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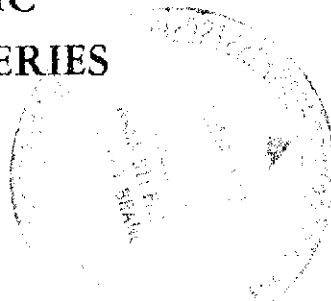
FACTORS INFLUENCING FLEXIBILITY, RESISTIVITY, AND ZINC DENDRITE PENETRATION RATE OF INORGANIC SEPARATORS FOR ALKALINE BATTERIES

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16. Abstract

Developmental work has resulted in a formulation which can improve the flexibility of the inorganic-organic-type separator for silver-zinc and nickel-zinc alkaline batteries. The effects of various fillers and reactive organic additives on separator volume resistivity are described. The effects of various inert fillers on the zinc dendrite penetration rate of the separator are shown. Conclusions regarding the operating mechanism of the separator are stated.

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FACTORS INFLUENCING FLEXIBILITY, RESISTIVITY, AND ZINC
DENDRITE PENETRATION RATE OF INORGANIC
SEPARATORS FOR ALKALINE BATTERIES

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SUMMARY

Efforts to improve the flexibility of the inorganic-organic separator have led to an initial understanding of the operating mechanism of the separator. Measurements of changes in volume resistivity, zinc dendrite penetration rate, and flexibility, resulting from substitution of materials, have provided this insight.

Flexibility of the separator can be controlled by limiting the filler volume content of the separator coating material. The volume resistivity of the separator appears to be controlled by reaction products resulting from the saponification of ester-type additives (plasticizers) and reactive fillers. The rate of zinc dendrite penetration is apparently controlled by the presence of unreactive fillers which create a physical barrier (tortuosity) against the zinc dendrite penetration.

INTRODUCTION

NASA has developed and tested a silver-zinc (Ag-Zn) cell which withstands heat sterilization and does not display the traditional life-limiting aspects of zinc electrode shape change (ref. 1). The separator used in the Ag-Zn cell belongs to a class of inorganic separators covered by the United States patents issued to the Astropower Division of McDonnell-Douglas Corporation. The particular separator material of interest is described in U. S. Patent 3,625,770 (ref. 2).

This inorganic-organic (I/O) separator consists of an asbestos bag which has been coated on the outside with a slurry coating composed of polyphenylene oxide (PPO) binder, a plasticizer (P-9750), and a filler mixture of pigmentary potassium titanate (PKT) and treated zirconium dioxide (ZrO_2). The solvent is chloroform ($CHCl_3$). The asbestos is fuel-cell-grade asbestos impregnated with 2-wt % PPO. Separator bags are then made by

gluing two sheets of the impregnated asbestos together along three edges, leaving an opening at the top. These bags are finally dip coated on the outside surface with the PPO/P-9750/PKT/ZrO_2 slurry. The principal drawback of this separator is that the coating material readily cracks when handled.

This separator material has been studied by both NASA and contractor personnel (ref. 3) in an effort to determine (1) the operating mechanism and (2) material substitutions to improve its flexibility. This report first describes the I/O separator; its constituents; and the effects of these constituents on flexibility, volume resistivity, and zinc dendrite penetration rate. Results are presented which show the effect on volume resistivity of substituting various reactive fillers and reactive organic additives (plasticizers). Data are then presented which show the effects of various inert fillers, both organic and inorganic, on inhibiting the rate of zinc dendrite penetration of the separator. Finally, based on these experimental data, several preliminary conclusions concerning the operating mechanism of this type of separator are stated.

The work described in this report was done in U.S. customary units. Conversion to SI units was for reporting purposes only.

INORGANIC-ORGANIC SEPARATOR AND VARIATIONS

Preparation of Inorganic-Organic Separator

The I/O separator described in reference 2 consists of a slurry coating on fuel-cell grade asbestos. As stated in the INTRODUCTION the coating consists of a binder, a plasticizer, a mixture of fillers, and a solvent. The binder is PPO resin, the plasticizer is a polymeric polyester, and the solvent is chloroform. The weight percent and volume percent of the binder and plasticizer are shown in table I.

The filler mixture consists of treated ZrO_2 and PKT in a weight ratio of 18:1. The weight percent and volume percent of each filler are shown in table I and are based on the theoretical percent of each in the dry film.

The formula for the I/O slurry is also shown in table I. This formula has two unusual characteristics for a coating material: its high filler volume content, and the large amount of plasticizer with respect to the binder. The PPO resin (binder) is only 10 wt % and 27 vol % of the total solids. The ratio of pigment (filler) to binder weight is 8:1. The filler volume content excluding plasticizer is 57 percent. This is well above the critical pigment volume concentration (CPVC) of 45 percent (ref. 4) required for good coating characteristics.

The plasticizer (P-9750)[1] is present in an amount equal to PPO in both volume and weight percent. In addition, this plasticizer is not completely soluble (i.e., not com-

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[1]Emery Industries, Cincinnati, O.

pletely compatible) with the PPO resin and as such should be considered an organic additive rather than a true plasticizer. The insolubility of the P-9750 in PPO is supported by the cloudiness and opacity of a cast film.

Scanning electron microscope (SEM) pictures of cast slurry films and separators reveal a porous surface. SEM side-view examination also reveals a porous coating from the surface to the asbestos substrate (ref. 5). This porosity is consistent with the high filler volume content (ref. 4).

Variations in Inorganic-Organic Formula and Other Formulations

The I/O formula was varied to evaluate the effects of constituents of the I/O slurry on volume resistivity and zinc dendrite penetration rates. In order to achieve a more flexible coating on asbestos, a truly flexible separator, it was necessary to formulate a new coating having a filler volume content ranging from 25 to 35 vol %. This involved the incorporation of different raw materials, plasticizers, and mixtures of fillers. The effects of these constituents on volume resistivity and zinc dendrite penetration rate were also measured.

Details of Tests and Measurements

Smatko, Weaver, and Kalhammer (ref. 3) cite 12 primary tests and five secondary tests considered necessary for separator characterization. This list was reduced to three tests so that the development program could progress more rapidly.

As long as the basic separator structure under consideration was PPO-impregnated, fuel-cell-grade asbestos with a PPO-based coating applied to it, the most critical tests were flexibility, volume resistivity, and zinc dendrite penetration rate measurements. In order to fully characterize the separator, other tests could be performed on materials after they had proved successful in cell tests. All results reported herein (on both the I/O formulation and other variations) are based on measurements where the asbestos substrate had been coated on both sides by either dipping or knife coating application. The I/O formulation applied in this manner represented the standard, and other formulations were compared with it.

Flexibility tests. - Flexibility tests were performed by carefully bending the separator around a mandrel of known diameter. Generally, diameters of 0.32, 0.63, 1.27, 1.95, 2.25, and 2.54 centimeters (1/8, 1/4, 1/2, 3/4, 7/8, and 1 in.) were used. Flexibility data published in the report indicate the smallest diameter mandrel over which the material was bent without visual cracking of the separator coating.

Volume resistivity tests. – The measure of separator resistance can be expressed as area resistivity or volume resistivity. For this report, all resistivity data are reported as volume resistivity (Ω-cm). All separator material tests for volume resistivity were preceded by an overnight immersion treatment in approximately 45 wt% potassium hydroxide (KOH) solution at 105° to 110° C. The test apparatus and procedure were based on those given by Salkind and Kelley in reference 6. In most cases, duplicate measurements were performed to establish precision. Resistivity measurements were performed in approximately 45-percent KOH at room temperature.

Zinc dendrite penetration tests. – Zinc dendrite penetration rate measurements were performed by following the technique and procedure described by Dalin and Solomon in reference 6. All separator samples were treated by an overnight immersion in approximately 45-percent KOH containing 76 g ZnO per 10^{-3} m^3 of solution. Treatment temperature was 105° to 110° C. Measurements of dendrite penetration were made in the KOH immersion solution at room temperature. Test results reported are based on a minimum of three measurements. Typically, four or five samples of separator material were tested to ascertain precision. Precision was normally less than ± 25 percent, including coating application and batch-to-batch formulations. Occasionally, a ± 50 percent value was encountered.

INORGANIC-ORGANIC SLURRY: COMPONENT AND COATING MEASUREMENTS

Measurements of flexibility, resistivity, and zinc dendrite rate were performed on the I/O formulation and variations of this formulation to determine the function of each component in separator performance. For these tests, asbestos was coated on both sides by dipping it into the slurry. This I/O standard had a measured volume resistivity ranging from 10 to 20 Ω-cm and a measured zinc dendrite penetration rate of 7×10^{-4} cm/min. And the separator material passed a bend test on a 1.9-cm- (0.75-in.-) diameter mandrel. Table II (item 3) shows these results.

The ratio indicated under each component in table II represents the weight ratio compared with that for the I/O formulation. The addition of PKT to the PPO and P-9750 coated on asbestos reduced the resistivity (table II, item 2) but had no effect on the zinc dendrite penetration rate when compared with that for the PPO and P-9750 combination (item 1). Decreasing the amount of ZrO$_2$ by a factor of 10 in the slurry formulation (table II, item 5) produced a factor-of-2 increase in the rate of zinc dendrite penetration (compared with item 3). This is also shown in figure 1. However, there was no measureable change in resistivity (table II, items 3 to 5). The flexibility of the coated asbestos markedly improved as the amount of ZrO$_2$ was reduced (1:1:1:0.1 formulation, item 5). The data presented in table II thus show (1) that PKT improved resistivity but had little effect on zinc dendrite penetration rate (see also ref. 5); (2) that ZrO$_2$ had a marked

effect on zinc dendrite penetration rate but had little effect on volume resistivity; and (3) that flexibility of the I/O formulation improved as the ZrO_2 content decreased. It was also observed that the flexibility improved with removal of PKT from the high pigment volume concentration (PVC) formulation.

As additional information, table II provides test data on the asbestos substrate with 2-percent-PPO impregnation (item 6) and coated with 13-percent PPO in chloroform (item 7).

PROBLEM OF FLEXIBILITY

Variations on the I/O formulation did not produce an adequately flexible separator. As a result a formula was developed which produced a separator of good flexibility (passed a bend test over a 0.32-cm (1/8-in.) mandrel) with a variety of filler mixture and which exhibited test behavior as good as or better than the I/O standard when test results were compared. This formula was developed by using PPO in chloroform, with a variety of plasticizers and fillers. The evaluation of these materials provided some further insight into separator operating characteristics.

Plasticizers

In general, a plasticizer is required to have certain essential properties related to the binder (resin) and the end use of the product (ref. 4). Some requirements applicable to this work would be

(1) Compatibility with the resin

(2) Resistance to extraction by water, solvents, etc.

(3) Resistance to chemical attack by alkali, acid, etc.

Because of the chemical structure of PPO and the alkaline environment, as mentioned earlier P-9750 does not meet the first requirement. In addition, because of the saponification of the polyester (the alkaline hydrolysis of an ester producing a salt of the organic acid and a glycol alcohol), P-9750 does not meet the third requirement. Therefore, this polymeric polyester plasticizer used with PPO should be considered as a "reactive" organic additive in this application.

The approach was to compare the flexibility of the separator with plasticizers both compatible and incompatible with the resin and to determine their effect on flexibility and volume resistivity. A formulation containing less than 45-vol % filler was used to ensure a good flexible film for comparing the volume resistivity of various plasticizers.

The substrate material used was a 0.0254-cm- (10-mil-) thick fiberglass mat impregnated with polystyrene. Fiberglass was used rather than asbestos because it

possessed a much lower volume resistivity (1.5 Ω-cm; last item, table III) than the 2-percent-PPO-impregnated asbestos (20 Ω-cm; item 6, table II). The lower volume resistivity of the fiberglass would not obscure the effects of the reactive plasticizer on resistivity. The various coatings were applied to the fiberglass mat on both sides by dipping.

The compatible plasticizers used with PPO were dibenzyl ether (DBE) and diallyl phthalate (DAP). When DBE and DAP were incorporated into the formula in table III, the coating materials were flexible, passing a bend test on a mandrel of 0.63-cm (1/4-in.) diameter. The volume resistivity of the DBE formulation was unacceptably high, while the DAP resistivity was closer to an acceptable value of 20 Ω-cm. DAP is an ester and is reactive with KOH.

Plastolein 9750 was tried in a reduced concentration along with another ester, dibutyl phthalate (DBP), and several long-chain fatty acids. The materials were all incompatible with PPO. Azelaic acid produced a highly brittle coating having a lower resistivity, possibly because of surface cracks. These data indicate that, for this class of materials and the substrate, an ester-type plasticizer is necessary to give the separator acceptable resistivity.

We postulated that separator volume resistivity was associated with the saponification products of the plasticizer, principally, the alcohol (glycol). In order to test this further, several Paraplex[2] polymeric polyester plasticizers with varying saponification numbers were mixed with PPO and chloroform solvent according to the formula given in table IV. These formulations were coated onto the fiberglass mat by dipping. The volume resistivity decreased linearly (correlation coefficient, R, -0.998) with increasing saponification numbers for the G-62, G-33, and G-50 plasticizers. But G-57, which had the highest saponification number, produced the highest resistivity. In order to determine the reason for the lack of correlation with G-57, the manufacturer was contacted. The manufacturer[2] provided the information that G-33, G-50, and G-57 were polyesters of adipic acid,[3] while G-62 was an epoxidized polyester of soybean oil. In addition, the G-33, G-50, and G-62 plasticizers all produce short-chain (two and three carbon) glycols, while the G-57 product alcohols were a mixture of a four-carbon glycol and a six-carbon alcohol. These product alcohols (glycols) are shown in table IV. By comparison, the P-9750 produces propylene glycol (short chain) upon saponification.

The solubility of short-chain glycols would be expected to decrease in a KOH solution with increasing carbon chain length. The correlation of volume resistivity with saponification number apparently holds if the product alcohol is a short-chain (two or three carbon) glycol. Hence, the function of the reactive organic additive (plasticizer) can be

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[2]Rohm and Haas Co., Philadelphia, Pa.

[3]The amount of free unreacted acid (carboxyl groups) in these plasticizers is less than 1 percent by weight.

viewed as producting, as a reaction product, a short-carbon-chain glycol soluble in KOH solution, which tends to improve volume resistivity.

Reactive Fillers

The incompatible plasticizers can be viewed as small globules of polyester dispersed in the PPO resin matrix. The globules react with the KOH solution to produce micropores containing reaction products. The same effect should be achieved with submicron-particle-size fillers which react completely with KOH. (Of course, short-chain alcohols would not be produced.)

Preliminary tests showed that the volume resistivity of the PPO resin on asbestos can be lowered by incorporating a reactive filler, such as calcium silicate, rather than by using reactive organic additives, such as a polymeric polyester. PPO-coated asbestos had a volume resistivity of about 200 Ω-cm. But PPO containing only calcium silicate (particle size, 0.03 μm) coated onto asbestos produced a linear decrease in volume resistivity with increasing volume percent filler when plotted on a semilog scale (correlation coefficient, R, -0.999), as shown in figure 2. The dispersion of the calcium silicate in PPO can be viewed as analogous to the dispersion of plasticizer globules.

Based on these observations, PKT was replaced with fillers that would improve coating resiliency and flexibility, would chemically react with KOH, and would form small micropores which might improve volume resistivity.

Three reactive fillers (calcium silicate ($CaSiO_3$), aluminum oxide (Al_2O_3), and silicon dioxide (SiO_2)), all having submicron-size particles, were selected for incorporation into the separator coating. Calcium silicate, reacting in the alkali-rich electrolyte, presumably forms a low-molecular-weight soluble silicate and insoluble calcium hydroxide. Aluminum oxide, reacting with KOH, forms soluble aluminate ions. Silicon dioxide, reacting with KOH, would tend to form soluble polymeric silicate anions.

The formulation shown in table V produced good flexible films except for those noted, which did not pass a bend test over a 1.27-cm- (1/2-in. -) diameter mandrel. The data presented in table V were obtained from dip coatings on asbestos. The $CaSiO_3$ data in table V and figure 3 show a good linear relation between volume resistivity and moles of reactive filler, with a correlation coefficient R of -0.984. Volume resistivity decreases with increasing filler content. These data show that the volume resistivity of separator formulations can be improved by using certain chemically reactive pigments.

ZINC DENDRITE PENETRATION RATE STUDIES

Comparison of Inert Fillers: Treated Zirconia and Magnesium Titanate

The effects of increasing the content of the inert fillers ZrO_2 and magnesium titanate[4] on zinc dendrite penetration rate are compared in figure 4. The number near each data point represents the weight (in grams) of filler used in the formula. The base formula tested is also shown. The PKT has been removed, and a small amount of submicron-particle-size SiO_2 (Cab-O-Sil) has been added along with the inert filler to improve film flexibility and volume resistivity. With the PKT removed from the formula, these coatings on asbestos were flexible enough to pass a bend test on a 0.63-cm-(1/4-in. -) diameter mandrel even at PVC's of greater than 50 percent. The linear fit of the magnesium titanate data was better than that for ZrO_2 ($R_{Mg_2TiO_3}$ = -0. 977 against R_{ZrO_2} = -0.932), although there is an apparent loss of linearity about the CPVC, approximately 45 vol %, for both. (The PVC for each filler in PPO is defined as cu cm (filler)/[cu cm (filler) + cu cm (PPO)].) The three lowest PVC values for ZrO_2 have an R of -0.999 (solid line in fig. 4(b)). (The vertical lines through each data point indicate the standard deviation about the point resulting from multiple measurements.) Based on the precision of the measurements, there is not much difference in zinc dendrite penetration response for ZrO_2 or magnesium titanate. Combining the data for both materials yields an R of -0. 95. The major advantage of magnesium titanate over treated ZrO_2 is its lower cost. Presently, the treated ZrO_2 is about nine times more expensive.

Figures 4(a) and (b) also show a data point denoted 0. This point indicates the response of the formula to the volume percent of Cab-O-Sil in PPO with no inert filler present. The increase and subsequent decrease in zinc dendrite penetration rate as inert filler content increased, probably relates to the packing effect of the fillers in the coating (ref. 4). An optimum condition resulting from just the right mixture of fillers in the formulation probably exists, but it has not been determined.

Effect of Various Inert Fillers

In addition to magnesium titanate as a replacement for the costly treated ZrO_2, a series of titanates and zirconates were evaluated to study their relative effects on both zinc dendrite penetration rate and volume resistivity. The results are shown in table VI. The formulation which would produce a flexible film having acceptable volume resistivity was used. Various inert fillers (treated ZrO_2, calcium titanate, magnesium titanate,

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[4]Magnesium Titanate C (product code, TICON MT(C), no. 504) product of TAM Division of NL Industries, Inc. , Niagara Falls, N. Y.

zinc magnesium titanate, lead titanate, calcium zirconate, and polyethylene microspheres) were incorporated at the weight shown (36 g). All formulations were ground 22 hours in a porcelain jar mill. The coatings were applied to 0.0254-cm- (10-mil-) thick asbestos (both sides) in two passes by using a knife edge (Gardner Blade). Total thickness (coating plus asbestos) is shown in table VI along with the density of the inert filler. The precision of the volume resistivity measurements is typically ± 10 percent, and that of the zinc dendrite penetration rate ± 25 percent. The results represent equal weight percent but not equal volume percent. There appears to be no correlation between zinc dendrite penetration rate and filler weight or volume percent. It is quite obvious that the formulation incorporating lead titanate is superior to treated ZrO_2 for inhibiting zinc dendrite penetration rate on both a weight percent and volume percent basis.

The data in table II show no significant increase in volume resistivity when the content of treated ZrO_2 was increased. This would indicate that there is little pertinent ion exchange or chemical interaction between K^+ and OH^- ions and the treated ZrO_2 filler.

The idea that the inert filler represents a physical barrier to zinc dendrite penetration was tested by using an organic filler to rule out any pertinent ion exchange or chemical effects. The filler was polyethylene (PE) microspheres. Results on zinc dendrite penetration rate and volume resistivity are shown in table VI along with the inorganic filler data. Data on the effect of increasing the PE content on zinc dendrite penetration rate and volume resistivity are shown in table VII. The formulation tested is also shown. The rate of zinc dendrite penetration decreased linearly as the PE weight content increased (fig. 5). The value of R was -0.994. All three data points are above the critical pigment volume content.

From the data in tables VI and VII it was concluded that, in addition to treated ZrO_2, other inert fillers, both organic and inorganic, are effective in stopping zinc dendrite penetration. The results on PE microspheres, an organic filler, indicate that the inert fillers act as a physical barrier against zinc dendrite penetration rather than having any pertinent chemical effect, such as ion exchange. Although no data have been collected to confirm this, the barrier effect is probably related to the tortuosity of the path through the plasticizer saponification products and resin matrix created by the packing effect of inert particles. The effect should be related to particle size, uniformity of particle size, the degree of "wettability" with the resin-plasticizer combination, and the homogeneity of filler dispersion and film coating on the asbestos.

CONCLUDING REMARKS

By using the preceding information, the details of an operating mechanism for the slurry coating used on the I/O separator in alkaline batteries can be put together. Significant details are as follows:

1. Acceptable volume resistivity is dependent upon the use of a ester-type plasticizer with polyphenylene oxide (PPO). Further, when saponified, this plasticizer must produce a short-chain (two or three carbons) glycol for optimum volume resistivity. The volume resistivity can be further improved by the incorporation of a soluble filler or fillers reactive with KOH.

2. Good flexibility is obtained by maintaining a reasonable volume ratio of filler to binder. The exclusion of fibrous pigments is desirable.

3. The zinc dendrite penetration rate is controlled by the presence of certain inert fillers. The tortuosity resulting from the presence of the inert filler retards the zinc dendrite penetration rate.

These points may be a simplification of the separator operating mechanism. But if true, the concept may not be unique to just the PPO/Plastolein 9750/pigmentary potassium titanate (PKT)/zirconium dioxide (ZrO_2) system on asbestos.

The final test of any separator used in the alkaline silver-zinc or nickel-zinc cells will be how well it performs in actual operation. Modification of the I/O formulation to improve flexibility may improve or impair the performance of the separator in cell operation. Only the results of cell tests on some of the formulations described in this report will show this.

Lewis Research Center,
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TABLE I. - INORGANIC-ORGANIC SLURRY

COATING FORMULA

Component	Weight, g	Dry weight, wt %	Dry volume, vol %
PPO (binder)	47	10	27. 7
CHCl$_3$	360	--	----
P-9750 (plasticizer)	47	10	27. 7
CHCl$_3$	60	--	----
PKT (filler)	19	4	3. 1
ZrO$_2$ (filler) treated (calcium stabilized)	356	76	41. 5

TABLE II. - RESISTIVITY AND ZINC DENDRITE

PENETRATION RATE OF SLURRY

COATING COMPONENTS

[Slurry coatings, 0.0051 to 0.0102 cm (2 to 4 mils) thick applied by dipping.]

Component[a]	Volume resistivity, Ω-cm	Zinc dendrite penetration rate, cm/min	Diameter of mandrel used in bend tests[b]	
			cm	in.
PPO:P-9750 (1:1)	23	1.53×10^{-3}	0.63	1/4
PPO:P-9750:PKT (1:1:1)	10	1.49	.63	1/4
PPO:P-9750:PKT:ZrO$_2$ (1:1:1:1)	16	.74	1.95	3/4
PPO:P-9750:PKT:ZrO$_2$ (1:1:1:0.5)	14	.84	1.95	3/4
PPO:P-9750:PKT:ZrO$_2$ (1:1:1:0.1)	15	1.52	1.27	1/2
2-Percent PPO[c]	20	1.6	.63	1/4
13-Percent PPO	180	<0.025	.63	1/4

[a]All coatings on asbestos except as indicated.

[b]Flexibility is good if separator material passes bend test on 0.63-cm (1/4-in.) mandrel, poor if it does not pass bend test on 1.27-cm (1/2-in.) mandrel.

[c]Impregnated into asbestos.

TABLE III. - EFFECT OF PLASTICIZER

FUNCTIONAL GROUP ON RESISTIVITY

[Slurry coating formula: PPO, 47 g; $CHCl_3$, 400 g; plasticizer, 14 g; PKT, 19 g; ZrO_2, 45 g; Cab-O-Sil, 1 g. Substrate: 0.0254-cm- (10-mil-) thick fiberglass impregnated with polystyrene. Coatings applied by dipping.]

Plasticizer	Compatible[a] with PPO	Volume resistivity, Ω-cm
Dibenzyl ether (DBE)	Yes	270
Dibutyl phthalate (DBP)	No	150
Diallyl phthalate (DAP)	Yes	33
Plastolein 9750 (P-9750)[b]	No	16
Stearic acid		26 500
Capric acid		4 500
n-Nonanoic acid		1 700
Azelaic acid		80
Fiberglass substrate	---	1.5

[a]Determined on the basis of clarity or opacity of film (consisting only of resin, solvent, and plasticizer) cast on glass.

[b]Plastolein (P-9750) is a polymeric polyester plasticizer. It is produced by the esterification of azelaic acid and 1,2 propylene oxide. It also contains a small amount (<2 percent) of pelargonic acid.

TABLE IV. - EFFECT OF POLYESTER PLASTICIZER

SAPONIFICATION NUMBER ON RESISTIVITY

[Slurry coating formula: PPO, 15 g; $CHCl_3$, 100 g; plasticizer, 5 g. Substrate, 0.0254-cm- (10-mil-) thick fiberglass impregnated with polystyrene. Coatings applied by dipping.]

Plasticizer[a]	Saponification number[b]	Resistivity, Ω-cm	Reaction product alcohol
Paraplex G-33[c]	435	21.7	1, 2-propylene glycol
Paraplex G-50[c]	500	12.6	1, 2-propylene glycol
Paraplex G-62[c]	183	48.8	Ethylene glycol
Paraplex G-57	526	168	2-ethyl hexanol; 1-3 butylene glycol

[a]"Paraplex and Monoplex Plasticizers - Summary of Physical and Performance Properties," Industrial Chemicals Department, Rohm and Haas Co., Philadelphia, Pa.

[b]Saponification number is defined as the milligrams of potassium hydroxide required to saponify 1 gram of fat (ester).

[c]Linear correlation coefficient, R, -0.998.

TABLE V. - EFFECT OF SOLUBILITY OR REACTIVITY

OF FILLER ON RESISTIVITY

[Slurry coating formula: 47 g; $CHCl_3$, 400 g; P-9750, 47 g; filler, as indicated, ZrO_2, 36 g. Substrate: 0.0254-cm - (10-mil-) thick asbestos sheet. Coatings applied by dipping.]

Filler	Filler weight, g	Moles	Particle size, μm	Surface area, m^2/g	Volume resistivity, Ω-cm
$CaSiO_3$[a]	19	0.16	[b]0.030	82-92	12.5
	36	.31			10.5
	53.5	.46			8.1
	[c]80	.69			6.6
Al_2O_3	19	0.19	[d]0.030	100	9.4
	[c]60	.59			7.8
SiO_2	[c]19	0.32	[e]0.012	200	4.8

[a]Linear correlation coefficient, R, -0.984.

[b]Product Bulletin "Silene EF, L," Chemical Division, Pittsburgh Plate Glass Co., Pittsburgh, Pa.

[c]Did not pass bend test over 1.27-cm- (1/2-in.-) diameter mandrel.

[d]Product Bulletin "Alon Fumed Alumina/Al_2O_3," Cabot Corp., Boston, Mass.

[e]Product Bulletin "Cab-O-Sil - How To Use It, Where to Use It," Cabot Corp., Boston, Mass.

TABLE VI. - EFFECT OF VARIOUS INERT FILLERS ON ZINC

DENDRITE PENETRATION RATE AND RESISTIVITY

[Slurry coating formula: PPO, 47 g; $CHCl_3$, 400 g; P-9750, 47 g; $CaSiO_3$, 19 g; filler, 36 g. Substrate: 0.0254-cm- (10-mil-) thick asbestos sheet. Coatings applied by knife edge. Diameter of mandrel used in bend test, 0.32 cm (1/8 in.).]

Filler	Density of filler, g/cm^3	Coating thickness cm	Coating thickness mil	Filler volume, vol %	Volume resistivity, Ω-cm	Zinc dendrite penetration rate, cm/min
Zirconium dioxide (treated)	[a]5.4	0.038	15	13.2	7.8	1.6×10^{-3}
Calcium titanate	[a]3.98	.035	14	17.0	16.6	1.2
Magnesium titanate	[a]3.36	.038	15	19.6	9.1	1.1
Zinc magnesium titanate	[a]4.2	.035	14	16.3	18	1.1
Lead titanate	[a]7.54	.043	17	9.8	23.1	.63
Calcium zirconate	[a]4.38	.035	14	15.7	10.9	1.2
Polyethylene (PE) micro-spheres (FN-510)	[b].92	.035	14	47.1	19.6	1.1

[a]TAM Division of NL Industries, Niagara Falls, N. Y.

[b]U. S. Industrial Chemicals Co., New York, N. Y.

TABLE VII. - EFFECT OF POLYETHYLENE

MICROSPHERE CONTENT ON ZINC

DENDRITE PENETRATION RATE

AND RESISTIVITY

[Slurry coating formula: PPO, 47 g; $CHCl_3$, 400 g;
P-9750, 47 g; Cab-O-Sil, 4.8 g; PE microspheres,
as indicated. Substrate: 0.0254-cm- (10-mil-)
thick asbestos sheet. Coatings applied by knife
edge. Linear correlation coefficient, R, -0.981.]

Weight of PE microspheres, g	PE volume, vol %	Volume resistivity, Ω-cm	Zinc dendrite penetration rate, cm/min
36	47.1	19.5	1.1×10^{-3}
71	63.7	12.5	.65
142	77.8	18.3	.45
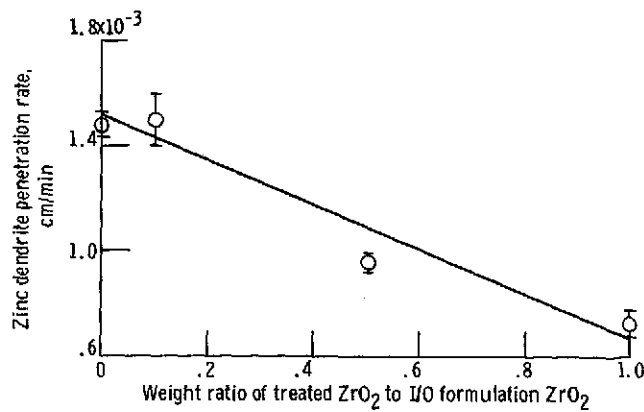
Figure 1. - Zinc dendrite penetration rate as function of vary-
ing amounts of ZrO_2 in I/O formulation. Linear correlation
coefficient, R, -0.9545.
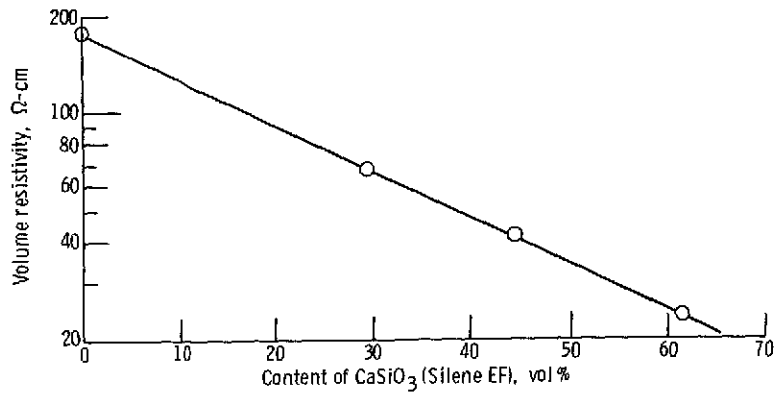
Figure 2. - Volume resistivity as function of volume percent of CaSiO₃ in PPO. Linear correlation coefficient, R, -0.9999; particle size, 0.03 μm; no other ingredients.
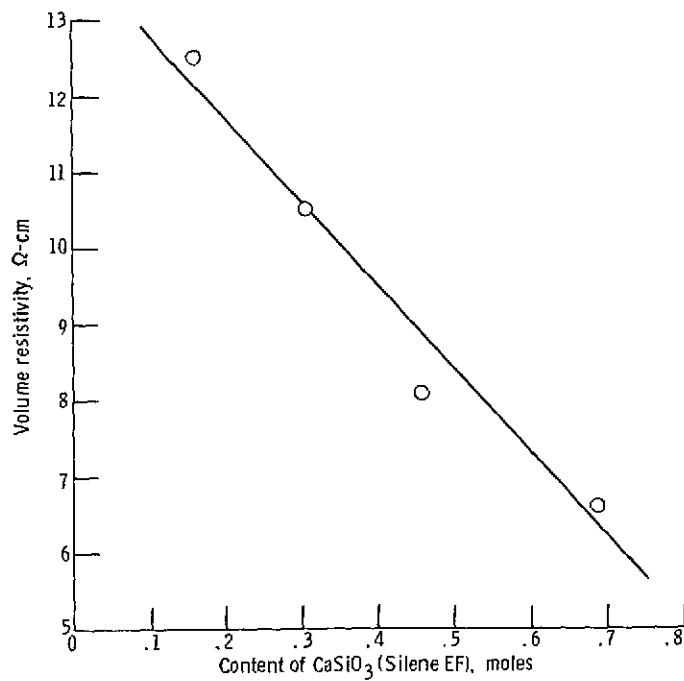

Figure 3. - Volume resistivity as function of moles of CaSiO₃ in coating formulation. (See table V for formula.)
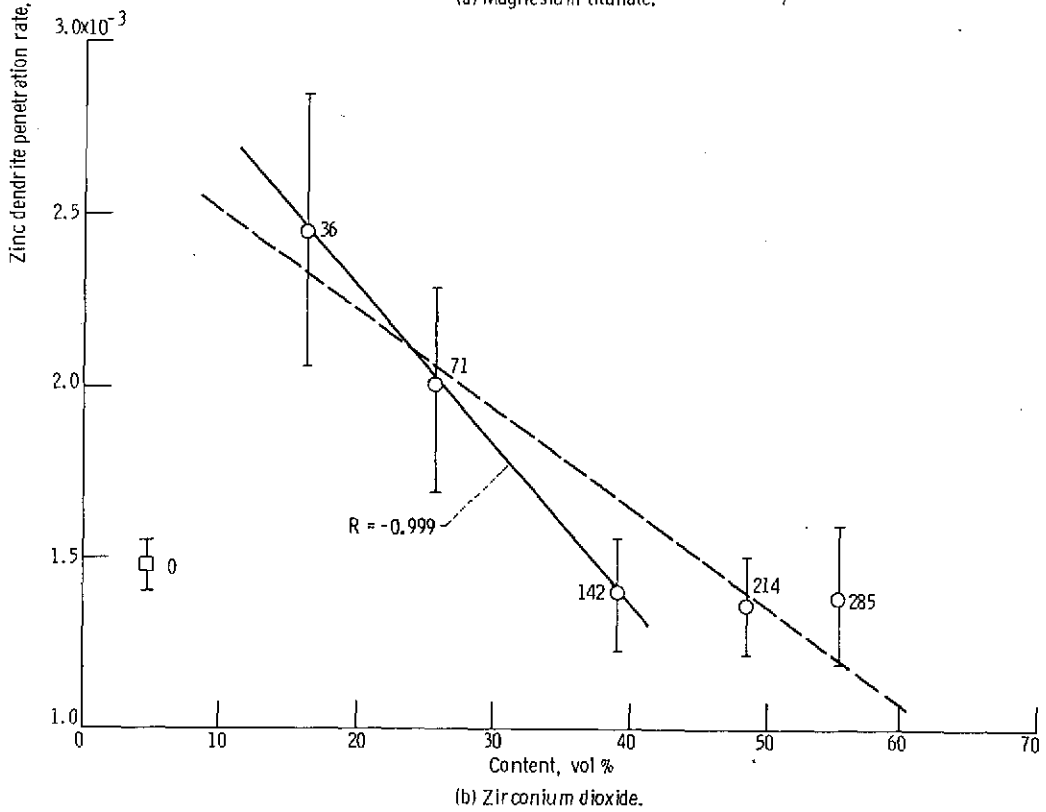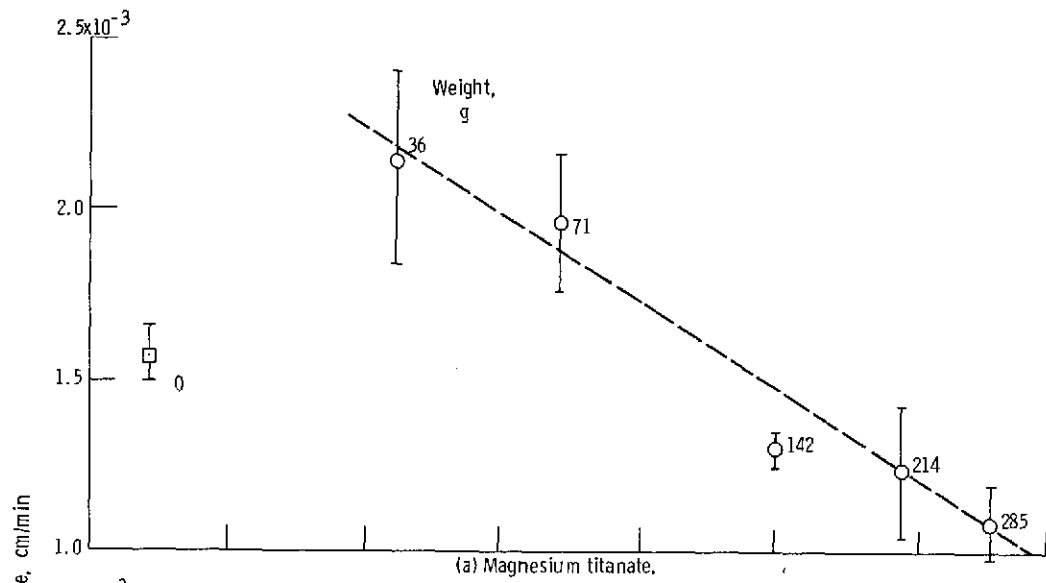
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Figure 4. - Zinc dendrite penetration rate as function of volume percent of magnesium titanate or zirconium dioxide in coating formulation. (Formula: PPO, 47g; CHCl₃, 400g; P-9750, 47g; Cab-O-Sil, 4.8g; magnesium titanate or zirconium dioxide as indicated.)
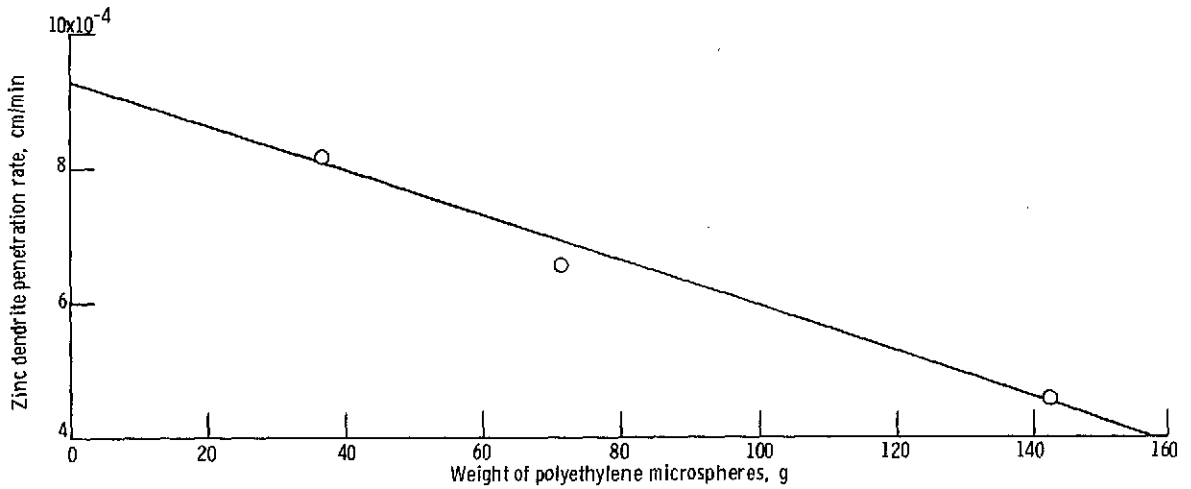
Figure 5. - Zinc dendrite penetration rate as function of polyethylene microsphere content in coating formulation. (See table VII for formula.)