**Registry No.** NaNbWO$_6$, 37300-85-9; KNbWO$_6$, 18662-25-4; RbNbWO$_6$, 18662-27-6; CsNbWO$_6$, 18662-30-1; Na$_2$NbWO$_6$, 87566-88-9; K$_2$NbWO$_6$, 87566-87-8; Rb$_2$NbWO$_6$, 87566-89-0; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2.

---

(27) Permanent address: Chemistry Department, Michigan State University, East Lansing, MI 48824.

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

**D. W. Murphy***
**J. L. Dye**[27]
**S. M. Zahurak**

*Received August 16, 1983*

## Surface Modification of Conducting Particles. A New Approach to Conducting Plastics

*Sir:*

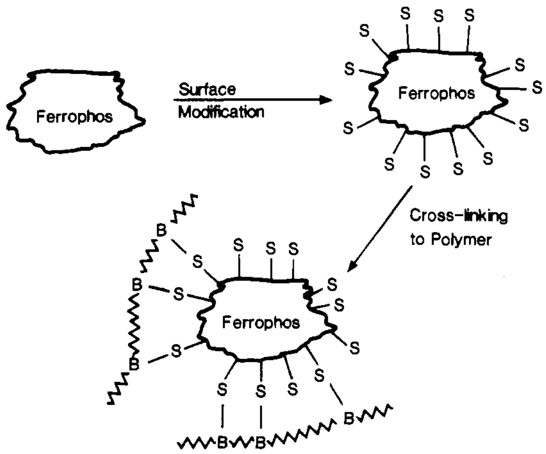
Conducting polymers have been the focus of avid study by chemists and physicists in recent years.[1] In addition to fundamental interest many potential commercial applications, e.g., batteries, radio-frequency interference, and electrophotography, are envisaged for conducting polymers. The most widely studied conducting polymers (e.g., polyacetylene) possess extended $\pi$ systems that are partially oxidized or reduced with dopants. These polymeric conductors are frequently brittle and react with oxygen.

An alternate approach to developing conducting polymers is to use refractory conducting inorganic particles and covalently bond them to a polymeric matrix. The resulting conductive polymer would maintain some of the physical properties of the polymer.

Herein, using ferrophosphorus[2] (**1**) as an exemplary conducting pigment, we demonstrate that both surface-modified[3] and polymer-bound conducting particles can be achieved without deleteriously affecting the conductivity of the conducting particle (Scheme I).

Silanation of **1** with either alkoxy- or chlorosilanes does not directly occur. Pretreatment of **1** with 1 M NaOH (3 days, 25 °C) leads to hydroxylation of **1**[4]. Hydroxylated **1** may be silanated with chlorosilanes, but not ethoxysilanes, in toluene. With use of (3-chloropropyl)dimethylchlorosilane the -OSiMe$_2$(CH$_2$CH$_2$CH$_2$Cl) pendant group is grafted onto **1**. The presence of this pendant group was confirmed with use of energy-dispersive X-ray (EDX) and ESCA analyses. The EDX spectra (Figure 1) show the presence of chlorine and enhanced abundance of silicon for the silanated **1**. With ESCA, chlorine is observed at a binding energy of 198.8 eV.

**Scheme I.** Generalized Procedure To Modify Ferrophosphorus[a]



[a] S is a surface group, and B is a point of attachment of S to a polymeric binder.

**Scheme II.** Reaction Sequences To Introduce EDX Tags to Styryl Groups on the Surface of **1**

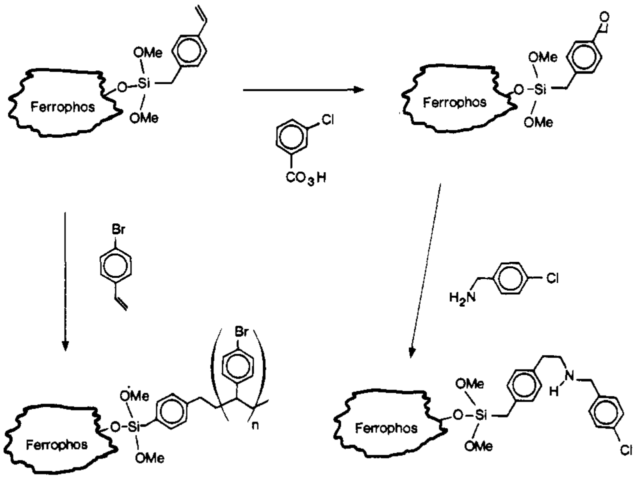
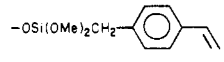


**Table I.** Surface Resistivity of Surface-Modified Ferrophosphorus

| | surface resistivity,[a] Ω/in. | |
|---|---|---|
| | Ferrophos:PVC[b] ratio[c] | |
| attached surface group | 9:1 | 8:2 |
| none (unmodified) | 4 | 9 |
| -OSiMe$_2$CH$_2$Cl | 3 | 7 |
| -OSiMe$_2$(CH$_2$)$_3$Cl | 3 | 7 |
| -OCH$_2$CH=CH$_2$ | 3 | 3 |
| -OCH$_2$CHCH$_2$<br>\ /<br>O | 3 | 8 |
| -OSiCl$_2$C$_{20}$H$_{42}$ | 3 | 6 |
|  | 8 | 31 |

[a] Nominally 75-$\mu$m thickness. [b] PVC = poly(vinyl chloride). [c] Weight basis.

Attachment of the alkoxy pendant group was achieved by reacting allyl alcohol (containing 5% LiMe) with **1** (1 day, 25 °C). Confirmation of allylalkoxylation of **1** required introduction of an EDX tag. We epoxidized the allyl alkoxide with *m*-chloroperbenzoic acid and subsequently reacted the epoxide with a tagged epoxide-sensitive reagent, *p*-chlorobenzylamine. The ESCA spectrum of the epoxidized functional group shows a new peak at 288.3 eV assignable to the C$_{1s}$ in the strained three-membered ring containing the electronegative oxygen. EDX spectra confirm the presence of chlorine resulting from the latter reactions.

---

(1) Seymour, R. B.; Ed. "Conductive Polymers"; Plenum Press: New York, 1981; *Chem. Eng. News* **1982**, *60* (16), 29–33; *Mol. Cryst. Liq. Cryst.* **1981–1982**, *77, 79, 81, 83, 85, 86.*

(2) Hooker Chemical Co. commercial Ferrophos product, nominally of Fe$_{16}$P composition with Mn, Ti, and Si impurities. Median particle size is 6.5 $\mu$m; 400 mesh and finer was used for the studies herein. Briel, G. In "Metallurgy of Ferroalloys", 2nd ed., Volkert, G., Frank, K. D., Eds.; Spinger-Verlag: New York, 1972; Chapter 7.

(3) Reviews include: Miller, J. S., Ed. "Chemically Modified Surfaces in Catalysis and Electrocatalysis"; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 192. Arkles, B. *CHEMTECH* **1977**, *7*, 766–778. Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135–141. Leyden, D. E.; Collins, W., Eds. *Midl. Macromol. Monogr.* **1980**, *7*. Pleuddemann, E. P. "Silane Coupling Agents"; Plenum Press: New York, 1982.

(4) Upon hydroxylation a new P Auger peak assignable to P$^{\mathrm{V}}$OH appears at 398.7 eV.

(5) Control reactions, e.g., *p*-chlorobenzylamine and unmodified **1**, hydroxylated **1**, or allyl alcohol modified **1**, did not result in positive EDX tests for chlorine.

0020-1669/83/1322-3681$01.50/0 © 1983 American Chemical Society

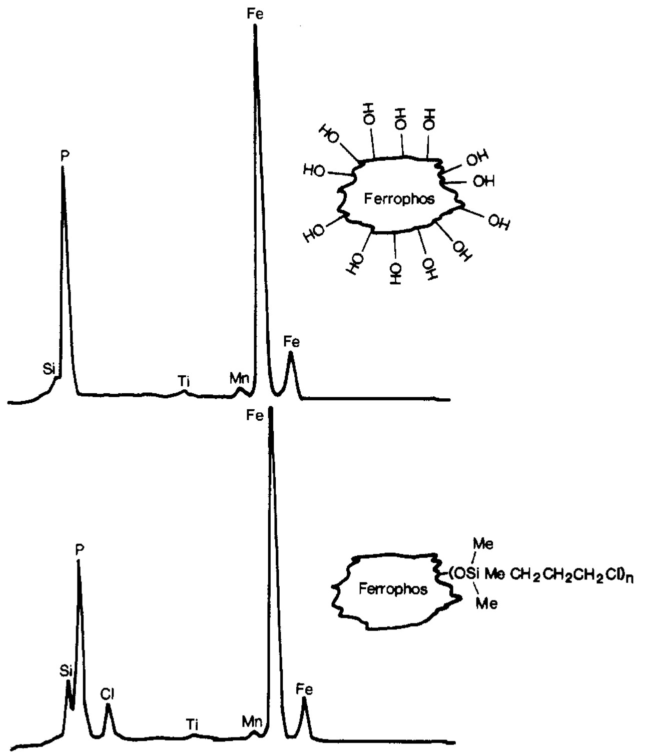


**Figure 1.** EDX spectra for hydroxylated Ferrophos (identical with that of unmodified Ferrophos) (top) and its reaction product with $ClSiMe_2C_3H_6Cl$ (bottom).

The conductivity ((resistivity)$^{-1}$) was not reduced by grafting of the pendant groups on the surface. The surface resistivities of 1 in. diameter pellets comprised of 9:1 (and 8:2) **1** in a polyvinylchloride matrix are given in Table I. The conductivity of the surface-modified **1** is comparable to and in some cases exceeds that of unmodified **1**: e.g., actual 75–100-$\mu$m epoxy-based films made with allyl alkoxy modified **1** exhibited lower surface resistivity (33 vs. 80 $\Omega$/in) and, thus, reduced the time to electroplate by 25% relative to that for comparable films based on **1**. Clearly the anticipated monolayer coverage of the organic pendant groups does not interfere with the interparticle contacts; thus, the conductivity is not substantially reduced.

Direct binding of the surface-modified **1** with a polymer was achieved by introducing a styryl group to the surface and cross-linking it with styrene.[6] The styryl group was introduced by treating **1** with tetrachlorosilane to nominally form $-OSiCl_3$ on the surface. Subsequent reaction with $ClMgCH_2$-$p$-$C_6H_4CH{=}CH_2$ in diethyl ether[7] and washing with methanol forms $-OSi(OMe)_2CH_2$-$p$-$C_6H_4CH{=}CH_2$ on the surface. Confirmatory epoxidation and amination (Scheme II) as well as the control reactions were carried out. Cross-linking of styryl-modified **1** was achieved with 4-bromostyrene by using 2,2′-azobis(2-methylpropionitrile) initiator (95 °C, 3 h). EDX spectra confirm via the presence of the bromine that direct binding of the polymer to the conducting particles occurred.[8]

Thus, we have shown that refractory conducting pigments may be surface modified with chlorosilanes or alkoxides without deteteriously affecting the conductivity. These surface-modified groups may be further reacted with reagents to introduce new functional groups to the surface and even cross-link with polymer matrices. Radiolabeling experiments using, e.g., $^3H$ and $^{14}C$, are required to determine the extent of surface coverage and degree of polymerization.

**Acknowledgment.** We thank Drs. Jasinski, K. Kem, P. DiGiacomo, and the late M. B. Dines for stimulating discussions and E. Shearin for technical assistance.

**Registry No.** Ferrophosphorus, 8049-19-2; chloro(3-chloropropyl)dimethylsilane, 10605-40-0; allyl alcohol, 107-18-6; polystyrene (homopolymer), 9003-53-6.

---

(6) Polymerization of epoxidized 1 with epoxy polymers was also demonstrated.
(7) Kem, K. U.S. Patent 3 649 668, March 14, 1972.
(8) Exhaustive washing (66 h) with toluene and methyl ethyl ketone was undertaken to remove any unpolymerized and un-cross-linked 4-bromostyrene.

* Address correspondence to E. I. du Pont de Nemours and Co., Wilmington, DE 19898.

Occidental Research Corporation
Irvine, California 92713
**Joel S. Miller***

*Received August 25, 1983*