

MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD A109789

**LEVEL II**

12

C81-620/201

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0636

Task No. NR 359-667

TECHNICAL REPORT NO. 4

Lanthanide Diphthalocyanines. Electrochemistry and  
Display Applications

by

M. M. Nicholson

Prepared for Publication

in

Industrial and Engineering Chemistry

Autonetics Strategic Systems Division  
Defense Electronics Operations  
Rockwell International  
Anaheim, California

January 1982

DTIC  
JAN 20 1982  
E

Reproduction in whole or in part is permitted for  
any purpose of the United States Government.

This document has been approved for public release  
and sale; its distribution is unlimited.

DTIC FILE COPY

01 18 82 078

391827

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-109789	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Lanthanide Diphthalocyanines. Electrochemistry and Display Applications	5. TYPE OF REPORT & PERIOD COVERED Technical 1 Sept. 1980 to 15 Aug. 1981	6. PERFORMING ORG. REPORT NUMBER C81-620/201
7. AUTHOR(s) M.M. Nicholson	8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0636	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
9. PERFORMING ORGANIZATION NAME AND ADDRESS Autonetics Strategic Systems Division Rockwell International P.O. Box 4192, Anaheim, CA 92803	11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217	12. REPORT DATE January 1982
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	14. SECURITY CLASS. (of this report) Unclassified	13. NUMBER OF PAGES 38
15. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in Industrial and Engineering Chemistry.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) rare earths diphthalocyanines electrochemistry electrochromism displays		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electrode films of lanthanide diphthalocyanines undergo a series of reversible color changes that make them potentially very attractive as flat-panel color display materials. Research on these compounds has revealed a complex scheme of electrode processes that is not yet fully characterized. The solid organic phases within the faradaic system include new room-temperature anion and cation conductors, as well as electronic semiconductors. Application of diphthalocya- nine electrochromics to practical display products will depend on development of adequate cycle life and a technique for matrix addressing.		

DD FORM 1 JAN 73 1473

UNCLASSIFIED  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

**LANTHANIDE DIPHthalOCYANINES. ELECTROCHEMISTRY AND DISPLAY APPLICATIONS**

**Margie M. Nicholson**

**Autonetics Strategic Systems Division, Rockwell International,  
Anaheim, California 92803**

**ABSTRACT**

Electrode films of lanthanide diphthalocyanines undergo a series of reversible color changes that make them potentially very attractive as flat-panel color display materials. Research on these compounds has revealed a complex scheme of electrode processes that is not yet fully characterized. The solid organic phases within the faradaic system include new room-temperature anion and cation conductors, as well as electronic semiconductors. Application of diphthalocyanine electrochromics to practical display products will depend on development of adequate cycle life and a technique for matrix addressing.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution _____	
Availability Codes	
_____ or _____	
Dist _____	
<b>A</b>	

Diphthalocyanine complexes of the lanthanide rare earths were first prepared and investigated by Russian scientists. These relatively new members of the phthalocyanine family have a sandwich structure resembling that of the ferrocenes. Moskalev and Kirin (1970a) reported that a film of lutetium diphthalocyanine on a transparent conductive tin oxide electrode underwent a series of striking color changes as the applied potential was varied in aqueous potassium chloride solution. That observation has led others to evaluate the rare-earth diphthalocyanines as electrochromic display materials and to investigate their basic electrochemistry. This research has emphasized the lutetium compound, although the electrochromism is known to occur in diphthalocyanines of all the lanthanide elements and of several other trivalent metals.

An exceptional range of chemical behavior is found in these systems. The discrete organic phases, characterized by different oxidation states of the dye, include electronic conductors, solid anion and cation conductors, and presumably ion exchangers. They may also include hydrates and oxygen adducts. Because of their close relationship to the chlorophylls and porphyrins, the diphthalocyanines might serve as dimeric model compounds for research on natural products.

This article provides a survey and critique of electrochemical investigations on the lanthanide diphthalocyanines. It then describes their display characteristics and status in relation to liquid crystals and other flat-panel display technologies. With further development

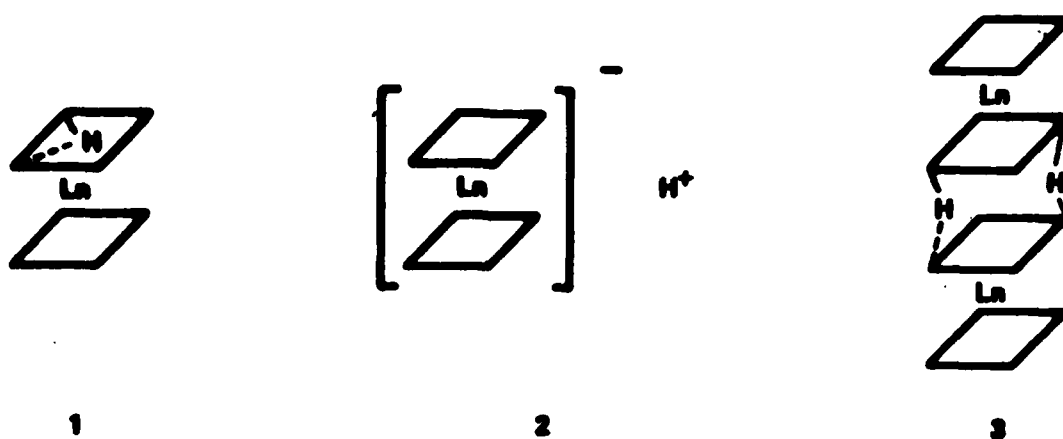
over the next several years, the multicolor diphthalocyanine electrochromics may be ready for application to military, industrial, and consumer products.

### Composition and Structure

Lanthanide diphthalocyanines are synthesized by heating the rare-earth acetate or chloride with *o*-phthalonitrile (Moskalev and Kirin, 1970b; Mackay et al., 1974). An exothermic reaction near 300° produces the desired material and a number of by-products, which may include monophthalocyanines. The crude solid reaction product is pulverized and washed in several organic solvents to extract lower molecular weight components. Further purification by liquid chromatography yields the diphthalocyanine, which may appear in both blue and green forms not yet fully distinguished from one another (Mackay et al., 1974). The chromatographic step can be eliminated by vacuum subliming the diphthalocyanine from the washed powder. In a thin layer, the resulting deposit is a bright green film with an optical absorption peak near 670 nm.

Figure 1 indicates the phthalocyanine ring structure and its conventional symbols. Pc denotes the phthalocyaninato group  $C_{32}H_{16}N_8$ . The presence of two of these units in the lanthanide (Ln) diphthalocyanine molecule is confirmed by elemental analysis (Mackay et al., 1974; Kirin et al., 1967; Chang and Marchon, 1981) and mass spectroscopy (Chang and Marchon, 1981). By analogy to other metal phthalocyanine

complexes, the formula is written  $\text{LnHPc}_2$ , or  $\text{PcLnPcH}$ , which implies a trivalent rare earth and a labile imino hydrogen. On this basis, a dipthalocyanine molecule could be represented by structure 1.



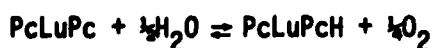
Structure 2, with the hydrogen ion delocalized, was suggested by Yamana (1977). Kasuga et al. (1980) later found crystallographic evidence that the eight central nitrogen atoms of the two rings are equivalent; this is consistent with an ionic or intermolecular hydrogen-bonded structure for the solid. Moskalev et al. (1979) proposed the hydrogen-bonded double-sandwich dimer 3 for solutions of americium and lanthanide dipthalocyanines in benzene. Structures 1-3 are only schematic and are not intended to show quantitatively the spatial or angular relationships of the rings.

Quite recently, Chang and Marchand (1981) have questioned the existence of the acidic hydrogen in lutetium dipthalocyanine on the basis of mass spectra, magnetic susceptibility, and electron paramagnetic resonance (EPR) data. The sum of isotopic masses in  $\text{LuHPc}_2$  is



is 1200, but a mass of 1199 was observed instead. Since the parent mass is prominent in the mass spectrum of metal-free phthalocyanine (Ely et al., 1973), a peak at 1200 would be expected for LuHPc<sub>2</sub>. Magnetic and EPR data showed the green form of lutetium diphthalocyanine to be paramagnetic, in agreement with EPR measurements of Corker et al. (1979). To account for the lower mass number and the paramagnetism, Chang and Marchand proposed the formula Lu(III)Pc<sub>2</sub>, with an unpaired electron, either in one ring or delocalized on the two rings. This is comparable to the formula PclnPc<sub>ox</sub> which Moskalev and Shapkin (1977, 1979) assigned to an anodic electrocrystallization product with an optical absorption peak at 682 nm. However, Chang's green material and Corker's had peaks at 665 nm; hence they must have differed from Moskalev's. Corker et al. attributed the paramagnetism of the green form to its existence as a salt LuHPc<sub>2</sub><sup>+</sup>A<sup>-</sup> containing a radical cation and an unidentified anion.

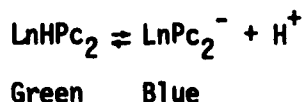
The writer proposes a variation of this: The paramagnetic green compound may be an oxygen complex such as PcluPch·O<sub>2</sub> or PcluPch<sup>+</sup>O<sub>2</sub><sup>-</sup>. A precedent is found in the EPR-active oxygen adducts of divalent-metal phthalocyanines, for which Raynor et al. (1977) suggested the structure M(II)Pc<sup>+</sup>O<sub>2</sub><sup>-</sup>. Decomposition of the oxygenated lutetium complex to LuPc<sub>2</sub> and HO<sub>2</sub>, or its equivalent in water and oxygen, could account for the mass spectral peak at 1199. The imino hydrogen should be restorable by reaction with water.



I

Influences of oxygen and water on the diphthalocyanine electrochemical processes have been observed in this laboratory (Nicholson and Pizzarello, 1980b) and are still under investigation.

There is distinct evidence in support of the protonated form  $\text{LnHPc}_2$ . First, electrode films of the proton-free compounds  $\text{UPc}_2$  and  $\text{ThPc}_2$  are not electrochromic (Moskalev and Alimova, 1975). This indicates a significant structural difference. Moreover, the infrared spectra of materials designated as  $\text{LnHPc}_2$  contain an imino hydrogen band and other features not found in the spectra of oxidized forms represented by Moskalev et al. (1979) as  $\text{PcLnPc}_{\text{ox}}$ . Finally, the visible spectra of lanthanide diphthalocyanines depend on pH. In a rather detailed study of dimethylformamide (DMF) - water solutions, Moskalev and Alimova (1975) interpreted this dependence in terms of the equilibrium



·II

and evaluated  $\text{pK}_a$ 's of 4.5 to 5.5 near 20°. Mackay et al. (1974) obtained similar results but noted that the straightforward acid-base equilibrium could be an oversimplification.

### Electrochemistry

The rare-earth diphthalocyanines have been investigated electrochemically as thin solid films and as solutions in organic and aqueous-organic solvents. They undergo a number of faradaic oxidation and

reduction reactions, which may differ in mechanism, or even in stoichiometry, for the solid and dissolved states. The experimental methods have included manual potential-step (Moskalev and Alimova, 1975; Moskalev and Kirin, 1972; Moskalev and Kirina, 1975) galvanostatic (Nicholson and Pizzarello, 1980a), potentiostatic (Nicholson et al., 1980) and optical (Nicholson and Pizzarello, 1980a; Nicholson et al., 1980) transients, cyclic voltammetry (Nicholson and Galiardi, 1977, 1978; Moskalev and Shapkin, 1978), and a novel solid-state moving-boundary technique (Nicholson and Pizzarello, 1979). Supplemental information has been obtained with radiotracers (Moskalev and Kirina, 1975; Pizzarello and Nicholson, 1980), visible absorption spectroscopy (Chang and Marchon, 1981; Corker et al., 1979; Moskalev and Kirin, 1972; Nicholson and Galiardi, 1977, 1978), EPR (Chang and Marchon, 1981; Corker et al., 1979), and magnetic susceptibility (Chang and Marchon, 1981). The solution studies have focused on the faradaic  $n$  values and identities of the reaction products. Research on the films has dealt with those questions and with the organic solid-state transport processes that can dominate the electrode kinetics.

It is evident from the diversity of proposed formulas in Table 1 that further work is needed to characterize the electrochemical reaction products. Disparities arise primarily from the assignment of different compositions to the green starting material:  $\text{LuH}(\text{Pc})_2$  by Moskalev and Kirin (1972) and Nicholson and Pizzarello (1979),  $\text{LuHPc}_2^+ \text{A}^-$  by Corker et al. (1979), and  $\text{LuPc}_2$  by Chang and Marchon (1981).

Further problems occur when the charge measurements yield nonintegral  $n$  values (Nicholson and Pizzarello, 1980a; 1979) or the reactions are incomplete (Corker et al., 1979). Oxygen complexes are not indicated in the table, but they may belong within the electrochemical scheme.

The variety of results obtained probably reflects the actual existence of more than one green starting material, for which the stabilizing conditions have not yet been determined. The phase rule predicts that two solid phases could exist in equilibrium with the gas if three chemical components, such as  $\text{LuPc}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$ , were sufficient, and both temperature and pressure were allowed to vary. This ideal situation may not be realized in practice, but an effort to establish and characterize it over a range of temperatures seems desirable.

In summary, the red, yellow, or brownish products result from loss of 1 or 2 electrons by the green form(s) of the diphthalocyanine. Reductions to blue and violet materials have been shown to occur with the gain of 1 to 3 or 4 electrons. Still further reduction would not be surprising, since phthalocyanines of divalent metals such as zinc or magnesium dissolved in organic solvents can accept up to 4 electrons per molecule (Clack and Yandle, 1972).

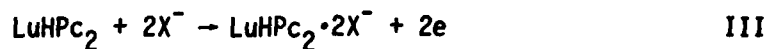
Anodic Processes. Initially, Moskalev and Kirin (1972) ascribed the electrochromism of lutetium diphthalocyanine at anodic potentials to complexation of the dye with oxygen or water. Although these processes may occur, it soon became evident that oxidation of the film

involved faradaic electron transfer. Moskalev and Kirina (1975) showed this indirectly by measuring the uptake of radioactive iodine from an iodide solution at a lutetium diphthalocyanine anode, and Nicholson and Galiardi (1977, 1978) demonstrated it coulometrically in potassium chloride.

With the moving-boundary technique illustrated in Figure 2, Nicholson and Pizzarello (1979) investigated the charge and material transport processes occurring within the solid dye film as it was anodically oxidized in the presence of ambient oxygen. The film was supported by an insulating alumina substrate. Under constant applied current, the green/red color boundary was propagated upward from the liquid contact. The boundary velocity was determined by measuring the propagation distance  $x$  as a function of time. The electric field within the red phase was mapped by raising the electrolyte level in successive increments and observing the corresponding voltage drops. The green film is an electronic semiconductor. It was concluded that the red product behaved as a solid anion conductor near 25°. For  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , the ion mobility was  $4 \times 10^{-6} \text{ cm}^2/\text{V-s}$ , and the approximate bulk resistivity in the red phase was 1,000 to 2,000 ohm-cm. Further results are given in Table 2.

Independently, Yamana (1979) used a similar qualitative technique with erbium diphthalocyanine films. He also attributed anodic color propagation from the electrolyte interface to the anion injection mechanism. Pizzarello and Nicholson (1980) confirmed with radiotracers

that chlorine and sulfur were present in the propagated red films at levels corresponding to  $n = 2$  or  $3$ . From these results and the tracer work of Moskalev and Kirina (1975), the anodic reaction of lutetium diphthalocyanine in a halide ( $X^-$ ) electrolyte has been written



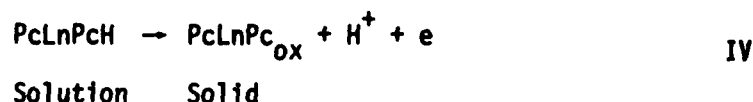
This process is not pH sensitive. However, the anodic boundary propagation requires some ambient water vapor and, with a sulfate solution, can also require oxygen (Nicholson and Pizzarello, 1980b). These ambient effects are not yet well understood; they suggest the existence of hydrates and possibly room-temperature oxygen carriers among the dye phases present.

Stabilities of red forms propagated in lutetium diphthalocyanine films with different anions were compared by observing changes in the absorption spectrum on open circuit for about 20 hr while the lower end of the film remained in the electrolyte (Pizzarello and Nicholson, 1981). Red films prepared with sulfate, chloride, or bromide ions were stable, while those prepared with the more mobile fluoride or acetate ions decayed to green with first-order rate constants near  $0.1 \text{ hr}^{-1}$ . Slow oxidation of water by the red dye species was the suggested cause of chemical color reversal.

The kinetics of the anodic process in lutetium diphthalocyanine films on tin oxide was investigated by recording galvanostatic and optical-absorption transients with the electrode completely immersed

in aqueous KCl (Nicholson and Pizzarello, 1980a). In this more usual cell configuration, the reaction occurred in milliseconds to seconds, while the lateral boundary propagations took several hours. Optical and electrical transition times marking the end of the oxidation process were in good agreement. The apparent n's ranged from 0.7 to 2.0 at current densities of 0.3 to 265 mA/cm<sup>2</sup>. The solid-electrolyte model also fit the galvanostatic transient data, with an ionic space charge in the red phase as the rate-controlling factor. Potentiostatic transients have been examined in lesser detail (Nicholson et al., 1980). They are somewhat more difficult to interpret but can be useful in correlating display switching characteristics with the basic electrochemistry.

Moskalev et al. (1979) and Moskalev and Shapkin (1978) used anodic electrocrystallization to isolate diphthalocyanines, including an americium compound, from the partially purified organic synthesis products. They gave the equation



for electrocrystallization from DMF solutions containing some water and hydrazine hydrate. A 1-electron transfer was confirmed for the reverse process by linear potential-sweep voltammetry. Although the hydrazine hydrate may not have been simply an inert solvent, it had no obvious effect on the cathodic scan (Moskalev and Shapkin, 1978). In its absorption spectrum, PcLuPc<sub>ox</sub> thus prepared differs from Nicholson's

red  $\text{LuHPc}_2^{++} \cdot 2\text{X}^-$  and from Chang's green  $\text{LuPc}_2$ . It resembles, instead, Chang's oxidized species designated as  $\text{LuPc}_2^+$ .

Corker et al. (1979) carried out essentially complete electrolyses of lutetium diphthalocyanine dissolved in DMF and examined the initial and final solutions by absorption spectroscopy and EPR. Formulas of the reaction products were derived from the magnetic changes rather than electrical charge measurements.

Chang and Marchon (1981) isolated a diamagnetic yellow-tan oxidation product from the chemical reaction of green lutetium diphthalocyanine with phenoxathiin hexachloroantimonate. Elemental analysis agreed with the composition  $\text{LuPc}_2^+ \text{SbCl}_6^-$ , and the change in magnetism indicated the loss of one electron. However, the optical absorption spectrum of the yellow-tan material resembled that of the yellow-red species which Corker wrote as  $\text{LuH}(\text{Pc})_2^{++}$ . At a molecular weight near 1,200, elemental analysis could not be expected to determine the presence of one additional hydrogen atom.

Cathodic Processes. The same questions concerning the green starting material can influence the formulation of the cathodic reactions. The original suggestion of Moskalev et al. (Moskalev and Kirin, 1970a; 1970b; Moskalev and Alimova, 1975) that the green-to-blue transformation of a lutetium diphthalocyanine film is due to field-induced acid ionization of the dye is contradicted by later findings that one or more electrons are gained in the process (Nicholson and Gallardi, 1977, 1978; Nicholson and Pizzarello, 1981). Nicholson and



Pizzarello recently investigated the cathodic electrochromism in HCl and KCl under a helium atmosphere by the moving-boundary technique. The results conform to a cation-injection model analogous to the anion-injection process found in the oxidations. Significantly, only light blue 1- or 2-electron reduction products were obtained in the propagations with metal cations, while dark blue to violet 3- or 4-electron products were obtained with the acid. A hydrogen-ion mobility of  $8 \times 10^{-7} \text{ cm}^2/\text{V-s}$  and an estimated bulk resistivity of 1,800 ohm-cm were determined in the dark colored material propagated from HCl. With the dye on tin oxide, completely immersed in aqueous KCl, both light and dark blue, as well as violet, cathodic products can be formed (Nicholson and Galiardi, 1977, 1978). Protonation of the dye in the neutral electrolyte may occur indirectly by coupled chemical reaction with cathodic hydrogen adsorbed on tin oxide, rather than by direct electron and proton injection into the organic solid (Nicholson and Pizzarello, 1981).

The blue and violet products are readily oxidized to green in air and tend to peel away from some inorganic substrates. They are also more soluble than the green form in organic solvents such as acetonitrile and dimethyl sulfoxide (Nicholson and Pizzarello, 1981). For these reasons, the reduced forms are more difficult to handle experimentally than the oxidation products.

Table 1 lists a variety of proposed cathodic products. Corker et al. (1979) showed that the absorption spectrum of lutetium

diphthalocyanine dissolved in DMF depended on the purity of the solvent and attributed the blue form to a reducing agent in the unpurified liquid. Chang and Marchon (1981) produced a spectrally similar blue solution in dichloromethane by first reducing the green form to violet with zinc amalgam and then converting it to blue by exposure to air. This blue form is not necessarily one of the electrochemical products. Further study of the cathodic electrochromism by electrochemical and spectroscopic methods is in progress in this laboratory. Kinetically, Billat et al. (1981) have noted faster coloration of lutetium diphthalocyanine in the cathodic regime than in the anodic, but details of their work have not yet been published.

The electrochemical kinetics, the participation of ions and other dissolved species, and the practical problem of adhesion all bear importantly on the use of diphthalocyanine films in electrochromic displays. The next section gives a technological perspective on these new display materials.

#### Display Applications

In display technology, electrochromics stand today where liquid crystals stood some years ago. The blue and white tungsten oxide electrochromic now meets performance requirements of electronic timepieces (Kaneko et al., 1981) but has not yet claimed a share of commercial or military display markets. The rare-earth diphthalocyanines are a newer system, very different chemically, and more exciting

aesthetically, but still awaiting the intensive development effort that must precede manufacturing. The potential applications include electronic games, appliances, automotive instrument panels, and industrial controls, as well as military devices ranging from simple bar graphs to battery operated emergency equipment, avionics displays, and large shipboard or ground-based information panels.

Table 3 summarizes the outstanding combination of display characteristics offered by lutetium diphthalocyanine. The other rare-earth complexes are not as well characterized but are expected to behave in a similar manner. Absorption spectra and representative Munsell color indices for lutetium diphthalocyanine in KCl at various applied voltages are given by Nicholson and Galiardi (1977, 1978). If a diphthalocyanine display is switched once per second, the average power density is about 1 to 3  $\text{mW}/\text{cm}^2$ , depending on the dye-film thickness and the color transition involved. This is an order of magnitude higher than the power required by liquid crystals, but several orders of magnitude lower than that of electroluminescent displays or light emitting diodes. Because an electrochromic display has open-circuit memory, it gains a further power advantage with less frequent switching. In comparison with other electrochromics, including some experimental organic materials (Kaufman, 1978), the rare-earth diphthalocyanines have greater color range, lower switching energy, and faster than usual response.

An electrochromic cell is illustrated schematically in Figure 3. The display plate consists of electrically isolated areas that may be independently addressed by application of a voltage pulse. The activated portion changes color, thus becoming visible against a contrasting background. Lutetium diphthalocyanine can assume red, green, blue, violet, or intermediate colors. However, it cannot become white or transparent, nor does it emit light. The cell in Figure 3 is to be viewed with front lighting. It therefore contains a white porous filler which serves as a reflective optical backing for the dye film and conceals the counter electrode. A diphthalocyanine display is also attractive as a color transparency projected on a large screen. The white filler is then omitted, and the counter electrode is shaped as an open frame around the viewing area. In most experimental display cells, the electrolyte has been aqueous KCl, and the counter electrode, Ag/AgCl.

The display capabilities of lutetium diphthalocyanine were first reported by Nicholson and Galiardi in 1977. Subsequent development has included a preliminary dot-matrix investigation (Nicholson et al., 1980) which demonstrated color contrast, resolution, and memory at 24 lines per inch and provided an engineering equivalent-circuit model for the dye electrode derived from potentiostatic transients. A typical dye film, in green/red switching, behaves as a pseudocapacitance of  $1,000 \mu\text{f}/\text{cm}^2$  in series with an area resistance of  $20 \text{ ohms}\text{-cm}^2$ . The corresponding time constant of 20 ms is a measure of the inherent switching time.

Two principal development tasks must be performed before detailed process technology can be established. The cycle life must be extended, and, for most applications, a means for matrix addressing must be devised. Electrochromic cells usually attain cycle lives far beyond those of secondary batteries, although both devices operate with faradaic mechanisms. The essential difference apparently is that display films are very thin ( $\sim 1,000 \text{ \AA}$  for LuHPC<sub>2</sub>) and have free access to the electrolyte. Early life testing as demonstrated more than  $5 \times 10^4$  cycles for red/green and red/blue switching of lutetium diphthalocyanine (Nicholson and Galiardi, 1979). The life limiting factors cannot be given in detail, but the usual effect is a gradual loss of color intensity, rather than catastrophic failure. Displays generally must have a life of  $10^6$  to  $10^8$  switching cycles. Since other electrochromic systems have exceeded  $10^7$  cycles, this is not a priori considered excessive for the diphthalocyanines. However, each electrochromic system is chemically unique and can achieve its full display capability only through intensive, specific laboratory experimentation. This developmental work has not yet been done for the rare-earth diphthalocyanines.

Although useful information can be displayed with graphic patterns or segmented alphanumeric characters of the sort used in digital watches, matrix displays in which the entire panel is covered by switchable dots are much more versatile. Electrical addressing of the matrix is a general problem in electrochromic display technology. From an engineering standpoint, it is desirable to construct a matrix panel

from parallel rows of display dots with each row of dots on a common electrical connector. This makes it difficult to control the individual dots during the switching process and in the memory mode, even when the counter electrode array is structured to cause selectivity. A preferred approach may be to incorporate an electronic drive matrix directly on the display panel, so that each dot has, in effect, a separate switch to the power supply. Integrated matrix drive using cadmium selenide thin-film transistors has been successfully developed by Brody et al. (1979) for electroluminescent and liquid-crystal panels at least 6 x 6 inches in size. Recently, Barclay et al. (1980) demonstrated a 1 x 1-inch viologen electrochromic matrix with integrated drive built on a silicon chip. With appropriate design and processing modifications, these matrix-drive concepts should be adaptable to diphthalocyanine electrochromic displays.

### Acknowledgements

Preparation of this article was supported in part by the Office of Naval Research. Figure 2 (Nicholson and Pizzarello, 1979) is reprinted by permission of the publisher, The Electrochemical Society, Inc. Figure 3 is reprinted from the article on electrochromics in the Encyclopedia of Materials Science and Engineering by permission of Pergamon Press Ltd.

Literature Cited

Barclay, D. J.; Bird, C. L.; Kirkman, D. H.; Martin, D. H.; Moth, F. T.,  
SID Intl. Symp. Digest 1980, XI, 124.

Billat, R.; Marcus, J.; Mercier, J. Abst. L-4, Mat. Res. Conf.,  
Santa Barbara, California, June 1981.

Brody, T. P.; Malmberg, P. R., Int. J. Hybrid Microelec. 1979, II, 29.

Chang, A. T.; Marchon, J. C., Inorg. Chim. Acta 1981, 53, L241.

Clack, D. W.; Yandle, J. R., Inorg. Chem. 1972, 11, 1738.

Corker, G. A.; Grant, B.; Clecak, N. J., J. Electrochem. Soc. 1979,  
126, 1339.

Eley, D. D.; Hazeldine, D. J.; Palmer, T. F., J. Chem. Soc.,  
Faraday Trans. 1973, 69, 1808.

Kaneko, N.; Tabata, J.; Miyoshi, T., SID Intl. Symp. Digest 1981,  
XII, 74.

Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.;  
Van Opdenbosch, N.; Pepe, G.; Meyer, Jr., E. F., J. Am. Chem Soc. 1980,  
102, 4835.



Kaufman, F. B., Conf. Record 1978 Biennial Display Res. Conf., 23,  
Publ. IEEE, New York, N.Y., 1978.

Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A., Russ. J. Inorg.  
Chem. 1967, 12, 369.

Mackay, A. G.; Boas, J. F.; Troup, G. J., Aust. J. Chem. 1974, 27, 955.

Moskalev, P. N.; Alimova, N. I., Russ. J. Inorg. Chem. 1975, 20, 1474.

Moskalev, P. N.; Kirin, I. S., Opt. Spectrosc. 1970a, 29, 220.

Moskalev, P. N.; Kirin, I. S., Russ. J. Inorg. Chem. 1970b, 15, 7.

Moskalev, P. N.; Kirin, I. S., Russ. J. Phys. Chem. 1972, 46, 1019.

Moskalev, P. N.; Kirina, N. I., J. Appl. Chem. U.S.S.R. 1975, 48, 370.

Moskalev, P. N.; Shapkin, G. N., Soviet Radiochem. 1977, 19, 294.

Moskalev, P. N.; Shapkin, G. N., Soviet Electrochem. 1978, 14, 486.

Moskalev, P. N.; Shapkin, G. N.; Darovskikh, A. N., Russ. J. Inorg.  
Chem. 1979, 24, 188.

Nicholson, M. M.; Galiardi, R. V., AD-A039596, 1977; SID Intl. Symp. Digest 1978, IX, 24.

Nicholson, M. M.; Galiardi, R. V., Rockwell International, Unpublished results, 1979.

Nicholson, M. M.; Pizzarello, F. A., J. Electrochem. Soc. 1979, 126, 1490.

Nicholson, M. M.; Pizzarello, F. A., J. Electrochem Soc. 1980a, 127, 821.

Nicholson, M. M.; Pizzarello, F. A., J. Electrochem. Soc. 1980b, 127, 2617.

Nicholson, M. M.; Pizzarello, F. A., J. Electrochem. Soc. 1981, 128, 1740.

Nicholson, M. M.; Pizzarello, F. A.; La Chapelle, T. J., AD-A085453, 1980.

Pizzarello, F. A.; Nicholson, M. M., J. Electron. Mat. 1980, 9, 231.

Pizzarello, F. A.; Nicholson, M. M., J. Electrochem. Soc. 1981, 128, 1288.

Raynor, J. B.; Robson, M.; Torrens-Burton, A.S.M., J. Chem. Soc.,  
Dalton Trans. 1977, 2360.

Yamana, M., Tokyo Denki Univ. Res. Rept. 1977, 25, 39.

Yamana, M., Ohyo Buts. 1979, 48, 441.

Table 1. Some Electrochemical Products of Lutetium Dipthalocyanine

Proposed Formula	State	Color	$\lambda_{max}$ (nm)	Magnetism	Reference
Anodic Products					
$[PcLuPcH]^+$	DMF solution	Green	600	Para	Corker et al., 1979
$PcLuPc^+ SbCl_6^-$	$CH_2Cl_2$ solution (chemical oxidation of $PcLuPc$ )	Yellow-tan	475, 688	Dia	Chang and Marchon, 1981
$[PcLuPcH]^+ \cdot X^-$	Film	Yellow	-	-	Suggested
$PcLuPc_{ox}$	Solid electrocrystallized from DMF-hydrazine hydrate solution ( $n = 1$ )	-	682	-	Moskalev et al., 1979 Moskalev and Shapkin, 1978
$[PcLuPcH]^{++}$	DMF solution	Yellow-red	690	Dia	Corker et al., 1979
$[PcLuPc]^{++}$	DMF solution	Red	-	-	Chang and Marchon, 1981
$PcLuPcH \cdot I_2$	Film	-	-	-	Moskalev and Kirina, 1975
$[PcLuPcH]^{++} \cdot 2Cl^-$	Film	Red	495, 695	-	Nicholson and Pizzarello, 1979, 1981

Continued

Table 1. (Continued)

Proposed Formula	State	Color	$\lambda_{max}$ (nm)	Magnetism	Reference
Cathodic Products					
PcLuPcH	DMF solution	Blue	612	Dia	Corker et al., 1979
PcLuPcH	Film from reduction of solid PcLuPcOx, DMF-hydrazine hydrate	-	-	-	Moskalev et al., 1979 Moskalev and Shapkin, 1978
PcLuPc <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub> solution (chemical reduction)	Blue	618	Dia	Chang and Marchon, 1981
[PcLuPcH] <sup>-</sup> ·Li <sup>+</sup>	Film	Lt blue	-	-	Nicholson and Pizzarello, 1981
[PcLuPcH] <sup>-</sup>	Film electroformed from DMF solution	Violet	-	Para	Corker et al., 1979
[PcLuPc] <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub> solution (chemical reduction)	Violet	341, 520, 670	Para	Chang and Marchon, 1981
[PcLuPcH] <sup>-</sup> ·2K <sup>+</sup>	Film	Lt blue	-	-	Nicholson and Pizzarello, 1981
PcLuPcH <sub>n+1</sub>	Film (2 ≤ n ≤ 4)	Dk blue to violet	-	-	Nicholson and Pizzarello, 1981

Table 2. Solid-State Electrical Properties in the Lutetium Diphthalocyanine System Near 25°

Film*	Proposed Formula	Mobile Species	Resistivity (ohm-cm)	Mobility (cm <sup>2</sup> /V-s) x 10 <sup>6</sup>	Reference
Green, vacuum sublimed	PcLuPch	Electrons or holes	400 to 1,100	-	Nicholson and Pizzarello, 1979
	PcLuPc	Electrons or holes	700	-	Billat et al., 1981
Red anodic oxidation products	PcLuPch <sup>++</sup> · 2Cl <sup>-</sup>	Cl <sup>-</sup>	1,300	4	Nicholson and Pizzarello, 1979 Nicholson and Pizzarello, 1979
	PcLuPch <sup>++</sup> · SO <sub>4</sub> <sup>=</sup>	SO <sub>4</sub> <sup>=</sup>	2,000	4	
Dark violet cathodic reduction product	PcLuPch <sub>n+1</sub>	H <sup>+</sup>	-	0.8	Nicholson and Pizzarello, 1981

\*Air present with green and red forms; oxygen complexes are possible.

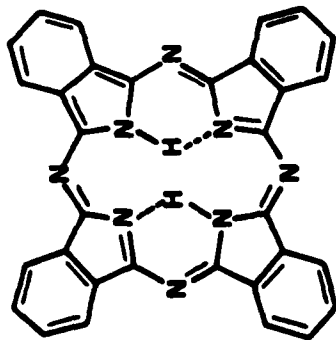
**Table 3. Display Characteristics of Lutetium Diphthalocyanine**

Advantages	Limitations
Many colors with a single display material	Requires night lighting.
Wide viewing angle; front or back lighting; enhanced visual effect in bright light	Contains liquid electrolyte.
Low input voltage (~1.5 to -1.5 V dc)	Requires further development for cycle life and matrix addressing.
Low switching energy (~0.5 to 2 mJ/cm <sup>2</sup> )	
Open-circuit memory (minutes to days)	
Fast response (10 to 50 ms)	
Wide operating temperature demonstrated experimentally (-50 to 100°)	

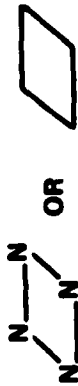
## Illustrations

1. The Phthalocyanine Ring Structure
2. Experimental Arrangement for Moving-Boundary Measurements
3. Schematic Design of Electrochromic Display Cell





**METAL-FREE PHTHALOCYANINE MOLECULE H<sub>2</sub>Pc  
CONTAINING TWO LABILE HYDROGENS**



**RHOMBOIDS REPRESENTING PHTHALOCYANINE  
RING WITH FOUR IMINO NITROGENS**

**FIGURE 1**

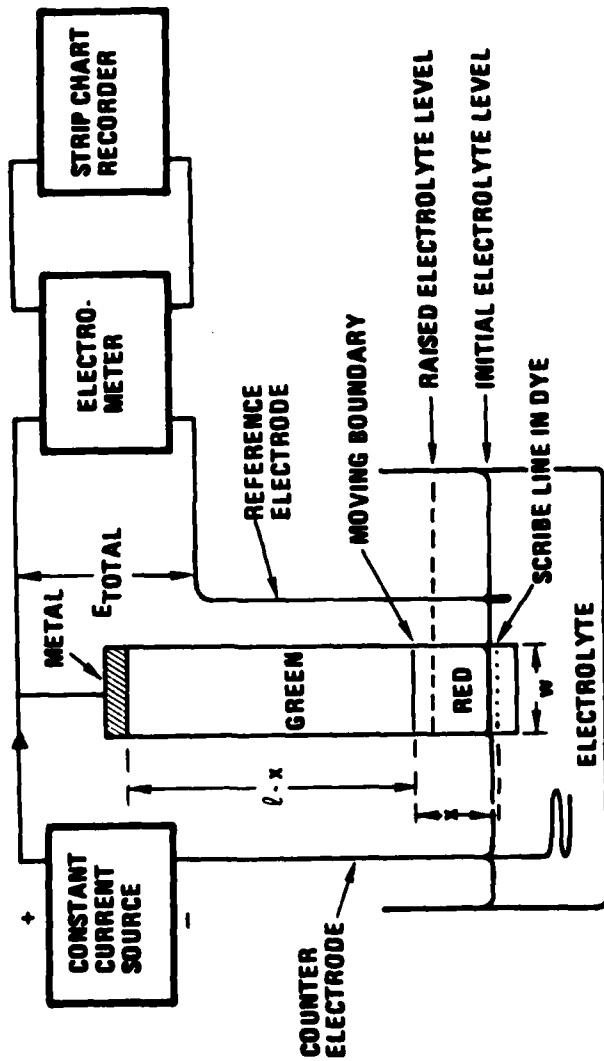


FIGURE 2

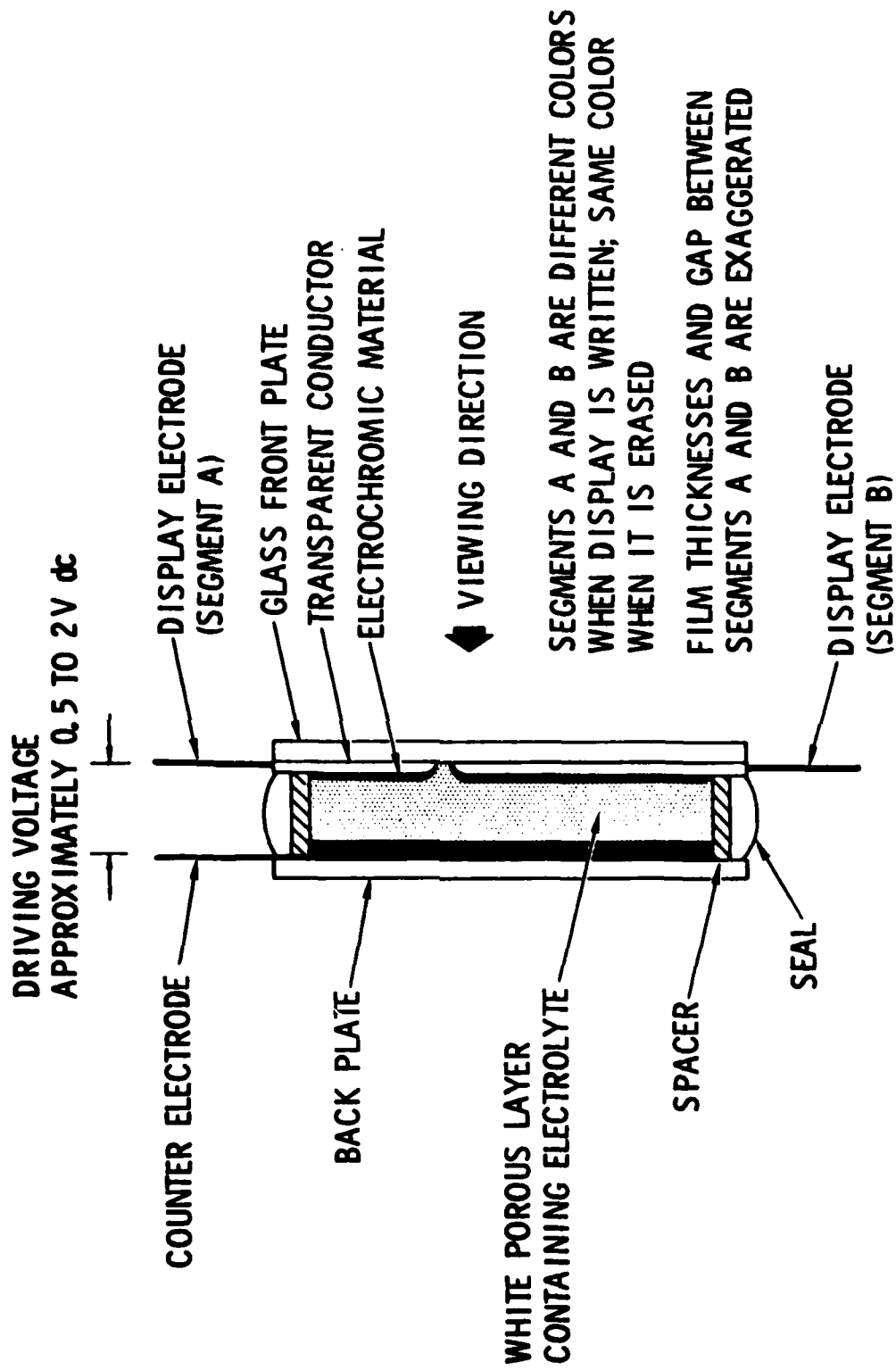


FIGURE 3

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Sasfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. N. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
<del>Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Hiraloma Avenue Anaheim, California</del>	<del>1</del>	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	Dr. Denton Elliott Air Force Office of Scientific Research Bolling AFB Washington, DC 20332	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. David Aikens Chemistry Department Rensselaer Polytechnic Institute Troy, NY 12181	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. A. P. B. Lever Chemistry Department York University Downsview, Ontario M3J1P3 Canada	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1	Mr. Maurice F. Murphy Naval Sea Systems Command 63R32 2221 Jefferson Davis Highway Arlington, VA 20360	1
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1	Dr. Stanislaw Szpak Naval Ocean Systems Center Code 6343 San Diego, CA 95152	1
Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1	Dr. Gregory Farrington Department of Materials Science & Engineering University of Pennsylvania Philadelphia, PA 19104	1
M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1	Dr. Bruce Dunn Department of Engineering & Applied Science University of California Los Angeles, CA 90024	1
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359No.  
Copies

Dr. Micha Tomkiewicz  
Department of Physics  
Brooklyn College  
Brooklyn, NY 11210 1

Dr. Lesser Blum  
Department of Physics  
University of Puerto Rico  
Rio Piedras, PR 00931 1

Dr. Joseph Gordon II  
IBM Corporation  
K33/281  
5600 Cottle Road  
San Jose, CA 95193 1

Dr. Robert Somoano  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 91103 1



**DAT  
FILM**