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The Use of Poly(Metal Phosphinates) as Antistatic Coatings, Multi-Purpose Fluid Thickeners, and Thermally Stable Coatings

Final Report

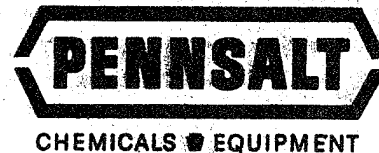
by G. H. Dahl, O. S. Sprout, Jr., N. D. Peschko, and B. P. Block

16 February 1967 - 15 November 1967

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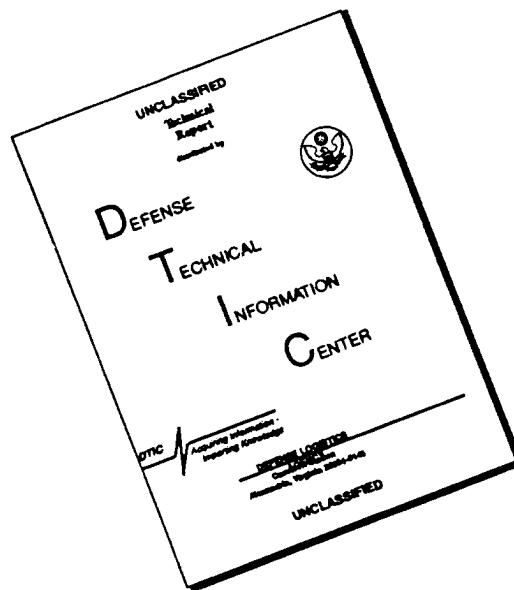
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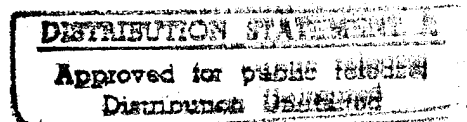
16 February 1967 - 15 November 1967

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This work was conducted at the Technological Center of Pennsalt Chemicals Corporation, King of Prussia, Pa. Many of the evaluations were made by personnel of the Aero Materials Department, Naval Air Development Center. Mr. Coleman Nadler was Project Engineer.

## Abstract

Water-repellent and transparent plasticized poly(metal phosphinate) compositions were developed for antistatic coatings on polyethylene. Coatings based on  $\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPBu}_2\text{O})_2$ ,  $\text{Cr}(\text{H}_2\text{O})(\text{OH})[\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$ ,  $\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPPh}_2\text{O})_2$ , and  $\text{TiO}(\text{OPPh}_2\text{O})_2$  all dissipated a 5 kV positive charge in one second or less. Coatings based on  $\text{TiO}(\text{OPPh}_2\text{O})_2$  also dissipated a 5 kV negative charge in one second or less and were essentially not tacky.

The tris(phosphinate)  $\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}][\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$  prepared in situ was found to be an effective thickener for a variety of lubricant fluids in the 5-14% concentration range. A thickener with substantially greater thermal stability was prepared by the reaction of  $\text{Cr}(\text{H}_2\text{O})(\text{OH})[\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$  with  $\text{Me}(\text{Ph})\text{P}(\text{O})\text{OH}$ . Greases made from DC550 and these thickeners exhibit drop points generally above 600° F. and good antiwear properties; however, their bearing performance is limited.

Coatings of  $\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}][\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$  pigmented with  $\text{TiO}_2$  adhere well to cold-rolled 1010 steel and exhibit good hardness and resistance to jet oil or water. They can tolerate 250° C. in air for one hour but degrade at 300° C. The use of more stable chromium(III) tris(phosphinates), i.e., tris(phosphinates) containing no alkyl groups other than methyl, for coatings was briefly explored. Although the coatings based on these showed superior resistance to jet oil and water, adhesion to the 1010 steel was not satisfactory for the formulations investigated.

## Table of Contents

	<u>Page</u>
Foreword	ii
Abstract	iii
I. Introduction	1
A. General	1
B. Symbolism	1
II. Experimental	4
A. Reagents	4
B. Sample Preparation	5
1. Antistatic Materials	5
2. Greases	6
3. Protective Coatings	7
C. Evaluation	8
1. General	8
2. Antistatic Materials	8
3. Greases	9
4. Protective Coatings	9
III. Results and Discussion	10
A. Antistatic Materials	10
B. Greases	17
C. Protective Coatings	22
IV. References	29

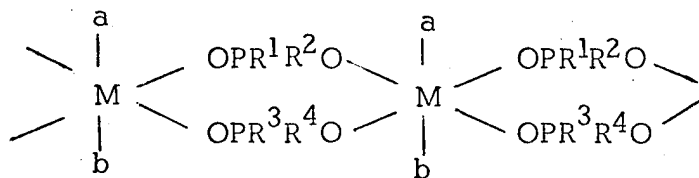
## List of Tables and Figures

	<u>Page</u>
Table 1. Meanings of Abbreviations	2
Table 2. Specific Resistance of $\text{CHCl}_3$ Solutions	11
Table 3. Properties of Poly(Metal Phosphinate) Coatings on Polyethylene	16
Table 4. Survey of Various Poly(Metal Phosphinates) as Thickeners for DC550	19
Table 5. Properties of Greases	21
Table 6. Preliminary Studies of Coatings of $\text{Cr}(\text{DO})(\text{MP})_2$ on Clean Cold-rolled 1010 Steel	23
Table 7. Effect of Using Partially Cured $\text{Cr}(\text{DO})(\text{MP})_2$ for Coating Cold-rolled 1010 Steel by Dipping in 1:1 THF:Toluene Solution	25
Table 8. Effect of Pigment Loading on Coatings of $\text{Cr}(\text{DO})(\text{MP})_2$ in Cold-rolled 1010 Steel	26
Table 9. Exploratory Studies of Tris(Phosphinate) Coatings Other than $\text{Cr}(\text{DO})(\text{MP})_2$	28
Figure 1. Resistivity of Chromium(III) Hydroxyaquo Bis(Phosphinates) in $\text{CHCl}_3$ as a Function of Concentration	13
Figure 2. Resistivity of Zirconium and Titanium Phosphinates in $\text{CHCl}_3$ as a Function of Concentration	14

## I. Introduction

### A. General

The poly(metal phosphinates), a novel family of coordination polymers, were discovered at Pennsalt Chemicals Corporation in studies partially sponsored by the Chemistry Branch of the Office of Naval Research. In general terms when there are two bridges per coordination center M these polymers can be formulated



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There may or may not be additional groups a and/or b bonded to M depending upon its coordination number. These polymers are unusual in that they possess a completely inorganic backbone consisting of metal atom centers and OPO bridges. The thermal and oxidative stability of this backbone far exceeds that of ordinary organic polymers. By appropriate choice of side groups and coordination centers it is possible to obtain polymers with a wide variety of properties.

Interest in exploiting these polymers led the Naval Air Systems Command to sponsor development studies in the areas of antistatic coatings, thickening agents to convert synthetic fluids to greases useful at elevated temperatures, thermally stable elastomers, and thermally stable coatings. The work reported here is a continuation of earlier studies<sup>1,2</sup> made in the first three areas under contract N156-46781 with the Naval Air Engineering Center. The development of antistatic coatings and fluid thickeners has continued, but the study of thermally stable elastomers has been replaced by the study of protective coatings. Each area investigated is discussed separately in this report.

### B. Symbolism

The polymers and certain other materials in this report are designated by abbreviations. A compilation of the abbreviations employed in addition to those used in Chemical Abstracts is presented in Table 1.

Table 1  
Meanings of Abbreviations

For Polymers

1. Co(DB) <sub>2</sub>	Co(OPBu <sub>2</sub> O) <sub>2</sub>
2. Co(DB)(DO)	Co(OPBu <sub>2</sub> O)(OPOc <sub>2</sub> O)
3. Co(DO) <sub>2</sub>	Co(OPOc <sub>2</sub> O) <sub>2</sub>
4. Co(DO) <sub>1.2</sub> (MP) <sub>0.8</sub>	Co(OPOc <sub>2</sub> O) <sub>1.2</sub> [OP(Me)(Ph)O] <sub>0.8</sub>
5. Co(DP)(MP)	Co(OPPh <sub>2</sub> O)[OP(Me)(Ph)O]
6. Cr(A)(H)(BDP)(MP)	Cr(H <sub>2</sub> O)(OH)[OP(p-C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> ) <sub>2</sub> O]- [OP(Me)(Ph)O]
7. Cr(A)(H)(DB) <sub>2</sub>	Cr(H <sub>2</sub> O)(OH)(OPBu <sub>2</sub> O) <sub>2</sub>
8. Cr(A)(H)(DO) <sub>2</sub>	Cr(H <sub>2</sub> O)(OH)(OPOc <sub>2</sub> O) <sub>2</sub>
9. Cr(A)(H)(DO)(MP)	Cr(H <sub>2</sub> O)(OH)(OPOc <sub>2</sub> O)[OP(Me)(Ph)O]
10. Cr(A)(H)(DP) <sub>2</sub>	Cr(H <sub>2</sub> O)(OH)(OPPh <sub>2</sub> O) <sub>2</sub>
11. Cr(A)(H)(MP) <sub>2</sub>	Cr(H <sub>2</sub> O)(OH)[OP(Me)(Ph)O] <sub>2</sub>
12. Cr(DH) <sub>0.9</sub> (DPDT) <sub>0.1</sub> (MP) <sub>2</sub>	Cr(OPHx <sub>2</sub> O) <sub>0.9</sub> (SPPPh <sub>2</sub> S) <sub>0.1</sub> [OP(Me)(Ph)O] <sub>2</sub>
13. Cr(DH)(MP) <sub>2</sub>	Cr(OPHx <sub>2</sub> O)[OP(Me)(Ph)O] <sub>2</sub>
14. Cr(DHP)(MP) <sub>2</sub>	Cr[OP(OH) <sub>2</sub> O][OP(Me)(Ph)O] <sub>2</sub>
15. Cr(DM)(DP) <sub>2</sub>	Cr(OPMe <sub>2</sub> O)(OPPh <sub>2</sub> O) <sub>2</sub>
16. Cr(DM)(MP) <sub>2</sub>	Cr(OPMe <sub>2</sub> O)[OP(Me)(Ph)O] <sub>2</sub>
17. Cr(DO)(MP) <sub>2</sub>	Cr(OPOc <sub>2</sub> O)[OP(Me)(Ph)O] <sub>2</sub>
18. Cr(DP)(MP) <sub>2</sub>	Cr(OPPh <sub>2</sub> O)[OP(Me)(Ph)O] <sub>2</sub>
19. Cr(DP) <sub>2</sub> (MP)	Cr(OPPh <sub>2</sub> O) <sub>2</sub> [OP(Me)(Ph)O]
20. Cr(MP) <sub>3</sub>	Cr[OP(Me)(Ph)O] <sub>3</sub>
21. G-Cr(A)(H)(DP) <sub>2</sub>	Green form of polymer 10
22. H-Cr(A)(H)(MP) <sub>2</sub>	High-molecular-weight form of polymer 11
23. R-Cr(A)(H)(MP) <sub>2</sub>	Polymer 11 prepared with revised stoichiometry
24. Mn(DB)(DO)	Mn(OPBu <sub>2</sub> O)(OPOc <sub>2</sub> O)
25. Mn(DO)(DP)	Mn(OPOc <sub>2</sub> O)(OPPh <sub>2</sub> O)
26. Mn(DO)(DP) <sub>0.2</sub> (MP) <sub>0.8</sub>	Mn(OPOc <sub>2</sub> O)(OPPh <sub>2</sub> O) <sub>0.2</sub> [OP(Me)(Ph)O] <sub>0.8</sub>
27. Mn(DO) <sub>1.2</sub> (MP) <sub>0.8</sub>	Mn(OPOc <sub>2</sub> O) <sub>1.2</sub> [OP(Me)(Ph)O] <sub>0.8</sub>
28. Mn(MP) <sub>2</sub>	Mn[OP(Me)(Ph)O] <sub>2</sub>
29. Ti(DP) <sub>4</sub>	Ti(OPPh <sub>2</sub> O) <sub>4</sub>
30. TiO <sub>0.5</sub> (DO)(DP) <sub>2</sub>	TiO <sub>0.5</sub> (OPOc <sub>2</sub> O)(OPPh <sub>2</sub> O) <sub>2</sub>
31. TiO(DO)(DP)	TiO(OPOc <sub>2</sub> O)(OPPh <sub>2</sub> O)
32. TiO(DO)(MP)	TiO(OPOc <sub>2</sub> O)[OP(Me)(Ph)O]
33. TiO <sub>1.1</sub> (DO) <sub>0.6</sub> (MP) <sub>1.2</sub>	TiO <sub>1.1</sub> (OPOc <sub>2</sub> O) <sub>0.6</sub> [OP(Me)(Ph)O] <sub>1.2</sub>
34. TiO(DP) <sub>2</sub>	TiO(OPPh <sub>2</sub> O) <sub>2</sub>
35. TiO(MP) <sub>2</sub>	TiO[OP(Me)(Ph)O] <sub>2</sub>
36. Zn(DB)(DF)	Zn(OPBu <sub>2</sub> O)[OP(C <sub>2</sub> H <sub>4</sub> C <sub>9</sub> F <sub>19</sub> ) <sub>2</sub> O]
37. Zn(DB)(DO)	Zn(OPBu <sub>2</sub> O)(OPOc <sub>2</sub> O)
38. Zr(DP) <sub>4</sub>	Zr(OPPh <sub>2</sub> O) <sub>4</sub>
39. ZrO(DB)(DO)	ZrO(OPBu <sub>2</sub> O)(OPOc <sub>2</sub> O)
40. ZrO(DP) <sub>2</sub>	ZrO(OPPh <sub>2</sub> O) <sub>2</sub>

Table 1 (continued)

Other abbreviations

1. DBCMP	$\text{ClCH}_2\text{P}(\text{O})(\text{OBu})_2$
2. DBP	$\text{o-C}_6\text{H}_4(\text{COOBu})_2$
3. DBS	$(\text{CH}_2)_8(\text{COOBu})_2$
4. o-DCB	$\text{o-C}_6\text{H}_4\text{Cl}_2$
5. DBBP	$\text{BuP}(\text{O})(\text{OBu})_2$
6. DEEP	$\text{EtP}(\text{O})(\text{OEt})_2$
7. EP	extreme pressure
8. Hx	$\text{n-C}_6\text{H}_{11}$
9. Oc	$\text{n-C}_8\text{H}_{17}$
10. TBP	$(\text{BuO})_3\text{PO}$
11. TCP	$(\text{Me}_2\text{C}_6\text{H}_3\text{O})_3\text{PO}$
12. TEP	$(\text{EtO})_3\text{PO}$
13. TGA	thermogravimetric analysis
14. THF	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$

## II. Experimental

### A. Reagents

Unless otherwise specified all reagents and solvents were obtained commercially and used without further purification. The phosphinic acids  $\text{Me}_2\text{P}(\text{O})\text{OH}$ ,  $\text{Bu}_2\text{P}(\text{O})\text{OH}$ ,  $\text{Hx}_2\text{P}(\text{O})\text{OH}$ ,  $\text{Oc}_2\text{P}(\text{O})\text{OH}$ ,  $\text{Me}(\text{Ph})\text{P}(\text{O})\text{OH}$ , and  $\text{Ph}_2\text{P}(\text{O})\text{OH}$  were in general prepared by methods previously described, <sup>3,4,5,6</sup> and  $(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{P}(\text{O})\text{OH}$  was prepared by a modification of published methods. <sup>7,8</sup> Technical  $\text{Ph}_2\text{P}(\text{S})\text{SH}$  (Lubrizol Corp.) was recrystallized from iso-PrOH to yield material melting 55-56°.

Most of the poly(metal phosphinates) were from Pennsalt stock made with appropriate stoichiometry by methods similar to those reported in the literature. <sup>3,9,10,11</sup>  $\text{Cr}(\text{A})(\text{H})(\text{BDP})(\text{MP})$  was prepared from  $\text{Cr}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  and an equimolar mixture of  $\text{Me}(\text{Ph})\text{P}(\text{O})\text{OH}$  and  $(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{P}(\text{O})\text{OH}$ . The reaction yielded two fractions which were combined and used to represent  $\text{Cr}(\text{A})(\text{H})(\text{BDP})(\text{MP})$  in preliminary evaluation.  $\text{H-Cr}(\text{A})(\text{H})(\text{MP})_2$  was made by aging a 3% (w/v)  $\text{CHCl}_3$  solution of the conventionally prepared polymer for three weeks at 55°, and  $\text{R-Cr}(\text{A})(\text{H})(\text{MP})_2$  was made with only a slight excess of  $\text{Me}(\text{Ph})\text{P}(\text{O})\text{OH}$  instead of the 15% excess usually employed. The manganese phosphinates were prepared in analogous fashion to the zinc and cobalt phosphinates <sup>9</sup>, the zirconium in analogous fashion to the titanium phosphinates. <sup>10</sup> The chromium tris(phosphinates) were formed during sample preparation (q.v.). In some cases prepolymers were made by the controlled reaction of chromium hydroxyaquo bis(phosphinates) with phosphinic acids. Their preparation is also included under Sample Preparation.

Other materials and their sources follow: technical grade TCP (80% para, 20% meta), Fisher; DBP, Matheson, Coleman, and Bell; DBBP and DEEP, Virginia-Carolina; DBCM, Aldrich; DBS, Commercial Solvents; USP stearic acid, Mallinckrodt; aluminum stearate No. 132, Witco; Santicizer 141 (2-ethylhexyl diphenyl phosphate), Monsanto; Kodaflex AD-2, Eastman Kodak via AMD; Catanac SP (35% iso-PrOH-H<sub>2</sub>O solution of  $(\text{C}_{17}\text{H}_{35}\text{CONHC}_3\text{H}_6\text{NMe}_2\text{CH}_2\text{CH}_2\text{OH})\text{H}_2\text{PO}_4$ , used after removal of solvents), Ucon LB-1715 [poly(alkylene glycol)], poly(ethylene glycol) 400, methoxy poly(ethylene glycol) 550, and 2-methoxymethyl-2,4-dimethyl-2,4-dimethylpentanediol, Union Carbide; Gafac PE 510 and RE 610 and Gafstat AS 710 ( $[\text{RO}(\text{CH}_2\text{OCH}_2)_n]_x\text{P}(\text{O})(\text{OH})_{3-x}$ ), General Aniline; Acryloid B-72 (polymerized ester derivative of acrylic and methacrylic acids), Rohm and Haas; Acrawax C (ethylenebis(stearamide)), Glyco Products; Zelek NK (Anionic fatty alcohol phosphate), duPont; and Cellosize QP 1500 (hydroxyethyl cellulose), Union Carbide. The lubricant

fluids DC550, di(2-ethylhexyl) sebacate, and Herculube A-PE were obtained in part commercially and in part from the Lubricants Branch of AMD. The  $\text{TiO}_2$  was obtained as Tripure R-610 from duPont. Mobil Jet Oil II (Mil L-23699A) was used in some experiments.

Polyethylene film (Transilwrap, 4 mils thick) was the substrate used throughout the antistatic coating studies. Cold-rolled 1010 steel was the substrate for the stable-coating studies.

## B. Sample Preparation

1. Antistatic Materials. Residue-free coating solutions containing the desired proportions of phosphinate polymer and plasticizer or other material at an initial total concentration of 6% (w/v) were prepared by stirring  $\text{CHCl}_3$  and the selected constituents overnight. Polyethylene plaques (4" x 6" x 0.004") were dipped in the solutions, briefly drained, suspended vertically, and air-dried away from drafts for a total of 15 minutes. The dip-and-dry procedure was repeated as necessary to produce uniform coatings of the desired thickness, 0.5 mil per side. Thickness of the coating was taken as one half the difference between 4 mils and the thickness of the coated plaque. By weighing the tared plaques after dipping the percentage add-on and weight per unit area of the coating could be determined. By monitoring the coating after 12 to 14 cycles it was generally possible to determine the additional dipping required for attainment of the desired thickness.

The solids content of each solution after completion of the dipping operation was determined by drying an aliquot of the final solution. Such solutions were generally somewhere in the range of two to five times the original concentration as a consequence of solvent evaporation. The pickup by the plaques was also about two to five times as great toward the end of the dipping. In addition to the increase in pickup because of progressive solution concentration, the built-up coatings also tended to retain solution more extensively. Variations in the weight and thickness of pickup observed between various coating compositions were due to factors such as the foregoing.

The finished specimens were stored in holders which prevented any contact of the coated surfaces until they were electrostatically tested. Although the properties of duplicate plaques were similar, the one more nearly fulfilling the requirements for film thickness, uniformity, etc., was submitted to AMD for testing.

Exploratory formulation of selected compositions to form unsupported films served as a basis for the choice of a number of compositions which were subsequently applied as coatings on polyethylene. Trial compositions were generally prepared as  $\text{CHCl}_3$  solutions containing 1 g. total solids per 40-50 ml. After the solutions were stirred several hours at room temperature, they were transferred to Teflon containers, covered loosely, and allowed to evaporate at ambient conditions. If evaporation was quite slow, the composition was finally dried for a few hours at  $80^\circ$ .

2. Greases. Method A. To a solution of 15 g. (0.038 mole) of  $\text{Cr(A)(H)(MP)}_2$  in THF or  $\text{CHCl}_3$  was added 10.97 g. (0.038 mole) of  $\text{Oc}_2\text{P(O)OH}$ . The reaction mixture was refluxed for 2 hr., and then the product was recovered by evaporation of the solvents and ground to a powder (about 60 mesh). A mixture of 5 g. of thickener and 45 ml. of DC550 was rapidly stirred and heated to  $80^\circ$  in an oil bath. After most of the thickener had dissolved, the temperature was increased to  $150^\circ$  while stirring was continued. Thickening occurred after 0.5-2 hr., and the grease was then heated for an additional hour. Setting of the grease was completed by heating it in a nitrogen atmosphere at  $160-170^\circ$  for 15 hr. without agitation. Greases based on  $\text{Cr(DH)(MP)}_2$  and  $\text{Cr(DH)}_{0.9}\text{(DPDT)}_{0.1}\text{(MP)}_2$  were prepared in the same way.

Variations in this technique appeared to affect the properties of the resultant grease. Different heating rates of the lubricant-thickener mixture seemed to have little effect, but attempts to prepare a grease with a preheated lubricant fluid gave poor results. Stirring the reaction mixture during grease preparation is important to prevent the formation of hard gels. Rapid stirring gives very smooth greases that tend to bleed less in oil-separation tests.

Most of the fractions of  $\text{Cr(A)(H)(MP)}_2$  used had intrinsic viscosities of 0.08 to 0.10 dl./g. in  $\text{CHCl}_3$ . One sample with an intrinsic viscosity of 0.3 dl./g. failed to give a satisfactory thickener. The ratio of acid to polymer in the thickener was varied from 0.5:1 to 1:1. The thickeners with ratios less than 1:1 tended to form greases in DC550 that were more gel-like in consistency than those in which the ratio was 1:1. These greases were not examined further.

Greases were made from the 1:1 thickeners and Herculube A-PE and di(2-ethylhexyl) sebacate by a similar technique except that the reaction temperature was kept below  $120^\circ$ .

Method B. A 5-g. sample of an equimolar mixture of Cr(A)(H)(MP)<sub>2</sub> and Me(Ph)P(O)OH was dissolved in a mixture of 27 ml. of CHCl<sub>3</sub> and 5 ml. of dioxane. After 1 week at room temperature a firm gel had formed. It was carefully ground in a mortar in the presence of 30 ml. of DC550 until a homogeneous, firm grease was obtained. The grease was then heated in a nitrogen atmosphere at 160-170° for about 15 hr. The same general technique was used for greases thickened with Cr(DM)(MP)<sub>2</sub>, Cr(DP)<sub>2</sub>(MP), and Cr(DM)(DP)<sub>2</sub>. The gel formation required from several days for the less sterically hindered phosphinate-acid combinations to several weeks for the more hindered systems. The time required for gel formation can be greatly shortened by heating.

3. Protective Coatings. In early experiments coating solutions were prepared by dissolving Oc<sub>2</sub>P(O)OH in an appropriate combination of solvents at room temperature and adding finely ground Cr(A)(H)(MP)<sub>2</sub> slowly with stirring. The mole ratio of 1.2 polymer to 1.0 acid and the concentration of 4-15% used in primers were changed to 1:1 and 26-38% for top coats. In later experiments a prepolymer similar to the one employed in the greases described in Section B.2 was prepared by mixing homogeneous 1:1 molar ratio solutions of the reactants and evaporating the mixture to dryness at room temperature. The ground, vacuum-dried solid was then heated to effect sufficient further reaction to impart resistance to jet oil without eliminating all solubility in solvents.

The other tris(phosphinate) prepolymers were made by variations of the same basic reaction. The technique employed was to dissolve the chromium hydroxyaquo bis(phosphinate) in a solution of the phosphinic acid by slowly stirring in portions of the bis(phosphinate). After the resulting solution was stirred at room temperature for a period of time, it was evaporated under a stream of nitrogen until solid started to form. If the solid was crystalline under the microscope (i.e., was unreacted acid), more solvent was added, and stirring was resumed. The partial evaporation and examination of the first solid to appear was then repeated. When acid crystals could not be detected, evaporation under nitrogen was continued to dryness, and the residue was further dried under vacuum at room temperature. Precuring was not necessary for the prepolymers of Cr(MP)<sub>3</sub>, Cr(DP)(MP)<sub>2</sub>, Cr(DM)(MP)<sub>2</sub>, and Cr(DP)<sub>2</sub>(MP) made in this way since their initial resistance to jet oil was satisfactory. They were, however, sufficiently soluble to permit coatings to be made from solution.

Paints were prepared by dissolving the prepolymer in the solvent and grinding in TiO<sub>2</sub> pigment on a roller in a 2- or 4-oz. jar containing 5 mm. glass beads. In some early runs 1/8" steel shot was used, but it caused foaming and darkening in formulations containing o-DCB, the preferred solvent. A typical formulation consisted of 1.200 g. of Cr(DO)(MP)<sub>2</sub> prepolymer cured at 160° for 1 hr., 0.648 g. of TiO<sub>2</sub>, and 31 ml. of 1:1 THF:o-DCB. It was milled for 6 hr. with glass beads and then dip coated onto the clean steel substrate. Some panels were given a second coat after air drying for 45 min., and then all coatings were air dried about 60 hr. before curing some for 1 hr. at 200°. (Only about 18 hr. air drying was actually necessary.)

The 1010 steel panels used as the substrate were cleaned in a boiling alkaline cleaner (Pennsalt F6<sup>®</sup>, 40 g./l.), rinsed, and dried with a high-pressure air jet. Cleaned strips were stored in a desiccator until used. Coatings were applied in three ways. Initially single drops of solutions were applied and later 1/2" x 6" strips were dipped in solutions. The most promising paint formulation was sprayed onto 4" x 6" panels with a Binks Model 15 spray gun at 50 lb. air pressure.

In general coatings were dried under mild forced draft at room temperature, examined, and then cured in an oven to complete the conversion to tris(phosphinate).

### C. Evaluation

1. General. During this study infrared spectra, intrinsic viscosities, and thermal behavior were routinely determined, respectively, with a Perkin-Elmer 337 grating spectrometer, a Cannon-Ubbelohde dilution viscometer, and a Chevenard or duPont thermobalance or a Perkin Elmer DSC-1B differential scanning calorimeter.

2. Antistatic Materials. Volume resistivity measurements on solutions of prospective antistatic materials were made at 30° as before.<sup>2</sup> The test solutions were stored at room temperature for two weeks, then for two weeks at 55°. The bottles were sealed with tape around the caps which were fitted with Teflon liners to prevent escape of CHCl<sub>3</sub>.

The antistatic performance of the coated samples was determined by I. H. Custis of AMD according to the procedure outlined in XAS-1152.<sup>12</sup>

3. Greases. The data on the performance of greases presented in the tables were obtained by the Lubricants Branch of AMD through the cooperation of L. Stallings.

4. Protective Coatings. Tests fairly standard to the paint industry were used to evaluate the coatings applied to 1010 cold-rolled steel. Adhesion was determined by the Scotch Tape test and by use of a 1/8" tapered mandrel initially without, but later with a Scotch tape test of the bend area. Hardness was determined by the pencil hardness test. Gloss was estimated visually or determined in a 60° Gardner Glossmeter. Thickness, thermal resistance, solvent resistance, and shelf life of formulations were also determined.

### III. Results and Discussion

#### A. Antistatic Materials

The ultimate goal of this phase of the study is the development of transparent, flexible, heavy duty packaging film which will not build up an electrostatic charge. Requirements for the desired film are given in the provisional specifications XAS-1152.<sup>12</sup> The primary purpose of the work during this period was to meet the specification of dissipating a charge of 5 kV in one second or less according to specified procedures. In the earlier work coatings of plasticized Cr(A)(H)(MP)<sub>2</sub> and Cr(A)(H)(DP)<sub>2</sub> on polyethylene appeared most promising. Although the coated films did not quite meet the specified discharge time, they were water repellent and transparent. The present work was devoted to improving the rate of discharge. It encompassed modification of the two promising polymers, exploration of other phosphinates and plasticizers, and incorporation of additives into the coatings.

Earlier work had suggested that there was sufficient correlation between the volume resistivity of solutions of the polymers in CHCl<sub>3</sub> and the discharge rate of coatings of the plasticized polymers on polyethylene that polymers could be screened by measuring volume resistivity of their solutions. The conclusion on the basis of volume resistivity that G-Cr(A)(H)(DP)<sub>2</sub> should give excellent antistatic coatings<sup>2</sup> has since been found to be correct as will be seen later, thus confirming the usefulness of this screening technique. Consequently the solutions of a number of poly(metal-phosphinates) have been examined. The solution resistivities are given in Table 2 as a function of concentration and time. Included are values for solutions of Cr(A)(H)(MP)<sub>2</sub>, Cr(A)(H)(DP)<sub>2</sub>, and G-Cr(A)(H)(DP)<sub>2</sub> which were stored for 8 months at 55° after initial measurements. Volume resistivities invariably increased as solution concentration decreased. The changes in resistivity during storage are not great and imply favorable stability of the polymers. Figure 1 is a plot of initial resistivities of solutions vs. concentration for Cr(A)(H)(DB)<sub>2</sub> and Cr(A)(H)(DO)<sub>2</sub> compared to G-Cr(A)(H)(DP)<sub>2</sub>, Figure 2 for Zr(DP)<sub>4</sub>, ZrO(DP)<sub>2</sub>, ZrO(DB)(DO), and TiO(DP)<sub>2</sub>. The results suggest that Cr(A)(H)(DB)<sub>2</sub>, ZrO(DP)<sub>2</sub>, ZrO(DB)(DO), and TiO(DP)<sub>2</sub> are as promising as G-Cr(A)(H)(DP)<sub>2</sub>. Plasticized coatings of some of them have been tested and confirm this promise.

Table 2  
Specific Resistance of  $\text{CHCl}_3$  Solutions

$\frac{\text{ohm-cm} \times 10^5}{\text{at } 30^\circ}$

Polymer	History	Concentration, g./100ml.												
		5.0	3.0	1.0	0.5	0.3	0.1	0.05	0.03	0.01				
Cr(A) (H) (MP) 2	Fresh	5.02	7.09	16.2	27.5	39.3	87.7							
	9 days, 55°	3.67	4.95	6.99	10.1	18.2	41.3							
	8 months, 55°	3.92	5.78	10.6	14.4	59.5	>100							
Cr(A) (H) (DP) 2	Fresh	2.78	3.77	7.63	12.3	17.2	37.7	63.2						
	9 days, 55°	gel	gel	6.89	13.7	69.4	>100	>100						
	8 months, 55°			9.26	20.9	59.5	>100	>100						
G-Cr(A) (H) (DP) 2	Fresh	0.70	1.02	2.37	3.95	5.71	13.6	24.7	35.9	98.0				
	9 days, 55°	1.36	2.08	4.78	9.00	13.9	42.0	>100	>100	>100				
	8 months, 55°	0.96	1.46	4.44	11.2	20.5	41.0	>100	>100	>100				
Cr(A) (H) (DB) 2	Fresh			1.27	2.22	3.33	8.20	15.7	23.2	56.2				
	14 days, ~25°			1.18	2.05	3.05	7.15	13.3	19.1	50.7				
	4 days, 55°			1.75	3.05	4.65	10.6	21.8	30.5	76.2				
	14 days, 55°			2.17	3.67	5.62	14.0	23.7	35.6	97.1				
Cr(A) (H) (DO) 2	Fresh			5.21	9.71	17.4	51.0							
	14 days, ~25°			3.95	6.66	9.90	32.3							
	4 days, 55°			4.85	8.93	13.3	35.6							
	14 days, 55°			4.27	7.63	13.3	41.0							
Zr(DP) 4	Fresh			9.71	15.0	20.1	44.4	76.3	89.3					
	14 days, ~25°			9.71	15.5	19.4	30.5	50.7	66.6					
	4 days, 55°			9.71	14.6	19.4	35.6	56.1	66.6					
	14 days, 55°			9.71	15.7	19.7	28.1	36.7	44.4					

Table 2 (continued)

<u>Polymer</u>	<u>History</u>	<u>Concentration, g./100 ml.</u>									
		<u>5.0</u>	<u>3.0</u>	<u>1.0</u>	<u>0.5</u>	<u>0.3</u>	<u>0.1</u>	<u>0.05</u>	<u>0.03</u>	<u>0.01</u>	
ZrO(DP)2	Fresh	0.96	2.25	4.92	10.2	16.2	53.7				
	14 days, ~25°	1.00	2.21	4.44	9.80	15.3	51.0				
	4 days, 55°	1.02	2.13	4.18	10.6	17.8	82.0				
	14 days, 55°	0.97	2.11	3.95	10.2	15.2	71.4				
ZrO(DB)(DO)	Fresh	0.67	1.59	2.74	3.95	17.8	27.4	76.3			
	14 days, ~25°	1.52	2.54	3.67	8.20	14.0	19.7	46.3			
	4 days, 55°	1.57	2.54	3.56	7.63	12.7	18.4	41.0			
	14 days, 55°	1.52	2.37	3.45	7.14	11.3	16.6	38.1			
TiO(DP)2	Fresh	4.27	6.71	9.26	18.4	30.5	42.7	106.			
	14 days, ~25°	3.23	4.85	6.29	12.5	18.4	26.6	53.4			
	4 days, 55°	3.14	4.65	6.29	12.3	18.7	24.8	56.2			
	14 days, 55°	1.97	3.14	4.27	8.20	13.3	17.8	44.4			

Figure 1

Resistivity of Chromium(III) Hydroxyaquo Bis(Phosphinates)  
in  $\text{CHCl}_3$  as a Function of Concentration

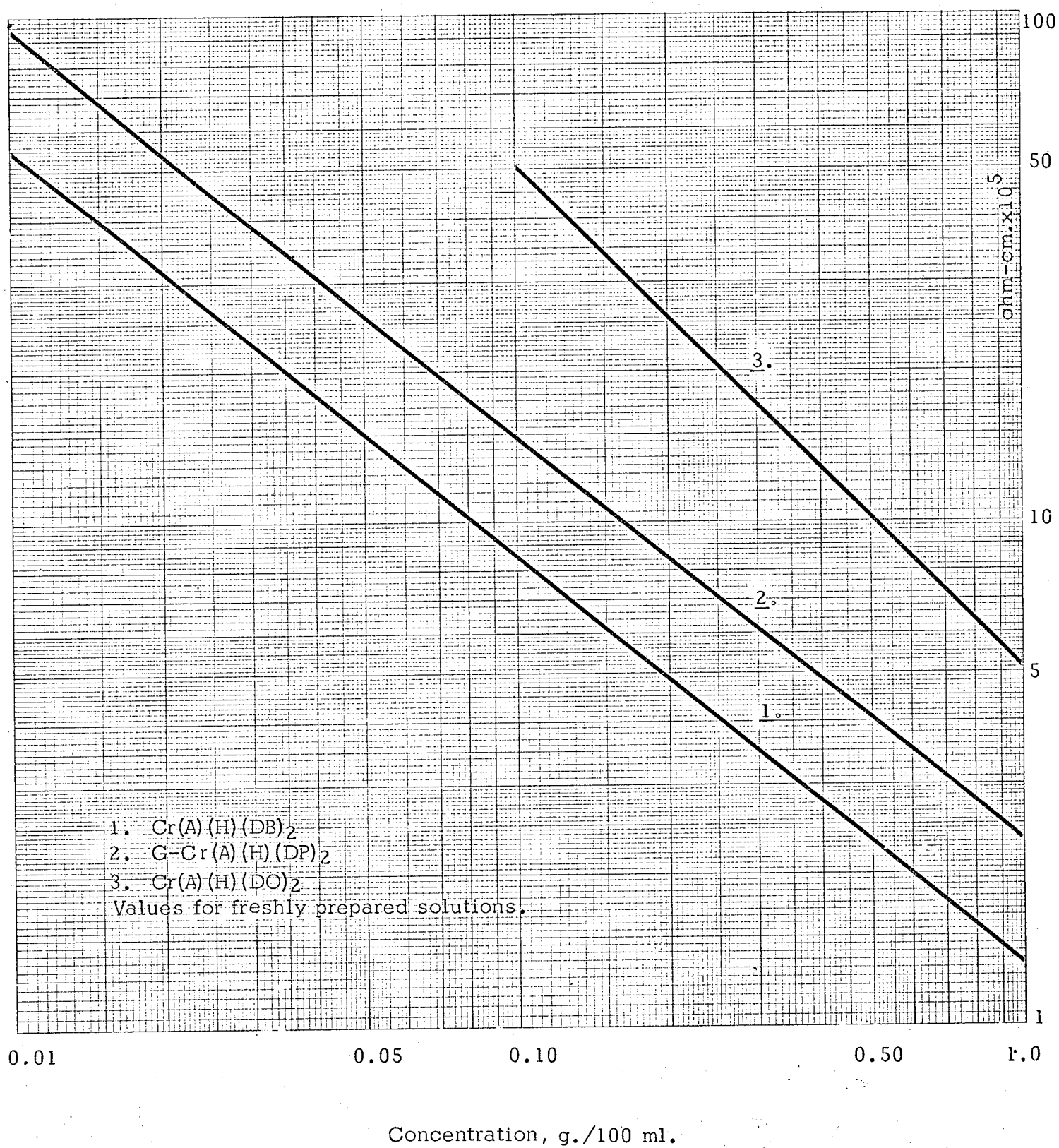
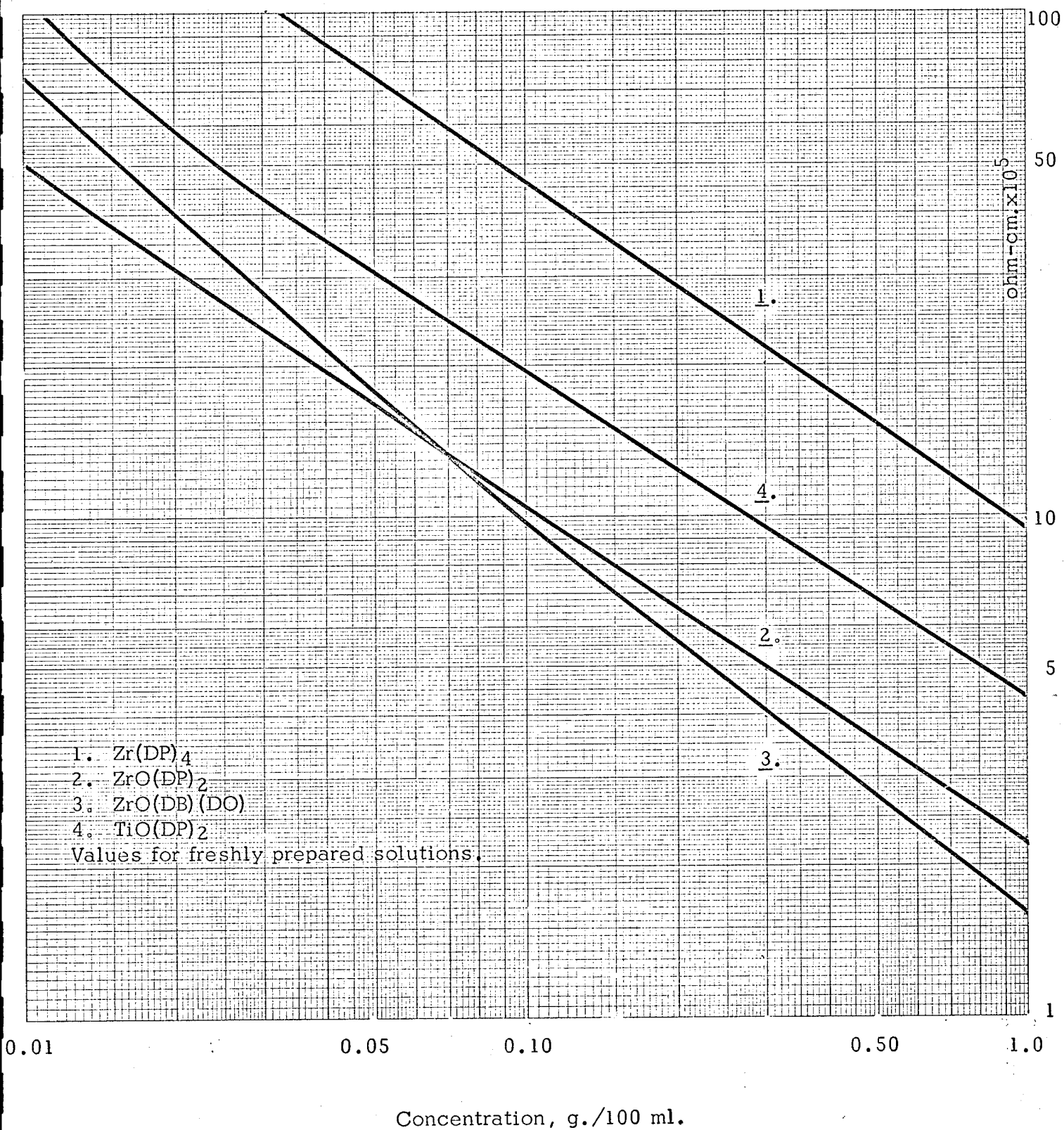


Figure 2

Resistivity of Zirconium and Titanium Phosphinates in  
 $\text{CHCl}_3$  as a Function of Concentration



Although attaining a suitable rate of dissipation of charge was the primary goal of this work with antistatic materials, once it was attained other properties were considered. These included transparency of coating, sensitivity of coating to water, and tackiness of coating. A wide range of additives was investigated in attempting to improve one or another of these properties without sacrificing discharge time. The esters TCP and DBP were very satisfactory plasticizers for Cr(A)(H)(DP)<sub>2</sub> and Cr(A)(H)(MP)<sub>2</sub>, but preliminary examination indicated they were less satisfactory with Cr(A)(H)(DB)<sub>2</sub>. Qualitative tests, however, indicated that of TCP, TBP, TEP, DBP, DBS, DBBP, DEEP, and DBCMP the most satisfactory for Cr(A)(H)(DB)<sub>2</sub> are TCP, DBP, and DBBP. In an attempt to improve the conductivity of Cr(A)(H)(MP)<sub>2</sub> coatings glycols and ionic antistats were also explored as plasticizers. None of the glycols considered (1,2-propanediol, Polyethylene glycol 400, Ucon LB-1715 (a polyalkylene glycol), methoxy polyethylene glycol 550, and 2-methoxymethyl-2,4-dimethylpentanediol-1,5) appeared sufficiently promising for more extensive testing. Of the four antistats surveyed (Kodaflex AD-2, Catanac SP, Gafstat AS-710, and Zelec NK) Zelec NK appeared unsatisfactory, and the range of compositions feasible with Kodaflex AD-2 and Catanac SP proved limited. Satisfactory films of ZrO(DB)(DO), in contrast to the chromium polymers, required hardening because it is semi-solid at room temperature. For this purpose Cr(A)(H)(MP)<sub>2</sub> with and without TCP or DBP, Cr(A)(H)(DB)<sub>2</sub>, and Zn(DB)(DO) were investigated, and it was found that acceptable films were obtained with 10% of one of the poly(metal phosphinates). Abherents were not screened as such because they obviously reduced the tackiness of the coatings without rendering them unsuitable for conductivity testing.

On the basis of the various screening tests mentioned polyethylene plaques were coated with a variety of compositions. The observations made on these samples are summarized in Table 3. Of the nine compositions that gave satisfactory decay rates in the positive cycle four also met the one-second requirement in the negative cycle. These four were all based on TiO(DP)<sub>2</sub>. Three of them were rated as very slightly tacky, the fourth as slightly tacky. The presence of water in the atmosphere enhanced the conductivity of the TCP-plasticized samples. Four different chromium hydroxy-aquo phosphinates gave satisfactory results in the positive cycle, and two of these gave decay rates lower than two seconds in the negative cycle. However, only one, Cr(A)(H)(BDP)(MP), gave a coating rated as very slightly tacky. The others definitely present a problem in being too tacky or in the case of Cr(A)(H)(DB)<sub>2</sub> in not adhering to the polyethylene well enough.

Table 3  
Properties of Poly(Metal Phosphinate) Coatings on Polyethylene

Composition of Coating				Final Coating Details				Nature of Coating				Electrostatic Properties (c)			
% Polymer	% Additive(s)	Reaction	Concn. of Soln. 9./100 ml.	No of Dips	% Add-on	mg./cm. <sup>2</sup>	mils./side	Coating	Charge (d) Sec.	Positive Cycle		Negative Cycle		Resid. Volt.	Resid. Volt.
										Decay Sec.	Decay Sec.	Charge Sec.	Decay Sec.		
34 G-Cr(A)(H)(DP)2	66 TCP		24.0	24	19.6	0.80	0.30	tr gr, VT	5.9	2.0	0	5.0	4.6	0	0
"	66 DBP		20.4	24	18.4	0.84	0.40	tr gr, VT	1.9	0.7	0	2.7	3.4	0	0
"	40 TCP		27.1	23	27.3	1.16	0.40	tr gr, NT	F	167	1.2 kV	188	195	3.8 kV	0
"	40 DBP		20.9	23	27.4	1.17	0.35	tr gr, NT	1.37	45	0	102	156	0	0
34 Cr(A)(H)(MP)2	66 TCP		29.4	16	35.7	1.54	0.60	tr gr, ST	4.4	1.3	0	3.4	4.1	0	0
40	60 TCP		31.1	22	41.4	1.87	0.50	tr gr, VST							
50	50 TCP		32.4	22	45.3	2.05	0.61	tr gr, NT							
60	40 TCP		21.2	17	26.4	1.18	0.40	tr gr, NT	289	326	0	304	300	1 kV	0
34	60 TCP	6 Cr(A)(H)(DB)2	30.1	21	39.2	1.66	0.45	tr gr, ST		13.8			9.4		
34	50 TCP	16 Kodaflex AD-2	41.6	16	86.8	3.64	1.0	tr gr, T		4.8			4.4		
same film at 70% rel. hum.															
34 Cr(A)(H)(MP)2	50 TCP	16 Gafstat AS-710	22.7	19	28.4	1.31	0.50	tr gr, ST							
34	50 TCP	16 Catanac SP	21.8	19	37.0	1.64	0.38	tr gr, oily							
40	60 Gafstat AS-710		13.6	15	36.1	1.59	0.50	tr gr, ST							
50	50 Gafstat AS-710		13.1	14	22.8	0.97	0.28	tr gr, NT							
50	50 Kodaflex AD-2		8.1	7	18.5	0.81	0.36	tr gr, NT							
50	40 Gafstat AS-710		13.9	13	26.5	1.18	0.42	tr gr, NT							
60	40 Kodaflex AD-2		9.9	9	46.4	2.09	0.63	tr gr, NT							
34 H-Cr(A)(H)(MP)2	66 TCP		31.0	15	41.8	1.82	0.60	tr gr, T	2.1	0.7	0	1.9	2.0	0	0
34	66 DBP		7.8	15	23.6	1.04	0.40	tr gr, VT	1.6	0.5	0	1.8	1.4	0	0
34 R-Cr(A)(H)(MP)2	66 TCP		31.4	23	43.2	1.85	0.42	tr gr, ST							
34	45 TCP	21 Gafac PE-510	27.8	21	39.5	1.65	0.45	tr gr, VT		9.4			10.5		6.3
34	32 TCP	34 Gafac RE-610	22.9	18	31.0	1.36	0.50	tr gr, T		23.5			25.4		25.4
34	16 TCP	50 Gafac RE-610	14.3	17	29.3	1.29	0.43	tr gr, ST		25.3			30.0		30.0
34 Cr(A)(H)(BDP)(MP)	66 TCP		30.7	25	26.8	1.17	0.36	tr gr, VST							
34 Cr(A)(H)(DB)2	66 TCP		24.4	22	23.4	1.04	0.70	tin gr, pwd	2.6	1.0	0	3.3	4.3	0	0
60	40 DBBP		19.6	18	19.6	0.87	0.43	tr gr, VST	F	162	2.1 kV	495	270	0	0
60	40 DBBP		13.2	18	26.4	1.13	0.47	tr gr, T							
34 TiO(DP)2	66 TCP		26.4	19	41.2	1.85	0.55	tr cl, VST							
same film at 50% rel. hum.															
60 TiO(DP)2	40 TCP		21.4	15	70.6	3.10	0.85	tr cl, NT							
same film at 50% rel. hum.															
34 TiO(DP)2	66 Santicizer 141		40.2	21	77.6	3.35	0.99	tr cl, VST							
34	56 TCP	10 Hydroxyethylcellulose (e)	22.7	16	17.5	0.81	1.53	het, NT							
34	64 TCP	2 aluminum stearate (e)	21.3	14	55.1	2.56	0.91	hz tin, NT							
34	65 TCP	1 Acrawax C (e)	25.1	20	38.6	1.66	0.62	hz tin, VST							
34	61 TCP	5 stearic acid	29.8	23	28.5	1.34	0.52	tr cl, ST							
34	56 TCP	10 Acryloid B-72	20.5	20	23.7	1.01	0.45	tr cl, VST							
90 ZrO(DB)(DO)	10 Cr(A)(H)(DB)2		24.9	20	18.5	0.76	0.15	tr gr, VST	99.4	40.4	0	40.3	72.2	0	0
90	10 Cr(A)(H)(MP)2		32.9	24	35.2	1.59	0.65	tr gr, VST	31.1	19.3	0	15.5	24.8	0	0
90	10 Zn(DB)(DO)		24.1	25	19.1	0.81	0.35	tr cl, NT							

(a) Based on acid number of additive where applicable.

(b) Abbreviations as follows: cl, clear; gr, green; het, heterogeneous; hz, hazy; NT, not tacky; pwd, powdery; ST, slightly tacky; T, tacky; tin, translucent; tr, transparent; VST, very slightly tacky; VT, very tacky.

(c) As reported by I. H. Custis of AMD, NADC. Most values are averages of two or three measurements.

(d) F means charged by friction.

(e) Present as finely divided, insoluble additive.

Several conclusions can be drawn from the data in Table 3. Only coatings containing a large amount of plasticizer are effective. Reduction of the plasticizer content below 60% to reduce tackiness results in too large an increase in decay rates although tackiness is reduced. In the samples measured the use of an ionic antistat as part of the plasticizer was deleterious. Small amounts of abherents, however, can be used without affecting the decay rate. The best polymer,  $TiO(DP)_2$ , contains one oxygen anion per metal center and aromatic side groups on the phosphinate bridges. It is tempting to conclude that the presence of oxygen groups is necessary for conductivity (probably an ionic mechanism) and that larger alkyl side chains interfere with the conductivity mechanism. Molecular weight and method of preparation have some effect on the conductivity of the chromium polymers and could perhaps be varied sufficiently to get better discharge times. It now appears that a colorless, transparent, water resistant, nontacky coating can be made from  $TiO(DP)_2$  that will meet the discharge requirements. It is likely that  $ZrO(DP)_2$  will also give satisfactory coatings. The chromium polymers appear less promising because of marked tackiness.

#### B. Greases

Although ultimate requirements call for greases with thermal stability up to  $1000^\circ F$ . our goal on the present contract was to prepare a grease with a service life of 500 hr. at  $450^\circ F$ . It was hoped that the thickener selected for this would also efficiently thicken other fluids to be used at lower temperatures. Finally it was expected that the thickener would impart good EP properties to the resultant grease.

Under the preceding contract a poly(metal phosphinate) acting as a multi-purpose grease thickener was developed.<sup>2</sup> The polymer,  $Cr(A)(H)(DO)(MP)$ , was found to thicken DC550, Herculube A-PE and di(2-ethylhexyl) sebacate in concentrations of 10% by weight or less. These greases also possessed good EP properties. The synthesis of the thickener, however, was sufficiently complex to make the preparation of greases with reproducible properties difficult.

Under the present contract our goals were:

- (1) to screen various poly(metalphosphinates) for thickener properties.
- (2) to develop a reliable synthetic procedure for the most promising thickener.

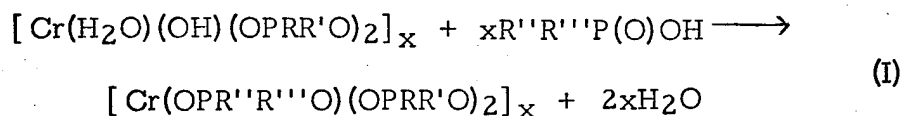
(3) to find the most suitable conditions for grease preparation.

(4) to supply grease samples to AMD for evaluation.

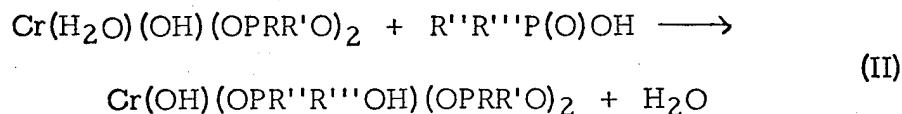
Selected phosphinates of titanium, zirconium, zinc, cobalt, and manganese were screened for grease forming properties in DC550 at 10% concentration. Their behavior is shown in Table 4. Of the compounds screened only some manganese phosphinates thickened DC550 to a grease at 10% concentration. The drop points of the greases, however, were quite low (230-280° F.), and all efforts to increase them were unsuccessful. Materials expected to yield high drop points were incompatible with the fluid.

Primarily as a result of our simultaneous efforts on poly(metal phosphinate) coatings we have been able to develop a variety of chromium phosphinate thickeners which are easily prepared and which have been found to retain the good EP properties shown by the copolymer thickener. These new thickeners are effective in DC550 (a poly(methylphenyl siloxane)) Herculube A-PE (a pentaerythritol ester), di(2-ethylhexyl) sebacate, and other fluids in concentrations of 5 to 14 per cent by weight.

Generally, these thickening agents were prepared from the reaction of a poly(metal bisphosphinate) with a phosphinic acid:



where R, R', R'', and R''' are alkyl and or aryl groups. The details of this reaction are not well understood, but it is believed that the evolution of water proceeds stepwise. The first step of the reaction is best initiated in a suitable solvent such as chloroform, dioxane or THF. The choice of solvent appears critical since attempts to prepare the thickener from the reactants in the presence of the fluid itself were unsuccessful. The intermediate product appears to be an adduct between the polymer and the acid formed by the displacement of the coordinated water

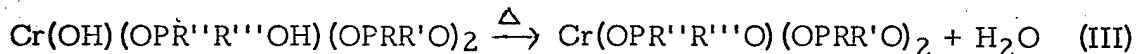


Infrared investigation of OH absorption in the range from 3700 cm.<sup>-1</sup> to 3200 cm.<sup>-1</sup> showed a progressive decrease in the absorption due to the coordinated water as the conversion to tris(phosphinate) took place.

Table 4  
Survey of Various Poly(Metal Phosphinates) as Thickeners for DC550

<u>Yield Grease</u>	<u>Some Thickening</u>	<u>Partially Soluble</u>	<u>Insoluble</u>
Mn(DB) (DO)	Co(DB) <sub>2</sub>	Co(DB) (DO)	Co(DP) (MP)
Mn(DO) (DP)	Co(DO) <sub>1.2</sub> (MP) <sub>0.8</sub>	Co(DO) <sub>2</sub>	Mn(MP) <sub>2</sub>
Mn(DO) (DP) <sub>0.2</sub> (MP) <sub>0.8</sub>	TiO <sub>0.5</sub> (DO) (DP) <sub>2</sub>	Ti(DP) <sub>4</sub>	TiO(DP) <sub>2</sub>
Mn(DO) <sub>1.2</sub> (MP) <sub>0.8</sub>	TiO(DO) (DP)		TiO(MP) <sub>2</sub>
	TiO(DO) (MP)		Zn(DB) (DP)
	TiO <sub>1.1</sub> (DO) <sub>0.6</sub> (MP) <sub>1.2</sub>		Zr(DP) <sub>4</sub>

After at least part of this initial reaction had taken place, the thickener was introduced into the lubricant. The elimination of the remaining water was then allowed to occur at elevated temperature and a grease resulted.



It is important that at least part of this reaction take place in the presence of the lubricant. All attempts to thicken fluids with fully cured tris(phosphinates) were unsuccessful.

The size of the organic substituents on the phosphorus in both the acid and polymer greatly influence the rates of the reactions described by equations II and III. Although the ultimate reaction product is a tris(phosphate) as outlined above, we have not identified the various intermediates obtained for the different thickeners.

Two methods have been developed to prepare greases with these thickeners. Method A involves the isolation of the initial reaction product of the phosphinic acid-bis(phosphate) reaction, equation II, which is then dissolved in the lubricant fluid and the solution heated with stirring to yield the grease. In Method B the reaction between phosphinic acid and bis(phosphate) takes place in a low-boiling solvent to give a gel. The gel is then mixed with the lubricant fluid to form the grease. In both cases it was found beneficial to cure DC550 greases by a final heat treatment at 160-200° for 5-15 hours. The mechanism of grease formation is not completely understood in either procedure, but it would appear that the matrix traps the fluid during formation of the gel in Method A, but that the fluid displaces the solvent from the gel matrix in Method B.

Thermogravimetric analyses were run on samples of tris(phosphinates) prepared in solvents and then heat-cured in the dry state until their infrared spectra showed complete reaction by the absence of OH absorption. Initial weight loss in air took place at 242° for Cr(DO)(MP)<sub>2</sub> and at 263° for Cr(DH)(MP)<sub>2</sub>. In an isothermal run at 232° Cr(DO)(MP)<sub>2</sub> lost 15.5% in weight over a period of 72 hours with approximately 60% of the total weight loss occurring during the first 24 hours. Thermal stability increases markedly when the long chain aliphatic groups are replaced. Initial decomposition is observed at 324° for Cr(MP)<sub>3</sub>.

Performance data for the greases are presented in Table 5. The greases made with DC550 all have high dropping points, ranging from 579 to 660°F. Variation of the concentration of the thickener Cr(DO)(MP)<sub>2</sub> within the range 7.4 to 10% appears to have little influence upon the bearing performance. Oil separation at 450°F. is quite high for the

Table 5  
Properties of Greases <sup>a</sup>

Fluid	Thickener	Concn. wt. %	Penetration	Oil Sepn.	Dropping Point °F.	Wear Scar, Shell 4-Ball, mm. 40 kg. 80 kg. 120 kg. 160 kg. 10 <sup>4</sup> r.p.m.	Bearing Life, Hr. 10 <sup>4</sup> r.p.m.				
DC550	Cr(DO)(MP) <sub>2</sub>	10	358	22 <sup>b</sup>	616	0.84	1.79	2.46	weld	62.0 <sup>b</sup>	
		10	346	12.6 <sup>b</sup>	660	0.92	1.80	2.17	weld	77.8 <sup>b</sup>	
		10	314	17.3 <sup>b</sup>	657	0.87	1.81	2.05	weld	90.3 <sup>b</sup>	
		7.4	264	18.2 <sup>b</sup>	627	0.86	1.37	2.69	weld	61.7 <sup>b</sup>	
		10	273	18.5 <sup>b</sup>	644	0.86	1.53	2.21	weld	110.7 <sup>b</sup>	
		8.3	216	13.2 <sup>b</sup>	617	0.84	1.92	2.35	weld	112.8 <sup>b</sup>	
		10	185	9.4 <sup>b</sup>	613	0.83	1.92	1.97	2.98	weld	124.3 <sup>b</sup>
		10	272	17.2 <sup>b</sup>	622	0.94	1.25	2.00	weld	140.8 <sup>b</sup>	
		10	334	13.4 <sup>b</sup>	628	0.83	1.96	2.35	weld	143.5 <sup>b</sup>	
		10	296	22.9 <sup>b</sup>	616	0.91	1.71	2.26	weld	108.5 <sup>b</sup>	
Hercolube A-PE	Cr(MP) <sub>3</sub>	12.5	299	17.6 <sup>b</sup>	579	0.89	1.20	2.20	weld	180.2 <sup>b</sup>	
	Cr(DO)(MP) <sub>2</sub>	10	327	16.4 <sup>c</sup>	517	0.54	0.59	2.09	weld	16.4 <sup>c</sup>	
Sebacate	Cr(DH) <sub>0.9</sub> (DPDT)(MP) <sub>2</sub>	10	248	30.4 <sup>c</sup>	543					92 <sup>c</sup>	
	Cr(DO)(MP) <sub>2</sub>	10	352	26.5 <sup>d</sup>	604						

<sup>a</sup>All data except Concn. supplied by I. Stallings, AMD, NADC

<sup>b</sup>at 450°F.

<sup>c</sup>at 350°F.

<sup>d</sup>at 250°F.

<sup>e</sup>average value

first six greases (12.6 to 22%), with no meaningful relationship between it and bearing performance. The last DC550-Cr(DO)(MP)<sub>2</sub> grease gave an oil separation of only 9.4%. In this case the thickener was allowed to gel the lubricant fluid completely without stirring, and the hard gel was then mechanically broken up into grease consistency. The last two DC550-Cr(DO)(MP)<sub>2</sub> greases (with the running times of 112.8 and 124.3 hours) were post-cured at 428°F. in a nitrogen atmosphere for 16.5 hours.

The higher running times with Cr(DH)(MP)<sub>2</sub> and Cr(MP)<sub>3</sub> are probably due to the higher thermal stabilities of the thickeners. Replacement of some of the Hx<sub>2</sub>P(O)OH with Ph<sub>2</sub>P(S)SH in the preparation of the thickener resulted in lower bearing life and did not improve the good EP properties of the grease. The thickener Cr(MP)<sub>3</sub> is clearly superior and merits further study.

The incomplete data on the Herculube and sebacate greases indicate that the former are unsatisfactory.

### C. Protective Coatings

Previous work had demonstrated that thin films of Cr(A)(H)(DP)<sub>2</sub> adhered well to aluminum to give coatings with good resistance to salt spray<sup>13</sup> and that Cr(DO)(MP)<sub>2</sub> formed tough films.<sup>2</sup> The present work was undertaken in order to evaluate the potential of tris(phosphinates) as high-temperature coatings for aircraft. The tris(phosphinate) Cr(DO)(MP)<sub>2</sub> was selected for orientation studies because of its tractability and solvent resistance, even though its thermal resistance is not as high as desired. Cold-rolled steel was used as the substrate, and the effect of variations in synthetic procedures, formulation, pre-cure, post-cure, application procedures, and substrate pretreatment, on selected properties of the finished coating was studied in statistically designed experiments (usually a 2<sup>3</sup> factorial design). The reaction products of a number of aquohydroxy chromium(III) phosphinates with various phosphinic acids were explored in the search for a more suitable tris(phosphinate) for high-temperature coatings. First the results with Cr(DO)(MP)<sub>2</sub>, and then the results with other tris(phosphinates), will be discussed.

On the basis of exploratory probes (see Table 6 for typical experiments) several facts about coating with Cr(DO)(MP)<sub>2</sub> became apparent. Of the solvents studied only THF, chloroform, benzene, toluene, and o-DCB dissolve both Cr(A)(H)(MP)<sub>2</sub> and Oc<sub>2</sub>P(O)OH in sufficient concentration for coating formulations. Mixed high- and low-boiling solvent systems are superior to single solvents, and a

Table 6  
 Preliminary Studies of Coatings of Cr(DO)(MP)<sub>2</sub> on Clean Cold-rolled 1010 Steel

Coating Solution			Coating Application			Coating Properties						
Solvent	Composition Moles Polymer:acid	g. solids/ 100 ml	Shelf Life Days to Gela	Method	Air Dry hr.	Cure °C. hr.	Appearance <sup>b</sup>	Thick- ness mil	Pencil Hard- ness	Adhesion <sup>c</sup> Mandrel Tape		
o-DCB <sup>d</sup>	1:1	26	27	Drop	17	120	4	Good, SG	0.4	2B	NG	NG
e			38	Drop	16	120	7	Good, SG	0.3	F	OK	OK
f		15	43	Drop	18	120	5	Good, G	0.5	6B	NG	NG
	1:0.8	35	18	Drop	18	120	4	Poor, D	0.2	F	NG	Poor
		24	25	Drop	18	120	5	Fair, G	0.2	HB	NG	Good
1:1 THF:toluene	1:1	37.5	11(9)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Fair, SG	1.6	9H	Fair	Good
1:1 THF:o-DCB	1:1	37.5	15(14)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Good, SG	0.9	HB	NG	Fair
1:1:1 toluene: o-DCB	1:1	37.5	10(7)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Poor, SG	0.6	6H	NG	Good
1:1 benzene: o-DCB	1:1	37.5	12(12)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Poor, SG	0.5	9H	Poor	Poor
2:1 THF:toluene	1:1	37.5	16(9)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Fair, SG	1.5	4H	Fair	Good
2:1 THF:o-DCB	1:1	37.5	16(16)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Fair, SG	0.8	2H	NG	Poor
2:1 toluene: o-DCB	1:1	37.5	9(7)	Dip	3	{ 70 198 } 1	{ 0.5 1 }	Poor, SG	0.6	5H	NG	Good

<sup>a</sup>where a number is given in parentheses, it indicates days to form a very viscous solution

<sup>e</sup>solution heated 2.5 hr. at 75° before coating

<sup>b</sup>G, glossy; SG, semiglossy; SM, semimatte; D, dull

<sup>c</sup>NG, no good

<sup>f</sup>solution used as primer for following solution

<sup>d</sup>substrate pretreated with 15% Oc<sub>2</sub>P(O)OH solution at room temperature for 3 days

1:1 mixture of THF and toluene is preferred. It forms solutions containing 36 g. of solids per 100 ml. of solvent which show low run-off and fair shelf life and give dip coatings of fair thickness, appearance, hardness, and adhesion to clean, untreated steel. Coating properties are not affected by varying the polymer to acid ratio from 1:1 to 1.2:1. The coatings must be cured at 195-200° to become insoluble in o-DCB and jet oil. Uncured coatings are tough and resilient but are attacked by jet oil at room temperature. Adequate coatings are not achieved in one dip, and multiple coating requires curing between coats.

Adhesion of Cr(DO)(MP)<sub>2</sub> to 2024 aluminum is better than to 1010 cold-rolled steel. Adhesion to the steel is better after alkaline cleaning than after manual cleaning with a household cleanser or after etching with HCl. Pretreatment of the cleaned steel with solutions of Oc<sub>2</sub>P(O)OH or priming with the diluted coating formulation also improves adhesion and hardness.

In order to impart immediate jet-oil resistance to the coating it was necessary to isolate the initial product of the polymer-acid reaction ("the resin") and to cure it before making the coating solution. Optimum conditions to impart resistance to jet oil while retaining some solvent solubility were a curing period of 1 hr. at 160°. Variations in resin preparation details had no important effect on coating properties. The resin treated in this fashion gives a solution in 1:1 THF: toluene with a concentration of 10 g./100 ml. of solvent that forms air-dried coatings of good appearance, thickness, and adhesion to steel with moderate hardness and adequate resistance to limited exposure to jet oil. Multiple coats may be applied after 30 min. drying at room temperature. After these coatings are cured, they are completely resistant to jet oil and are considerably harder, but some adhesion is lost. The experimental data are summarized in Table 7.

Pigment loading with TiO<sub>2</sub> was investigated in an attempt to improve the properties of the coating. Table 8 summarizes the results. Pigment loading was found to improve appearance, hardness, and adhesion of both uncured and cured coatings, with an optimum TiO<sub>2</sub> to resin weight ratio of 35:65. Due to the high viscosity of the precured-resin solutions dispersion of the pigment was difficult, and formulation of paints with much more than 10 g. of solids per 100 ml. of solvent was not possible under the conditions employed. An attempt to make a master mix by milling a suspension of the resin and TiO<sub>2</sub> and recovering the solid mixture produced a material which yielded good paint dispersions when dissolved in a solvent with stirring. Curing this product was difficult, however, and conditions necessary to develop jet oil resistance while retaining

Table 7

Effect of Using Partially Cured Cr(DO)(MP)2 for Coating Cold-rolled  
1010 Steel by Dipping in 1:1 THF:Toluene Solution

°C.	Curing of Resin		g. solids/ 100 ml.	Shelf Life Days to Gela	Curing of Coating °C. hr.	Coating Properties				
	hr.	%wt. loss				Appear- ance b	Thickness mils	Pencil Hardness	Mandrel	Adhesion <sup>c</sup> Tape
0			39.8	16 (12) gels at once	197 2	Fair, G	0.5	H	NG	Good
175	2	3.85	3.7	8 (7)	{ 197 1	Fair, D	0.2	B	OK	OK
	0		39.2		{ 197 1	Fair, D	0.2	6H	NG	Poor
150	1	3.8	10	2-3(1)	{ 197 1	Fair, SG	0.2	H	OK	OK
160	1	4.1	10	2-3(1)	{ 197 1	Fair, SG	0.2	6H	NG	OK
					{ 197 1	Fair, SG	0.2	H	OK	OK
170	1	4.3	10	2-3(1)	{ 197 1	Fair, SG	0.2	3H	NG	Fair
					{ 197 1	Fair, SG	0.5	H	OK	OK
	0		39	13(6)	{ 197 1	Fair, SG	0.5	5H	NG	Poor
160 <sup>d</sup>	1	4.2	10	3(1)	{ 197 1	Fair, D	0.5	2B	NG	OK
					{ 197 1	Poor, D	0.5	7H	NG	Poor
					{ 197 1	Good, G	0.5	2B	OK	NG
					{ 197 1	Good, G	0.5	2H	NG	Fair
160 <sup>e</sup>	1	5.2	10	3(1)	{ 197 1	Good, G	0.5	HB	NG	Good
	0		39	12(6)	{ 197 1	Fair, D	0.5	7H	NG	Fair
					{ 197 1	Poor, D	0.5	7H	NG	Fair
					{ 197 1	Good, G	0.5	H	NG	Good
					{ 197 1	Good, G	0.5	4H	NG	OK
	0		39	40-70	{ 197 1	Good, SM	0.7	3H	OK	OK
160 <sup>f</sup>	1	3.7	10	5(1)	{ 197 1	Good, SG	0.7	7H	NG	Fair
					{ 197 1	Good, G	1.5	2B	OK	OK
	0		39	40-70	{ 197 1	Good, G	1.6	3H	NG	OK
					{ 197 1	Good, SM	0.6	3H	OK	OK
					{ 197 1	Good, SG	0.6	8H	NG	OK
160 <sup>g</sup>	1	3.4	10	1-16	{ 197 1	Good, G	0.9	2B	OK	OK
					{ 197 1	Good, G	1.0	3H	NG	OK

a-c See Table 6

d Very dilute reactants

e Acid solution added to polymer solution

f Polymer solution containing 10% water added to acid solution

g Polymer solution added to acid solution

Table 8  
Effect of Pigment Loading on Coatings of Cr(DO)(MP)<sub>2</sub> on Cold-rolled 1010 Steel

Solvent	Coating Solution				Shelf Life Days	Curing of Coating		Coating Properties				
	Resin <sup>g</sup> g./100 ml.	TiO <sub>2</sub> g./100 ml.	Total Solids g./100 ml.	Hours Milled		°C.	hr.	Appear- ance <sup>b</sup>	Thickness mils	Pencil Hardness	Adhesion <sup>c</sup> Mandrel Tape	
1:1 THF: toluene	30 <sup>g</sup>	30	60	2	>148			Good, SM	0.6	2H	NG	OK
						197	1	Good, SM	0.8	4H	NG	OK
	40 <sup>g</sup>	22	62	6.8	>143			Fair, SM	1.6	9H	NG	OK
						197	1	Flaked	1-2	4H	NG	NG
	40 <sup>g</sup>	10	50	6	138			Good, D	1.5	F	NG	OK
						197	1	Good, D	1.0	9H	NG	Fair
	2.4	2.4	4.8	1.5	>148			Good, D	0.4	6H	Poor	OK
						197	1	Good, D	0.7	8H	Poor	OK
	2.8	1.5	4.3	6.5	122			Good, D	0.5	4H		OK
						197	1	Good, D	0.3	9H	NG	OK
	3.6	0.9	4.5	6	>137			Good, D	0.4	2H	NG	OK
						197	1	Good, D	0.5	B	NG	OK
	2.25	2.25	4.5	17.3	113			Good, D	0.6	4H	NG	OK
						197	1	Good, D	0.4	7H	NG	OK
	1.35	1.35	2.7		>135			Fair, D	0.4	9H	NG	OK
					197	1	Fair, D	0.4	9H	NG	OK	
2.92	1.58	4.5	17.3	113			Fair, D	0.6	3H	Fair	OK	
					197	1	Fair, D	0.7	5H	NG	Good	
1.95	1.05	3.0		>135			Good, D	0.5	9H	Good	OK	
					197	1	Good, D	0.4	9H	NG	OK	
1:2 THF: toluene	1.95	1.05	3.0	2	>127			Good, D	0.5	8H	NG	Good
						197	1	Good, D	0.4	8H	NG	Good
2:1 THF: o-DCB	2.92	1.58	4.5	22.3	>134			Good, D	0.9	3H	OK	OK
						197	1	Good, D	1.0	7H	OK	OK
1.95	1.05	3.0	2	>127			Fair, D	0.5	9H	Good	OK	
						197	1	Fair, D	0.3	9H	Good	OK
3.90	2.10	6.0	6	>126			Good, D	0.5	9H	OK	OK	
						197	1	Good, D	0.5	9H	OK	OK
1:1 THF: o-DCB	1.95	1.05	3.0	2	>127			Fair, D	0.3	9H	OK	OK
						197	1	Fair, D	0.3	9H	OK	OK
3.90	2.10	6.0	6	>126			Good, SM	0.3	7H	OK	OK	
						197	1	Good, SM	0.4	8H	Good	OK
6.50	3.50	10.0	5.5	>122			Good, D	1.0	3H	Poor	OK	
						197	1	Good, D	1.3	5H	Poor	OK
			21 <sup>h</sup>	>114			Good, SG	0.2	6H	OK	OK	
						197	1	Good, SG	0.2	7H	OK	OK
i			21 <sup>h</sup>	>106			Good, SG	0.2	7H	OK	OK	
						197	1	Good, SG	0.2	8H	Poor	OK
j			21 <sup>h</sup>	>106			Good, SG	0.1	7H	OK	OK	
						197	1	Good, SG	0.1	8H	Poor	OK
k			21 <sup>h</sup>	Did not disperse completely								
2.34	1.26	3.6	6	>92			Good, SM	0.2	4H	Poor	OK	
						197	1	Good, SM	0.2	6H	Poor	OK
						{197	1					
						{250	1	Good, SM	0.2	9H	Poor	OK
						{197	1					
						{300	1	Good, SM	0.2	9H	NG	NC

b, c See Table 6.

<sup>g</sup> Resin not cured before use if marked <sup>g</sup>. If unmarked, it was cured at 160° for 1 hr.

<sup>h</sup> Resin and TiO<sub>2</sub> milled in THF, recovered, and stirred into solvent.

<sup>i</sup> Resin cured at 160° for 2 hr.

<sup>j</sup> Resin cured at 170° for 1 hr.

<sup>k</sup> Resin cured at 190° for 1 hr.

some solvent solubility were not found (formulations marked <sup>h</sup> in Table 8) .

A TiO<sub>2</sub>-loaded paint was made thin enough for spraying (the last formulation in Table 8) and applied by spraying. Uniform coatings were obtained with 7-10 gloss (out of 39), 0.2-0.3 mil thickness, 3-6H hardness, good adhesion by the Scotch Tape test, and fair to poor adhesion by the 1/8" tapered mandrel and impact tests both before and after curing. The air-dried uncured coating was not attacked by jet oil or water for 24 hr. at room temperature. Cured spray-coated panels were placed in a cold oven, heated to 250 or 300° and held at the elevated temperature for 1 hr. before cooling back to room temperature. At 250° hardness increased and gloss and adhesion were unchanged, but at 300° the coating was discolored and loosened from the substrate.

These results with the Cr(DO)(MP)<sub>2</sub> coatings were sufficiently promising to encourage us to explore other tris(phosphinates) with greater thermal stability. Cured samples, nominally tris(phosphinates) as designated, were found by TGA in air to start losing weight at the indicated temperature with rapid loss commencing at the temperature in parentheses: Cr(DO)(MP)<sub>2</sub> 242 (242), Cr(MP)<sub>3</sub> 324 (421), Cr(DM)(MP)<sub>2</sub> 315 (406), Cr(DM)(DP)<sub>2</sub> 312 (354), Cr(DP)<sub>2</sub>(MP) 265 (329), and Cr(DP)(MP)<sub>2</sub> 300 (353). Apparently Cr(MP)<sub>3</sub> is the most stable thermally of the tris(phosphinates) studied. The uncured resins are all soluble to some extent in THF, chloroform, and o-DCB; Cr(MP)<sub>3</sub> is also soluble at least to some extent in DMF, 1,4-dioxane, methylene chloride, toluene, xylene, and benzene. The uncured films from these solutions on glass and steel tended to craze on drying but were not attacked by jet oil in 24 hr. at room temperature and were harder and more brittle than uncured Cr(DO)(MP)<sub>2</sub> films. Table 9 summarizes the exploratory dip coating studies on 1010 cold-rolled steel with these tris(phosphinates). Although most of the coatings were crazed, they were still adherent, except where flaking was observed, and could be tested by the standard methods. In general adhesion appears to be a problem with the more stable tris(phosphinates).

Table 9  
Exploratory Studies of Tris(phosphinate) Coatings Other Than Cr(DO)(MP)<sub>2</sub>

Polymer System g./100 ml.	Coating Solution			Curing of Coating hr. at 200°	Coating Properties					
	Other Solids g./100 ml.	Solvent	Total Solids g./100 ml.		Appear- ance	Thickness mils	Pencil Hardness	Adhesion <sup>a</sup> Mandrel Tape		
Cr(MP) <sub>3</sub>	28		CHCl <sub>3</sub>	28	0	Good	0.3	6H	NG	OK
	6.7		1:1 THF:o-DCB	6.7	1	Crazed	0.6	B-F	None	
					0	Good	<0.1	9H	NG	OK
					1	Good	<0.1	9H	NG	NG
28	Cr(DO)(MP) <sub>2</sub>	3	CHCl <sub>3</sub>	31	0	Good	1.0	5H	NG	Fair
					1	Poor	1.0	3H	NG	Fair
18.3	Unox Epoxide 221	1.7	CHCl <sub>3</sub>	20	0	Good	0.7	4H	NG	OK
					1	Poor	0.8	H	NG	NG
5.0	TiO <sub>2</sub>	2.7	CHCl <sub>3</sub>	7.7	0	Fair	<0.1	9H	NG	OK
					1	Poor	<0.1	9H	NG	Very Poor
b	18		7:10 1,4-di- oxane:CHCl <sub>3</sub>	18	0	Good	<0.1	4H	NG	OK
					1	Good	<0.1	4H	NG	NG
c	25		1:5 1,4-di- oxane:CHCl <sub>3</sub>	25	0	Crazed and Flaked - rubs off				
<sup>b</sup> Cr(DHP)- (MP) <sub>2</sub>	10		DMF	10	0	Good	<0.1	9H	NG	OK
					1	Good	<0.1	9H	NG	OK
<sup>c</sup> Cr(MP) <sub>3</sub>	25		1:5 1,4-diox- ane:CHCl <sub>3</sub>	25	0	Crazed and Peeled - rubs off				
Cr(DM)- (MP) <sub>2</sub>	28		CHCl <sub>3</sub>	28	0	Crazed and Flaked off				
	19.5	TiO <sub>2</sub>	10.5 1:1 THF:o-DCB	30	0	Crazed and Flaked off				
	25.2	Cr(DO)- (MP) <sub>2</sub>	2.8 CHCl <sub>3</sub>	28	0	Very Poor	1.0	3H	NG	OK
					1	Very Poor	1.0	5H	NG	OK
Cr(DM)- (DP) <sub>2</sub>	28		CHCl <sub>3</sub>	28	0	Crazed	1.0	2H	NG	Fair
					1	Crazed	1.0	H	NG	Poor
	19.5	TiO <sub>2</sub>	10.5 1:1 THF:o-DCB	30	0	Crazed	0.3	6H	NG	Very Poor
					1	Crazed, Flaked	0.4	4H	NG	NG
Cr(DP) <sub>2</sub> - (MP)	28		CHCl <sub>3</sub>	28	0	Crazed	0.8	H	NG	OK
					1	Crazed	0.8	F	NG	Poor
	18	Cr(DO)- (MP) <sub>2</sub>	2 CHCl <sub>3</sub>	20	0	Good	0.1	4H	NG	OK
					1	Good	0.1	6H	NG	OK
	18.7	Cr(DO)- (DP) <sub>2</sub>	9.3 CHCl <sub>3</sub>	28	0	Poor	0.3	5H	NG	OK
					1	Poor	0.3	3H	NG	Very Poor
Cr(DP)- (MP) <sub>2</sub>	28		CHCl <sub>3</sub>	28	0	Crazed	1.0	4H	NG	OK
					1	Crazed	1.0	4H	NG	NG

<sup>a</sup> NG indicates adhesion was no good.

<sup>b</sup> Substrate treated with Fosbond 20.

<sup>c</sup> Applied over preceding coating as top coat.

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13. ABSTRACT Water-repellent and transparent plasticized poly(metal phosphinate) compositions were developed for antistatic coatings on polyethylene. Coatings based on $\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPBu}_2\text{O})_2$ , $\text{Cr}(\text{H}_2\text{O})(\text{OH})[\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$ , $\text{Cr}(\text{H}_2\text{O})(\text{OH})-(\text{OPPh}_2\text{O})_2$ , and $\text{TiO}(\text{OPPh}_2\text{O})_2$ all dissipated a 5 kV positive charge in one second or less. Coatings based on $\text{TiO}(\text{OPPh}_2\text{O})_2$ also dissipated a 5 kV negative charge in one second or less and were essentially not tacky. The tris(phosphinate) $\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}][\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$ prepared in situ was found to be an effective thickener for a variety of lubricant fluids in the 5-14% concentration range. A thickener with substantially greater thermal stability was prepared by the reaction of $\text{Cr}(\text{H}_2\text{O})(\text{OH})[\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$ with $\text{Me}(\text{Ph})\text{P}(\text{O})\text{OH}$ . Greases made from DC550 and these thickeners exhibit drop points generally above 600°F. and good antiwear properties; however, their bearing performance is limited. Coatings of $\text{Cr}[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}][\text{OP}(\text{Me})(\text{Ph})\text{O}]_2$ pigmented with $\text{TiO}_2$ adhere well to cold-rolled 1010 steel and exhibit good hardness and resistance to jet oil or water. They can tolerate 250°C. in air for one hour but degrade at 300°C. The use of more stable chromium(III) tris(phosphinates), i.e., tris(phosphinates) containing no alkyl groups other than methyl, for coatings was briefly explored. Although the coatings based on these showed superior resistance to jet oil and water, adhesion to the 1010 steel was not satisfactory for the formulations investigated.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Inorganic Polymers Poly(Metal Phosphinates) Phosphinic Acids Chromium Titanium Cobalt Manganese Zinc Zirconium Applications Antistats Greases Thickeners Protective Coatings						

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