Kirk-Othmer Encyclopedia of Chemical Technology.

ANTISTATIC AGENTS

Electrification is the process of producing an electric charge on an object. If the charge is confined to the object it is said to be electrostatic. The term static electricity refers to accumulated, immobile, electrical charges in contrast to charges in rapid flow, which is the subject of electrodynamics.

Static electricity was described as early as 600 BC by the Greek scientist Thales of Miletus, who observed that amber attracts small particles of dust when rubbed with animal fur. William Gilbert (1540–1603), an English scientist, discovered that many other materials behave like amber when rubbed. There have been many attempts made at investigating the origin and nature of electrostatic charges in various materials. As far back as 1757 Wilcke (1) noted that various substances such as amber, silk, wool, etc, could be arranged in a triboelectric series. It was assumed earlier that electric charges are generated by the mechanical work dissipated in friction, hence the name triboelectricity. A triboelectric series can be defined as a grouping of materials arranged according to their electrostatic susceptibility, the first in the series being positively charged with respect to all the others, and the last in the series being negatively charged with respect to all the others. Wilcke showed that rubbing any two of the substances together produces opposite charges, the one that precedes in the series becoming positively charged. Since that time many such lists have been published (2–7), some of which are shown in Table 1. A widely accepted triboelectric series is that listed in the Electronics Industry Association (EIA) Standard 541, which is also listed in Table 1 (8). There are certain similarities among the tables, eg, wool and polyamides are located on the positive end of the series whereas polyesters appear on the negative end; however, several inconsistencies also exist. Overall, it is possible to predict the signs of the charges for a given pair of materials when rubbed together, especially when these materials are sufficiently far apart in the series; however, the magnitude of charge generated is difficult to predict. Kinetic effects play an important role in static generation and render it unpredictable. Many other factors such as differences in the molecular surface structure of materials, presence of surface impurities, intensity of contact, electrochemical and thermochemical effects, etc, may also be responsible for the inconsistency of the triboelectric series (9).

Static is a surface phenomenon. When two surfaces are brought into contact, electrons pass across the interface in both directions. This exchange is not symmetrical, and even with two identical bodies one of the two acquires an excess of electrons at the expense of the other. As long as contact is maintained, there is no further effect. However, when the surfaces are separated part of the charge is discharged into air, and the remainder is left on the material. One of the two bodies has an excess of electrons and the other has a shortage of electrons, ie, the objects are electrically charged with the same magnitude of charge but opposite signs. The magnitude of the charge depends on the rate of separation of the two bodies. The electrons in a conductor move freely, thus the excess of electrons is eliminated by backflow. However, the electrons in an insulator are not mobile, and the phenomenon of static electricity becomes noticeable.

Coulomb (1736–1806) stated the law of repellency between similarly charged bodies and attraction between oppositely charged bodies, and Faraday (1791–1867) described the laws of electrostatic induction. The inductive principle known as Faraday's ice-pail method is still in use in modern measuring equipment.

Table 1. Triboelectric Series

Reference 2	Reference 3	Reference 4	Reference 7	Reference 8
wool	glass	wool	platinum	quartz
nylon	human hair	nylon	formvar	glass
silk	nylon yarn	viscose	filter paper	mica
viscose	nylon polymer	cotton	cellulose	human hair
polyethylene	wool	silk	acetate	celluloid
Cordura[a]	silk	acetate	cellulose	nylon
human skin	viscose	Lucite[a]	triacetate	wool
fiber glass	cotton	poly(vinyl alcohol)	polyethylene	fur
glass	paper	Dacron[a]	aluminum	silk
acetate	ramie	Dynel[b]	polystyrene	aluminum
Dacron[a]	steel	Velon[c]	natural rubber	paper
chromium	hard rubber	polyethylene		cotton
Orlon[a]	acetate	Teflon[a]		steel
	Orlon[a], Saran[d]			wood
	polyethylene			amber
				sealing wax
				hard rubber
				nickel, copper,brass,
				silver,old platinum
				sulfur
				acetate rayon
				polyester
				Orlon[a], Saran[d]
				polyurethane
				polyethylene
				polypropylene
				PVC
				silicon
				Teflon[a]

[a] DuPont trademark.
[b] Union Carbide trademark.
[c] Firestone trademark.
[d] Dow trademark.

The density of static charge accumulated by an insulator is limited due to leakage through air, and therefore the attraction and repulsion of charged bodies are also limited. The breakdown potential of air at atmospheric pressure is 30,000 V/cm; thus the maximum charge that can exist on a plane surface is about 3.3×10^{-9} C/cm^2 (10 esu/cm^2) (10). Such charges are sufficient to hold only small particles. Increasing the density of the charge beyond the breakdown potential of air causes a discharge through an electric spark.

During the first half of the nineteenth century one of the few significant researchers of static was Helmholtz (1821–1894), who introduced a comprehensive theory of electricity and also developed the contact potential theory of the electrification of insulators by contact. Also, P. E. Shaw showed the influence of chemical and physical conditions of surfaces on static generation. Many problems have arisen in recent decades in the textile, paper, and plastic industries because of the introduction of new insulating materials, particularly synthetic fibers and plastics, as well as increased processing speeds. This has led to an accelerated pace of research into the generation and discharge of static electricity in insulators.

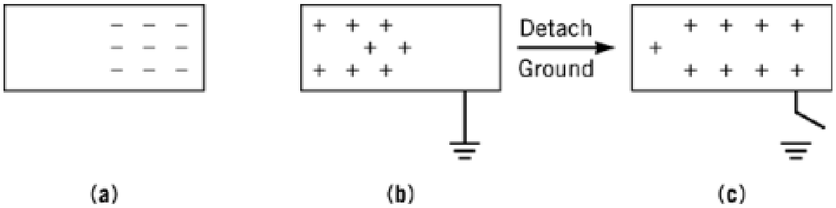

Fig. 1. Acquisition of static charge by induction.

1. Nature of Charge Generation

Objects are thought of as developing static charges either by tribocharging or by an induction mechanism. Tribocharging involves the rubbing together of two objects to form the charge. Induction is a process by which an outside electrical field charges an object.

1.1. Tribocharging

The root word "tribo" is from the Greek word meaning "to rub." When two objects contact they have the potential for the transfer of electrons from the surface of one object to the surface of the other object. Electron transfer can occur simply by touching the objects together and then quickly separating the objects. The more the objects are rubbed against each other the more the electrons are excited, and the greater the potential for electron transfer. Electrons are removed from the surface atoms of one material more readily than from the other material; the surface with the electron deficit thus develops a positive charge. The surface accepting these electrons has an excess of electrons and therefore acquires a negative charge. Whether a material is an acceptor or a donor is determined by their relative positions along the triboelectric series (11).

The magnitude of the static electric charge developed by tribocharging is dependent on the intimacy of contact between the two surfaces, the amount of rubbing, the coefficient of friction of the two surfaces, the speed at which the two surfaces are separated, and the conductivity of the materials. The first three factors are somewhat interrelated. The closer the contact between the two surfaces, the more opportunity exists for the transfer of electrons. When the two surfaces are in contact the overall charge is neutral; a static charge does not establish until the two surfaces are separated. If the surfaces are separated slowly, the electrons have time to return to their normal state. If they are separated quickly, the electrons do not have time to return to their normal state and remain on the surface that is closer to the negative charge end of the triboelectric series.

The rubbing of the two surfaces need not be a continuous, repetitive motion. Actions as simple as walking across a room or sitting in a chair can generate a static charge.

1.2. Induction

An object can acquire a static charge from another charged object by induction. If a charged object A is brought into the vicinity of a neutral object B and the neutral object is grounded, the neutral object acquires a charge of opposite polarity by induction (Fig. 1). In this example, the electrons on object B are repelled by the negative charge on object A. The electrons flow to the ground, leaving a positive charge on the object. If the ground is removed, C, the object retains the positive charge even after the inducing object A is removed. If the object remains grounded after the inducing object is removed, the electrons flow from the ground and return the neutrality of the object. In the example, if object A had been positively charged, the object B would have attracted electrons from the ground and would have been negatively charged.

2. Effects of Static Electricity

2.1. Repellency of Similarly Charged Objects

Mutual repulsion of fibers having similar charges causes difficulties in many textile processing procedures. Repulsion causes filaments in a charged warp to bend away from one another, ballooning of a bundle of slivers (12), excessive fly (very short fibers) during processing, and increases in hairiness of the yarn produced. Difficulty in folding fabrics into layers is especially disturbing in dyeing and finishing plants where long lengths of dry fabrics must be handled.

2.2. Attraction of Oppositely Charged Objects

Mutual attraction of oppositely charged fibers leads to difficulties in carding, drawing, weaving, knitting, roving, spinning, etc, due to tangled fibers and yarns. Charged fibers are attracted to adjacent parts of the spinning machinery and thus interfere with processing (13–15). Static attraction of dirt and fly from the air produces dark localized stains on fabrics left on looms during weaving (fog marking) and soiling of packages of nylon yarn (16). For the consumer, many annoyances occur frequently as a result of mutual attraction of oppositely charged fabrics. Examples are clinging of apparel to the body and to undergarments (17–20). Static can contribute to the soiling of garments, draperies, and other textile products by attracting oppositely charged particles of dust and dirt from the atmosphere to a charged fabric (21–23). One of the most severe outcomes of mutual attraction of oppositely charged fabrics is failure of parachutes to open.

Static phenomena due to the attraction of oppositely charged objects are evident in many other industries. Electrostatic charges tend to accumulate on the surface of plastic articles during fabrication, and these charges attract dust and dirt particles to the surface, causing fabrication problems. Dust attracted to finished consumer products makes them unattractive for sale. The generation of electrostatic charges is particularly troublesome in the fabrication of sheets, films, or filaments because the static charges tend to cause the articles to cling together or to the processing equipment (24). Electrostatic charges are also accumulated during the subsequent use of the fabricated article and cause excessive pickup of dust and dirt particles by bottles, film wrap, and resin powders. Static buildup on phonograph records attracts dirt and dust, consequently impairing the quality of sound reproduction. It also causes accelerated wear of the stylus and the record (25). Electrically charged resin powders are troublesome since the charge causes them to adhere to processing equipment, packaging materials, and other surfaces, thus causing various difficulties in their preparation and utilization. Accumulated electrostatic charge on photographic films can cause adhesions of surrounding dust onto the surface of the film, which impairs the quality of the film. Discharge of such films during processing causes fogging. In the paper industry, electrostatic charges developed on paper during printing prevent proper layering of the sheets.

2.3. Static Electric Discharge

When a charged object comes into contact with an object of lower charge or into contact with a ground, a static electric discharge occurs. If the charged object has come into contact with an ungrounded object, the discharge continues until the charge on each object is equivalent. If the object comes into contact with a grounded conductor, then it completely discharges.

The contact between the two objects is not required to be a physical touching of the two objects. If the charge on the object is greater than the dielectric strength of air, the charge will pass over the air gap to the other object.

The static electric discharge can be a small annoyance, such as shock received when a person touches a doorknob after walking on a charged carpet, or the discharge can be catastrophic. Static electric discharge can cause explosions in areas where flammable gases are in use and in grain elevators when the grain dust reaches

Table 2. ESD Susceptibility of Various ElectronicDevices

	Range of ESD susceptibility	
Device type	Potential, V	Energy, μJ
MOSFET	100–200	0.5–2.0
EPROM	100	0.5
JFET	140–7000	0.98–2.45
OP-AMP	190–2500	1.62–312.5
CMOS	250–3000	3.13–450
Schottky diodes	300–2500	4.5–312.5
film resistors(thick, thin)	300–3000	4.5–450
bipolartransistors	300–7000	4.5–2.45
Schottky TTL	1000–2500	50–312.5

combustible levels. Perhaps the most famous example of the dangers of static electric discharge is that of the German airship, the Hindenberg, which ignited its hydrogen, causing the airship to burn.

Static electric discharge is a serious problem in the electronics industry. Electronic devices are extremely sensitive to static electric discharges. Examples of the sensitivity to electrostatic discharge (ESD) are given in Table 2 (26).

The energy from an electrostatic discharge on an integrated circuit chip causes localized heating in the chip, which melts areas of silicon in the chip. This melting destroys the circuits engraved on the silicon. Temperatures have been known to reach 760°C at certain points on the chip. The temperature is highest at positions of restricted current flow on the chip (27).

Electrostatic charges are also generated when liquids move in contact with other materials, liquid or solid, eg, during pumping of gasoline. Serious industrial hazards caused by static in chemical and related fields have been described (28), and a study of accidents in the chemical industry revealed that 115 out of 1600 accidents, or 7%, were ascribed to static electricity (29) (see Plant safety).

Accumulation of electrical charges on textiles, plastics, and other materials of insulating character causes problems which occur with greater frequency as the relative humidity decreases, particularly during winter months. Heated rooms in winter provide an environment in which static phenomena are frequently apparent.

2.4. Useful Applications

Suggestions have been made for uses of static electricity in the textile (9) and other industries, but the number of commercially successful applications is few. One well-known use of static electricity in the textile industry is the process of flocking, in which short fibers (flocks) are embedded vertically and cured in an adhesive-backed substrate, usually fabric or paper, to make a large range of velvetlike materials. Static charges are generated by a high voltage source and are used to control the deposition of the short fibers onto the backing (30). Other successful applications are in the lay-down of fibers in the process of spunbonded nonwoven fabrics (31, 32) and in electrostatic polishing of pilo fabrics (see Nonwoven textiles).

Electrostatic fields generated by high voltage electrodes are employed in electrostatic spray painting where the charge first attracts the spray to the object and then repels the excess spray from it (see Coating processes). Avoiding soiling due to the attraction of dust and dirt particles by static is applied in air filters (33) (see Air pollution control methods). The Shirley Institute has developed perhaps the most novel application of static phenomena, the detection of footprints on carpets and other floor coverings (31).

Other suggested applications include the use of electrostatic fields in electrostatic printing (see Printing processes) (34), shearing machines (35), and measurements of yarn hairiness and moisture content of fabrics (31). Other examples are utilization of static electricity in fiber processing (35), cleaning of cotton and wool fibers from trash (35–38), separation of long and short fibers (35, 59), separation of wool from synthetic fibers

(40), open-end spinning of yarns (41, 42), and straightening of filling thread in shuttleless looms (41). It has been claimed that negative static charges generated on undergarments made of synthetic fibers have considerable therapeutic effects on rheumatic illnesses such as arthritis, rheumatism, etc (43, 44).

3. Methods of Controlling Static Charges

The amount of electrostatic charge developed on a material represents a balance between the rate of generation and the rate of dissipation. Good conductors disperse a static charge quickly; however, textiles and plastics have a high surface resistivity and charge decay can occur only at a low rate. For example, it has been calculated that a given charge on a polystyrene surface would take three years to decay to a negligible value (45). It is feasible to reduce accumulation of static charges by either reducing the rate of generation or by increasing the rate of dissipation.

3.1. Preventing Static Generation

The most logical remedy to static problems is prevention of static generation. Reduction of friction generally results in reduction of static, but friction is essential for many processes and cannot be excessively reduced. Moreover, it cannot be regarded as a true remedy since charges are actually generated whenever two materials in contact are separated, regardless of rubbing. Also, charges can be generated by induction from another charged object, although static-shielding containers that provide protection from static charging by induction can be purchased.

Another method reported to reduce charge generation is changing the electrical potential of the contacting elements (31, 46, 47). Perhaps the most popular suggestion to eliminate static generation utilizes the rank of materials in the triboelectric series. This includes either impressing countercharges on the charged material by contact with materials on the other side of the triboelectric series (48–50), or neutralizing the charge generation by blending two kinds of fibers with a tendency to attain opposite charge (2, 7). The blending technique, however, is generally not effective since it is practically impossible to predict the exact composition of the optimum blend of two fibers that will generate equal but opposite static charges.

3.2. Increasing Rate of Static Dissipation

Since it is not feasible to prevent the generation of static electricity, all practical remedial measures are based on increasing the rate of charge dissipation or charge leakage. Static charges on polymers dissipate or decay through two processes, namely surface and volume conductivity of charges through the substrate, and loss of charge by radiation to the air (51, 52). The radiation process has a significant effect on charge decay and in some polymers, ie, nylon-6,6, the evidence strongly suggests that the loss of charge by radiation is greater than by the conductivity process. Even for polymers that are conducting, ie, wool and cellulose, it is found that the rate constant for radiation is approximately equal to that for conduction (51). The following comprise the main practical methods for increasing the rate of static dissipation.

3.2.1. Grounding

Use of a grounded bar, rod, or roll to discharge static charge buildup is effective for conductive materials which contain a charge. Grounding is ineffective for insulators since the electrons on an insulator are not sufficiently mobile to travel to ground. For partially conductive materials, grounding can be somewhat effective for the area of the object in contact with the ground. Grounding of a partially conductive material is best attempted by contacting the entire surface of the object, eg, using a string of copper tinsel stretched across a roll of paper on a computer printer.

3.2.2. Ionization

If a charge is located on an insulator, there is in principle no way by which the charge may be removed. If, however, the charged insulator is completely surrounded by a conducting fluid in contact with all points of the surface, the charge or the field from the charge may be neutralized by oppositely charged ions being attracted to the insulator. Although this scenario in principle could be established by using a conducting liquid, the only practical solution is to surround the charged body with ionized air (53).

Static eliminating devices that ionize the atmosphere around the device are available. Static eliminators are divided into two main groups: silent (corona) discharge eliminators, such as inductive eliminators, or high voltage eliminators which initiate an impact ionization of the air by applying strong electrostatic fields, and radioactive eliminators that provide a multitude of ions from independent ion sources (9).

3.2.3. Increasing Conductivity

Increasing the electrical conductivity of the material by increasing its electrolytic (ionic) or electronic conductivity is another means of controlling static charges. The electrolytic conductivity can be improved by increasing the moisture content of the surrounding atmosphere (humidification), by application of internal or external antistatic agents, or by chemically modifying the material. Chemical modification is especially used for textile fibers and involves surface modification to increase hygroscopic properties (54, 55) or grafting of functional groups leading to ionic configurations or greater moisture sensitivity (56). The electrical conductivity of the material can also be improved by increasing its electronic conductivity. This can be achieved by coating fibers with a thin layer of a conductor such as silver or carbon black, by blending fine metal fibers with static-prone fibers in the textile material, or by incorporating carbon black in plastics.

3.2.4. Humidification

Adding moisture to air has long been used to control static and to help dissipate static electricity in textile mills (see Air conditioning). Moisture does not improve the electrical conductivity of the air, but it increases the electrical conductivity of materials absorbing moisture. A definite limit to humidification is imposed by discomfort and corrosion problems, and in some cases high humidity has to be avoided due to its deleterious effects on the materials or on the processing performance. Also, humidification alone has effective limits; for example, lightning, which is a static electric discharge, occurs during rainstorms. Humidification within a tolerable range is the most widely used antistatic process in the processing of materials of limited static propensity such as cotton and rayon, but this does not suffice with other materials such as wool, synthetic fibers, plastics, etc; the use of suitable antistatic agents in the processing of such materials is essential. Antistatic agents are also used to eliminate static problems that arise in consumer use. Antistatic agents prevent the bulk of static problems, but almost all of them rely on atmospheric moisture for their effectiveness; humidity control therefore remains a requirement for the smooth processing of hydrophobic materials.

4. Measuring Static Charges

Static charges can be characterized by several techniques (57). A simple test is to suspend an object 2 cm above a shallow dish containing cigarette ashes. A charged object attracts the ashes to its surface; the amount of ashes attracted is proportional to the charge on the object. More scientifically vigorous tests are available by measuring surface resistance, field voltage, coulombic charge, and charge decay rate.

4.1. Field Voltage

A field voltmeter measures a static charge by putting a conductive plate in the field of charge around a charged object. The plate is always positioned the same distance from the charged object. By estimating the dielectric constant of the object and knowing the area and the distance, the capacitance of the object can be estimated

$$C = \frac{KE_oA}{x}$$

where C = capacitance, K = dielectric constant, $E_0 = 8.85 \times 10 - 14$ F/cm, A = area, and x = distance. After capacitance and charge are determined, voltage can be calculated by the formula: voltage = charge/capacitance.

For an accurate measurement using a field voltmeter, the meter must be calibrated (or zeroed) before a test. The charge on a grounded conductor is measured. A grounded conductor should have a charge equal to zero, which means the voltage would be zero. Therefore, the field meter should read zero (Fig. 2**a**).

In practice, field voltage is a quick and easy test. Several companies manufacture small handheld voltmeters. However, the test is error-prone. The capacitance of the object is needed for an exact measurement, and the meter must be held an exact distance from the object being measured. If the distance is different from the one used by the manufacturer to calculate the voltage, then the voltage reading on the meter will be different from the actual voltage. The voltmeter does not measure the entire charge, but only the charge directly in front of the plate. Voltmeters have the advantage of being easy to use and can measure voltages on large or immovable objects that would not fit into other test devices.

4.2. Faraday Cage

One of the best means of measuring a static charge, typically in coulombs, is by means of a Faraday Cage. When a charged object is put inside a conductive box, the Faraday Cage, a charge is induced on the box. This charge is of opposite polarity but equal magnitude to the charge on the object. The Faraday Cage can simply be connected to an electrometer, and the charge on the cage measured. The cage should be grounded before the test to bring its charge to zero, and the ground should be removed before the object is put into the cage. In practice the Faraday Cage should be inside of but insulated from a second Faraday Cage. The second Faraday Cage shields any outside charges from interfering with the test. If the Faraday Cage is deeper than it is wide, it does not require a lid to give an accurate reading. An object put into the Cage falls to the bottom of the cage so that very little of its charge is lost through the air out of the top of the top of the cage (Fig. 2**b**).

Faraday Cage measurements have the advantage of measuring the total charge on an object and also are equally effective for testing conductive as well as insulating objects. One disadvantage of the test is that the object to be tested must fit into the cage.

4.3. Surface Resistivity

Resistance is the measure of the conductivity of a material. Conductive materials have the ability to dissipate static charges. Therefore, resistance is a good measure of the ability of an object to dissipate a static charge. Since static electricity is primarily a surface phenomenon, the resistance along the surface of the object is of most interest.

Surface resistance is measured by placing two electrodes on the surface of the object to be tested. A d-c voltage is applied to one electrode and an ammeter is attached to the other electrode. The current travels from one electrode to the other by traveling across the surface of the object. When the current is measured and the applied voltage is known, resistance can be calculated by the formula: resistance = voltage/current.

Resistance measurements change with an alteration in voltage, and the voltage used to run a test should be compared when evaluating resistivity results. The proper voltage to use is often listed in the test organizational procedures that specify surface resistance test methods. The most common test method is provided by the American Society of Testing and Materials (ASTM) in standard D257. The Electrical Overstress/Electronics Industry Association has found that ASTM D257 is a good procedure for conductive materials and insulators but is not accurate when testing static dissipative materials. They have proposed a variation on ASTM D257

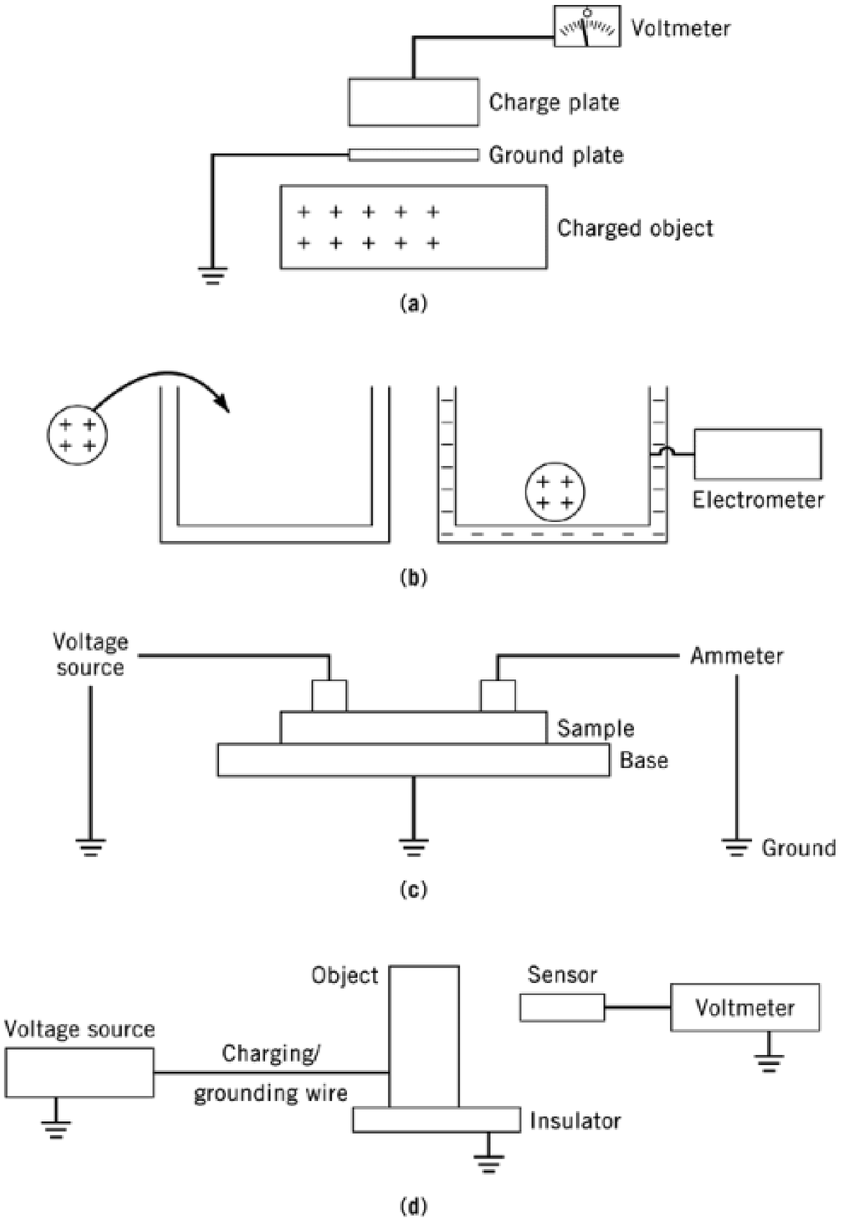

Fig. 2. Measuring static charge. (**a**) Field voltage measurement; (**b**) Faraday cage; (**c**) surface resistivity measurement; and (**d**) static decay test.

in their standard DS11.11 (58). ASTM D257 is run with a 500 V d-c charge. EOS/ESD DS11.11 is run with a 100 V d-c charge for materials with a resistance above $1.0 \times 10^6\ \Omega$ and a 10 V d-c charge when the resistance is below $1.0 \times 10^6\ \Omega$.

The terms resistance and resistivity are both used when referring to the resistance of an object to current flow. Surface resistance is the measure of electrical resistance along the surface of an object. However, the current flow is not limited to the surface of the object. Some of the current passes through the bulk of the object from one electrode to the other electrode. Surface resistivity includes the dimensions of the object in its measurement (Fig. 2**c**).

$$\text{Surface resistivity} = \frac{\mathit{Area}}{\mathit{Thickness}} \times \text{Resistance}$$

4.4. Static Decay

A static decay test measures the length of time required for the charge on an object to decay once the object has been grounded. The test suspends an object from conductors or ground. A charge is induced on the object using a d-c voltage source. The charge on the object is determined by a voltmeter. The charged object is grounded and the drop in voltage is measured by the voltmeter (Fig. 2**d**). The test is usually run in a Faraday Cage to prevent outside charge sources from interfering with the test. A typical charging voltage is 5000 V d-c. The test method is described in Federal Test Method Standard 101B Method 4046 (59).

The static decay test is a good measure of the static dissipative nature of an object. However, the test is controlled by the object's resistance to ground. Objects that have a high resistance, such as insulators, will not readily accept an induced charge or decay an induced charge. The static decay test is most suited for objects with resistances of 10^{12} or less (52).

4.5. Tests Simulating Use Conditions

Several simulation tests involving wear and use testing have been developed. The first and only one to be adopted as a standard in the United States is AATCC Test Method 134-1975 for measuring the electrostatic propensity of carpets (60). In this test a person wearing standard neoprene and leather sole shoes and carrying a probe connected to an electrometer walks on a carpet for 30 to 60 s until the measured body voltage builds up to a maximum.

A test that does not involve a human test subject has been adopted as AATCC Standard Test Method 115-1973 called Electrostatic Clinging of Fabrics: Fabric-to-Metal Test (61). This test is used for evaluating lightweight fabrics, and is based on the principle of frictional charge generation by rubbing with a fabric of different composition. The charged fabric is allowed to cling to a grounded metal plate and the time for declinging is measured.

Subjective tests using humans have also been described, such as the sail test (62) and others (63–65). As might be expected, the results of these tests are not very reproducible.

4.6. Tribocharging Tests

Since a common source of a static charge is by tribocharging, a lot of effort has been expended in developing tribocharging tests. In general, the results of such tests are not reproducible, and the tests are effective only for the narrow range of materials used in developing the tests. The tests usually involve rubbing a cloth (usually wool) against an object or sliding an object down a quartz or Teflon rod; if the object is not suitable for sliding down a rod, then a quartz or Teflon disk is slid down the object. The charge on the object or the disk is then measured. The EOS/ESD Association is attempting to develop a standard reproducible tribocharging test under standard DS11.2 (53).

4.7. Significance of Static Charge Measurements

Attempts have been made to correlate static charge measurements to a set of standards that would ensure that articles meeting the standard would not pose static electric problems. Most of the tests have only provided general guidelines for static protection. For problems such as static-induced dust attraction no standards exist, and performance measures are strictly subjective. The electronics industry and the National Fire Protection Association have developed standards based on the surface resistivity and static decay tests. These standards have evolved over time and will no doubt be modified in the future. The current standards are as follows: EIA-541 for static dissipative materials requires a surface resistivity of 10^5–10^{12} Ω and a static decay rate of 99% charge decay in less than 2.0 s (66). The National Fire Protection Association Standard 99 for materials used in areas containing flammable gases requires a surface resistivity of $1.0 \times 10^{13}\ \Omega$ or less and a static decay rate of a 90% charge decay in less than 0.5 s (67). Since it is recognized that most antistatic agents function by attracting atmospheric moisture, the standards specify the test to be run in a 15% rh atmosphere.

5. Static Dissipative Materials

The term antistatic traditionally referred to materials having a surface resistance between the resistance of conductors and insulators. The resistance values of an antistatic material were considered to be in the range of 10^9 to 10^{14} Ω. The antistatic property of a material is not a dependent function of material resistivity, which is an intrinsic property used to define the material's degree of conductivity without regard to other materials. A material's propensity to form a static charge depends on the nature of the material itself, the material with which it is in contact, and the means of surface separation. In the Electronics Industry Association Standard 541, the term antistatic no longer refers to a material's ability to resist triboelectric charge generation (68).

Materials that have the ability to dissipate a charged formed, by any means including tribocharging and induction, on the material are referred to as static dissipative. There is a correlation between static dissipation and surface resistance. EIA-541 currently defines the static dissipative range as 10^5 to 10^{12} Ω.

The term antistatic agent is generally used to describe a substance that is added to a material to make that material static dissipative. The two biggest markets for antistatic agents are textiles and plastics.

5.0.1. Antistatic Agents for Textile Materials

Antistatic finishes are defined as antistatic agents in combination with water, mineral oil, composite finishes applied by producers during fiber manufacture, oils used to facilitate throwing or coning, textile softeners or lubricants, and hand building compounds. The terms antistatic agents and antistatic finishes have often been used interchangeably in the literature.

Effective antistatic agents must act at a relative humidity below 40%, preferably below 15%. The agent must form a film on various surfaces and be applied from a solution or dispersion in water or other inexpensive solvents. The antistatic agent must not interfere with subsequent processing of the product, impair the hand, or affect color, odor, appearance, and performance properties of the substrate. It should be nontoxic and nonflammable.

5.1. Function

Antistatic agents can function either by reducing the generation of charge, by increasing the rate of charge dissipation, or by both mechanisms. The way in which rate of generation is diminished is not completely understood; however, it seems likely that the presence of the antistatic agent at the interface reduces the intimacy of contact between surfaces and therefore the net charge transfer (9). Evidently most lubricants function this way, and it is often desirable to combine antistatic action with lubrication (69) (see Lubrication and lubricants).

Most antistatic agents operate by increasing the rate of charge dissipation. Good correlation has been shown between the surface resistivity of a material and its charge decay rate (70). Moreover, there is a direct correlation between the effectiveness of an antistatic agent and its ability to lower the surface resistivity of a polymeric material (70, 71). It is believed, however, that static charges on polymers are lost through two processes, namely surface and volume conductivity of the charge through the substrate, and loss of charge through air by radiation. The radiation process is at least as important as the conduction process in effecting charge dissipation (51, 72).

5.2. Chemical Classification

Substances of high electrical conductivity are effective antistatic agents. Numerous chemicals have been proposed and reviewed (73–75). In general, most antistatic agents belong to one of the following classes (76): nitrogen compounds such as long-chain amines, amides, and quaternary ammonium salts; esters of fatty acids and their derivatives; sulfonic acids and alkyl aryl sulfonates; polyoxyethylene derivatives; polyglycols and their derivatives; polyhydric alcohols and their derivatives; phosphoric acid derivatives; solutions of electrolytes in liquids with high dielectric constants; molten salts; metals; carbon black; semiconductors; and liquids with high dielectric constant, such as water, which are usually volatile and have a temporary effect only.

5.3. Role of Atmospheric Moisture in Static Protection

Water is outstanding among liquids because of its low cost, absence of toxicity, and nonflammability. Furthermore, although volatile, water can be continuously replenished from the atmosphere. Most nonmetallic antistatic agents utilize the conductivity of water for charge dissipation and ensure its presence by their hygroscopic nature. The amount of moisture absorbed in equilibrium with atmospheres of various relative humidities at a given temperature represents a moisture absorption isotherm for the antistatic material. A reduction of atmospheric humidity reduces the effectiveness of antistatic agents. A small quantity of adsorbed water is essential for ionization in the process of antistatic protection (77, 78). In contrast, substances such as carbon black and metallic filaments do not rely on the presence of moisture to dissipate the static charge.

Most organic polymers absorb significant amounts of moisture from the atmosphere; the amount absorbed is a function of the relative humidity. The absorption isotherms of polymers depend on the affinity for, and accessibility to, water molecules. Pure water has a specific resistance of 10^8 Ω/cm; in general, therefore, it has a resistance 10^8 times lower than an organic polymer. Moreover, water usually contains dissolved electrolytes that increase its conductivity a thousandfold. The conductivity of a polymer increases significantly by absorption of even small quantities of moisture. The efficiency of an antistatic agent depends on the degree of its hygroscopicity, the distribution of moisture, and its ability to supply mobile ions to the aqueous layer it forms with absorbed water (79). Hygroscopicity alone is sufficient for antistatic action of a finish, as demonstrated by the effectiveness of nonionic antistatic agents, since stray electrolytes are usually present in the form of impurities. However, the degree of efficiency of an antistatic agent can be increased by the addition of electrolytes.

Experimental observations (80) relating moisture content to specific resistance R_s for polymeric fibrous materials are shown in Figure 3. Most natural fibers such as cotton (qv), silk (qv), and wool (qv), are hydrophilic in nature, and synthetic polymers such as polyolefins (see Olefin polymers), polyamides, polyesters, and polyacrylonitrile are comparatively hydrophobic (see Fibers, acrylic; Polyamides, fibers; Fibers, polyesters). Therefore, under identical conditions, synthetic fibers as a group are better insulators and are more staticprone than natural fibers. In a certain range, however, nylon shows lower resistance than the more hydrophilic viscose (rayon) for the same moisture content (see Fibers, regenerated cellulosics). The range of resistivity, even in the incomplete range of moisture content, embraces eight orders of magnitude. Under the same moisture conditions, hydrophobic fibers tend to show lower conductivity compared to hydrophilic fibers. This lower conducting efficiency is perhaps related to a lower dielectric constant and, consequently, a lower degree of ionization of the hydrophobic polymer. However, both synthetic and natural fibers become increasingly static-prone as the moisture content of the fiber is reduced. The exceptional position of wool indicates that moisture is preferably

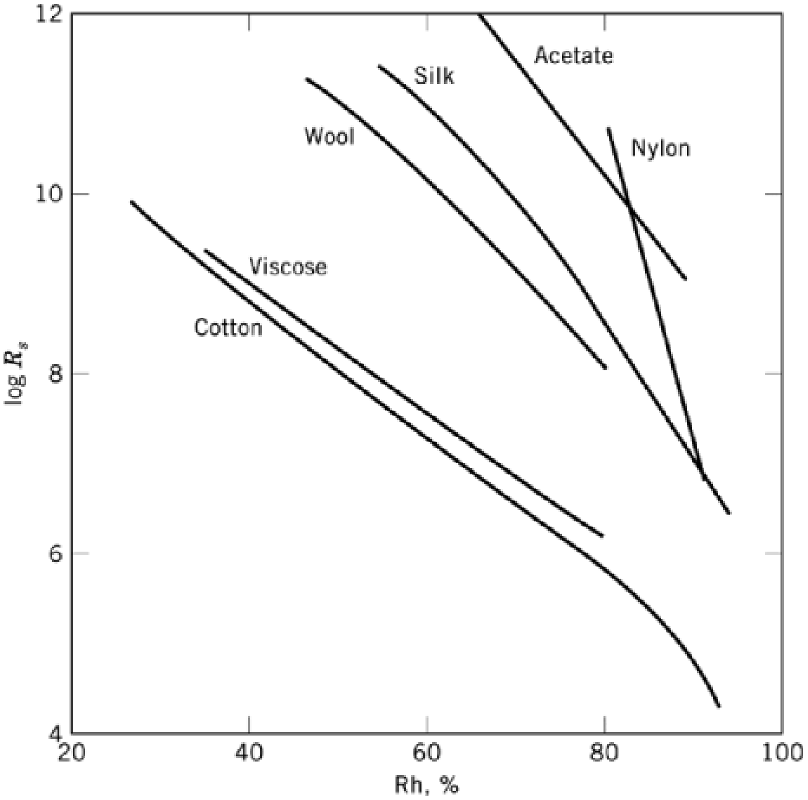

Fig. 3. Relationship of moisture content and relative humidity to specific resistance R_s of polymeric, fibrous materials. Courtesy of Butterworth Publications, Ltd.

absorbed by the interior of the wool (cortex) rather than the periphery (cuticle or epicuticle) of the fiber. Static propensity of fiber assemblies, such as of yarns and fabrics, is related to the properties of the component polymers; however, this is complicated by a form factor, mainly by the varying density of the structure (81).

Static electrification may not be a property of the basic structure, but of a new surface formed by a monomolecular layer of water (82). All textile fibers at a relative humidity, at which a continuous monomolecular layer is formed, actually do have the same charge density. This is attributed to the absence of ionic transport which cannot occur in a monomolecular layer. At higher moisture levels than required to form a monomolecular layer, ionic conductivity can occur because of excess water molecules and by hydration of the ions. At very low moisture-regain levels, all materials acquire the same charge (83).

The antistatic efficiency of absorbed water in a hydrophilic fiber is due to the submicroscopic, continuous channels it forms in the fiber. In contrast, a hydrophobic fiber that has been coated with an antistatic agent has a high surface conductivity. The increased conductivity of the treated hydrophobic fiber is due to a surface layer, even though a larger portion of the absorbed moisture may still be inside the fiber. The ratio of water to material is higher in a good antistatic layer than in a hygroscopic fiber so that the conductivity effect of moisture on an antistatic surface can be higher than in a hygroscopic fiber. An effective antistatic agent should therefore form a surface layer of aqueous solution, preferably of high ionic concentration; however, there is no clear distinction between the surface and volume conductivity of textile fibers.

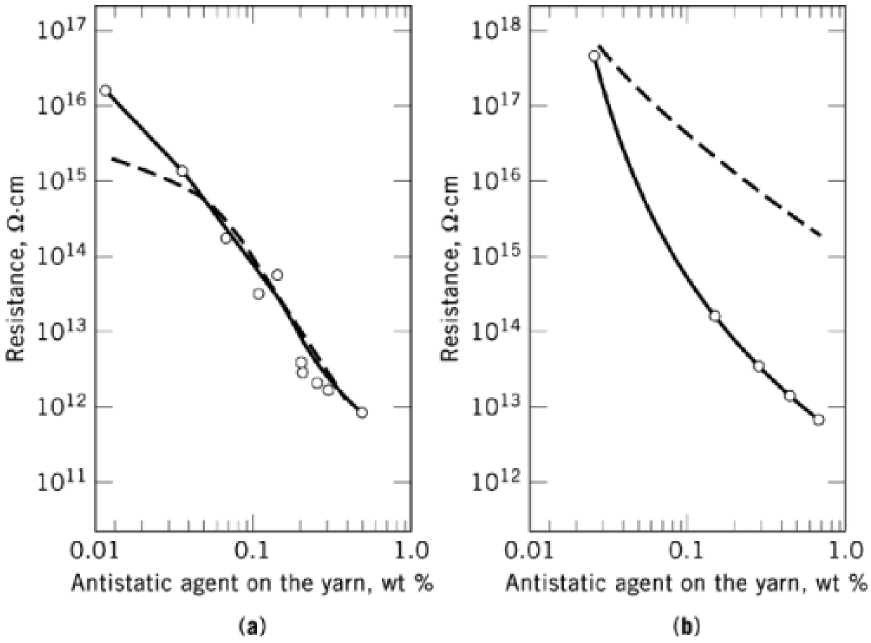

Fig. 4. (**a**) Yarn resistance in Ω·cm vs amount of antistatic agent on the yarn. The agent is the ethyl sulfate salt of an amine. (**b**) Resistance vs amount of nonionic, hygroscopic agent on the yarn. Dotted lines are calculated from the specific resistance of the dry bulk solution; solid lines are experimental yarn resistance. Courtesy of *Textile Research Journal*.

Charge decay rates of polymers have been correlated to their chemical structures (51). The presence of groups such as –Cl, –CN, and $-COOCH_3$ in a polymer contributes less to antistatic protection than hydrophilic groups such as –COONa, $-SO_3Na$, and $-OCH_2CH_2-$ contribute. However, it is difficult to explain the superiority of $-CON(CH_3)_2$ groups over $-SO_2NH_2$ groups. A study of such factors as the mode of distribution of absorbed water, mobility of ions inside the swollen polymer, dissociation of ionizable groups, skin and core effects in polymers, etc, might provide a more general correlation between chemical structure and charge decay.

5.4. Quantitative Relationship of Conductivity and Antistatic Action

Assuming that an antistatic finish forms a continuous layer, the conductance it contributes to the fiber is proportional to the volume or weight and specific conductance of the finish. As long as the assumption of continuity is fulfilled it does not matter whether the finish surrounds fine or coarse fibers. Assuming a cylindrical filament of length 1 cm and radius r, denoting the thickness of the finish layer as Δr and the specific conductance of the finish k, the conductance K of the finish layer is given by the equation (84):

$$K = k\frac{2\pi r\Delta r}{l}$$

The specific conductance of the finish on the filament k is not necessarily the specific conductance it exhibits in its bulk condition. For instance, absorption of ions from the finish by the fiber can reduce the conductivity. The specific conductance greatly depends on the amount of moisture present. Figure 4**a** shows the experimentally observed resistance of yarn as a function of the amount of antistatic agent applied in comparison to the calculated resistance. Below 0.05% of antistatic agent the experimental values show a lower conductivity than calculated; this may be due to a lack of continuity of the antistatic agent.

Unless some measures are taken to ensure uniformity, about 0.1% is needed for antistatic protection of textile fabrics. The exact amount depends on the efficiency of the agent, relative humidity, temperature, diameter of fiber, fabric structure, and degree of antistatic protection desired. Figure 4**b** shows that the observed surface conductivity of a nonionic agent is higher than the calculated value. This might be attributed to impurities or to the absorption of excess moisture. Even the experimentally observed conductivities are approximately one order of magnitude lower than the values for the nonionic antistatic agents considered in Figure 4**a** at the same concentration.

In another investigation (71), nine different antistatic agents were applied at various concentrations to a nylon fabric, and the magnitude of charges generated by rubbing against aluminum plates in a reproducible manner was compared with the fabric resistivity. A linear relation holds between the logarithms of charge and resistivity. In view of the broad confidence limit of the charge values, these results confirm the relationship between antistatic protection and resistivity.

From a quantitative study of the effect of lubricating oils in static generation by yarns, the role of dynamic coefficient of friction was compared with that of electrical conductivity (85). In order to avoid static difficulties in yarn processing, the yarns must have a low coefficient of friction and, more importantly, have the highest possible conductivity. Whatever the coefficient of friction may be, the voltage approaches zero if the conductivity becomes high enough (85).

Although it has been generally demonstrated (15, 77, 86–89) that antistatically treated fabrics exhibit increased surface conductivities, many examples have been found where static behavior is not always related to the conductivity of the fabric (90) or the material. One of the main reasons for this is the fact that static charges decay not only by conduction but also by radiation.

5.5. Durability of Finishes

The required extent of durability depends on the use of the treated article. For example, an antistatic finish that is removed after several launderings would be termed nondurable for blankets to be used in hospitals and motels where static protection through over fifty launderings is desirable. However, the same finish applied to blankets for household use which would be laundered once or twice per year could be termed durable. Antistatic finishes have been widely reviewed (73–75, 77, 86, 90–95).

5.5.1. Nondurable Antistatic Finishes

Most surface-active agents reduce static properties of materials to which they are applied and are classified as nondurable antistatic agents. They appear to work on the basis of moisture absorption, and their effectiveness decreases as the humidity (and temperature) in the atmosphere is reduced, reaching a cutoff in effectiveness when ionization is inhibited. Antistatic agents are often combined with lubricating oils to allow emulsification of the oils and to facilitate their removal during scouring and dyeing of textile materials (69). Surface-active agents of the nonionic or cationic type are commonly used as the antistat, and compatibility with lubricants becomes an added requirement.

The structures that render a substance surface-active are its hydrophobic hydrocarbon residue and a terminal hydrophilic group. Synthetic fibers treated with the separate components or a mixture fail to achieve the antistatic efficiency provided by the surface-active molecule derived from the two components. The hydrophobic portion of the surface-active agent is attached to the hydrophobic surface, and the hydrophilic groups are repelled. As a result of this orientation, the fiber surface is covered with a radiating hedgehog structure. Orientation of these molecules at the fiber surface with the formation of an electrostatic shield probably has a specific effect on the static behavior (20, 90, 96). This is difficult to prove because the mechanism of charge generation is not completely known. Regardless, surface-active agents are generally hygroscopic, nonvolatile compounds with good lubricating power that can provide useful antistatic protection to various substrates.

Table 3. Antistatic Agents for Textiles

Trade name	Manufacturer	Chemical type
	Durable antistats	
Aerotex Antistatic D	American Cyanamid Corp.	
Aston 123	Refinex Onyx	polyamine resin
Cirrasol Z	ICI Americas	
Nonax 1166	Henkel	polyamine resin
Permalose T	ICI Americas	nonionic
Stanax 1166	Standard Chemical Products	polyamine resin
	Cationic antistatic softeners	
Ampitol VAC	Dexter Chemical Co.	quaternary ammonium
Avitex DN	DuPont	cationic
Kemamine Q9702C	Humko Chemical	quaternary ammoniumcompound
	Unclassified	
Antistatin D	BASF	
Arkostat AC	Hoechst	
Aston MS	Refinex Onyx	quaternized (cationic)fatty aminecondensate
Aston AP	Refinex Onyx	amine condensate
Cassastat	Cassella	cationic
Catanac SN	American Cyanamid Corp.	cationic
Elfugin UW	Sandoz	
Igepal CO 430	GAF Corp.	nonylphenol ethyleneoxide
Neutro-stat[a]	Simco Co.	
Siligen APE[b]	BASF	quaternary ammoniumcompound
Statexan HA	Bayer	
Tinorex TC	CIBA-GEIGY	
Zelec DP	DuPont	cationic
Zero C	Lutex Chemical Corp.	nitrogeneous polymer

[a] Spray.
[b] For polyester.

Surface-active agents increase the conductivity of oils quite significantly (97), and addition of water, probably dissolved at the interface with the surfactant, further increases the conductivity. Nonionic and cationic surface-active agents are preferred to anionic surface-active agents probably because of their higher solubility in oils and higher hygroscopicity. Many anionic surfactants have adequate antistatic efficiency, but they are used less frequently.

The relationship between chemical constitution and antistatic action of an array of surface-active agents has been evaluated (92). Residual amounts of surface-active detergents in hydrophobic garments after laundering can also be effective in aiding charge dissipation. Some examples of commercial nondurable antistatic agents are given in Table 3. Nondurable antistatic agents are suitable for textile processing aids in such operations as spinning, winding, weaving, and fiber manufacture, but cannot provide the material with antistatic protection in consumer use.

5.5.2. Durable Antistatic Finishes

The difficulty with nondurable finishes, as far as the consumer is concerned, is that they are water-soluble and thus easily removed by washing. An effective antistatic finish must be durable and capable of withstanding repeated laundering and dry-cleaning cycles. Only a small number of durable antistatic agents are available for textiles. Semidurable antistatic finishes for textile materials based on compounds of limited solubility and moderate resistance to wet treatments were known in the early 1950s.

Some commercial durable antistatic finishes have been listed in Table 3 (98). Early patents suggest that amino resins (qv) can impart both antislip and antistatic properties to nylon, acrylic, and polyester fabrics. Cyclic polyurethanes, water-soluble amine salts cross-linked with styrene, and water-soluble amine salts of sulfonated polystyrene have been claimed to confer durable antistatic protection. Later patents included dihydroxyethyl sulfone [2580-77-0], hydroxyalkylated cellulose or starch, poly(vinyl alcohol) [9002-86-2] cross-linked with dimethylolethylene urea, chlorotriazine derivatives, and epoxy-based products. Other patents claim the use of various acrylic polymers and copolymers. Essentially, durable antistats are polyelectrolytes, and the majority of useful products involve variations of cross-linked polyamines containing polyethoxy segments (92, 99–101).

Polyelectrolytes (qv) carry ionizable repeating groups and combine the characteristics of polymers and electrolytes in one molecule. These polymers are linear and soluble, but upon cross-linking they form an insoluble three-dimensional network. The giant polyelectrolyte molecule is insoluble in water but still hygroscopic and capable of ionization. A three-dimensional network cannot be deposited on textiles from solution but the monomers can be deposited together with a suitable catalyst and then polymerized and insolubilized by drying and curing *in situ*. Cross-linked polyelectrolytes are also known as ion-exchange resins (qv). The resin produced must be hygroscopic but, when swollen with water, it must have sufficient mechanical strength to withstand the abrasive action of laundering and drying. In addition, the resin must display high ion-exchange capacity in the neutral pH range.

N-Alkylation of amines provides one route to polyelectrolytes (100). Alkylation of the amine with a hygroscopic polymer not only provides hygroscopicity, but also ionizable groups required for efficient antistatic performance. The ratio of hygroscopic to ionizable groups can be controlled by the proper choice of raw materials. For instance, alkylating a primary amine with poly(ethylene glycol dihalide) as the hygroscopic component produces a polyamine that contains oxyethylene interspacing groups. The polyamine contains preponderately tertiary amine groups along the polymer chain, and the end groups may be tertiary amines and/or halide groups. This polymer is capable of undergoing further reaction, resulting in cross-linking of the individual polymer chains to a giant three-dimensional thermosetting resin. Cross-linking occurs mainly at the tertiary nitrogen-forming polyquaternary groups, with some tertiary and quaternary groups at the chain ends. The resulting structures are, in effect, ion-exchange resins. Amines that have been used in this manner include diethylenetriamine [111-40-0] and hexamethylenediamine [124-09-4]. A very suitable dihalide is the diiodide of poly(ethylene glycol). Other polyfunctional alkylating agents can be used in place of halides, eg, compounds containing oxirane groups (polyepoxides) and polyfunctional compounds containing both oxirane and halide groups, eg, epichlorohydrin.

Whether a polyelectrolyte is dissolved in water or is immobilized in it by cross-linking, its conductivity is not appreciably affected. In a solution, transport of electrical charges is accomplished by migration of the ions and their compensating ions (gegenions) to the electrodes. In the cross-linked ion-exchange resin, however, the polymeric ion is fixed but its gegenions and water can move. In this case the transport of charges occurs about as fast as if the polymeric ion were dissolved. The conductivity of a water-swollen polymer is therefore determined not only by the amount of dissolved electrolytes present, but also by the amount of ionizable groups linked to the polymer by covalent bonds or van der Waals forces. Atmospheric moisture also plays an important role in the performance of a durable antistatic finish. The effectiveness of a durable antistatic treatment decreases as the temperature and humidity decrease, and cutoff occurs where the moisture content of the atmosphere is low, usually at some temperature in the range of -30 to 0°C.

Cross-linked finishes are not permanent in the true sense of the word; however, under optimum conditions the finish can last for the useful life of the material. Wet abrasion during laundering is probably the principal cause of gradual removal of the finish. In order to retain antistatic protection for extended use, an excess of finish is often applied. The extent of chemical interaction between the durable antistatic agents and the fiber substrates to which they are applied is not perfectly understood. Certain oxidizing agents such as hypochlorite bleaches tend to depolymerize and remove some durable antistatic finishes. Some of the durable finishes have also produced undesirable side effects on textile materials, ie, harsh hand, discoloration, and loss of tensile properties.

5.6. Application of Antistatic Finishes

Antistatic finishes are commonly applied to textile materials by padding (dipping and squeezing off excess finish), exhausting (absorption from solution due to affinity of the antistat for the textile material), spraying, and coating (see Textiles, finishing). For instance, exhaust application is possible with cationic finishes which have an affinity for the anionic groups in polymeric materials. After application, the textile is dried. Durable antistatic finishes require cross-linking of the resin. Cross-linking is usually achieved by subjecting the treated, dried material to heat curing. A catalyst is often incorporated to accelerate insolubilization.

5.7. Effect of Aging on Antistatic Protection

Aging is known to improve the laundering resistance of durable antistatic finishes that have been incompletely cross-linked by curing, but a gradual reduction of static protection on aging has been observed with some nondurable antistats (77). Although volatilization of the antistatic agent was thought to be the cause, migration of the antistatic agent from the surface to the interior of the polymer fiber may be responsible for this effect. Migration into the interior dilutes the antistatic agent and destroys its continuity. Migration in the opposite direction, from the interior of the polymer to its surface, is the action mechanism of durable antistats for plastics, and will be discussed later. Exposure to high temperatures can accelerate this migrating-aging effect. Extraction and reapplication with a solvent can restore the static protection. This verifies that loss of effectiveness can be due to migration rather than volatilization or decomposition (90).

5.8. Soiling of Antistatic Finishes

Soiling of fabrics having a tendency for accumulation of charges has been assumed to be an electrostatic phenomenon, and therefore it follows that if static is eliminated, soiling will be reduced. However, most antistatic agents have been developed and used for reasons other than the reduction of soiling.

The relationship between static and soiling as understood prior to 1952 has been reviewed (102). The conclusions drawn from this survey were that most soil particles are uncharged or only lightly charged; the charged particles may be attached to fabrics and held mechanically by a soft tacky layer; uncharged particles may be strongly attracted to charged fabrics. Even though two-thirds of all airborne soil particles may be negatively charged, airborne soil pickup is only slightly influenced by static (103).

The effect of nontacky antistats such as lithium chloride [7447-41-8] on the soiling of clothing has also been studied (22). No difference was noted on the cuffs and collars in soiling between treated and untreated polyester and polyacrylonitrile shirts; however, on polyester and nylon slips significant reduction of soiling was noted near the hemline of the treated garment. The effect of nonionic, anionic, and cationic antistats, including durable and nondurable antistats on the soiling and soil removal properties of textile materials, has been examined (21, 103–105). One study showed that a significant percentage of soiling of women's slips was due to static, especially at the hemline. Antistatic agents had no effect on areas where contact soiling occurred. Some antistatic agents, because of tackiness, increased soiling, and this varied from agent to agent (105). The evaluated nondurable agents helped soil removal in contrast to durable antistatic treatment where soil removal was more difficult. Several other workers have attempted to establish the relationship between static and soiling (106–108).

Various hydrophilic finishes have been used in connection with soil release and soil redeposition during laundering. These finishes can impart a degree of antistatic protection to the treated materials; however, the main functions of these finishes are to release soil and to prevent the redeposition during laundering.

5.9. Inherently Static-Free Textile Fibers and Fabrics

The antistatic agents discussed previously are applied to the surface of the material to provide a conductant surface layer, and their application increases the electrolyte (ionic) conductivity of the surface, thus reducing the propensity of the material to accumulate electrostatic charges. They are therefore called external antistatic agents, and even the so-called durable antistatic agents do not provide permanent protection. Thus there have been many efforts to develop fibers that are inherently static-free. One method involves incorporation of internal antistatic additives in the bulk of the polymer before spinning, and a second method consists of coating the fiber with conducting metals or carbon black and incorporating fine metal fibers in the textile material. Both methods increase the electrical conductivity of the whole material rather than the surface conductivity alone. However, the first method increases ionic conductivity, whereas the second increases the electronic conductivity.

5.9.1. Internal Antistatic Agents

Most of the commercially available antistatic fibers which contain internal antistatic agents are polyamides. Permanently antistatic nylon carpet yarns were introduced in the mid-1960s by the DuPont Company under the trade name of Antron. The first static-resistant nylon fibers containing internal additives and intended for apparel use became commercially available in late 1967 when the Monsanto Textiles Company introduced Ultron (109). The antistatic protection in Ultron fiber products is permanent and withstands textile processing as well as multiple launderings and dry-cleanings for the product's lifetime. Similar modifications were built into Monsanto's nylon carpet yarns (110) where the antistatic protection is also permanent to mill processing and subsequent cleaning treatments. Similar nylon fibers have been developed by other fiber producers. Examples include Antistat Celon (Courtaulds), Perlon Antistatic (Bayer), and Ecstatic (Enkalon), which are all nylon-6 type, and Counterstat (ICI), which is a nylon-6,6 (see Polyamides, fibers). Other examples of carpet antistatic fibers are Anso X (Allied Chemical), Enkalon IT and Enkastat (Akzo), and Nylon L (Toray) which are all nylon-6 types (111).

The type of internal additive and the exact composition of these inherently antistatic fibers have not been published. However, the patent literature (112, 113) suggests that these fibers contain 2–10% of a polyethoxylated compound, such as poly(ethylene glycol), mol wt 20,000. The additive is uniformly dispersed in the bulk of the polymer before spinning and may partially form chemical linkages with reactive groups in the polymer. During spinning, the additive is trapped inside the spun fiber, thus only the surface antistat is removed during subsequent processing and washings. Consequently, the fibers maintain their antistatic properties after laundering, even though the internal additives are water-soluble and can be partially extracted. These internal antistatic agents appear to work on the basis of moisture absorption from the atmosphere to increase the electrolyte conductivity of the fiber. For melt-spun fibers, the internal additive has to be thermally stable at the spinning temperature. Also, it must not adversely affect the dyeing characteristics of the fibers; obviously these requirements limit the list of potential additives.

The incorporation of metal salts of amphoteric surface active agents (Mostat Series) as internal antistatic agents in polypropylene fibers has been reported (95). Metal salts of alanine, amidoamine, and imidazoline-type amphoteric surface-active agents show excellent performance as internal antistatic agents and also improve the dyeing ability of the fibers with acid dyes.

5.9.2. Incorporation of Metals and Carbon Black

The incorporation of metals and carbon black increases the electrical conductivity of the whole material, and their effectiveness does not depend on the moisture content of the fiber. They can easily dissipate electrostatic charges. Early methods involved the blending of small percentages of metallic fibers with organic fibers. The metallic fibers dissipate electrostatic charges even when these fibers fail to provide a continuous, electrically conducting path because of low concentration in the blend. They apparently act as dipoles that interact with the electrostatic field of the static charges, thus increasing delocalization of the charges and accelerating their dissipation (56). Typically these fibers are included in amounts varying form 0.1–2.0 wt % of the fiber content, and they reduce the static propensity of carpets made from such blends by 50–75% (114). Stainless chrome–nickel steel fibers were developed in the United States in the mid-1960s; since then others have been produced in Europe and Japan. The three main commercially available types are (*1*) Staple stainless steel fibers, such as Brunsmet (Brunswick Corporation) and Bekinox (Bekaert), that can be blended with static-prone fibers prior to spinning to eliminate static problems in carpets (111, 115) and in garments used in explosive atmospheres (29, 116); (*2*) spun yarns consisting of a blend of about 87% polyamide and 13% stainless steel fibers, such as Brunslon (Brunswick Corporation) and Bekitex (Bekaert), that can be combined with continuous filament carpet yarns and tufted to produce static-resistant carpets (111, 117). Also available is Tenavelle (Teijin) a spun yarn of polyester and stainless steel fiber, which is used in industrial fabrics (118); and (*3*) monofilament yarns that have an aluminum core coated with either a plastic material (Zefstat, Dow Badische) (111, 119) or with polyamide (MFD, Allied Chemical) (112) and are primarily used in carpets. For the best results, the steel fibers should be distributed evenly in both yarn and pile, and care must be taken that mechanical or chemical damage during processing does not result in loss of conductivity.

The principle of blending a conduction fiber with a static-prone fiber has been known for years. A mixture of a substantial quantity (30–40%) of a hydrophilic fiber such as cotton or rayon with a hydrophobic static-prone fiber such as a polyester can produce a static-free blend under ordinary conditions. However, blocking the hydrophilic groups by cross-linking of the cotton with bifunctional reagents such as dimethylolethylene urea or addition of a water-repellent finish such as a silicone resin increases the static propensity of such a blend.

Durable antistatic nylon fibers consisting of a filament or a staple fiber coated with a thin layer (on the order of 1 cm) of a conductor such as silver or nickel have been developed (31), eg, Metalian (Teijin) and X-Static (Rohm & Haas) (111). Ultron advanced-generation BCF nylon carpet yarns were introduced to offer static protection and soil-hiding characteristics (119). These properties result from a combination of fiber properties and a fine carbon black-containing conductive filament. The carbon black appears as a hairline stripe on the side of the conductive filament. One conductive filament in the yarn bundle offers complete antistatic protection and is invisible in the finished carpet. Other fiber producers have developed similar nylon carpet fibers containing conductive carbon black, such as Antron III (DuPont) and F901 (The Dow Chemical Company). These fibers are primarily used in carpets by incorporating one conducting filament into a regular nylon yarn; carpets containing as little as 0.1 wt % of conductive filaments show satisfactory antistatic properties (31). Also available are polyester fibers containing conductive carbon black, such as Epitropic (ICI) and Dacron III (DuPont) (112). The principal advantages of these fibers are their high effectiveness in dry conditions and their resistance to cleaning and wear (111) (see Carbon, carbon black).

Special types of carbon black may be incorporated in latexes used for backing of carpets to enhance their conductivity. Nylon carpets backed with such conductive latex offer excellent antistatic properties even at 10% rh (110).

5.9.3. Consumption of Antistatic Agents in Textile Applications

In textile finishing of synthetic fibers and their blends, durable antistatic agents represent a potential market of a million kg/yr or more; however, volumes have not been disclosed. Many thousands of metric tons of nondurable antistatic agents are also used in textile processing, and the volume increases as use of synthetic fibers and production speeds increase. Antistatic action in textile finishing is often combined with lubrication and softening. Almost all nondurable antistatic lubricating oils are formulated with surface-active agents, usually of the cationic or nonionic types. Moreover, surface-active agents are frequently used by themselves as nondurable antistatic agents. Thus the complexity of antistatic formulations and their multipurpose uses in textile finishing agents make it difficult to determine the actual volume of this market. One estimate is

Table 4. Lubricant-Antistat Combinations in EVA Films

Film composition	Surface resistivity, Ω/sq	Triboelectric voltage
EVA 0.4% fatty amide wax	2.1×10^{13}	823
EVA 59% carbon black	3.2×10^{11}	3199[a]
EVA 59% carbon black 0.4% fatty amide wax	5.0×10^{10}	1850

[a] Detector saturated.

that approximately 250 t/yr of antistats are used in textile mill applications. This does not include antistats formulated for use on synthetic fibers during manufacturing and for home laundry application.

Antistatic compositions are being sold for application during household laundering to be added in the rinse cycle or during tumble drying. Most of these products, listed as antistatic agents for textiles, are nondurable and based on cationic and nonionic surface-active agents (see SURFACTANTS). Durable antistatic agents for textiles are few and most of them are variations of cross-linked polyamines containing polyethoxy segments.

5.9.4. Antistatic Agents for Plastics

Plastics are excellent insulators and have a great tendency to generate and retain static charges. Static charges on bottles and other packaging products charge dust particles in the air by induction. The dust particles acquire a charge of the opposite polarity than the plastic package, and so are attracted to the package. The dust attracted to the packages of consumer products makes them less attractive for selling. Dust attracted to phonograph records wears down the record and the phonograph needle when the record is played. Plastic resin powders are subject to an explosion hazard when they generate a static charge. Static charged sheets of plastic are difficult to separate. Static charged plastic products are an explosion hazard in areas where flammable gases are used. Electronic circuit chips are susceptible to damage from static charged plastic packaging.

Antistatic agents may be applied to the surface of the finished article or incorporated in the bulk of the polymer during processing (see Plastics processing). They function by decreasing the rate of charge generation, by increasing the rate of charge dissipation, or by both mechanisms (73, 76).

The way in which the rate of charge generation is reduced is not entirely understood, but it was found (95) that metal salts of amphoteric surface-active agents (Mostat Series) form a molecular layer at the interface, and the presence of this layer reduces the intimacy of contact and therefore the net charge transfer. There is also an indication that mold lubricants can function in this manner (45), and poly(ethylene glycol) oleates were found to be more effective than poly(ethylene glycol) laurates in reducing the rate of charge generation on poly(vinyl chloride) surfaces (120). Fatty amides reportedly reduce charge buildup on plastics. Fatty amides are lubricants and are thought to reduce tribocharging (see Amides, fatty acid). They are often used in conjunction with a static dissipative-type antistatic agent to both reduce the tribocharging and dissipate any charge that might form (121). Combining the lubricant and the static dissipative additive are necessary because propensity to tribocharge and surface resistivity do not correlate. Studies show that ethylene vinyl acetate (EVA) film with an amide lubricant has a very low propensity to tribocharge, but has a surface resistivity higher than the accepted static dissipative range. EVA film containing a static dissipating amount of carbon black exhibits large triboelectric voltages. By combining an amide lubricant and the carbon black, the EVA film becomes both static dissipating and produces smaller triboelectric charges (Table 4) (122).

5.10. Types of Antistats

Plastics are rendered static dissipative by either adding a conductive material to the plastic in sufficient quantity that there is a three-dimensional conductive pathway through the plastics, or by adding to the plastic a surfactant-type chemical that will attract moisture to the surface of the plastic. Since water is a conductor, the surface layer of moisture then dissipates a static charge. The source of conductive material can be either an inherently conductive polymer, a metal or metal-containing material, or carbon black. The conductive additive can, if desired, be added to the plastic at a concentration sufficient to make it static dissipative, but not completely conductive. Surfactant-type additives are of several different chemical types. They can be applied to the surface of the finished plastic article or incorporated in the bulk of the polymer during processing (see Plastics processing).

5.10.1. Inherently Conducting Polymers

Conducting polymers are polymers with a pi-electron backbone capable of passing an electrical current. These polymers generally are not sufficiently conductive as neat polymers but require the inclusion of an oxidizing or reducing agent (dopant) to render them conductive.

Common conductive polymers are polyacetylene, polyphenylene, poly-(phenylene sulfide), polypyrrole, and polyvinylcarbazole (123) (see Electrically conductive polymers). A static-dissipative polymer based on a polyether copolymer has been announced (124). In general, electroconductive polymers have proven to be expensive and difficult to process. In most cases they are blended with another polymer to improve the processibility. Conductive polymers have met with limited commercial success.

5.10.2. Metal-Containing Polymers

Metal-containing polymers function simply by adding sufficient quantities of a metal to form a three-dimensional conduction pathway through the plastic. The metal is in the form of a powder, micrometer-sized needles, or as a thin coating on glass spheres, carbon fibers, or mica. The metals normally employed are nickel, zinc, stainless steel, copper, and aluminum. At higher levels these materials make the polymer capable of shielding electromagnetic impulses (EMI) (125).

The metal fillers act as a reinforcing material that results in added strength and stiffness (126). They color the plastic gray for nickel, zinc, stainless steel, and aluminum, and brown for copper. Metal additives are more expensive than carbon black or surface-active agents, but they get extensive use in EMI shielding applications.

5.10.3. Carbon Blacks

The high electrical conductivity of carbon black is utilized where its color is not objectionable and its reinforcing action is used (see Fillers; Composites). Carbon black increases the electrical conductance of the polymer to which it is added, and therefore its effectiveness does not depend on moisture absorption (see Carbon, carbon black).

Vulcanized rubber is an insulator (volume resistivity is 10^{15} Ω-cm), and the static generated by rubber tires created serious problems in vehicles until the introduction of electrically conductive carbon black as a reinforcing pigment. An excellent correlation was found between the potential generated and the resistivity of the tires (127, 128) (see Rubber natural).

Airplanes in flight acquire the same potential as the surrounding atmosphere, and, upon landing, the plane might be at high potential with respect to the ground. To bring the airplane to ground potential before the passengers step out, highly conductive tail-wheel tires have been developed. Some of these have rim-to-tread resistivities of only $2 \times 10^3\ \Omega$ as compared to about 10^{10} Ω for ordinary tires.

A minimum of 10 to 35 parts carbon black to 100 parts of rubber is required to obtain a resistivity in the order of 10^4 Ω-cm. At that loading the carbon black particles, which have an average radius of 10 nm, form grapelike aggregates that provide continuous paths for the electrical current. Special purpose rubbers containing even more carbon black have resistances as low as 1 Ω-cm (129). The electrical resistivity of rubber with carbon black is sensitive to strain history, probably because of temporary disruptions of the continuity of the carbon black aggregates.

Other rubber products that require high conductivity are belts, hoses, footwear, and rubber products used in hospital operating rooms. Fabrics have been woven with viscose yarns containing carbon black for operating room use (130). Conductive linoleum or asphalt tiles are also based on high loads of carbon black. Too high a conductivity of flooring, however, increases the danger of electrical shock and fire hazards caused by circuit insulation defects (131).

The carbon blacks used in plastics are usually different from the carbon blacks used in rubber. The effect of carbon black is detrimental to the physical properties of plastics such as impact strength and melt flow. Electroconductive grades of carbon black have much higher surface areas than conventional carbon blacks. The higher surface areas result in a three-dimensional conductive pathway through the polymer at much lower additive levels of the carbon black. The additive concentrations of electroconductive carbon blacks is usually $\frac{1}{4}$ to $\frac{1}{3}$ that of a regular carbon black (132).

Carbon black finds use in lower cost products. Vinyl audio records are a commonly recognized use of carbon black, but it is also useful in vinyl video albums (133).

5.10.4. Surfactant-Type Antistats

Inherently conductive antistats have the advantage of not being dependent on atmospheric moisture to function. Their drawbacks include expense, coloration of the plastic, and alteration of the mechanical properties of the plastic. The added stiffness caused by conductive fillers may not be a problem with a rigid container, but it can be a problem for a flexible bag.

Surfactant-type antistats find the widest use because of their low cost and minimal effect on the mechanical properties of the plastic. Ease of use is another favorable aspect to surfactants. They can be mixed with the bulk of the plastic prior to processing or can be applied to the surface of the finished plastic article as the need dictates.

Internal surfactant antistats are physically mixed with the plastic resin prior to processing. When the resin is melted, the antistat distributes evenly in the polymer matrix. The antistat usually has some degree of solubility in the molten polymer. However, when the polymer is processed (extruded, molded, etc) into its final form and allowed to cool, the antistat migrates to the surface of the finished article due to its limited solubility in the solidified resin. The molecule of a surface-active agent is composed of a polar hydrophilic portion and a nonpolar hydrophobic portion. The hydrophilic portion of the surfactant at the surface attracts moisture from the atmosphere; it is the moisture that has the static dissipative effect.

Because the antistatic effect only occurs after the surfactant has migrated to the surface, the solubility of the surfactant in the polymer is an important consideration. Surfactants can generally be classified as one of four chemical types: cationic, where the hydrophilic portion has a positive charge; anionic, where the hydrophilic portion has a negative charge; nonionic, where the hydrophile does not have a charge; and amphoteric, where the molecule contains both positive and negative charges. Figure 5 shows the effect of changing surfactant type on the surface resistivity of two different polymers (134).

Cationic, anionic, and amphoteric surfactants derive their water solubility from their ionic charge, whereas the nonionic hydrophile derives its water solubility from highly polar terminal hydroxyl groups. Cationic surfactants perform well in polar substrates like styrenics and polyurethane. Examples of cationic surfactants are quaternary ammonium chlorides, quaternary ammonium methosulfates, and quaternary ammonium nitrates (see Quarternary ammonium compounds). Anionic surfactants work well in PVC and styrenics. Examples of anionic surfactants are fatty phosphate esters and alkyl sulfonates.

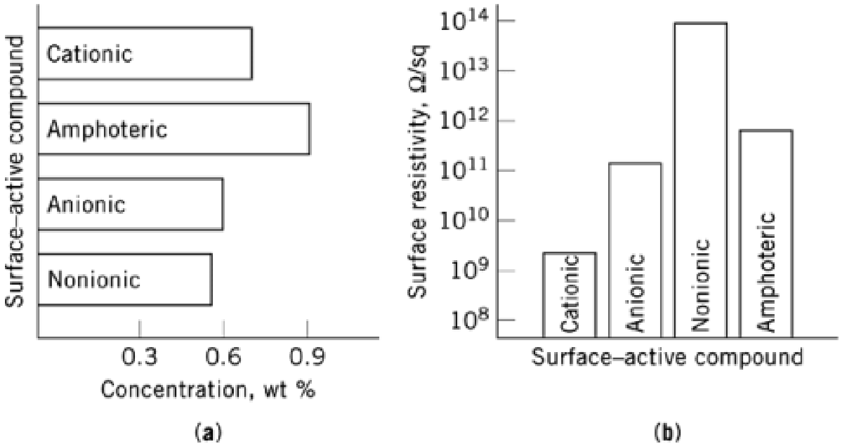

Fig. 5. Effect of surfactant type on surface resistivity. (**a**) Concentration of surface-active compound in low density polyethylene (LDPE) required to achieve 10^{10} Ω/sq surface resistivity; and (**b**) effect on surface resistivity of an acrylic polymer. Concentration of surface-active compound is 0.3%.

Table 5. Static Decay Times of Ethoxylated FattyAmines in High Density Polyethylene

Ethoxylatedamine[a]	Time, s
coconut	0.93
tallow	2.01
oleyl	1.26
stearyl	>100

[a] At 1500 ppm.

Table 6. Effect of Ethoxylated Oleyl Amines on Static Decay in Polyolefins

	Static decay time, s			
Antistat, ppm	LDPE	LLDPE	HDPE	PP
1000	0.37	1.07		>100
1500			1.26	
3000	0.23		1.01	7.93
4000				0.65

Nonionic surfactants perform well in nonpolar polymers such as polyethylene and polypropylene. Examples of nonionic surfactants are ethoxylated fatty amines, fatty diethanolamides, and mono- and diglycerides (see Amines, fatty amines; Alkanolamines). Amphoteric surfactants find little use in plastics (134).

Varying the fatty acid portion of the surfactant can have an effect on antistatic performance. In the example given in Table 5, ethoxylated coconut amine results in the shortest static decay time, whereas ethoxylated stearyl amine results in the longest static decay time (135).

In the same class of polymers, an antistat can exhibit different degrees of effectiveness. As seen in Table 6 the performance of ethoxylated oleyl amine varies among polyolefins. The data for polypropylene (PP) also shows the concentration dependence of antistats.

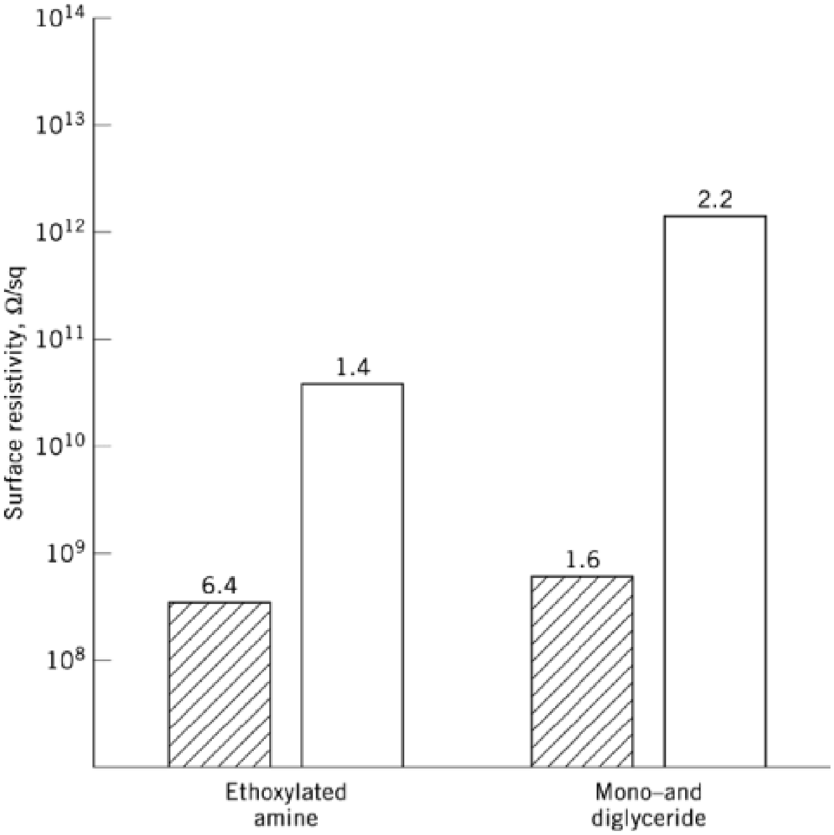

Fig. 6. Effect of humidity on antistat performance. ▨, 50% rh; □, 15% rh.

Table 7. Effect of Relative Humidity on Charge Generation

	Electrostatic voltage at	
Charge generation source	10–20% rh	65–90% rh
walking across carpet	35,000	1,500
walking over vinyl floor	12,000	250
working at bench	6,000	100
pick up polymeric bag	20,000	1,200
chair padded with polyurethane foam	18,000	1,500

Since surfactant-type antistats function by attracting atmospheric moisture to the plastic, the relative humidity (rh) has a significant effect on antistat performance (Fig. 6). Relative humidity also has an effect on charge generation (Table 7).

There are many commercial surface and internal antistatic additives (136). Table 8 lists several of the internal antistats along with the polymers for which they are recommended. Surface-applied antistats are not included because they function independent of polymer type.

Internal antistats are considered permanent antistats. This permanence is based on the concept that most plastic products are disposable, so that the antistat is not required to last long. The antistatic effectiveness of an internal antistat can decrease over time. One study showed large increases in surface resistivity on antistatic

Table 8. Commercially Available Internal Antistatic Agents and the Polymers for Which They Are Recommended[a]

Trade name[b]	Manufacturer	ABS	LDPE	HDPE	PP	PS	Concentration, %
		Amines					
Armostat 310	Akzo (Noury) USA		x	x	x		0.05–0.5
Armostat 410	Akzo (Noury) USA	x	x	x	x	x	0.05–2.0
Atmer 163	ICI Americas	x	x	x	x	x	0.5–5.0
Hexcel 273C	Hexcel		x	x	x		0.05–0.2
Hexcel 273E	Hexcel		x	x	x		0.05–0.3
Hostastat FA14	Hoechst Celanese		x	x	x		0.1–0.5
Hosastat FA18	Hoechst Celanese		x	x	x		0.1–0.5
Kemamine AS-650	Humko Chemical	x	x	x	x	x	0.05–2.0
Kemamine AS-975	Humko Chemical		x	x	x		0.05–0.5
Kemamine AS-989	Humko Chemical		x	x			0.1–0.3
Kemamine AS-990	Humko Chemical		x				0.1–0.5
Varstat T22[c]	Sherex		x	x	x	x	0.05–0.5
		ABS	Acrylic	PS	RPVC	PU	
		Quartery ammonium compounds[d]					
Cyastat 609[c]	American Cyanamid	x	x		x		0.5–2.0
Cyastat LS[c]	American Cyanamid	x		x	x		0.5–2.0
Cyastat SN	American Cyanamid	x	x		x		1.0–2.0
Cyastat SP	American Cyanamid				x		1.0–2.0
Larostat 377 DPG	Lonza Chemical					x	1.0–2.0
Larostat SC	Lonza Chemical	x	x		x		
Markastat AI-12[e]	Argus					x	3.0–5.0
Markastat AL-33	Argus	x	x			x	0.5–1.5
		LDPE	HDPE	PP	PS	FPVC	
		Esters					
Atmos 150	Humko Chemical	x	x	x			0.2–1.5
Dimul SK	Humko Chemical	x	x	x	x		0.2–2.0
Glycostat	Lonza Chemical	x	x	x	x	x	0.5–2.0
Hostastat FE-20[f]	Hoechst Celanese	x	x	x	x	x	0.5–2.0
Hostastat HS1[f],[g]	Hoechst Celanese				x	x	0.1–3.0
Markastat AL-14	Argus					x	3.0–7.0
Myrj 45[d]	ICI Americas	x	x				0.5–2.0

[a] Ref. 136. LDPE = low density polyethylene; HDPE = high density polyethylene; PP = polypropylene; PS = polystyrene; FPVC = flexible PVC; RPVC = rigid PVC; and PU = polyurethane.

[b] Has some FDA approvals unless otherwise noted.

[c] Also useful for FPVC.

[d] Not approved by FDA.

[e] Also useful for polyacetate.

[f] Also useful for ABS and RPVC.

[g] FDA approved for PVC.

bags stored at 71°C for six months. Antistatic bags stored at room temperature showed only a small increase in surface resistivity (137). Loss of antistatic effectiveness is attributed to the volatility of the antistatic agent. The antistat does not easily wear off the plastic, but it can be removed with solvents and/or repeated wear.

5.10.5. Surface Applied Surfactants

Antistat agents can be applied directly to the surface of a plastic part. Usually the antistat is diluted in water or in a solvent. The antistat solution is applied by spraying, dipping, or wiping on the surface. The water or solvent dries leaving a thin film that attracts moisture. Since it is applied to the surface, migration through

Table 9. Estimated USA Volume of AntistaticAgents Used in Plastics[a]

Year	t
1960	182
1963	318
1966	681
1969	1135
1972	1300
1973	1790
1974	1830
1975	1600
1976	1800
1983	3300

[a] See refs. 129, 145, and 146.

the resin is not a factor. In practice, the quaternary ammonium compounds find the most use. They are soluble in water and effective at low concentrations.

The antistatic protection provided by surface treatment is excellent while it lasts. However, surface treatments provide only temporary protection. The antistat layer is extremely vulnerable to rubbing and wiping, especially when wet (45). Loss of antistatic agent can also occur by diffusion from the surface into the bulk of the material on storage (77, 78). Several attempts have been made to obtain more durable antistatic coatings with varying degrees of success using reactive resins and surface grafting (122, 138–144).

5.11. Consumption of Antistatic Agents for Use in Plastics Applications

Antistatic agents are widely used in the plastic industry, and their economic significance is greater than in the textile industry. Food and drug packaging accounts for well over half the market, and FDA acceptable products such as polyethylene, poly(vinyl chloride), and polypropylene film and bottles are predominant. The use of antistatic agents in medical and surgical applications of flexible poly(vinyl chloride) and polyethylene film and sheet has increased, providing higher safety in places where a buildup of static charges can trigger explosions (145). The use of antistatic agents in plastics used for the electronics industry has grown to the point that virtually all of these plastic products contain some type of antistatic agent (see Electronic materials).

Determining the exact consumption of antistatic products is difficult due to commercial secrecy. The world consumption for hydrophilic-type antistatic agents has been estimated for 1983 at 11,400 t, with an average growth rate of about 6.0% per y (146). The estimated average consumption of hydrophilic-type antistatic agents in the United States over time is given in Table 9.

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