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NONFLAMMABLE, ANTISTATIC, AND HEAT-SEALABLE FILM

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FOREWORD

The work described herein, which was conducted by the Pennwalt Corporation, was performed under NASA Contract NAS 9-8356 with Mr. Jack Naimer, R and D Technology Branch, NASA Manned Spacecraft Center, as Technical Monitor. Some data presented in this report were obtained by Mr. I. H. Custis of the Naval Air Development Center in Philadelphia under NASA - Defense Purchase Request No. T-799650.

ABSTRACT

Antistatic, heat-sealable, and self-extinguishing films, 2.5, 4 and 6 mils thick, were prepared from polyvinylidene fluoride and polyvinylidene chloride resins. Numerous compounds were studied as internal antistatic additives in cast films and as additives to resinous surface coatings. Conductive laminates, 4 and 7 mils thick, were prepared by heat pressing a wire mesh or a printed silver grid between films of polyvinylidene fluoride.

Static properties were evaluated by two different methods and at different levels of humidity. Films containing pyridinium or ammonium chloride derivatives or conductive grids were found to have static propensities of less than 5 nanocoulombs at 57% relative humidity and dissipation times of 0.6 to 2 sec for a 5 kv charge both at 50 and at less than 15% relative humidity. Water resistance and mechanical properties were also studied for these films.

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SUMMARY

The objective of the work described in this report was the development of a nonflammable, transparent, heat-sealable, antistatic polymer film.

Two commercial, self-extinguishing polymer resins known to form heat-sealable films were selected and modified to obtain antistatic properties. Most of the work was done with a polyvinylidene fluoride polymer.¹ The second resin, a vinylidene chloride-acrylonitrile copolymer,² was selected as a representative of the group of self-extinguishing polyvinylidene chloride resins. The problem of developing films with antistatic properties was approached in three different ways:

- a. Formulation of internal antistatic agents.
- b. Development of self-extinguishing antistatic surface coatings.
- c. Preparation of conductive laminates.

Several hundred compounds were screened as internal antistatic additives by examining films cast from solutions containing the resin and antistatic agents. For polyvinylidene fluoride best performance was

¹Kynar.

²Saran F-300.

obtained with several cationic type compounds, in particular pyridinium and ammonium chloride derivatives which were present in the resin at 2.5 to 4% concentration. A combination of 2% laurylpyridinium chloride and 1% cetyldimethylbenzylammonium chloride gave an antistatic propensity of less than one nanocoulomb at $57 \pm 3\%$ relative humidity (R.H.), well below the specified limit of 5 nanocoulombs at 65% R.H. For these samples the time required to dissipate a charge of 5 kv was slightly above one second at both 50 and less than 15% R.H. By comparison antistatic Nylon RC-AS-2400 was found to have charge dissipation times of 8.5 and more than 300 sec at 50 and less than 15% R.H., respectively, and its antistatic propensity ranged from 20 to 40 nanocoulombs at $57 \pm 3\%$ R.H. Although completely water resistant antistatic agents with sufficient activity to meet the requirements could not be obtained, most films with good initial antistatic performance recovered their antistatic properties rapidly even after repeated exposure to running water.

Antistatic agents that were found to be effective in polyvinylidene fluoride generally did not perform as well in the vinylidene chloride-acrylonitrile copolymer. Several amine derivatives such as N,N-bis(2-hydroxyethyl)-alkylamine and complex phosphate ester derivatives gave good antistatic propensity values in the copolymer, but charge dissipation data were not as good for these samples as for polyvinylidene fluoride films.

Although less work was done with surface coatings, experiments showed that formulations consisting of antistatic agents and a self-extinguishing proprietary resin, RC 3584, may be spray coated on polyvinylidene fluoride film to give a durable antistatic surface coating.

Laminates, 4 and 7 mils thick, with excellent antistatic performance were prepared by heat pressing a fine wire mesh between two polyvinylidene fluoride films. For these samples the dissipation times for a charge of 5 kv at 50 and less than 15% R.H. were 0.5 and 0.6 sec, respectively. The static propensity was too low to be measurable. A different type of conductive film was obtained by incorporating a printed silver grid between two polyvinylidene fluoride films. Static propensity values ranged from less than 1 to 20 nanocoulombs, and charge dissipation times of 0.5 to 17 sec were found for these samples.

INTRODUCTION

The use of flammable polymer films in applications where fire or explosion hazards exist is undesirable. Because plastics are poor conductors and tend to accumulate and retain electrical charges, an additional safety problem arises, for electrostatic discharges may result in fire or explosion. Although there are several polymer resins from which heat-sealable and nonflammable films can be made, their antistatic behavior leaves much to be desired. The major part of the work presented in this report was devoted to making self-extinguishing polymer films antistatic.

Although much progress has been made toward understanding the nature and distribution of static charge in organic polymers, knowledge is still very limited. Some believe that static buildup is a surface phenomenon (ref. 1), whereas others contend that there is a distribution of static charge throughout the bulk (ref. 2). Since static electricity is frequently generated by friction, surface treatment with agents that

impart lubricity has been used to reduce the static propensity of plastic films. However, mere contact may suffice for any material to become charged. Therefore, a more effective way to prevent static charging is to make the polymer sufficiently conductive that the charge can be dissipated to ground. Most antistatic agents are believed to function in this way. Water seems to play an important role in antistatic behavior, and coatings with hygroscopic agents make polymer surfaces more conductive. Accidental presence of stray electrolytes further aids in charge dissipation. Because most antistatic surface coatings exhibit water solubility and poor mechanical properties, they are easily washed or wiped off. However, a number of water resistant antistatic compositions have been developed recently, for example, crosslinked polymers as textile finishes and metal phosphinates as coatings for polyethylene (refs. 3,4,5,6). Plastics may be given more permanent antistatic protection by incorporating the antistatic agent into the bulk of the resin. If the agent is slightly incompatible with the resin, it can migrate to the surface and reduce the surface resistivity of the plastic. Abrasion or prolonged exposure to water may remove the antistatic agent from the surface, but it will eventually be replenished by migration from the bulk of the polymer. The rate of recovery of antistatic properties is most likely determined by the degree of incompatibility of the antistatic agent with the plastic. The presence of foreign matter may decrease some of the mechanical properties of the polymer film, and it is therefore desirable to keep the amount of antistatic agent to a minimum.

Metals and carbon black have been used to make plastics conductive, but ordinarily such products are not transparent. Surface coatings of metals

on polymer films can be abraded and may also cause capacitance effects that tend to retain rather than dissipate charge.

There is no generally accepted method to evaluate the static propensity of polymers. Ideally, a test method should duplicate as closely as possible the conditions and mechanism by which a polymer film may be expected to accumulate and dissipate static charges. Numerous techniques have been developed to measure antistatic performance, ranging from the simple and qualitative ash test to more elaborate methods requiring sophisticated instrumentation. The determination of electrical conductivity is a quantitative method useful for the evaluation of electrical properties of polymers (ref. 7). A possibly more meaningful indicator of antistatic performance is the measurement of time necessary to dissipate a given charge to zero volts or some other value (refs. 8,9). Another technique is to determine the amount of static charge generated on test samples in a reproducible way under controlled conditions. In the work described in this report the last two methods were used to evaluate the antistatic performance of test samples.

RESULTS AND DISCUSSION

A survey of available materials led to the selection of polyvinylidene fluoride and a vinylidene chloride-acrylonitrile copolymer for the preparation of test films, because both resins are self-extinguishing according to ASTM D568. Although vinylidene chloride-acrylonitrile copolymer is primarily designed for coatings, polyvinylidene chloride resins and polyvinylidene fluoride can be made into heat-sealable films with good mechanical

properties.

In order to develop a film sufficiently antistatic to meet the specified requirement several approaches were followed in the hope that one or more would achieve the desired objective:

- a. Films with internal antistatic agents.
- b. Films with durable antistatic coatings.
- c. Laminated films with a metallic conductor.

Progress made in each area was followed by static propensity measurements. The methods used to obtain these measurements will be discussed first in order that the data can be better understood.

Antistatic Performance Measurements

Static propensity data were obtained with a fabric charge tester in combination with an electrostatic voltmeter. In this test method test samples are pulled through rollers by means of a spring-operated lever. The generated charge or a fraction of it leaks off through one of the metal rollers to a range multiplier and is measured in nanocoulombs with the electrostatic voltmeter. The individual measurements vary sufficiently that an average value has to be calculated. The values so determined are reproducible, and, though they have no absolute meaning, they permit a comparison of antistatic behavior of test samples.

Apart from the level of humidity which obviously influences static behavior, the nature of the film surface was found to affect the data obtained by this method. An irregular surface generally gave a much lower static propensity than a smooth surface. If the two sides of a test film differed slightly in surface properties, the results obtained depended

upon which side faced the grounded roller during the test procedure. Well lubricated or slippery surfaces give erroneous data by this method. In a few instances the data were excessively scattered and therefore useless.

Additional data on the antistatic performance of the most promising test samples were obtained by a different method. Dissipation times of positive and negative charges of 5 kv were measured by Mr. I. H. Custis of the Aero Materials Department of the Naval Air Development Center in Philadelphia. His techniques permit the measurement of dissipation times as low as 1 sec or less at 50 and at less than 15% R.H. (ref. 9). There are a few exceptions, but in general the data obtained by the two methods agree.

Films with Internal Additives

Although coatings are believed to give more effective antistatic protection to polymer films, the incorporation of antistatic agents into the bulk of the polymer is preferred because of greater durability. We therefore screened several hundred compounds with antistatic potential to find compositions that would most efficiently protect the film from charge accumulation. In order to speed up evaluation, test samples were cast from solutions containing the polymer resin and antistatic agents. After the solvent was removed, the test films were conditioned at ambient temperature and the desired humidity. Static performance data were then obtained by the techniques discussed in the previous section. The data in Table 1 indicate that a number of internal antistatic formulations meet or exceed the requirement of a maximum static propensity of 5 nanocoulombs at 57% R. H. and 70°C. For several antistats this could be achieved at a concentration of 3%. The static propensity values in Table 1 are averages of at least two measurements. Each sample was remeasured after several

days to confirm the initial results. The preparation of the best performing samples was also repeated to make sure that the data were reproducible. Dissipation times obtained for a charge of 5 kv at different humidities in many cases parallel the static propensities obtained (Table 1). A value of 1 sec or less is the goal for antistatic packaging film as outlined in the provisional specification XAS-1152 of the Naval Air Systems Command. It is remarkable that short discharge times are retained for several internal antistats even at less than 15% R.H. Combinations of antistats were also tried to find possible synergistic effects. Although the existence of such effects could not be clearly established for all the different conditions under which the films were tested, the presence of a second component in some instances improved the physical properties of the film. For example in Table 1 the composition in item 3 is preferred over that in item 4, in which one of the components was omitted, because films prepared with the single antistatic agent curled excessively.

The best samples were also examined at $45 \pm 2\%$ R.H. Antistatic behavior was not as good as at the higher humidity, but several samples still appeared to meet the required antistatic performance of less than 5 nanocoulombs. For several samples static propensity values vary more with a change in humidity than do charge dissipation times. A direct correlation of antistatic data obtained by the two methods is therefore not possible.

Several attempts were made to develop a water insoluble composition by modifying compounds with known or expected antistatic properties such as Gafstat AS-710, Gantrez AN and polyvinylpyridines. Although insoluble derivatives could be prepared, none proved to be adequately antistatic when incorporated into the polymer resin.

The water resistance of films containing the most promising internal antistatic agents was also examined. To do this, test samples were treated with cold running water for one half hour once a day, and their antistatic performance was determined after each treatment. The data on the static propensity after 4 and 8 leachings are shown in columns I and II, respectively, in Table 1. All samples show a marked decrease in antistatic properties immediately after leaching, but recovery is good. Another set of samples was immersed in running water and was leached continuously for 5 hours. This resulted in a reduction in antistatic performance, but here also a substantial recovery was noted after several hours (column III, Table 1). Because of ease of formulation, overall antistatic performance, and physical properties of the film, a combination of 2% of laurylpyridinium chloride and 1% cetyldimethylbenzylammonium chloride is recommended as an internal additive to give polyvinylidene fluoride film the desired antistatic properties. A listing of less successful experiments with internal additives is given in Appendixes A and B.

In other attempts to develop an antistatic film with internal additives the static properties of films consisting of two polymers selected from opposite ends of the triboelectric series were investigated. Films made up of 50% polyvinylidene fluoride and 50% nylon resin³ showed a static propensity of less than one nanocoulomb, but charge dissipation times were high, varying from 43 to more than 300 sec at the different humidities (Item 18, Table 1). In contrast very rapid charge dissipation

³Elvamide 8061.

was observed for polyvinylidene fluoride films containing 2.5 to 0.5% gold chloride which was photochemically reduced in situ to elemental gold. The static propensity values increased from 15 to 180 nanocoulombs for these samples (Items 15-17, Table 1). Although these samples dissipate static charge rapidly, they obviously also acquire it readily.

Several compounds were also found to give good antistatic performance in vinylidene chloride-acrylonitrile copolymer films (Table 2). For example 5% stearamidopropyldimethyl- β -hydroxyethylammonium dihydrogen phosphate (Catanac SP) or N,N-bis(2-hydroxyethyl)alkylamine (Armostat 310) reduced the static propensity from 140 to less than 1 nanocoulomb. Although excellent values of charge dissipation times of less than 1 sec were achieved at 50% R.H., the values increased to 8 to 14.7 sec at the lower humidity.

Surface Coatings

An antistat is likely to be more efficient on the surface of the polymer than when incorporated into its bulk so some effort was devoted toward developing a durable antistatic coating for polyvinylidene fluoride film. Since the surface treatment may be applied after the film has been made, the possibility of decomposition during processing is avoided. To improve the abrasion resistance of such coatings antistatic agents were incorporated into various resins. Although a film made of a nylon resin (Elvamide 8061) containing 5% tetrakis(hydroxymethyl)phosphonium chloride (THPC) had excellent charge dissipation times of less than 1 sec, the same formulation gave mediocre results when sprayed on polyvinylidene fluoride film (Item 2, Table 3). Adherent coatings were also obtained with an acrylic resin (Acryloid AT-50) containing different antistatic agents, but

their static propensity values were not promising. A reaction product of a methylvinylether-maleic anhydride copolymer (Gantrez AN) and THPC was spray coated on polyvinylidene fluoride film to give a coating with good static propensity, but the charge dissipation values were unsatisfactory (Item 5). To retain the self-extinguishing properties of the polyvinylidene fluoride substrate most of the coatings work was done with a self-extinguishing proprietary resin RC 3584. According to the results in Table 3, Catanac SP and cetylpyridinium chloride appear to be the most promising additives for this system.

Antistatic Laminates

The possibility of developing a transparent conductive plastic film by incorporating a metallic grid was also explored. Antistatic properties should be permanent and independent of the dimensions of the film as well as humidity. A wire mesh, made of 0.0005-in. Chromel-R wire, was heat-laminated between polyvinylidene fluoride films. Depending upon the thickness of these films laminates 4 mils and 7 mils thick were obtained. Both antistatic propensity and charge dissipation tests gave excellent values, less than 1 nanocoulomb and less than 1 sec, respectively, even at low humidities (Table 4). A microscopic investigation revealed some exposed metal fibers for the thinner films but a completely smooth surface for the 7 mil laminates. In a different approach a rectangular silver mesh was printed on a polyvinylidene fluoride film which was then heat laminated to a second film. Again excellent discharge times were obtained although static propensities were slightly higher than for the wire mesh laminates. Incorporation of small amounts of antistatic agents into the films from which the laminates were made improved the static

propensity values but did not influence dissipation times at 50% R.H.

The high value for the time required to dissipate a positive charge of 5 kv at less than 15% R.H. is puzzling.

Physical Properties

Tests of physical properties were performed mainly on cast polyvinylidene fluoride film containing the most promising antistatic agents. With the exception of samples containing dispersed gold all films including laminates and those with surface coatings were found to be more or less transparent. Only films containing a nylon resin or having an acrylate or nylon in the surface coating were not self-extinguishing according to ASTM D568-61. Other data are shown in Table 5. Tensile strengths at yield for these cast, unoriented films are slightly below 5000 psi, the same as for cast polyvinylidene fluoride film without additives. Since oriented polyvinylidene fluoride films can be made with tensile strengths in excess of 25,000 psi, the desired value of 13,500 psi for the antistatic films should be readily achieved by orientation. None of the tested samples was found to have the desired abrasion resistance of 5 mg or less. Average values range from 7.9 to 15.9 mg after 1000 cycles and 500-g load according to ASTM D1044. Folding endurances were determined on 2.5-mil films with an MIT tester by ASTM D2176. Several samples were found to exceed substantially the folding endurance of pure cast polyvinylidene fluoride films of 167,000. This may be due to a plasticizing effect of the additives. However, there is some evidence that the folding endurance decreases with age of the sample. For oriented films not containing additives folding endurances in excess of 500,000 have been obtained. Hydrostatic resistance tests were performed according

to Fed. Spec. CCC-T-191b, Method No. 5512. As shown in Table 5 the data vary from 20 to 45 psi for 2.5-mil films. Again, substantially higher values can be expected for oriented samples.

Late in the program the need for a material with a higher tear resistance than is characteristic for polymer films arose. The present studies indicate that a highly tear-resistant, self-extinguishing and antistatic fabric or reinforced film can be developed based in part upon the knowledge gained so far.

EXPERIMENTAL

Materials

Polyvinylidene fluoride resin and the proprietary resin RC3584 were supplied by our Plastics Department and the vinylidene chloride-acrylonitrile copolymer resin was obtained from the Dow Chemical Co., Midland, Michigan. The substrate for surface coatings was 3-mil blown polyvinylidene fluoride film supplied by our Plastics Department. The additives screened for antistatic activity were obtained mainly from commercial sources under their respective trade names. Some were obtained from our Fluorochemicals Department. An acrylic resin, Acryloid AT-50, was supplied by Rohm and Haas Co., Philadelphia, and a nylon resin, Elvamide 8061, was obtained from E. I. du Pont de Nemours & Co. The wire fabric used for conductive laminates was knitted from 5×10^{-4} in. Chromel-R wire and was manufactured by Fabric Research Laboratories, Inc. Dedham, Mass. Eccocoat CC-2 obtained from Emerson and Cuming, Inc., of Canton, Mass., was used to print conductive silver grids on Kynar film.

Equipment

Fabric charge tester Model SWE 1190 and SWE 1170 Electrostatic Voltmeter with a No. 1170-500 probe manufactured by the Sweeney Manufacturing Co. of Denver, Colorado, were used for antistatic testing. The conditioning of samples and the measurement of their antistatic properties were performed in a chamber in which the relative humidity was controlled by constant humidity baths. Saturated solutions of sodium nitrite and of magnesium nitrate were used to maintain the relative humidity at $57 \pm 3\%$ and $45 \pm 2\%$, respectively. A Bendix model 566 Psychrometer was used to measure relative humidities. Tests of the physical properties of antistatic films were done with instruments meeting the specifications of the various ASTM procedures.

Films with Internal Antistatic Agents

Test samples, 3 in. x 8 in., were cut from films cast from solutions containing 20% polyvinylidene fluoride and from 0.4 to 1.0% antistat in dimethylacetamide. Whenever necessary, antistats were first dissolved in small amounts of other solvents such as ethanol or isopropanol and then added to the polymer solution with rapid mechanical stirring. Films were cast on 12 in. x 12 in. glass plates by means of a doctor blade. After standing at room temperature for 10 min the films were cured at $125-135^\circ$ for 0.5 to 1 hr depending upon the thickness of the film.

Antistatic vinylidene chloride-acrylonitrile copolymer films were cast from methyl ethyl ketone solutions containing 20% resin and 1% antistat. Films were cast on glass plates with a doctor blade, and after standing at room temperature for 30 min they were cured at 85° for 30 min.

Surface Coatings on Polyvinylidene Fluoride Film

A typical spray solution for applying 0.5 to 1.5 mil-thick coatings on polyvinylidene fluoride film consisted of 9 parts resin RC 3584, 0.5 parts cetylpyridinium chloride, 61 parts cyclohexanone, 20 parts methyl isobutyl ketone, 4.5 parts dimethylacetamide and 5 parts ethanol. A Binks air-powered sprayer or an aerosol propelled suction sprayer was used to apply the coatings which were cured at 150° for 5 min in a circulating air oven.

Conductive Laminates

A fabric knitted from 5×10^{-4} in. Chromel-R wire was heat laminated between 3 or 1.5 mil polyvinylidene fluoride films at 350° F for 10 min at 60 psi.

Other conductive laminates were made by drawing a rectangular grid of fine lines on 2.5 mil polyvinylidene fluoride film using a conductive fluid resin Eccocoat CC-2. The fluid, which contained suspended silver particles, was diluted with an equal volume of acetone and then applied with a drawing pen. The lines were approximately 0.04 in. wide and 1 to 1-1/2 in. apart. The grid was air dried for 30 min, and then a second film was heat laminated over it. Good laminates were obtained by pressing at 350° F and 625 psi for 5 min.

CONCLUSIONS

The purpose of the work described in this report was the development of a self-extinguishing, antistatic and heat-sealable film. Test samples that meet or exceed the desired antistatic performance were obtained by incorporating antistatic agents into self-extinguishing and heat-sealable

polyvinylidene fluoride and vinylidene chloride-acrylonitrile copolymer resins. The best agents for polyvinylidene fluoride were lauryl- and cetylpyridinium chloride and cetyldimethylbenzylammonium chloride and for the vinylidene chloride-acrylonitrile copolymer stearamidopropyl-dimethyl- β -hydroxyethylammonium dihydrogen phosphate and N,N-bis(2-hydroxyethyl)alkylamine. Conductive laminates also meeting the required antistatic properties were prepared by heat laminating a wire mesh or a silver grid between thin polyvinylidene fluoride films. Work on the development of a self-extinguishing antistatic spray coating for polyvinylidene fluoride film showed promising results. Abrasion resistance, tensile strength and folding endurance for cast antistatic polyvinylidene fluoride films are lower than desired.

REFERENCES

1. Woodland, P. C. and Ziegler E. E., Modern Plastics 28, 95 (1951).
2. Skinner, S. M., Gaynor, J. and Sohl, S. W., Modern Plastics, 33, 127 (1956).
3. Pretka, J. E., U. S. Patent 3,021,232 (1962).
4. Boardman, H., U. S. Patent 3,382,096 (1968).
5. Owen, J. B. and Sagar, H., U. S. Patent 3,391,019 (1968).
6. Dahl, G. H., Sprout, O. S. Jr., Peschko, N. D. and Block, B. P., Contract N00156-67-C-1783, Final Report, March 1968.
7. 1965 Book of ASTM Standards, Part 27, page 78-97 American Society for Testing and Materials, Philadelphia.
8. Shashoua, V. E., J. Polym. Sci. 33, 65 (1958).
9. Custis, I. H., Package Engineering 12 (12), 78 (1967).

Table 1. Performance Data of Polyvinylidene Fluoride Films with Selected Internal Antistatic Agents

Item No.	Additives		Static Propensity (nanocoulombs)						Dissipation Time (seconds)				
	No. a	%	57±3% R.H.						50% R.H.		<15% R.H.		
			Initial	Initial	I ^b ,e	II ^c ,e	III ^d ,e	+	-	+	-		
R-1	-	-	150	-	-	-	-	-	-	-	-	-	-
R-2 ^f	-	-	20-50	-	-	-	-	-	-	-	-	-	-
1	unknown	-	60	85	-	-	-	-	8.24	8.80	-	-	300
2	2.0	-	7	<1(6.5)	6(6)	-	-	28(1.5); 7(20)	0.63	0.62	0.91	0.91	1.11
3	1.5	-	26	<1(22)	20(5)	-	-	25(2.5); -	1.18	0.91	1.65	1.65	1.49
4	2.0	-	1	12(5)	13(5.5)	-	-	11(1.5); 5(20)	1.13	0.72	1.17	1.17	1.76
5	3.0	-	8	8(6)	13(6.5)	-	-	30(1.5); 7(20)	0.70	0.66	1.00	1.00	1.11
6	2.5	-	1	8(2.5)	6(5.5)	-	-	-	1.15	0.92	1.37	1.37	1.33
7	2.0	-	35	5(2.5)	16(5.5)	-	-	-	0.84	0.67	1.32	1.32	1.33
8	2.0	-	7	11(5)	8(5.5)	-	-	12(2.5); 3(25)	1.73	1.55	2.41	2.41	2.60
9	5.0	-	-	<1(6.5)	28(6.0)	-	-	-	0.79	0.92	1.00	1.00	1.20
10	2.0	-	5-30	16(22)	15(5.0)	-	-	22(2.5); -	2.51	2.34	2.71	2.71	2.75
11	2.0	-	-	<1	15 ^g (1.5)	-	-	-	0.76	0.74	5.30	5.30	4.58
12	2.0	-	-	<1	39(70)	-	-	-	12.07	16.9	286.8	286.8	210.0
13	1.0	-	-	<1	25 ^g (17)	-	-	-	2.31	2.4	30.9	30.9	37.05
14	2.5	-	-	<1	55 ^g (20)	-	-	-	0.63	0.67	1.04	1.04	0.75
15	2.5	-	-	8	5 ^g (25)	-	-	-	1.06	0.90	4.76	4.76	5.3
16	2.5	-	-	15	-	-	-	-	0.71	0.83	1.17	1.17	0.75
17	1.0	-	-	90	-	-	-	-	2.38	2.63	2.42	2.42	1.59
18	0.5	-	-	180	-	-	-	-	1.55	1.25	6.50	6.50	4.00
19	50	-	-	6	-	-	-	-	43.9	50.6	300 ^h	300.0 ^h	-
20	2.5	-	5	<1	60(75)	70(6)	-	-	-	-	-	-	-

^aSee Table 6 for listing of antistatic agents
^bSamples leached for 30 min four times
^cSamples leached for 30 min eight times
^dSamples leached continuously for 5 hr

^eFigures in parentheses indicate hours elapsed between last water treatment and static propensity measurement
^fRC-AS-2400, a nylon reference film
^gSample leached once for 30 min
^hExperiment was terminated after 300 seconds

Table 2. Performance Data of Vinylidene Chloride - Acrylonitrile Copolymer Films with Selected Internal Antistatic Agents

Item No.	Additive		Static Propensity (nanocoulombs) 57±3% R.H., 75±2°F	Dissipation Time (seconds)						
	No. ^a	%		50% R.H.		<15% R.H.		+ -	-	
				+	-	+	-			
R-1	-	-	170	-	-	-	-	-	-	-
1	5	5	<1	0.7	-	12.00	-	14.72	-	-
2	21	5	<1	8.44	0.65	120.0	120.0	125.0	-	-
3	9	5	2	300 ^{b,c}	7.96	300 ^{b,c}	300 ^{b,c}	300 ^{b,c}	-	-
4	10	5	<1	32.8	70.40	Sample accepted only 4.5 kv	-	-	-	-
5	11	5	<1	0.97	0.93	8.03	8.03	10.21	-	-
6	12	5	<1	6.84	1.66	300 ^c	300 ^c	271.8	-	-
7	3	5	2	-	-	-	-	-	-	-
8	13	5	1	-	-	-	-	-	-	-
9	14	5	2	-	-	-	-	-	-	-
10	15	8.3	<1	-	-	-	-	-	-	-
11	16	5	1	-	-	-	-	-	-	-
12	17	5	1	-	-	-	-	-	-	-
13	18	5	1	-	-	-	-	-	-	-

^aSee Table 6 for listing of antistatic agents

^bSample accepted less than 5 kv of charge

^cExperiment was terminated after 300 seconds

Table 3. Performance Data for Antistatic Coatings on Polyvinylidene Fluoride Film

Item No.	Coating Resin	Additive		Static Propensity (nanocoulombs)		Dissipation Time (seconds)			
		No. ^a	%	57±3% R.H.		50% R.H.	<15% R. H.		
				Initial	Leached ^b		+	+	
1	Elvamide 8061	-	-	6	-	102.0	108.0	90.0 ^c	300.0 ^{c,d}
2	"	19	5	1	3	78.0	108.0	300.0 ^c	300.0 ^{c,d}
3	Acryloid AT-50	4	5	15	18	-	-	-	-
4	"	23	5	20	-	-	-	-	-
5	-	20	100	1	6	136.0	136.0	240.0 ^c	300.0 ^{c,d}
6	-	4	100	4	-	-	-	-	-
7	RC 3584	3	0.4	<1	-	-	-	-	-
8	"	5	5	<1	8	-	-	-	-
9	"	5	1.5	1.5	15	-	-	-	-
10	"	4	10	80	-	-	-	-	-
11	"	9	10	25	150	-	-	-	-
12	"	19	10	140	-	-	-	-	-
13	"	21	10	4	-	-	-	-	-
14	"	22	10	23	-	-	-	-	-

^a See Table 6 for listing of antistatic agents

^b Sample was leached in water for 30 min.

^c Sample accepted less than 5 kv of charge

^d Experiment was terminated after 300 seconds

Table 4. Performance Data for Selected Conductive Polyvinylidene Fluoride Laminates

Item No.	Conductor	Additive		Static Propensity (nanocoulombs) 57±3% R.H.	Dissipation Time (seconds)			
		No. ^a	%		50% R.H.	<15% R.H.	-	
1	Chromel-R mesh	-	-	1	0.53	0.52	0.63	0.58
2	Silver Grid	-	-	4	0.67 ^b	0.71	1.04	0.5
3	"	-	-	3	0.63	0.63	1.25	0.50
4	"	-	-	20	1.21	0.85	2.42	0.63
5	"	3	1.0	8 ^c	0.50	0.63	0.88	0.63
6	"	5	1.0	<1	0.65	0.50	17.10	4.68
7	"	5	1.0	6 ^c	0.63	0.67	6.80	0.73
8	"	7	2.0	<1	0.68	0.50	27.20	2.26

^aSee Table 6. for listing of antistatic agents

^bResult obtained at 65% R.H.

^cFilm leached with water for 30 minutes

Table 5. Physical Properties of Cast Antistatic Polyvinylidene Fluoride Films Selected from Table 1.

Item No. ^a	Tensile Strength (ASTM-D 882) psi	Abrasion Resistance (ASTM-D 1044) mg ^b	Folding Endurance (ASTM-D 2176) cycles ^c	Hydrostatic Resistance (CCC-T-191b, No. 5512) psi ^c
1	4593	15.9	211,871	22
2	4394	9.7	92,543	35
3	4948	12.9	230,843 ^d	20
4	4836	15.6	78,989	24
5	4820	11.5	-	-
6	4883	14.7	-	-
7	4762	11.9	202,452	-
8	-	-	60,204	-
9	4264	7.9	137,809	45
10	-	12.8	156,800	28
11	-	11.2	250,700	25
12	-	7.4	186,200	37
13	-	14.9	205,800	24
14	-	13.6	308,800	21

^aSame as in Table 1

^b1000 cycles and 500-g load

^cTest samples were 2.5 mils thick

^dValue appeared to be decreasing with age of the sample

Table 6. Description of Antistatic Agents

No. ^a	Name	Chemical Description	Source
1	Dehyquart C	Laurylpyridinium chloride	Henkel International
2	Acetoquat CDAC	Cetyldimethylbenzylammonium chloride	Aceto Chemical Co.
3	Acetoquat CPC	Cetylpyridinium chloride	Aceto Chemical Co.
4	3222-173-4	Proprietary fluorocarbon derivative	Pennwalt Corp.
5	Catanac SP	Stearamidopropyldimethyl- β -hydroxyethylammonium dihydrogen phosphate	American Cyanamid Co.
6	Electrosol S-1-X	Unavailable	Alframine Corp.
7	Antaron FC-34	Complex fatty amido compound	General Aniline & Film Corp.
8	Gafac RE-610	Free acid of complex phosphate ester	General Aniline & Film Corp.
9	AMS 313	Amphoteric Compound	Armour Industrial Chemicals
10	AMS 303	Amphoteric Compound	Armour Industrial Chemicals
11	Armostat 310	N,N-bis(hydroxyethyl)alkylamine	Armour Industrial Chemicals
12	Lubrol PE	Unavailable	I.C.I. Organics, Inc.
13	Gafac LO-529	Sodium salt of complex phosphate ester	General Aniline & Film Corp.
14	---	A magnesium salt of Gafstat AS-710	Laboratory preparation
15	Armostat 100V	Unavailable	Armour Industrial Chemicals
16	Aromox 18/12	Amine	Armour Industrial Chemicals

Table 6. (continued)

No. ^a	Name	Chemical Description	Source
17	FC 134	Fluorocarbon derivative	3M Company
18	Amine S	Heterocyclic tertiary amine	Geigy Industrial Chemicals
19	THPC	Tetrakis(hydroxymethyl)phosphonium chloride	Hooker Chemical Corp.
20	---	Unidentified reaction product of THPC and Gantrez AN	Laboratory preparation
21	Gafstat AS-710	Free acid of complex phosphate ester	General Aniline & Film Corp.
22	Antara LF-205	Barium salt of complex phosphate ester acid	General Aniline & Film Corp.
23	3222-155-3	Proprietary fluorocarbon derivative	Pennwalt Corp.
24	---	Sodium tetrachloroaurate(III)	Fisher Scientific Co.
25	Elvamide 8061	Nylon resin	E.I. du Pont de Nemours & Co.
26	Zelec DP	Unavailable	E.I. du Pont de Nemours & Co.

^aNumbers are the same as those given to antistatic agents in Tables 1-4.

APPENDIX A

LESS EFFECTIVE ANTISTATS IN POLYVINYLIDENE FLUORIDE

The following compounds, listed by classes, were judged unsatisfactory when present at 5% conc. in polyvinylidene fluoride because of poor antistatic performance or in some cases because of their adverse effect on the physical properties of the films.

1. Commercial Fluorocarbon Compounds

FC 95	3M Company
FC 98	" "
FC 126	" "
FC 128	" "
FC 134	" "
FX 161	" "
FC 170	" "
MP 53	Pennwalt Corp.
Pentel 22	" "

2. Commercial Antistats and Surfactants

Acetoquat CTAB	Aceto Chemical Co.
Amine S	Geigy Industrial Chemicals
Ammonyx 27	Onyx Chemical Co.
AMS 303	Armour Industrial Chemicals
AMS 313	" " "
Antara LF-200	General Aniline & Film Corp.
" LF-205	" " " "
" LM-400	" " " "
" LM-405	" " " "

Antara LM-505	General Aniline & Film Corp.
Antistat 61	Charles Pfizer and Co., Inc.
Antistat C 1028, Hallco	The C. P. Hall Co.
Antistat C 1029, Hallco	The C. P. Hall Co.
Aromox 18/12	Armour Industrial Chemicals
Arquad 303	" " "
Aston AP	Onyx Chemical Co.
Barquat SB-25	Barlow Chemical Corp.
Carbowax 1500	Union Carbide Chemicals
Drewplast 017	Drew Chemical Corp.
" 029	" "
" 032	" "
" 050	" "
Electrosol S-1-X	Alframine Corp.
Ethomeen 18/60	Armour Industrial Chemicals
Gafac GB-520	General Aniline & Film Corp.
" LO-529	" " " "
" RE-610	" " " "
" RE-960	" " " "
Gafstat AD-510	" " " "
" AE-610	" " " "
" AS-610	" " " "
" AS-710	" " " "
Hyamine 3500	Rohm and Haas Co.
Lubrol CF-50	I.G.I. Organics, Inc.
" PE	" " "

Lubrol PX	I.C.I. Organics, Inc.
Negomel AL 5	" " "
Norane R	Sun Chemical Corp.
Onamine RO	Onyx Chemical Co.
Priminox T 15	Rohm and Haas Co.
Rane-pel	Crown-Metro Corp.
Zelec DP ¹	E. I. du Pont de Nemours & Co.
Zelec NE	" " " " "

3. Combinations of Commercial Antistats or Surfactants²

Acetoquat CDAC (2.0)	and	Electrosol S-1-X (2.0)
" " (2.0)	"	Zelec DP (1.6)
" " (2.0)	"	Fluorocarbon complex (2.0)
" CPC (2.0)	"	Electrosol S-1-X (2.0)
" " (2.0)	"	Zelec DP (1.6)
" " (2.0)	"	Acetoquat CDAC (2.0)
" " (2.0)	"	Zelec NE (2.0)
AMS 303 (2.5)	"	Antara LM-400 (2.5)
" " (2.5)	"	Catanac SP (2.5)
" " (2.5)	"	Electrosol S-1-X (2.5)
" " (2.5)	"	Antara LF-200 (2.5)
Antara LF-205 (2.5)	"	Electrosol S-1-X (2.5)
" LM-400 (2.5)	"	Dehyquart C (2.5)
Aston AP (2.5)	"	Eponite 100 (1.0) ³

¹This compound had good antistatic properties (cf. Table 1), but the film containing 5% was not transparent.

²Per cent present in resin indicated in parentheses.

Dehyquart C (2.5)	and	Eponite 100 (1.0) ³
" (2.0)	"	Zelec DP (1.6)
Electrosol S-1-X (2.5)	"	Gafac RE-610(2.5)
" (2.0)	"	Stateeze (2.0)
Stannox 1166 (5.0)	"	Eponite 100 (1.0) ³
Zelec NE (2.0)	"	Fluorocarbon complex (2.0)

4. Unidentified derivatives prepared from commercial compounds and various reagents to obtain less water soluble or more effective antistatic agents.

Products of:

1. Complex organic acids and tetrakis(hydroxymethyl)phosphonium chloride.
2. Fluorocarbon acids and barium hydroxide.
3. Free acids of complex phosphate esters and sodium, barium, titanium, magnesium and zinc compounds.
4. Complex amines and Eponite 100³.
5. Gantrez AN⁴ and simple and complex alcohols.
 - " " polyvinylpyrrolidones.
 - " " chromium nitrate.
6. Ionac PP2000 series⁵ and cetyl chloride.
 - " " " methyl iodide.

³Epoxy resin, Shell Industrial Chemicals

⁴Poly(methyl vinyl ether/maleic anhydride), General Aniline & Film Corp.

⁵Vinylpyridine polymers and copolymers, Ionac Chemical Co.

5. Miscellaneous Compounds:

Acrysol ASE-60	Rohm and Haas Co.
Boron phosphonate, laboratory preparation	
	Pennwalt Corp.
Cab-O-Sil	Cabot Corp.
Copper powder	Ablestik Adhesive Co.
Molybdenum chloride, laboratory preparation	
	Pennwalt Corp.
" cluster derivatives, laboratory preparations	
	Pennwalt Corp.
Organic ammonium silicate	Philadelphia Quartz Co.
Phosphinates of Cr and Ti, laboratory preparations	
	Pennwalt Corp.
Polyvinylpyridine, PP 2000	Ionac Chemical Co.
" " PP 2020	" " "
" " PP 2040	" " "
Sulfonic acid derivative, laboratory preparation	
	Pennwalt Corp.
Tetraethyl orthosilicate	Fisher Scientific Co.

APPENDIX B

LESS EFFECTIVE ANTISTATS IN POLYVINYLIDENE CHLORIDE-
ACRYLONITRILE COPOLYMER

The following commercial compounds failed to give satisfactory antistatic performance when present in vinylidene chloride-acrylonitrile copolymer films at 5% concentration:

Acetoquat CDAC	Aceto Chemical Co.
" CPB	" " "
Ammonyx 27	Onyx Chemical Co.
" DME	" " "
Antara LM-405	General Aniline & Film Corp.
" LM-505	" " " "
Antistat 61	Charles Pfizer and Co., Inc.
Arquad 2HT-75	Armour Industrial Chemicals
Aston AP	Onyx Chemical Co.
Aston AP, Eponite 100	" " ", Shell Industrial Chem.
Atlas G-3780A	Atlas Chemical Industries, Inc.
Barquat SB 25	Barlow Chemical Co.
Carbowax 1500	Union Carbide Chemicals
Drewplast 017	Drew Chemical Corp.
" 029	" " "
" 032	" " "
" 050	" " "
Eponite 100	Shell Industrial Chemicals
Ethomeen 18/60	Armour Industrial Chemicals
Ethoquad 18/25	" " "

Gafac GB-520	General Aniline & Film Corp.
Gafstat AE-610	" " " "
" AD-510	" " " "
" AS-610	" " " "
" AS-710, Eponite 100	" " " "
	Shell Industrial Chemicals
Hyamine 3500	Rohm and Haas Co.
Lubrol CF	I.C.I. Organics, Inc.
" PX	" " "
Kodaflex A-D-2	Eastman Chemical Products, Inc.
Negomel AL 5	I.C.I. Organics, Inc.
Onamine RO	Onyx Chemical Co.
Phosphinates of Cr and Ti, laboratory preparation	
	Pennwalt Corp.
Stateeze 100	Fine Organics, Inc.
Titanium derivative of Gafac RE-610, laboratory preparation	
	Pennwalt Corp.