on the surface. Powder coating has the advantage of being the most environmentally friendly spray painting process. Not only is there no solvent to contend with, but there is little wastage of the paint due to the high transfer efficiencies and the fact that excess powder can be collected and reused. Powder coating is widely used in applications where it is desired to have a durable protective coating, whereas liquid painting is still the preferred method when a high-quality, smooth, decorative finish is desired.

Electrostatic Separation

It is well known that electrostatic methods are ideally suited to separate small particulates that are otherwise similar but consist of one component that is a conductor and the other an insulator. In this case it is possible to segregate the particles by utilizing either corona or induction charging and the fact that the materials have charge relaxation times that can differ by orders of magnitude. Thus they will retain charges for different times, which can be used to separate the materials through differences in their electrostatic adhesion.

However, the use of contact electrification allows separation of materials to take place when the differences in the material characteristics are much more subtle. For example, consider the case of two insulating plastics that exchange charge when contacted. If these materials are then exposed to an external electric field, Coulomb forces will attract the materials to opposite electrodes, thus producing separation. The practical application of this requires three stages: (1) material preparation, (2) material contact, and (3) exposure to the separating field. Materials suitable for separation must have the components to be separated as discrete (or at least majority) constituents. This normally means that bulk materials must be chopped or ground into small particles, which has the added advantage of exposing fresh surfaces of the materials. Depending on the type of material, mean sizes ranging from microns to millimeters may be successfully separated. It is important to ensure that the contacting surfaces are free of contaminants, such as dirt and moisture. To prevent condensed moisture from forming on such materials, it is usually necessary to prepare and treat the materials in an atmosphere with a relative humidity less than approximately 50%. Contacting the materials together can take place in many ways and, depending on their size range, may include the use of fluidized beds, vibratory feeders, rotating drums, and the interior of inclined rotating cylinders. By careful selection of the material used in the construction of the apparatus, third-body charge exchange can take place, which may further enhance the charge difference between the two materials. Once charged, the particles are exposed to an external extraction field and segregated into separate components. This may be achieved in many ways depending on the equipment geometry. One common method is to allow the particles to drop by gravity and to superimpose a horizontal electric field to deflect the particles toward one electrode depending on the sign of the particle's charge. Such a process can be repeated to produce the desired recovery and purity. Electrostatic separation has been used successfully to separate materials in the mining industry (iron ore), cement industry (fly ash and carbon), the recycling industry (commercial plastic waste), and other industries.

NUISANCES AND HAZARDS

As mentioned earlier, when charges are separated, energy is required. This energy W accumulates as charge builds up according to the relation

$$W = \frac{1}{2} Q^2/C = \frac{1}{2} CV^2$$

where Q is the charge on the capacitor of capacitance C and V is the electric potential of the object. Since $Q = CV$, it can be seen that the potential increases linearly with Q whereas the energy increases as its square. If the charge cannot escape to ground, eventually the potential will increase to a point exceeding the breakdown strength of air and the energy is released in a discharge. The form of this discharge depends on a number of factors but generally takes the form of either a corona, brush, propagating brush, or spark discharge (see CONDUCTION AND BREAKDOWN IN GASES). The energy released in these discharges can range from fractions of a millijoule in the case of corona to many joules in the case of sparks. The breakdown of air is accompanied by a number of byproducts, including electromagnetic radiation, acoustic energy, and chemical byproducts such as ozone. Depending on the circumstances, this may create problems ranging from nuisances affecting personal comfort or equipment operation to environmental or explosion hazards. Following are some of the activities that often lead to problems.

Materials Handling

Since charge may transfer between materials in contact, any time one material is moved relative to another, the possibility for charge buildup exists. This is a problem in many industries and may be associated with moving solids (primarily in particulates or films) and liquids. Although charges always transfer between dissimilar surfaces, it is only in cases where they cannot flow back on separation that a net charge will accumulate. Normally this means that one or both of the materials must be an insulator for problems to occur. Since modern industry is using more insulating materials, particularly plastics, in place of conductors, such as metals, or semiconductors, such as wood, this is an issue of increasing concern. In the case of particles, problems may occur as they are moved through pipes or within vessels or are transferred from one container to another. As they become charged, they repel one another and are difficult to handle. The charge remaining on the original container may be significant and can cause shocks to the worker handling it or may discharge to nearby metal. If organic solvents or fine dust clouds are present, as they may be in many industrial processes, an explosion hazard may exist. Generally these problems are greater for small particles that, because of their high specific surface area, tend to generate high values of Q/M. In the case of film or sheet materials that are moved at high speed over rollers, larger amounts of surface area are exposed to contact. Even in cases where the rollers are grounded, very large charges can accumulate on the surfaces of the films if they are insulating, leading to problems in handling the film or creating a discharge hazard. There are a number of ways to alleviate these problems. The first is to ensure, if possible, that the surfaces in contact are conductive enough to prevent the accumulation of charge as they separate. Alternatively, if charges are present upon separation, they should be allowed to leak to ground quickly or to be neutralized in situ. Charges will normally dissipate from all but the most hydrophobic materials if the relative humidity is equal to or greater than approximately 50% and the surface is in contact with ground. Alternatively, a number of commercial antistatic agents (conducting materials or highly polar molecules that attract water to the surface due to the high polarity of water) are available that, when coated in microscopic layers on the surface, will increase the surface conductivity. Another approach is to neutralize the surface charge by using passive corona ionizers consisting of sharp points or fine wires connected to ground. Here the electric field created by the surface charge will cause air ionization and will attract oppositely charged ions to the surface, reducing but not completely eliminating the charge. Active ionization is also possible where the separating surfaces are exposed to copious amounts of air ions of both signs such that neutralization of the charges will occur. This can be accomplished by exposing air in the vicinity of the surfaces to either an ac corona discharge or a low-level radioactive source producing alpha or beta emissions. Selective absorption of the opposite sign charge will then occur, resulting in essentially complete elimination of the surface charge.

For the case of liquids, charge separation will occur between the container walls and the liquids as the liquid is pumped through pipes or stirred and agitated, as often occurs in industrial processes. Most aqueous-based liquids are sufficiently ionic to have high enough conductivities to allow charges to neutralize rather than accumulate. However, many pure organic solvents are highly resistive and, coupled with the fact that they are often very flammable, present particular hazards. Often, small quantities of ionic additives are used to increase the conductivity to sufficient levels. However, if this is not feasible and the possibility of charge accumulation exists, the process can be carried out in an inert environment to prevent the possibility of an explosion. Charge separation also can occur when liquids splash against a surface and break into smaller droplets. This will occur even if the liquid is a good conductor like water, as witnessed by the fact that excess negative ions are usually found in the air near waterfalls and breaking waves. Several major explosions of oil supertankers in the 1970s were believed to be caused by charge separation and accumulation due to this mechanism. Similar problems have been documented in situations as diverse as the pumping of fuel into planes and automobiles and flour mill explosions.

Electrostatic Discharge Damage

As very large scale integrated (VLSI) electronic devices have become more microscopic, conductor widths and insulator thicknesses have become smaller. Typical devices now have element dimensions that are submicron. The result has been that conductive elements have become very susceptible to thermal overload and burnout due to stray currents, which can be accidentally coupled into the circuit often by indirect means. Similarly, the thin insulators used in such devices are susceptible to dielectric breakdown by relatively modest voltages that result in very high electric fields. Voltage levels capable of producing such damage are easily obtained by contact charging between the devices and such common items as table tops, packaging, or human handling. As a result, special techniques must be adapted for the manufacture and assembly of these devices to ensure that unwanted charge is eliminated before it has a chance to accumulate and cause damage. As with material handling hazards, one solution is to ensure that all surfaces involved are conductive enough to allow charge to leak to ground. However, in addition it is necessary to protect the device both during manufacture and its end use application from induced or triboelectric charge by ensuring that it is electrically shielded within a grounded conductive Faraday cage. Special protection circuits are often integrated into the design of the chip to protect it against conductive charge incursions. In the case of contact by humans, care must be taken in the type of clothing worn since many synthetic fabrics are highly insulating and rubber-soled shoes can insulate the body from ground. To be sure that no charge can accumulate, grounding straps are often attached to the wrists or ankles of assembly workers. Charge can come from unusual places, and there are examples of damage occurring by the charge generated by the sudden suction removal of solder during the attempted repair of printed circuit boards. The economic impact of unwanted electric discharge damage to the multi-billion-dollar VLSI industry has led to a separate industry dedicated to the prevention of such unwanted failures.

MEASUREMENT OF CHARGE

Imagine that a material has been triboelectrically charged. How is the charge measured? Perhaps the easiest method, if the material is sufficiently small, is to put it into a Faraday cage, which is simply a metal container attached to a Coulomb meter (which integrates the current that flows through it). When the charged material is placed into the cage, it induces an equal but opposite charge on the inner surface of the cage that, because of charge neutrality within a conductor, leaves a charge on its outer surface equal to the material charge. Charge then flows from the ground plane, through the meter, to the metal Faraday cage to neutralize this charge. This measures the total charge on the sample.

Usually, the sample cannot be easily placed in a Farday cage. If the insulating material is placed on a ground plane, as shown in Fig. 1(a), then charge triboelectrically placed on the surface will induce charge in the ground plane to neutralize the surface charge. Under some circumstances this induced charge can be measured as it flows to the metal ground plane. If it cannot be measured, an alternative approach based on electrostatics is possible.

The electric field E in the sample in Fig. 1(a) is directly related to the charge per unit area σ on the surface by

$$E = \frac{\sigma}{K\epsilon_0}$$

where K is the dielectric constant of the material and ϵ_0 is the permittivity of free space (8.85×10^{-12} F/m). The voltage drop V across the sample is the field times the thickness of the sample L

$$V = \frac{\sigma L}{K\epsilon_0} \tag{1}$$

This is the surface potential above the sample that remains constant for distances small compared to the sample size. However, note that the electric field in air above the sample is zero. There are two ways to measure the charge on the sample in this situation. First, a probe ground plane can be brought into the vicinity of the surface, as shown in Fig. 1(b). Charge will be induced on the probe ground plane that can be measured with a Coulomb meter. The charge that flows into the ground plane is derived as follows: Assume the charge per unit area induced in the probe ground plane is σ_1 and the charge per unit area induced in the ground plane under the sample is σ_2. By charge conservation, $\sigma_1 + \sigma_2 = \sigma$. The electric field in the material is $\sigma_2/K\epsilon_0$ and the electric field in the air is σ_1/ϵ_0. The voltage drop in the material must equal the voltage drop in air (since both planes are grounded), giving

$$\frac{\sigma_2 L}{K\epsilon_0} = \frac{\sigma_1 d}{\epsilon_0}$$

which, together with charge neutrality, can be solved for σ_1. The charge measured by the Coulomb meter is Q_1, which

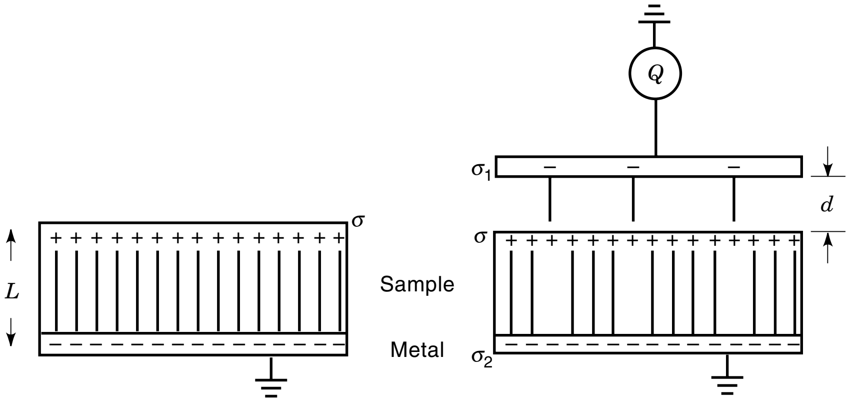

Figure 1. (a) An insulating material of thickness L and dielectric constant K is placed on a metal ground plane. The charge per unit area triboelectrically placed on the surface induces a counter charge in the metal ground plane. (b) If a probe ground plane is placed above the surface of the insulating material, charge is capacitively induced in the probe ground plane.

equals $\sigma_1 A_1$, where A_1 is the area of the probe ground plane.

$$Q_1 = \sigma A_1 \frac{L/K}{L/K + d}$$

Q_1 is linearly proportional to σ, the charge per unit area on the sample, and the area of the probe ground plane. It also depends on the spacing between the sample and the probe ground plane d, which implies that measurement of this spacing is necessary.

The second method makes use of the fact that even though the electric field above the sample is zero when no probe plane is present [see Fig. 1(a)], there is an electrostatic surface potential on the sample given by Eq. (1). This can be detected by electrostatic voltmeters, which were originally developed for the electrophotographic industry (5). These instruments have the great advantage that they are not sensitive to the spacing between the probe and the sample. They work by introducing a probe plane above the sample, as in Fig. 1(b), but the probe plane is set to the electrostatic surface potential of the sample. This is accomplished by adding a small hole in the probe plane and detecting the electric field in the hole that is proportional to the difference in voltage between the probe plane and the sample. This difference is brought to zero by appropriate circuitry. Then the voltage on the probe plane equals the electrostatic potential of the sample. Knowing the sample's thickness and dielectric constant, the charge per unit area can be calculated using Eq. (1).

There are some important insulator-insulator charging experiments that have been done with mixtures of insulating powders used in the electrophotographic industry. The two powders called toner and carrier have sizes that differ by at least an order of magnitude. The powders exchange charge on mixing. However, the mixture remains net neutral. The charge exchanged between the particles is measured using a modified Faraday cage. In this application the Faraday cage has screens on both ends with holes that are larger than the toner but smaller than the carrier. An air jet (see Fig. 2) blows the toner out of the cage. The change in mass of the Faraday cage and the charge that leaves the cage can be measured, giving the charge-to-mass ratio, Q/M, of the toner. This quantity is an average value. It is also possible to measure the distribution of charge on the toner particles. The interested reader is referred to the literature for a discussion of the measurement of toner charge distributions (see Sect. 4.4.4 and 12-4.4.4 of Ref. 1).

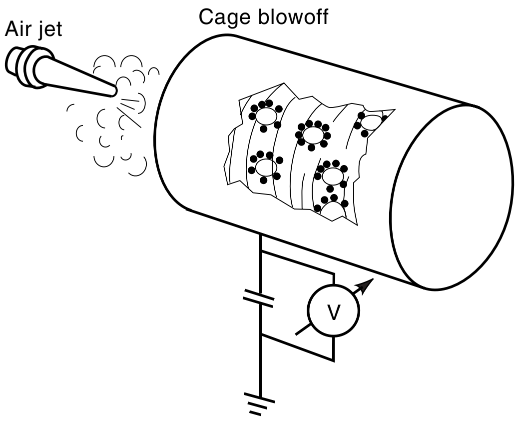

Figure 2. A modified Faraday cage useful for measuring the charge exchanged between mixtures of insulating powders. The cage has screens on both ends whose holes are larger than the smaller powder and smaller than the larger powder. By blowing the smaller powder out of the cage with an air gun, the charge-to-mass ratio of the smaller powder can be determined (6).

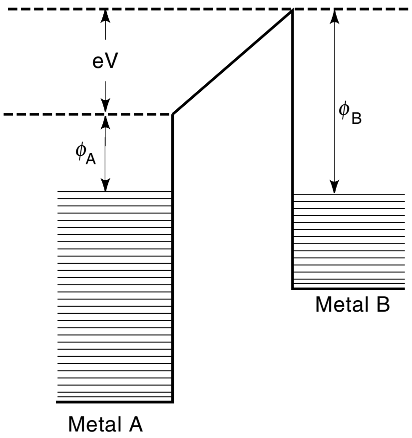

Figure 3. Two metals in close proximity exchange charge until, in equilibrium, their Fermi levels are coincident.

MECHANISMS OF TRIBOELECTRIFICATION

Applications that make use of triboelectrification were discussed previously. Applications generally require a charged condition. The control of the triboelectric charge is therefore necessary. Unfortunately, triboelectricity remains one of the least understood scientific fields (Chap. 4 of Ref. 1, and Ref. 2). Its understanding and eventual control will require skills from the disciplines of electrostatics, surface physics, and surface and polymer chemistry. In industries today, control of the charging process is achieved by empirical methods, which are time consuming and costly.

The current status of our understanding of charge transfer phenomena can most easily be explained by considering metal-metal charging and insulator charging separately. The charge transfer phenomena governing metal-metal contact are well understood. Whenever an insulator is involved in the charging process, significant questions arise.

Metal-Metal Contact Charging

Consider two metals with different work functions ϕ_i. If they are brought together (Fig. 3) and electrons are allowed to exchange by tunneling, a contact potential difference V_c is created across the interface given by

$$V_c = (\phi_B - \phi_A)/q$$

and the charge Q exchanged by electron tunneling is

$$Q = C_{AB} V_c$$

where C_{AB} is the capacitance between the two adjacent bodies. As the two bodies are separated, C_{AB} decreases (and consequently Q decreases) until charge exchange by tunneling stops at a separation of about 1 nm. The final observed charge is

$$Q = C_0(\phi_B - \phi_A)/q$$

where C_0 is the capacitance at a spacing of approximately 1 nm.

The experimental results (2) of making a single contact with a 0.4 cm diameter chromium plated ball against 1.3 cm diameter balls electroplated with different metals are shown in Fig. 4. The contact potential difference was measured in situ for the identical contact points used in the charge measurements. Clearly, both the trend with contact potential difference V_c and the magnitude of the charge appear correct. The small discrepancy between theory and experiment can be traced to the roughness of the metal surfaces, which affects the calculation of the capacitance.

Insulator Charging

This field has considerable experimental disagreement and controversies. For example, it has been claimed that the work function derived from charging experiments of Teflon is both larger and smaller than the work function of gold. It also has been claimed that Teflon does not charge against gold. Others claim that the charge exchanged to Teflon is not influenced by the metal used for charging. It is difficult to imagine any more disagreement than this. It is also relatively obvious that the most likely source of the disagreement is different surface conditions of the Teflon in each experiment. Another important example of the controversies in the field is the experiments of Davies (7), who did the logical extension of the metal-metal charging experiment mentioned previously. If one can define a polymer work function, then the charge exchanged between a metal and a polymer would depend on the energy difference between the work function of the metal ϕ_M and the work function of the polymer ϕ_I. If one measures Q, the charge exchanged for a series of metals, then the value of the work function at $Q = 0$ should be ϕ_I, the insulator work function. Such a linear relationship was, in fact, observed by Davies and others. However, a tabulation of ϕ_I for a wide range of polymers (Nylon 66, polystrene, polyethylene terephthalate, polytetrafluoroethylene, polycarbonate, polyimide, polyvinylchloride) reveals a curious fact: The values show very little variation, from 4.08 eV to 4.85 eV. Davies's result is curious for another reason. Many solid-state physics texts treat insulators as though they are wide-bandgap semiconductors. A problem occurs when the band gap exceeds 2 eV. Traps in the bandgap are so deep that at room temperature they cannot come into thermodynamic equilibrium in reasonable times. The release time is generally written as ν_e^{-1} exp (ϕ/kT), where ν_e is an attempt to escape frequency (10^{14} s^{-1}), ϕ is the depth of the trap from the conduction or valence band, k is Boltzmann's constant, and T is absolute temperature. For a trap depth of 0.5 eV, the release time is 5 μs; for a 1 eV trap, the release time is 2000 s; for a trap of 2 eV, the release time is 10^{20} s. The polymers used in Davies's experiment are believed to have forbidden gaps of 7 eV. Therefore concepts requiring thermodynamic equilibrium, such as work function, may not be useful for such materials.

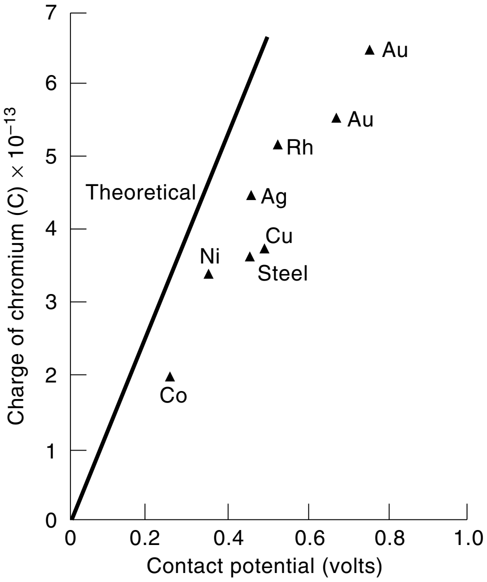

Figure 4. Charge on a Cr sphere after contact with a sphere of another metal, plotted against the contact potential difference between the metal and Cr. The line marked "theoretical" is the prediction of a theory based on tunneling between closely spaced smooth metals (2).

Despite the controversies, there is general agreement that the concept of a triboelectric series is valid, suggesting that a single mechanism can account for the charging of insulators. As mentioned in the Introduction, a triboelectric series is a list of materials such that if a material is above another, it always charges positively when contact is made between the two materials. Furthermore, there is good evidence that metal-insulator charging and insulator-insulator charging are based on the same phenomenon. For example, Davies (8) found that the charge exchange between two insulators can be predicted from a knowledge of the charge they acquired against metals. Duke and Fabish (9) found the same experimental result. In addition, there is good evidence that triboelectricity is a surface phenomenon. These results have led people to suggest the surface state theory of toner charging, which assumes that triboelectric charging is determined by the filling or emptying of "states" on the surface of insulators driven by work function differences. The manifestations of this theory in mixtures of insulating powders have led to new insights into the mechanism of charging.

Physics of Charging in Mixtures of Insulating Powders

The surface state theory assumes that charge is exchanged between the surface states of the two materials, driven by the surface work function difference between the materials. The two limits of the theory are schematically indicated for an insulator-insulator contact in Fig. 5. In the low-density surface state theory, charge is exchanged to fill the states between the two work functions [Fig. 5(a)], from the surface of the material with the lower work function to the surface of the material with the higher work function. In the high surface state theory [Fig. 5(b)], charge exchange is large enough to raise the insulator with the larger work function (before charging) to the energy level of the insulator with the smaller work function.

Triboelectric charge exchange between two insulating powders (toner and carrier) is used in the field of electrophotogra-

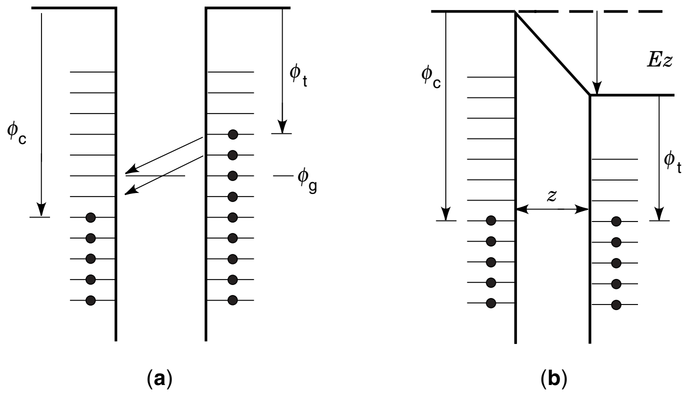

Figure 5. Schematic diagram of the insulator-insulator contact for the (a) low- and (b) high-density surface state theory: ϕ_t and ϕ_c are the surface work functions (energy difference from highest occupied level to vacuum) on the insulators and Φ_g is the final common work function after charge is exchanged. A dash at the interface represents a surface state, a dot on the dask indicates a filled surface state before contact, and an arrow indicates the movement of charges during charge exchange.

phy. This system has empirically been made triboelectrically reproducible in order to make copying and laser printing reproducible. With this system, an experiment was identified that is consistent with only one of the two proposed surface state theories of insulator charging. The argument is as follows: Consider the predictions of the charge-to-mass ratio Q/M of the toner versus the toner concentration C (the ratio of the mass of the toner to the mass of the carrier) in the two limits of the theory. In the low surface state theory, it is assumed that there are N_c states per unit energy per unit area on the carrier and N_t states per unit energy per unit area on the toner. Assume that after charge exchange, carrier surface states are filled between the carrier work function ϕ_c and an intermediate energy ϕ_g and the toner surface states are emptied between the toner work function ϕ_t and ϕ_g. Then, after mixing to equilibrium, it can be shown that the inverse of the charge-to-mass ratio M/Q is given by (10)

$$\frac{M}{Q} = RC\left(\frac{\rho_c}{3\Delta\phi e N_c}\right) + r\left(\frac{\rho_t}{3\Delta\phi e N_t}\right) \qquad (2)$$

where R (r) is the carrier (toner) radius and $\rho_{c(t)}$ is the carrier (toner) density and $\Delta\phi$ is the difference between the carrier and toner work functions. This equation suggests that a measurement of M/Q plotted against C will be a straight line with a slope proportional to R and an intercept proportional to r. These predictions are in accord with numerous experimental observations, one of which is shown in Fig. 6.

In the high-density surface state theory, charge is exchanged so that an electric field is created to offset the change in work functions at the interface ($\phi_c - \phi_t$). The electric field E_e in the interface is $(\phi_c - \phi_t)/ez$, where z is the distance between the insulators at which charge exchange ceases. Based on this model, it can be shown that (11)

$$\frac{M}{Q} = RC\left(\frac{\rho_c}{3\epsilon_0 E_e}\right) + r\left(\frac{\rho_t}{3\epsilon_0 E_e}\right) \qquad (3)$$

Note that this equation also predicts that M/Q plotted against C will be a straight line with a slope proportional to R and an intercept proportional to r. Equation (3), the high-density limit, is identical to Eq. (2), the low-density limit, with $\Delta\phi e N_c$ and $\Delta\phi e N_t$ replaced with $\epsilon_0 E_e$. There is an important difference between these equations: The slope-to-intercept ratio of M/Q versus C is determined entirely by known parameters $R\rho_c/(r\rho_t)$ in Eq. (3); it is determined by the product of this parameter and N_t/N_c in Eq. (2). This result has obvious experimental implications.

These predictions can be compared with experimental measurements of M/Q versus C. Figure 7 shows a compilation of the slope to intercept ratio for virtually every published experiment up to 1994 (11). The center line represents exact agreement between experiment and the prediction of the high-density surface state theory. The other two lines represent agreement within a factor of 2. The result is that the experimental slope-to-intercept ratio agrees with the prediction of the high-density surface state theory within a factor of 2 for almost all of the experiments with no adjustable parameters. One must therefore conclude either that the surface state density (per unit area per unit energy) on the carrier and toner particles are equal ($N_c = N_t$), within a factor of 2, for all of the different toner-carrier systems characterized by these sets of data, taken with different toners and carriers at different laboratories, which seems unlikely, or that the high-density limit is the correct description of the data.

Despite the encouraging success of this macroscopic model of triboelectric charging, the transition to a microscopic model, which identifies materials parameters with the electric field created at the interface, has not been achieved. The primary difficulty with the high-density surface state theory is that the exchanged charge per unit area predicted, $\epsilon_0\Delta\phi/z$, using reasonable estimates of the parameters, is orders of magnitude (9×10^{-3} C/m^2) higher than observed (3×10^{-5}

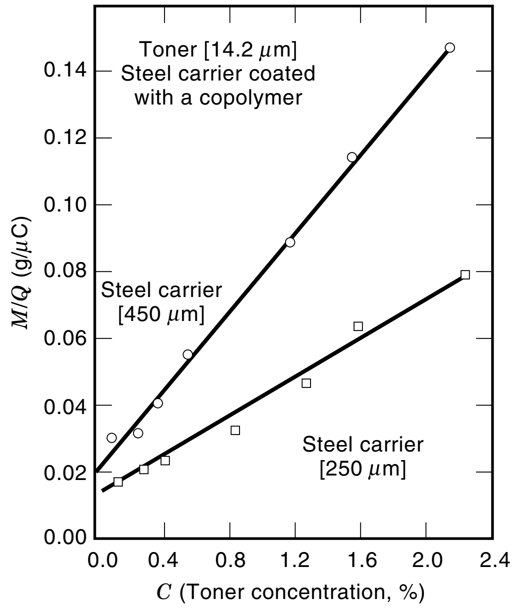

Figure 6. The mass-to-charge ratio plotted against the toner concentration for two difference carrier diameters (10) (Reprinted with permission of IS&T: The Society of Imaging Science and Technology, sole copyright owner of *Photographic Science and Engineering.*)

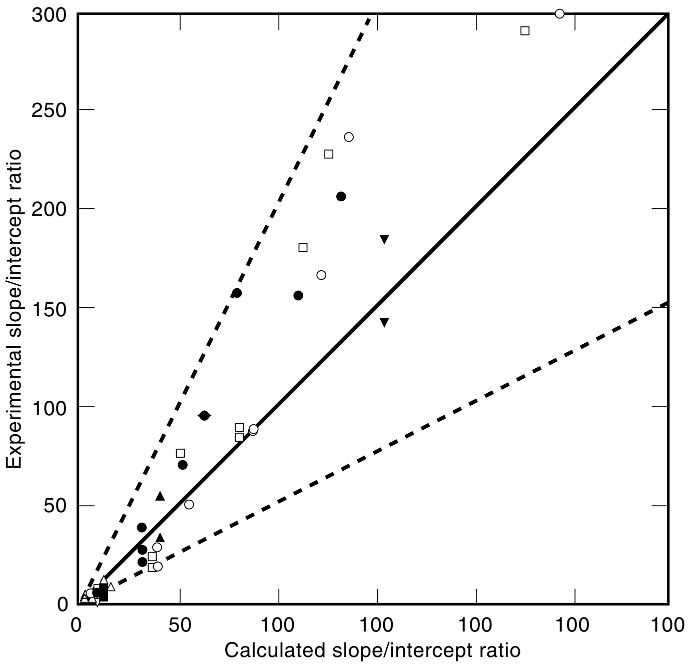

Figure 7. Comparison of experimental and calculated values (from the high-density surface state theory) of the slope to intercept ratio of M/Q versus C data (11). (Reprinted by permission of Elsevier, copyright holder.)

C/m^2) (for a 10 μm diameter particle charged to 20 μC/g). This results from assuming a typical solid-state work function difference of $\Delta\phi = 1$ eV and a tunneling cutoff distance of $z = 1$ nm. This makes it difficult to associate these parameters with real materials parameters, which is the goal of a microscopic theory of insulator charging.

The role of return currents caused by air breakdown as the particles separate has been discussed recently by Matsuyama and Yamamoto (12). Their experiments were done with insulator-metal contacts. Figure 8 shows Paschen's curve, which describes the conditions under which air breakdown occurs (if the potential difference between the surfaces at a contact gap d is above the curve) and the potential of a charged particle as it approaches and then leaves a metal plate. In Fig. 8 it is assumed that the initial charge on the particle is less than required to contact Paschen's curve, so no charge is lost prior to contact. During contact, it is assumed that sufficient charge is transferred to make the potential curves meet on separation. Charge relaxation occurs due to gaseous breakdown during separation. The final charge on the particle is determined by the particle's potential curve being tangent to Paschen's curve. Therefore, the particle's final charge is uniquely determined by its diameter and dielectric constant. For 3.2 mm diameter polymer particles used in the experiment, quantitative agreement between theory and experiment was obtained. For a 10 μm polymer particle, the particle's final predicted Q is 0.25 pC and Q/M is 500 μC/g if air breakdown limits the charge.

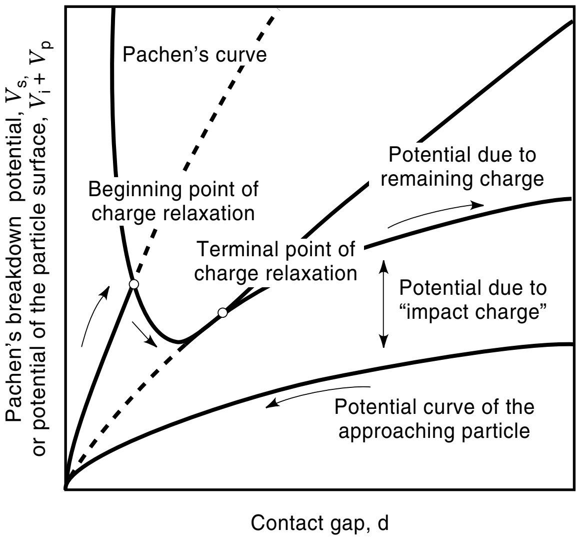

Figure 8. Schematic diagram of a model determining the charge on a particle after separation from a metal plane and gaseous breakdown (12).

Surface Chemistry of Insulator Charging

That the surface of insulators and not the bulk is involved in insulator charging is well supported both experimentally and theoretically. There are many reported experiments (see Refs. 1 and 2 for reviews, and Ref. 13 for an example of recent work) that show that when only the surface is chemically changed, the triboelectric charging is observed to change. Theoretically, the basic argument is the one presented previously regarding the movement of charges in wide-bandgap materials—the times required for charges to be released from deep traps in the bulk of an insulator are much longer than charging experiments.

The importance of surface water in insulator charging has been discussed in several reviews. Morris (14) states that "the part played by water in ionic charging is not clear. It may be essential in providing an aqueous layer between the 'contacting' surfaces in which the ions can diffuse. However, this layer would have to be extremely thin or discontinuous in order to avoid rapid surface leakage of the charge on separation of the contact." Medley (15) suggests that polar polymers, such as used in textiles and ion-exchange resins, in the presence of the acidic or basic groups promote water absorption. Water absorption by acidic and basic groups is enhanced by the high polarity of water molecules. One ion remains firmly bound to the polymer matrix and the other is free to take part in the charge exchange. For example, consider the strongly basic resin De-acidite FF and the strongly acidic permutit sulphonated polystyrene. In the presence of water, one obtains

$$R \cdot NOH \rightarrow RN^{+} + OH^{-}$$
$$R \cdot SO_3H \rightarrow RSO_3^{-} + H^{+}$$

That is, free H^+ and OH^- ions are available for charging. On shaking the powders of these resins from filter paper at 30% relative humidity, Medley found that the De-acidite FF became consistently positive and the permutit became consistently negative, the free ions having presumably been transferred to the filter paper. Other acids and bases were found to behave similarly. These ideas provide a rationale for extensive experiments done over many years. For example, experiments in which powders were slid off glass, sulfur, platinum, and paraffin wax coated plates revealed a strong correlation between the sign and magnitude of charging and the acidic or basic properties of the powders. Experiments on glass have shown that charging depends on the acidic nature of the surface, with basic materials charging positive and acidic materials charging negative. Related experiments by Sereda and Feldman (16) and Pence et al. (17) have shown charging peaks at one monolayer of surface water for textiles and toner, respectively.

Additives called charge control agents (CCA) (Section 12-4.4.3 of Ref. 1, and Refs. 18 and 19) increasingly are being added to toner used in electrophotographic technology to control the toner charge. Charge control agents are added to either the toner surface or bulk. Examples of surface charge control agents are fumed silica and highly fluorinated polymeric materials. Bulk charge control agents that are melt

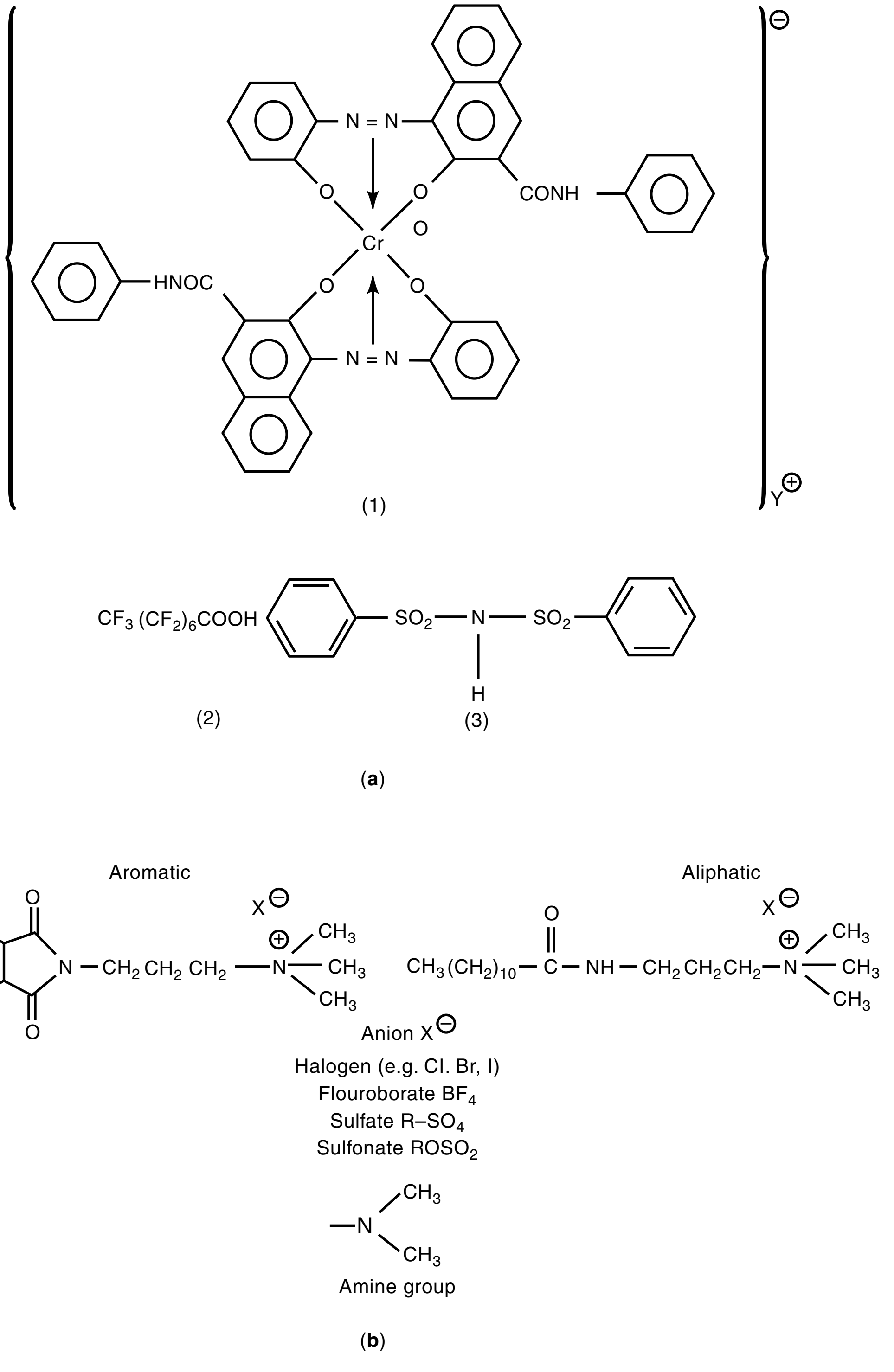

Figure 9. (a) Examples of negative charge control agents: (1) is a metal complex, (2) is a perfluorooctanoic acid, and (3) is a sulfonimide. (b) Examples of positive charge control agents. They can be aromatic or aliphatic. A list of counterions is shown at the bottom of (b) (19). (Courtesy of Society for Information Display.)

blended into the toner polymer differ for negative and positive toners. Metal complex dyes shown in Fig. 9(a) have been suggested as charge control agents for negative toners. Bulk charge control agents for positive toners can be amines and quaternary ammonium salts [Fig. 9(b)]; in either case they may be aliphatic or aromatic (both with long aliphatic hydrocarbon chains). The counterion can be halogens, fluoroborates, sulfates, or sulfonates. These materials are ionic surfactants very similar in chemical structure to the antistatic agents used to treat fabrics (19). Birkett and Gregory (18) have proposed that the charging process probably involves transfer of the counterion of the charge control agent on the toner surface to the carrier surface upon contact. They suggest that this mechanism qualitatively explains why 2 : 1 chromium or cobalt complex azo dyes having a proton as a counterion are observed to be particularly effective charge control agents: (1) The proton, being the smallest counterion, is highly mobile, and (2) the single negative charge in the dye anion is delocalized over an extremely large π-system, resulting in an easy removal of the proton. Gruber (19) has argued that the charging rate should be faster for a more weakly bound ion, which can be measured by acidity (which was observed). There have been several attempts in the literature to observe the transfer of a counterion of the charge control agent by surface science tools. This experiment has the difficulty that so few ions are needed to account for all of the charging (1 atom in 10^4–10^5) that small amounts of contamination easily confound the interpretation of this experiment. One article in the literature is especially interesting: Law et al. (20) used the charge control agent cesium 3,5-di-*t*-dibutylsalicylate, which has as its mobile ion Cs. Cs was in fact detected on the carrier by X-ray photoemission spectroscopy (XPS). Even more convincing, a linear relationship was observed between the measured charge exchange and the amount of Cs seen on the carrier. However, since the sensitivity of XPS to surface atoms is about 1%, 100 Cs atoms had to have transferred to the carrier surface for every one active in the triboelectrification. All of the aforementioned experiments clearly suggest that ion transfer is occurring during triboelectrification. In fact, the correlation of triboelectric charging with the presence of mobile ions on CCA is the basis of empirical approaches used to choose new materials as CCAs. However, Anderson (21) recently published results that show that the Q/M of toner with a CCA with a free cation (positive ion) increases both negatively and positively as the charge control agent concentration increases, simply by changing carrier coating. Furthermore, Anderson argues that there must be more ionic species available for charge exchange than just those introduced by the CCA because even polystyrene can charge to both polarities depending on the carrier used.

Discussion

There are some puzzling inconsistencies in the preceding discussions, some of which were pointed out. In addition, there is very strong evidence that the acidic or basic nature of a material determines the sign of the charge exchange. However, if it were assumed that this implies that a mobile ion moves from one material to the other driven by diffusion alone, a clear contradiction occurs with the insulator-insulator charging experiments shown in Figs. 6 and 7. These results demonstrate that the charge on a toner particle depends on the number of toner particles on a carrier particle ($1/Q$ is linear in the toner concentration). How does a mobile ion on a toner, “considering” whether to transfer to a carrier particle, “know” that there are other toner particles on the carrier? Speaking less anthropomorphically, noting that mobile ions are present does not specify the driving force for the charge exchange. The evidence for gaseous breakdown in the insulator-metal experiment is strong. Can this be generalized to the insulator-insulator charge exchange results? These experiments predict that the particle’s final charge depends only on the diameter and dielectric constant of the particle. But toners (of basically the same size and dielectric constant) are observed to have highly variable charge, depending on the carrier surface material and the addition of charge control agents added to the toner (at the 1% level). Furthermore, the predicted Q/M for typical 10 μm diameter particles is 500 μC/g, much higher than ever observed. These well-known results would appear to indicate that toner charging cannot be determined by gaseous breakdown alone; probably gaseous breakdown represents an upper limit. Some other mechanism is controlling toner charging in the practical case.

The experimental demonstration that the high-density surface state theory describes toner charging, and therefore probably all insulator charging, is interesting. But accounting for the magnitude of the electric field at the interface at which toner charging ceases remains an unsolved problem. This result does help to resolve one controversy: whether electrons or ions determine insulator charging. Assume that some unknown mechanism determines the electric field at which charging ceases. Then any ions or electrons that are available are exchanged between the two materials until the electric field is achieved. If more ions or electrons are available, the rate of charge exchange is probably increased, as shown by Gruber (19). However, this is not the whole story, because the presence of CCA, which can provide mobile ions in the toner-carrier experiments, is also known to change the magnitude of the charge exchange. A consequence of this reasoning is the following: If no electrons or ions are available, then charge exchange should not be observed, which is exactly what Harper (22) claimed to have observed. It would appear that the key to a better understanding of the mechanism of triboelectrification of insulators is for an interdisciplinary team of chemists and physicists to understand the material parameter(s) that determine the electric field at the interface at which charging ceases.

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TRIBOELECTRIFICATION. See TRIBOELECTRICITY.

TRIMMING OF CIRCUITS. See CIRCUIT TUNING.

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TTL. See TRANSISTOR-TRANSISTOR LOGIC.

TUBES, CATHODE-RAY AND TELEVISION. See CATHODE-RAY TUBES.

TUBES, MICROWAVE. See MICROWAVE TUBES.

TUBES, RECTIFIER. See RECTIFYING CIRCUITS.

TUNABLE FILTERS. See ELECTRO-OPTICAL FILTERS.

TUNING OF CIRCUITS. See CIRCUIT TUNING.