

Measurement of Triboelectric Position

VINCENT J. WEBERS, *E. I. du Pont de Nemours & Co., Inc.,
Photo Products Department, Research Division, Parlin, New Jersey*

INTRODUCTION

Quantitative techniques are available for determining the relative ability of surfaces to dissipate electrostatic charges,¹ but little has been done to develop convenient techniques for measuring the tendency of a surface to acquire charges from other surfaces. In practical situations, particularly at low relative humidity where resistivities are very high, avoidance of charge generation may be more important than charge dissipation as a means of preventing undesirable effects of static charges.

A group of surfaces of interest may be arranged in a *triboelectric* series such that any member of the series will become negatively charged if rubbed or otherwise contacted by any member above it, and positively charged by a member below it. A number of such series have been published.²⁻⁴ Their orders have not always been found to be reproducible, and such factors as relative humidity, temperature, cleanliness of the samples, pressure of contact, geometric factors, renewal of surface by rubbing, or transfer of material during contact,⁵ have been indicated as possibly responsible for these variations. Study of the relative effect of each of these variables has been hampered by lack of a simple convenient method for assessing triboelectric position.

We have developed a simple technique for the electrical characterization of a surface by determining the signs and relative magnitudes of the induced electrical charges developed when the sample is pressed in contact with a number of reference materials. After a few determinations have been made, the reference set can be arranged in the order of the triboelectric series and thus provides a simple scale to which the triboelectric position of other substances can be related. The technique is similar to the "sandwich" procedure used by Henry,⁴ but it allows a more rapid determination of charges developed on contact with a larger number of reference surfaces.

EXPERIMENTAL

As shown in Figure 1, a 1 cm.² film (b) of each reference substance was affixed with Permacel P-50 double-faced pressure-sensitive tape (c) to the jaws of spring-loaded clamps (ordinary spring-loaded clothespins, which exert a force of about 1.0 kg., were quite satisfactory). During the assem-

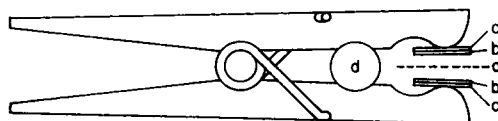


Fig. 1. Reference sample clamp: (a) sample to be measured; (b) reference surface; (c) 14 mil. double-faced adhesive tape; (d) spacer rod.

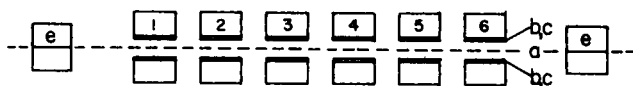


Fig. 2. Open assembly of clamps: (a) sample to be measured; (b, c) reference surface and mounting tape; (e) mounting clamps; (1-6) reference sample clamps.

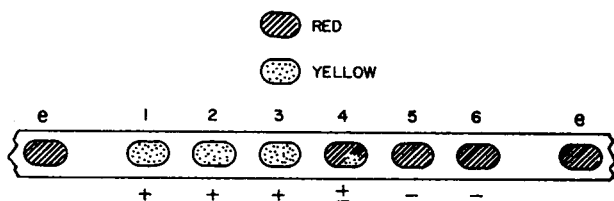


Fig. 3. A typical "triboelectrogram"; red (crosshatched) indicates negative charge; yellow (dotted) indicates positive charge.

bly, the tape and samples were exposed to α -radiation from a polonium source (Nuclear Products Co., El Monte, Calif.), to dissipate any previously induced charges. A set of six to nine such clamps were mounted in parallel and simultaneously held open by means of a rod (d).

The film sample (a) to be tested was in the form of a strip $\frac{1}{2}$ to 1 in. wide. Both the reference substances and the film strip were conditioned for several hours at constant temperature and humidity and were then exposed to radiation from the polonium source. The film strip was supported by clamps (e) (Fig. 2). about $\frac{1}{2}$ in. above a flat surface, the rod (d) was removed, and the assembly of clamps was allowed to close and touch the sample.

After 5 min. the clamp assembly was removed from the sample by reversal of the clamping procedure, and the film sample was removed from its mounting clips and sprayed with a mixture of charged fluorescent powders from a polyethylene wash bottle⁶ (Neon Red D-12 and Saturn Yellow D-17, Switzer Brothers, Cleveland, Ohio). By mixing the powders for 16 hrs. in a roller mill the red pigment became positively charged and the yellow pigment negatively charged.

About 10 ml. of the mixed powder was placed in a 250 ml. polyethylene wash bottle, and expressed in a series of short puffs. After spraying, the film sample showed a series of colored spots at the positions where the reference surfaces had made contact. A typical "triboelectrogram" is illus-

TABLE I
Reference Substances in Triboelectric Order

Order no.	Substance
6	Polycation coating ⁷ on polyethylene terephthalate support
5	Gelatin coating on polyethylene terephthalate support
4	Cellulose triacetate film
3	Photographic emulsion on cellulose triacetate support
2	Aluminum foil
1	Polyethylene terephthalate film

trated by Figure 3. These spots were red where the film was negatively charged and yellow where the film was positively charged. The use of fluorescent powders of the same or similar names from other sources gave poorer color contrast and led to some difficulty in discriminating positive from negative charges. The amount of powder deposited on a spot gave a rough measure of the magnitude of the charge at that spot.

When the charges developed were of low intensity, resulting in a very faint spot, or when the sample itself was colored, the spots were easily distinguished under ultraviolet radiation. The spots were sharply defined when the sample had low conductivity at the relative humidity used for measurement, but were enlarged and somewhat diffuse if the sample possessed a moderate conductivity. If too much time elapsed between the removal of the clamps and the spraying with powder, or if the conductivity was appreciable, the spots would be lost.

To illustrate the technique, a number of samples were tested at about 18% R.H., the reference substances being those listed in triboelectric order in Table I. These reference substances were commercial materials, not cleaned or etched, except for the aluminum foil, which was washed with hexane to remove an oil film. In the table, a substance with a higher order number indicates that the reference substance acquires a positive charge from a greater number of test samples than does one with a lower number.

Samples to be tested were obtained in the form of self-supporting films, or were coated on both sides of polyethylene terephthalate film base by dipping the film base in a suitable solution and drying. The results of testing of various samples are shown in Table II. Each substance tested is given a rating indicating its triboelectric position relative to the standard samples in Table I.

It will be noted in Table II that there was a certain lack of reproducibility. However, replicate determinations usually gave an unequivocal result (see polymethyl methacrylate in Table II). When a sample was slightly conductive, the area in contact was not sharply defined and a "halo" of the opposite charge was often observed around the spot. This halo was due to charging by induction of the area around the spot, and it

TABLE II
Trielectrical Measurements of Various Samples

Material tested	Order no.						Relative triboelectric position
	1	2	3	4	5	6	
Polyethylene film	-	-	-	-	-	-	0
Polyvinyl butyral ^a	-	-	-	-	-	-	0
Polyethylene terephthalate sample 1	-	-	-	-	-	-	0
Polyethylene terephthalate sample 2	+	-	-	-	-	-	1
Polyacid ^b	+	-	-	-	-	-	1
Polyacrylic acid ^c	+	-	-	-	-	-	1
Cellulose acetate/butyrate ^d	+	-	-	-	-	-	1
Polyacrylamide ^e	+	+	+	-	-	-	3
Polycation ^f	+	+	+	±	-	-	4-5
Polymethyl methacrylate ^g sample 1	+	+	+	±	+	-	5
Polymethyl methacrylate sample 2	+	±	±	+	+	-	5
Polyethyl methacrylate ^b	+	+	+	+	+	-	5
Polybutyl methacrylate ⁱ	±	+	+	±	±	-	5
Polyvinyl acetate ^j	+	+	±	+	±	±	4-6
Gelatin sample 1	+	+	+	+	+	-	5
Gelatin sample 2	+	+	±	+	+	+	6
Polyethylene imine ^k	+	+	+	+	+	+	6
Polyethylene oxide ^l	0	0	0	0	0	0	Indeterminate

^a Butacite polyvinyl butyral, Polychemicals Dept., Du Pont.

^b Carbolon 934, B. F. Goodrich.

^c Acrysol A-1, Rohm & Haas.

^d "1/2 second" EAB cellulose acetate/butyrate, Eastman Chemical Products.

^e Polyacrylamide-100, American Cyanamid.

^f Zelec DX, Organic Chemicals Dept., Du Pont.

^g Acryloid A-101, Rohm & Haas.

^h Lucite 42, Polychemicals Dept., Du Pont.

ⁱ Lucite 44, Polychemicals Dept., Du Pont.

^j Vinac beads, grade B-100, Colton Chemical.

^k PEI polyethylene imine, Chemirad.

^l Polyox polyethylene oxide WSR-35, Union Carbide Chemicals.

was disregarded in assessing triboelectric position. When conductivity was too high, no determination could be made (see polyethylene oxide in Table II).

It might be expected that making contact between a test sample and a reference substance of the same material would result in zero charge, but minor shifts in triboelectric position was usually observed, probably because of physical differences in the samples (see Table II, gelatin against gelatin, polyethylene terephthalate against polyethylene terephthalate). It is of interest that Henry⁴ noted similar effects.

DISCUSSION

From the experimental data above it may be seen that the technique presented will allow assignment of triboelectric position in a series relative

to a particular group of reference materials of interest. We have routinely used a set of thirty-six reference surfaces (four assemblies of nine clamps each), chiefly of reference materials used in the photographic industry. The average time required was about 15 min. per film sample tested. It appeared that this group of thirty-six surfaces contained a great proportion of materials which would be regarded, on an absolute basis, as having triboelectric positions quite close to each other. This is probably because the photographic emulsions, film bases, x-ray intensifying screens, and the like were originally selected for use because, among other things, they did not lead to static discharges upon touching each other. It is hoped that standard reference materials will be devised so that absolute assignments might be made and results in one laboratory compared with those in another.

Although insufficient work has been done to warrant firm conclusions, some of the measurements we have obtained indicate that triboelectric properties of a surface may be correlated with the nature or orientation of groups in a polymer surface, or may give some clue to the nature or orientation of adsorbed substances or surface contaminants. For example, poly-anionic materials such as polyacrylic acid were shown to be at the negative end of the triboelectric series, while the polycationic materials of Tables I and II were found at the positive end. These results would lend some support to the hypothesis that static charges arise in the case of these substances through transport of mobile counterions across the interface.

These measurements of triboelectric position differ from the "charge selective power" parameter σ used by Shashoua,⁸ which was found to be positive for acrylic acid and negative for various polycations. The triboelectric position measured here is concerned with charge generation and measures the net effect of spontaneous charge migration across an interface, while the static propensity tester of Shashoua^{1,8} is concerned with charge dissipation, and measures rates of disappearance of positive and negative charges under a potential gradient.

The polymeric methacrylates and polyvinyl acetate are found grouped together in Table II at about the same relative position near the positive end of the scale. This suggests that these polymeric films have common groupings in the surface. These are more likely to be ester groupings, —COOR, than alkyl groups, since hydrocarbon surfaces such as polyethylene (Table II), and others examined in this laboratory were found at the negative end of the scale. On the other hand, the highly crystalline, biaxially oriented, aromatic polyester polyethylene terephthalate was found at the negative end of the triboelectric scale. This suggests that the nature and/or orientation of groups in the surface is quite different in the latter from that of the aliphatic polyesters. Biaxially oriented polyethylene terephthalate is known to have the —COOR group approximately coplanar with the benzene ring, this plane lying parallel with the film surface.⁹⁻¹¹

In the expanded series of thirty-six reference films, reference substances

4, 5, and 6 of Table I were found to be quite close to the positive end of the series, and re-examination of polyacrylamide showed that it was somewhat closer to the positive end of the scale than to the middle. At about the same level was a urea-formaldehyde resin; both are slightly below gelatin film. These similar electrical properties may arise from the presence of amide groupings in the surface, which are common to all three substances.

It is suggested that reproducible surfaces suitable for absolute reference standards might be obtained by adsorption to a suitable substrate of molecules carrying specific functional groups, so that a high population of these groups would appear in the surface of the film.

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Synopsis

A convenient technique is presented for determination of triboelectric characteristics of a film sample relative to a group of reference surfaces and to other film samples, with the use of inexpensive, easily assembled equipment. It consists of pressing a number of reference surfaces into contact with a test film, determination of the sign and intensities of the charges generated, by spraying with an indicating powder, and estimation of triboelectric position of the test sample by the distribution of positive and negative charges generated. With this technique, relative triboelectric characteristics were determined for films of various polymers. The measurements give some insight into the relation between polymer structure and triboelectric characteristics.

Résumé

On présente une technique facile en vue de la détermination des caractéristiques triboélectriques d'un échantillon de film comparé à un groupe de surfaces de référence et à d'autres échantillons de films, et ne demandant qu'un équipement peu coûteux facilement assemblable. Cette technique consiste à presser une nombre de surfaces de référence en contact avec un tillon du échanfilm; elle nécessite la détermination du signe et des intensités des charges provoquées par vaporisation d'une poudre indicatrice et une estimation de position triboélectrique de l'échantillon test par la distribution des charges positives et négatives produites. En employant cette technique, les caractéristiques triboélectriques relatives pour des films de divers polymères ont été déterminées. Ces mesures ont été employées pour obtenir quelques aperçus sur la relation existante entre la structure polymérique et les caractéristiques triboélectriques.

Zusammenfassung

Ein bequemes Verfahren zur Bestimmung der triboelektrischen Eigenschaften einer Folienprobe im Vergleich zu einer Gruppe von Bezugsoberflächen und zu anderen Folienproben unter Benützung einer wohlfeilen und einfach aufzubauenden Messeinrichtung wird angegeben. Das Verfahren besteht darin, eine Reihe von Bezugsoberflächen gegen eine Testfolie zu pressen, das Vorzeichen und die Stärke der erzeugten Aufladung durch Besprühung mit einem Indikatorpulver zu bestimmen und die triboelektrische Lage der Testprobe durch die Verteilung der erzeugten positiven und negativen Ladungen zu ermitteln. Mit diesem Verfahren wurden die relative triboelektrische Charakteristik von Folien aus verschiedenen Polymeren bestimmt. Diese Messungen wurden zur Gewinnung einer gewissen Einsicht in die Beziehung zwischen Polymerstruktur und triboelektrischer Charakteristik benützt.

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