

## Antistatic Polystyrene

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### Synopsis

Mechanical blends of polystyrene with small amounts of poly(2-methyl-5-vinylpyridine) furnish molded objects which acquire by means of a surface treatment with chemical agents (which react with the pyridic nitrogen) satisfactory antistatic protection. Methods of measure of the static charge are discussed along with the conditions of applications of the quaternizing agents.

Plastics show a general tendency toward facile charging of static electricity, especially under friction. Many theories have been developed to explain this behavior.<sup>1-5</sup> Methods have been suggested which practically eliminate this phenomenon. Some of these methods facilitate the removal of the electrical charge from the plastic surface. Upon increasing the relative humidity, the plastic shows a tendency to attract less dust from the atmosphere. This is probably not due to an increase in the surface conductivity but to the greater humidity of the atmospheric dust.<sup>6</sup> Similarly, increase of air conductivity by ionization produces antistatic effects.<sup>6,7</sup>

Generally it is preferable to increase the conductivity of the polymer surface. This is usually accomplished by covering the surface with destaticizing materials. A number of materials are used for this purpose.<sup>8</sup> In general, these are nitrogen compounds, sulfonic acids, polyglycols, etc., i.e., materials which are strongly hygroscopic and which protect the plastic. They increase the surface moisture content, thereby creating a thin conductive layer on the surface.<sup>5</sup>

These substances, which have normally a temporary effect, may be applied from solutions, by spraying the surface of the molded objects, etc. Due to the hydrophobic character of the majority of plastics<sup>4</sup> this humidity remains localized on the surface. On aging, washing, etc. the destaticizer agent which is weakly linked to the plastic is removed from the surface. Therefore, it is easy to see that it is difficult to get permanent antistatic protection with such a treatment. The problem is to obtain good surface conductivity on the polymer by linking this layer strongly to the surface.

In the present work we attempted to prepare a permanent antistatic protection for polystyrene by making use of the fact that a mixture of polystyrene with small amounts of polyvinylpyridine has physical properties which are substantially similar to those of the polystyrene alone. We in-

tended to render such a mixture antistatic by treating its surface with a substance which would quaternize the pyridine nitrogen, thereby creating a polar and conductive surface. As a matter of fact, it is well known that the quaternary salts of vinylpyridines are strongly hydrophilic and form solutions of high conductivity.<sup>9</sup>

## RESULTS AND DISCUSSION

Commercial injection-molding polystyrene was used, both transparent and white (containing  $\text{TiO}_2$ ) types. The molecular weight was 90,000–100,000. Poly-2-methyl-5-vinylpyridine (PVP) of varying molecular weights was prepared from commercial monomer via suspension polymerization. The physical properties of this homopolymer have been previously described.<sup>10</sup> Polystyrene–polymethylvinylpyridine blends (95/5 and 97.5/2.5 PS/PVP) were obtained by mixing the homopolymers in a rotating bottle for 15 min. at room temperature. The mixture was then extruded twice and then granulated and injection-molded.

The working temperatures were usually equal to or somewhat higher than that used for polystyrene, and depended on the molecular weight of PVP. The physical properties (tensile, impact, hardness, etc.) of these blends are essentially similar to those of PS alone and depend on the molecular weight of PVP. As far as the color is concerned, some discoloration was noted in blends with the transparent (crystal type) polystyrene. This discoloration is not very noticeable in colored blends.

### Measurement of the Static Charge

Of the various methods suggested for the determination of the static charge<sup>2,6,7,11–13</sup> we have adopted the so-called dust-spraying method, in conjunction with a measure of the electric potential present on the surface (statometer).

The dust-spray method is based on the fact that when dust is sprayed on the surface of a plastic, its orientation indicates the intensity of the charge existing there.

The measurements were performed as follows. Injection-molding samples of disk form with a diameter of 105 mm., 2 mm. thick, were used. The specimens (both as such or treated with quaternizing agents) were dried at 40°C. under vacuum over phosphorus pentoxide to constant weight. They were then transferred to a thermostatic room at 25°C., 50% R.H. and conditioned up to constant weight, i.e., until they reached equilibrium with the relative humidity (few weeks).

The measurements were carried out by spraying the specimen with dust formed by zinc stearate and carbon black and observing the way in which the dust deposited.

The tests were performed by using dust which had been previously dried over phosphoric anhydride at 50% R.H. It is known<sup>5,14</sup> that the formation of designs of crows' feet type indicates high charge, whereas spots indicate



Fig. 1. Very high charge (unrubbed white polystyrene).

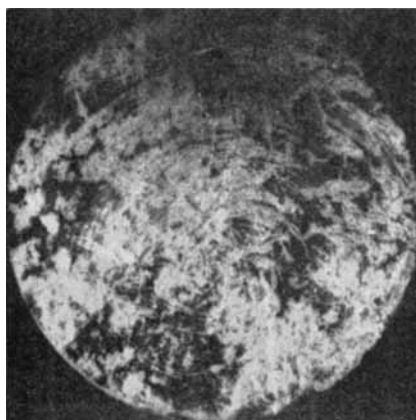


Fig. 2. High charge (rubbed).

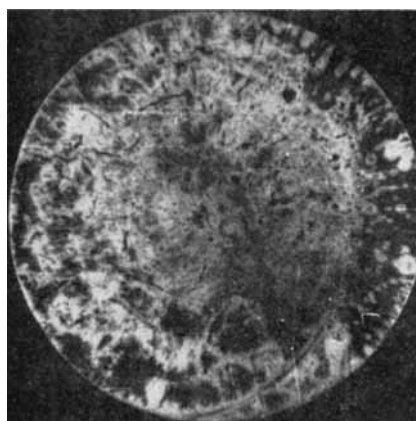


Fig. 3. Medium charge (rubbed).

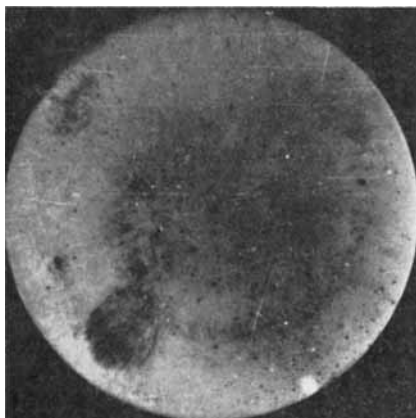


Fig. 4. Very low charge (rubbed).

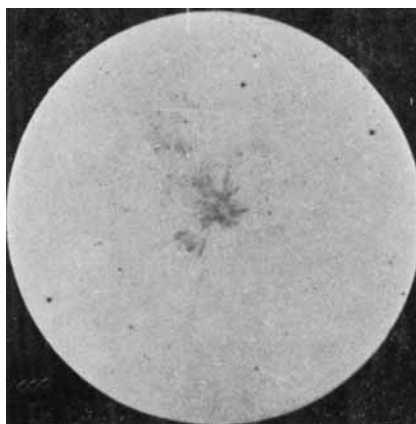


Fig. 5. No charge (rubbed).

medium charge and a diffuse smudge indicates low charge. If the design is observed carefully it is possible to detect greater or lesser charges. For example, the presence of few crows' feet shows a high charge, while the presence of large crows' feet with net contours shows a very high charge (Fig. 1).

In order to ensure greater reproducibility, the specimens were previously discharged with a humid rug and then rubbed with a rotating disk covered by a wool rug (we checked that this rug was discharged before every test). The specimen was held against the rug by a spring with a constant rubbing pressure. Rubbing lasted 10 sec. and the rubbing disk rotated at a speed of about 1450 rpm. Readings were taken 45 sec. after rubbing.

For these rubbed specimens, the designs obtained from dust deposition differed from those obtained for the unrubbed ones. It can be stated in general that high charges are indicated by strong circular orientation and a few crows' feet, medium charge by orientation spots, and low charge by

very low or no orientation or smudge. A specimen which does not attract dust may be considered as having a very good surface conductivity. Figures 1-5 indicate the assignment of charge we gave to the various dust figures on the specimen.

The surface potential readings were performed with Baldwin Dunlop Statigun Mark IV equipment.<sup>7</sup> The conditioning of specimens, rubbing, etc., were the same as above. The electrode was placed 210 mm. from the specimen. Owing to relatively fast charge decay, readings were taken at strictly identical time intervals after rubbing (45 sec.).

As far as the practical evaluation of the antistatic protection is concerned, the dust spray method is probably more reliable than the surface potential methods. As a matter of fact, Woodland and Ziegler,<sup>5</sup> in their extensive study of the patterns obtained on the surface of the plastic by use of fluorescent dust, reached the conclusion that the determination of the amount of charge with a statometer can often be meaningless. In fact, by spraying the polymer with mixtures of colored dusts, which are attracted differently by positive and negative charges, it was shown that polymer surface areas charged with opposite signs exist side by side. Therefore, it can be seen that a statometer which gives the total charge value may be in error, i.e., if the plastic surface is divided into two areas of equal but opposite signs we may get a "zero" reading. In this case, a more complicated and thorough examination of the entire surface of the plastic with the statometer is required. In Table I, the values of static charge determined for various materials by the dust spraying method and by the statometer are reported for comparison. One set of values is given for samples rubbed before reading for 30 sec. as described above. Data are given also for specimens measured without previous rubbing (i.e., a charge simply induced by molding). It is evident that it is advisable to take the readings on specimens which were previously rubbed in order to obtain more reproducible results. Preliminary tests had shown no difference in static charge (both dust and statometer) in specimens rubbed for a time varying from 5 to 30 sec.

Satisfactory agreement between the values read by the statometer and the dust method was obtained. The statometer readings in the reproducibility measurements show satisfactory agreement. The charge sign is the same in all readings. This obviously refers only to specimens which were rubbed, because the specimens tested after molding show a charge value (obviously lower in absolute value) which varies in sign. This probably is due to the fact that the unrubbed specimens are more heterogeneous than the rubbed ones. However, if the signs of the charge are ignored, it is seen that even for the unrubbed specimens there is satisfactory agreement of the absolute values obtained from the statometer and the dust spray method.

#### Surface Treatment with Quaternizing Agents

Blends of PS containing 2.5 and 5% PVP, prepared as described above, were used. Preliminary tests showed that when these specimens were

TABLE I  
Static Charge Measurements on Various Polymers

Sample	Polyethylene <sup>a</sup>				Polystyrene <sup>b</sup>				PS(white) +5PVPb			
	After 48 hr.		After 65 hr.		After 24 hr.		After 48 hr.		Transparent	White	Sta- tom- eter, v./cm. <sup>o</sup> Dust	Sta- tom- eter, v./cm. <sup>o</sup> Dust
	Sta- tometer, v./cm. <sup>o</sup>	Dust	Sta- tometer, v./cm. <sup>o</sup>	Dust	Sta- tometer, v./cm. <sup>o</sup>	Dust	Sta- tometer, v./cm. <sup>o</sup>	Dust	Sta- tometer, v./cm. <sup>o</sup>	Dust		
	Very high	Very high	Very high	Very high	High	High	High	High	Low	High		
1	-90	Very high	-90	Very high	-23	High	-56	High	-2.3	Low	-25	High
2	-100	Very high	-100	Very high	-18	High	-80	High	-0.1	Low	-27	High
3	-110	Very high	-90	Very high	-20	High	-80	High	-6.7	Low	-38	High
4	-100	Very high	-90	Very high	-29	High	-56	High	-2.3	Low	-40	High
5	-110	Very high	-80	Very high	-31	High	-67	High	0.0	Low	-40	High
6	-110	Very high	-90	Very high	-56	High	-	-	+2.1	Low	-51	High
7	-135	Very high	-90	Very high	-31	High	-	-	+4.2	Low	-36	High
8	-110	Very high	-80	Very high	-36	High	-	-	+8.4	Low	-25	High
9	-110	Very high	-80	Very high	-34	High	-	-	+6.3	Low	-37	High
10	-110	Very high	-100	Very high	-36	High	-	-	+9.0	Low	-30	High
11	-	-	-	-	-14	High	-	-	+6.5	Low	-35	High
12	-	-	-	-	-34	High	-	-	+11	Low	-33	High
13	-	-	-	-	-41	High	-	-	+8.5	Low	-34	High
14	-	-	-	-	-43	High	-	-	+13	Low	-40	High
15	-	-	-	-	-23	High	-	-	+6.5	Low	-	-

<sup>a</sup> Specimens rubbed 30 sec. before testing; 50% R.H.; readings made 24, 48, 65 hr. after molding; specimens were stored in conditioned room, 25°C., 50% R.H.

<sup>b</sup> Tests made 75 sec. after molding; specimens were not rubbed before test; 50% R.H.

<sup>c</sup> Instrument sensitivity, X1.

TABLE II  
 Static Charge Measurements on Treated and Untreated PS (white) + PVP specimens by the Dust Method

Conditioning after treatment	Static charge after various treatments							
	Immersion in water, 2 hr., 50°C.				Immersion in ABM 50% 2 hr., 50°C. <sup>a</sup>			
	PS + 2.5 PVP	PS + 5 PVP	PS (transp.)	PS (white)	PS + 2.5 PVP	PS + 5 PVP	PS (transp.)	PS (white)
After 1 week in conditioned room, 25°C., 50% R.H.	Low	Low	Low	Low	Low	Low	Low	Low
After additional 3 days in vacuum desiccator over phosphoric anhydride	Medium high	Medium high	Medium	Medium	Low	Low	Medium	Medium high
After 1 additional week in conditioning room, 25°C., 50% R.H.	High	High	Medium	High	Low	Low	Medium	Medium high

<sup>a</sup> Bromine found (% w/w): white polystyrene, nil; PS + 2.5 PVP:0.05 PS + 5 PVP:0.15.

sprayed with strong quaternizing agents, such as hydriodic acid or ethylene iodobromide, satisfactory antistatic products were obtained, but their surfaces were extensively damaged. The same specimens (or specimens from polystyrene alone) which were superficially sprayed with commercial destaticizer liquid showed good antistatic properties which disappeared with time.

In Table II the results obtained by using as quaternizing agent monobromomalonic acid (ABM) are shown. ABM, prepared according to Conrad and Reinbach,<sup>15</sup> was absorbed onto the specimens from concentrated aqueous solution. The molded specimens were immersed in the acid solution, then washed thoroughly with water and conditioned at 25°C. and 50% R.H.

It can be seen from the Table II that the results of antistaticity are satisfactory. In order to obtain significant data it was necessary to dry the sample thoroughly after immersion in the ABM solution, and then to condition it to allow absorption of surface moisture and then to take the reading. Water absorbed in the ABM bath which was not eliminated during one week of conditioning at 25°C. caused a false reading, since the surface of the specimens was too conductive.

As a matter of fact, the specimens containing polystyrene alone showed a low charge, not only after the ABM solution treatment, but also after immersion in distilled water.

On the other hand, after drying over phosphoric anhydride for 3 days, the specimens which were simply treated with water and the polystyrene treated with ABM showed a charge of medium intensity which was conserved after subsequent conditioning, indicating that the absorbed water had been eliminated. Blends treated with ABM did not lose such antistatic behavior.

A few tests have been performed by coating dried ABM on the surface of the 5.0 blends. The specimens covered with solid ABM were kept in a desiccator for 14 hr. at 25°C. and then washed with water, dried, conditioned, and tested by the dust-spray method. This operation was carried out under vacuum in a desiccator in view of the high hygroscopicity of ABM. The resulting samples were apparently unmodified. While specimens which were not treated with ABM showed medium charge, the treated ones gave practically zero charge. These results were reproduced after an interval of one month.

In Table III the data obtained by using weak organic acids are given. The specimens were immersed in aqueous solutions (concentration 50%) of the reactant, thoroughly washed with water, and dried at 50°C. under vacuum over phosphoric anhydride to constant weight. They were then conditioned at 25°C., 50% R.H., for different lengths of time. After a few weeks at equilibrium the following were determined: (1) the increase in weight (the humidity, particularly on the surface, absorbed after drying); (2) the total water content by the Fisher method (titration of the specimen dissolved in benzene); (3) the amount of acidic groups present on the speci-



TABLE III  
Static Charge Determined on PS + PVP Samples (Dust Method)

Blend (white PS), % PVP	Treatment <sup>a</sup>		Total water (Fischer titration), %	Acid, m.eq.	Static charge (50% R.H., 25°C.)		
	Quat. agent (sol. 50%) <sup>b</sup>	Tempera- ture, °C.			Time, hr.	Weight increase % <sup>b</sup>	After 7 days
—	—	—	—	—	High	High	High
—	H <sub>2</sub> O	25	—	0.05	Medium high	Medium high	Medium high
2.5	H <sub>2</sub> O	25	—	—	Low	Low medium	Low medium
2.5	AM	25	—	—	Low	Low	Low
2.5	AC	25	0.2	0.1	Low	Medium	Medium
5	AC	25	0.15	0.6	Medium	Medium	Medium
5	H <sub>2</sub> O	25	—	—	Very low	Very low	Very low
5	AM	25	0.5	0.9	Low	Very low	Very low
5	AC	25	0.3	0.8	Very low	Very low	Very low
2.5	AM	50	—	—	Low	Very low	Low
2.5	AM	50	0.35	1.2	Very low	Low	Very low
2.5	AM	50	0.3	1.3	Nil	Very low	Very low
5	AM	50	0.4	1.3	Nil	Nil	Nil
5	AM	50	0.45	2.4	Nil	Nil	Nil
2.5	AC	50	—	0.7	Low	Low medium	Low medium
2.5	AC	50	0.15	—	Medium	Medium	Medium
2.5	AC	50	0.3	0.9	Low	Low	Low
5	AC	50	0.6	1.0	Very low	Very low	Very low
5	AC	50	0.4	1.0	Very low	Very low	Very low
2.5	—	—	0.25	—	Medium high	Medium high	Medium high
5	—	—	0.3	—	High	High	High
—	AM	50	—	—	High	High	High
5	H <sub>2</sub> O	50	—	0.2	Medium high	Medium high	Medium high

<sup>a</sup> After treatment, specimens were washed thoroughly with water, dried under vacuum over P<sub>2</sub>O<sub>5</sub> to constant weight and then conditioned at 25°C, 50% R.H.

<sup>b</sup> AM = malonic acid, AC = citric acid.

<sup>c</sup> Determinations made after 21 days. The values were constant after 10 days.

men (titration in benzene with sodium methylate). Lastly the surface charge was determined by the dust-spray method. Measurements on conditioned specimens were repeated at one week intervals for three weeks. In general it was observed that better results were obtained with malonic acids (AM). At 50°C. with 4 hr. treatment, antistatic specimens are obtained which do not attract dust sprayed on the surface.

On the other hand, polystyrene alone, as such or immersed in water or in malonic acid solution under various conditions, shows high charge. Blends with 2.5 and 5.0% PVP, as such or immersed in water, also show a high charge. Results obtained from titration (Table III) show that the greater amount of acid is absorbed by specimens which contain greater amounts of PVP or which are heated for a longer period of time.

It seems that the amount of water in the specimen is not important as far as antistaticity is concerned. As a matter of fact, the amount of water absorbed after conditioning (very probably on the surface) depends only on the amount of PVP contained in the blend. Weight increases of +0.11% and +0.16%, respectively, were obtained for specimens containing 2.5 and 5% PVP, independent of the particular treatment to which they were subjected. The amount of the water in the specimen (Fisher) appears to be independent of the antistatic protection. Therefore it seems that the surface humidity (obviously within certain limits) may be independent of the ease of dispersion of the static charge.

The results in Table III refer to mixtures obtained with white polystyrene. The specimens show no appreciable variation on the surface, except for some loss of gloss due to microscopic surface attack. As an example, such surfaces resemble those of rubber-modified impact polystyrenes. On the other hand, samples obtained from transparent polystyrene show greater corrosion. Correspondingly, under the same conditions, the obtained antistatic values are greater.

Impact-type polystyrenes were not considered in this work (of exploratory character). We assumed that surface deterioration could be better evidenced on normal types. We feel that by working with other (more reactive) quaternizing agents on rubber-modified polystyrenes, antistatic products with practically unmodified surfaces can be obtained with greater ease and rapidity of treatment.

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### Résumé

En mélangeant mécaniquement du polystyrène avec de petites quantités de poly-(2-méthyl-5-vinylpyridine) on obtient des objets moulés qui possèdent une protection anti-statique satisfaisante par un traitement de surface avec des agents chimiques (qui réagissent avec l'azote pyridinique). On discute des méthodes de détermination des charges statiques ainsi que des conditions d'application des agents de quaternation.

### Zusammenfassung

Aus mechanischen Mischungen von Polystyrol und kleinen Mengen von Poly(2-methyl-3-vinylpyridin) erhält man Spritzgussartikel, die durch Oberflächenbehandlung mit chemischen Substanzen (die mit dem Pyridinstickstoff reagieren können), gute anti-statische Eigenschaften bekommen. Messmethoden für die statische Aufladung sowie Anwendungsbedingungen der Quaternisierungsmittel werden diskutiert.

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