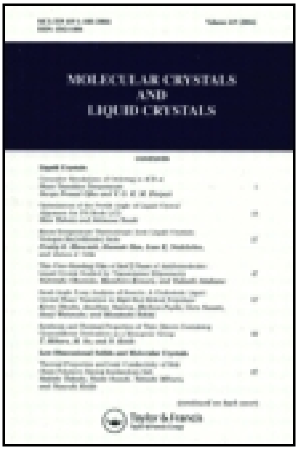

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Surface Modification Of Conducting Particles. A New Approach To Conducting Polymers.

Joel S. Miller [a] [b]
[a] Occidental Research Corporation
[b] E.I. du Pont de Nemours & Co., Inc., Experimental Station Bldg. 328, Wilmington, DE, 19898

Version of record first published: 20 Apr 2011.

To cite this article: Joel S. Miller (1985): Surface Modification Of Conducting Particles. A New Approach To Conducting Polymers., Molecular Crystals and Liquid Crystals, 121:1-4, 321-324

To link to this article: http://dx.doi.org/10.1080/00268948508074882

Mol. Cryst. Liq. Cryst. 1985, Vol. 121, pp. 321-324
0026-8941/85/1214-0321/$10.00/0

Printed in the United States of America

SURFACE MODIFICATION OF CONDUCTING PARTICLES. A NEW APPROACH TO CONDUCTING POLYMERS.[1]

JOEL S. MILLER*
Occidental Research Corporation‡

Abstract Conducting polymers based on binding a highly conducting inert inorganic solid and insulating polymer matrices have been prepared. Films prepared with the surface modified pigments exhibit surface conductivities comparable to and in some cases greater than those prepared from unmodified pigments.

INTRODUCTION

Intrinsically conducting polymers have been the focus of intense study by chemists and physicists in recent years. An alternate approach to developing conducting polymers is to use refractory conducting inorganic particles and covalently bond them to a polymeric matrix; thus, 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, Fig. 1.

RESULTS AND DISCUSSION

Silanation of 1 with either alkoxy or chlorosilanes does not directly occur. Pretreatment of 1 with NaOH leads to hydroxylation

---

* Current address: E.I. du Pont de Nemours & Co., Inc.
Experimental Station Bldg. 328, Wilmington, DE 19898

‡ Deceased

of 1[4]. Hydroxylated 1 may be silanated with chlorosilanes, e.g., using chloropropyldimethylchlorosilane the $-OSiMe_2(CH_2)_3Cl$ pendant group is grafted onto 1. The presence of this pendant group was confirmed using energy dispersive X-ray (EDX), Fig. 2, and ESCA analyses (Cl is observed at a binding energy of 198.8 eV).

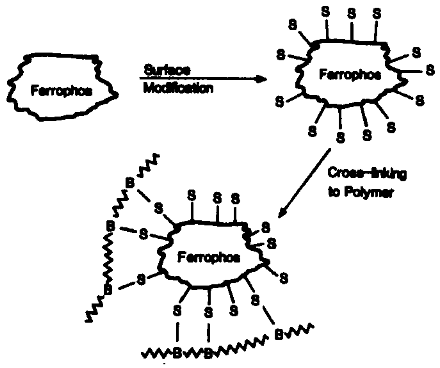

FIGURE 1 Generalized Procedure To Modify Ferrophosphorus S is a surface group, and B is a point of attachment of S to a polymeric binder.

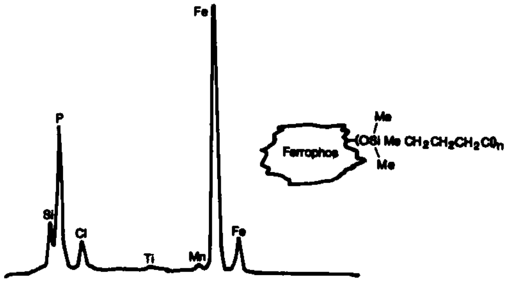

FIGURE 2 EDX spectra for Ferrophos surface modified with $ClSiMe_2C_3H_6Cl$ (bottom).

Attachment of the alkoxy pendant group was achieved by reacting allyl alcohol (containing 5% $LiCH_3$) with 1. Confirmation of allylalkoxylation required introduction of an EDX tag. Thus, after epoxidization with *m*-chloroperbenzoic acid we reacted the epoxide with *p*-chlorobenzylamine to introduce the EDX active Cl tag, Fig. 3. 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.

The conductivity was not deleteriously affected by grafting of the pendant groups on the surface. The surface resistivity of 1 inch diameter pellets comprised of 9:1 1 in a polyvinylchloride matrix are comparable to and in some cases exceeds that of unmodified 1. Actual 75-100 μm epoxy based films made with allyl alkoxy modified 1 exhibited lower surface resistivity (33 vs. 80 ohm/in) and, thus, reduced the time to electroplate by 25% relative to comparable films based on 1, Fig. 4.

Direct binding of the surface modified 1 with a polymer was achieved by introducing a styryl group to the surface and crosslinking it with styrene.[1,6] Crosslinking of styryl modified 1 was achieved with 4-bromostyrene using 2,2'-azobis(2-methylpropionitrile) initiator. EDX spectra confirm via the presence of the bromine in the crosslinked product.[8]

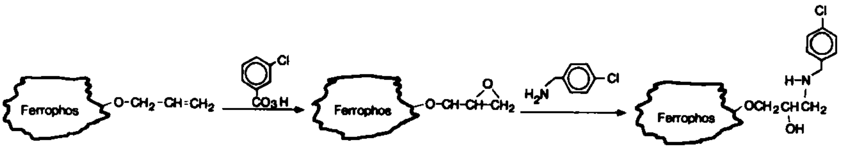

FIGURE 3 Epoxidation and amination of allyl alkoxide pendant to a Ferrophos particle.

SUMMARY

Thus, we have shown that refractory conducting pigments may be surface modified with chlorosilanes or alkoxides without deleteriously affecting the conductivity. These surface modified

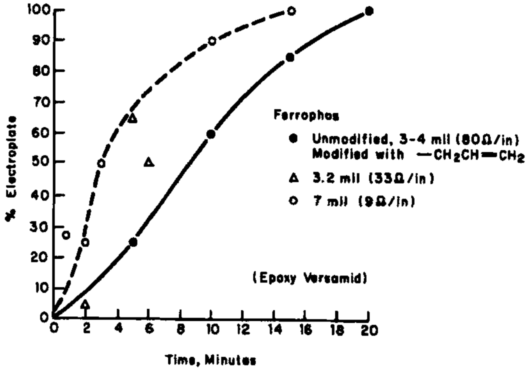

FIGURE 4 Plating time for unmodified and allyl alkoxide modified Ferrophos.

groups may be further reacted with reagents to introduce new functional groups onto the surface and even crosslink with polymer matrices to form a conducting polymer.

REFERENCES

1. J.S. Miller, Inorg. Chem., 22, 2681-2682 (1983).
2. Hooker Chemical Co. commercial Ferrophos™ product. Nominally of $Fe_{1.6}P$ composition with Mn, Ti, and Si impurities. Median particle size is 6.5 μm; 400 mesh and finer was used.
3. Reviews: e.g., J.S. Miller, ed. "Chemically Modified Surfaces in Catalysis and Electrocatalysis," A.C.S. Symp. Ser., 192, 1982; D.E. Leyden, W. Collins, eds., "Silylated Surfaces," Midland Macromolecular Monographs, Vol. 7, Gordon and Breach, Inc., 1980; and E.P. Pleuddemann, "Silane Coupling Agents," Plenum Pub. Corp., New York, N.Y., 1982.
4. Upon hydroxylation a new P Auger peak assignable to $P^{V}OH$ 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.
6. Polymerization of epoxidized 1 with epoxy polymers was also demonstrated.
7. K. Kem, U.S. Patent #3,649,668 (March 14, 1972).
8. Exhaustive washing (66 hrs) with toluene and methylethylketone was undertaken to remove any unpolymerized and uncrosslinked 4-bromostyrene.