

AD-A021 534

THE CHEMISTRY AND APPLICATIONS FOR THE
SOLUBILIZATION OF CHROMATE SALTS IN
NONPOLAR ORGANIC MEDIA - PART II

Jack Ohr, et al

Naval Air Development Center
Warminster, Pennsylvania

23 December 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

A021534

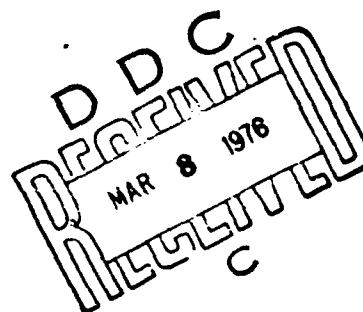


THE CHEMISTRY AND APPLICATIONS FOR
THE SOLUBILIZATION OF CHROMATE SALTS IN
NONPOLAR ORGANIC MEDIA - PART II

J. Ohr and K. G. Clark
Air Vehicle Technology Department
NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

23 December 1975

FINAL REPORT
AIRTASK NO. ZF 61412001
Work Unit No. GC312



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

Reproduce by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Government Printing Office
Washington, D.C. 20540

Prepared for
DIRECTOR OF NAVAL LABORATORIES
Department of the Navy
Washington, D. C. 20360

NOTICES

REPORT NUMBERING SYSTEM - The numbering of technical project reports issued by the Naval Air Development Center is arranged for specific identification purposes. Each number consists of the Center acronym, the calendar year in which the number was assigned, the sequence number of the report within the specific calendar year, and the official 2-digit correspondence code of the Command Office or the Functional Department responsible for the report. For example: Report No. NADC-73015-40 indicates the fifteenth Center report for the year 1973, and prepared by the Crew Systems Department. The numerical codes are as follows:

CODE	OFFICE OR DEPARTMENT
00	Commander, Naval Air Development Center
01	Technical Director, Naval Air Development Center
02	Program and Financial Management Department
03	Anti-Submarine Warfare Program Office
04	Remote Sensors Program Office
05	Ship and Air Systems Integration Program Office
06	Tactical Air Warfare Office
10	Naval Air Facility, Warminster
20	Aero Electronic Technology Department
30	Air Vehicle Technology Department
40	Crew Systems Department
50	Systems Analysis and Engineering Department
60	Naval Navigation Laboratory
81	Administrative and Technical Services Department
85	Computer Department

PRODUCT ENDORSEMENT - The discussion or instructions concerning commercial products herein do not constitute an endorsement by the Government nor do they convey or imply the license or right to use such products.

Routing slip form with checkboxes for 'Copy Section' and 'Copy Section'. The 'Copy Section' checkbox is checked. There is a signature 'A' at the bottom left of the form.

APPROVED BY:

P. D. Stogis

DATE: 23 December 1975

P. D. STOGIS
 Commander, USN
 Deputy Director, AVTD

U N C L A S S I F I E D

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NADC-75308-30	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE CHEMISTRY AND APPLICATIONS FOR THE SOLUBILIZATION OF CHROMATE SALTS IN NONPOLAR ORGANIC MEDIA - PART II	5. TYPE OF REPORT & PERIOD COVERED FINAL	
	6. PERFORMING ORG. REPORT NUMBER NADC-75308-30	
7. AUTHOR(s) Dr. J. Ohr and K. G. Clark	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Air Development Center Air Vehicle Technology Department Warminster, Pennsylvania 18974	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AIRTASK ZF 61412001 Work Unit No. GC 312	
11. CONTROLLING OFFICE NAME AND ADDRESS Director of Naval Laboratories Department of the Navy Washington, D.C. 20360	12. REPORT DATE 23 December 1975	
	13. NUMBER OF PAGES 14	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Macrocycle Polyether Chromate Anion Complex		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The hexavalent anionic partner to the dibenzo-18-crown-6 and 18-crown-6 complexes made according to U. S. Patent Application Serial No. 511328 (Allowed) by Ohr and Clark was determined to be Chlorochromate, CrO₂Cl⁻. The complexes when dissolved in small amounts in paint coatings provide good corrosion protection to aircraft metals such as aluminum, steel, and magnesium; but are impractical for Fleet use at this time because of their poor storage stability properties.		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

U N C L A S S I F I E D

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

I N T R O D U C T I O N

The Part I report demonstrated that it was possible to impart a high degree of corrosion inhibition to organic solvent-based aircraft topcoats without seriously affecting their color by dissolving (not dispersing) therein small amounts of complexed hexavalent chromium salts (references (a) to (f)) prepared according to the authors' patented method (reference (g)). The report covered by this investigation explores the chemical nature of the complexes; i.e., the anionic species containing the hexavalent chromium, and the practicality of using the complexes as paint additives at this time to solve Fleet corrosion problems. We choose to designate the hexavalent chromium complexes as "AMChromes", regardless of macrocycle source.

The work reported herein was conducted under AIRTASK NO. ZF 61412001, IED Work Unit No. GC 312.

E X P E R I M E N T A L P R O C E D U R E S

Preparation and Purification of 18-Crown-6 (reference (h))

A three-liter, three-neck flask equipped with mechanical stirrer, reflux condenser, and addition funnel is charged with triethylene glycol (112.5 g, 0.75 mole) and tetrahydrofuran (600 ml). Stirring is commenced and 60% KOH solution (109 g of 85% KOH in 70 ml water) is poured in. The solution warms but does not boil. After about 15 min of stirring (when the solution darkens) a solution of 3,6-dioxo-1, 8-dichlorooctane (140.3 g, 0.75 mole) in THF (100 ml) is added in a stream. After the addition is complete, the solution is heated at reflux and stirred vigorously for 18 hours. The solution is allowed to cool and the bulk of the THF is evaporated under reduced pressure. The resulting thick brown slurry is diluted with 500 ml dichloromethane and filtered. The salts removed by filtration are washed with more dichloromethane to remove adsorbed crown, and the combined organic solution is dried over $MgSO_4$, evaporated to minimum volume (aspirator vacuum), and then distilled at high vacuum. The distillation should be carried out at the lowest possible pressure; a typical fraction contains 80 g and is collected over 100-160°C at 0.2 mm Hg.

To 50 g of crude 18-crown-6 (bp 125-160°C, 0.2 mm) in a 250 ml Erlenmeyer flask is added 125 ml acetonitrile. The resulting slurry is heated on a hot plate to effect solution. A magnetic stirring bar is added and the neck equipped with a $CaSO_4$ drying tube. The solution is stirred vigorously as it is allowed to cool to ambient temperature, and fine white crystals of crown-acetonitrile complex are deposited. The flask is finally cooled in an ice-acetone bath to precipitate as much complex as possible, and the solid then collected by rapid filtration. The hygroscopic crystals are transferred to a 500 ml round-bottom flask equipped with a magnetic stirring bar and vacuum take-off. The acetonitrile is removed from the complex at high vacuum (0.1 - 0.5 mm) with gentle heating ($t \leq 40^\circ C$) over two to three hours. The pure, colorless crown (20 - 30 g, 40 - 60%) crystallizes on standing and

shows no ions above $m/e = 265$ in the mass spectrum and no significant hydroxyl vibration in the 3500 cm^{-1} region of the infrared. The pure crown has mp $36.5 - 38.0^\circ\text{C}$ (lit. mp $39 - 40^\circ\text{C}$) (reference (1)); nmr (60 MHz, CCl_4): 3.56 ppm (singlet); ir (neat): 2875 (alkane CH), 1450 and 1350 (alkane CH), and 1120 cm^{-1} (ether link); mass spectrum: M and M+1 at 264 and 265, other fragments at $m/3 = 89, 87, 59, 45, 44, 43,$ and 31. See Figures 1 and 2 for IR and NMR of compound.

Preparation of the Potassium Chlorochromate of 18-Crown-6 (reference (g))

A 0.7M solution of 18-crown-6 was prepared in methylene chloride and 200 ml of it was placed in a 500 ml separatory funnel. Next, 500 ml of an acidified aqueous solution of hexavalent chromate was prepared as follows: 50 gm K_2CrO_4 , 500 ml water and 96 gm of 37% constant boiling HCl. A 200 ml portion of this solution was added to the same separatory funnel. The funnel was vigorously shaken and the organic phase removed, dried over MgSO_4 , filtered, evaporated to about 125 ml and crystallized at -5°C . The product is orange crystals which decomposes over a long range of temperature beginning at approximately 150°C .

Elemental Analysis:	Theory	Found
LC	32.84	32.92
HE	5.51	5.62
LC1	8.08	7.66

Further proof that the complex is as designated is indicated by the data of Table I which shows that the maximum molar extinction coefficient values for the complex and for the potassium chlorochromate salt per se are reasonably close for the same wave lengths. See Figures 3 and 4 for IR and UV spectra of complex.

Preparation of Potassium Chlorochromate (Prepared according to Mellor) (reference (j))

A 6 Molar HCl solution was prepared by diluting 85 grams of 38% HCl to 150 ml with water. To this was added 25 grams of potassium dichromate while heating and stirring. The solution was allowed to crystallize undisturbed for three days at room temperature and then suction filtered. The orange crystals were dried under vacuum. See Figures 5 and 6 for UV and IR spectra of compound.

Preparation of Potassium Chlorochromate of Dibenzo-18-Crown-6

The preparation was very similar to the potassium chlorochromate of 18-crown-6 above. The crystals were orange-yellow.

	Theory	Found
LC	44.90	44.53
HE	4.52	4.39
LC1	6.64	7.00

See Figure 7 for UV of complex.

TABLE I

COMPARISON OF UV ABSORPTION DATA FOR THE POTASSIUM
CHLOROCHROMATE COMPLEX OF 18-CROWN-6 vs POTASSIUM CHLOROCHROMATE PER SE

COMPLEX (1)

λ_{MAX}	A	ϵ_{MAX} (l/g-cm)	ϵ_{MAX} (l/mol-cm) (2)
363	0.64	2.71	1190
354	0.64	2.69	1180
283	0.91	3.86	1695
244	1.07	4.53	1990

SALT

λ_{MAX}	ϵ_{MAX} (l/mol-cm)
363	1180
353	1160
282	1650
240	1780

NOTES:

(1) Complex values are from Figure 4

(2) A molecular weight of 439 was assumed based on the complex, (18-Crown-6) (KCrO₃Cl). Since a concentration of 0.236 gm/liter was prepared, this corresponds to a 5.37×10^{-4} Molar solution. These values were used for c in the Beer-Lambert expression $A = \epsilon bc$

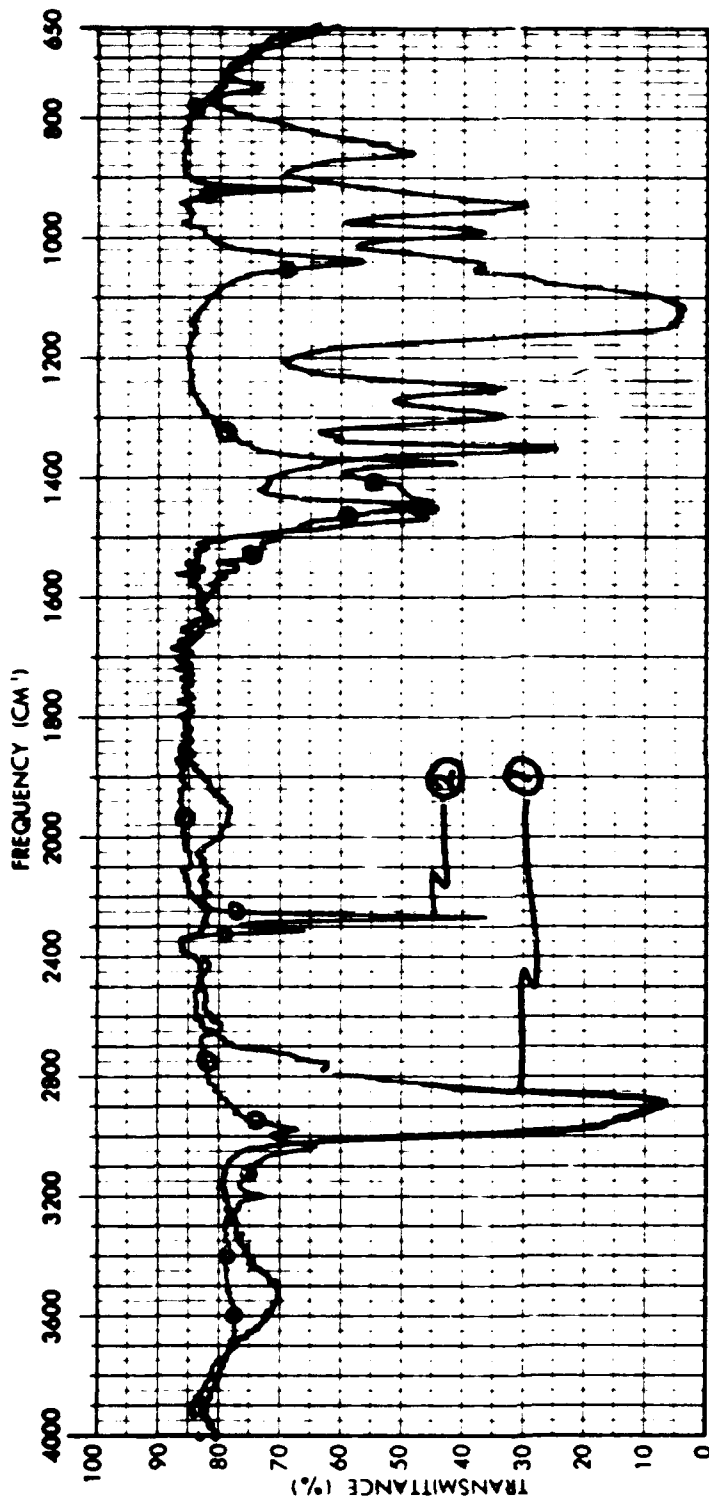


FIGURE 1 — IR of 18—CROWN—6 vs THE PURIFICATION SOLVENT, ACETONITRILE.

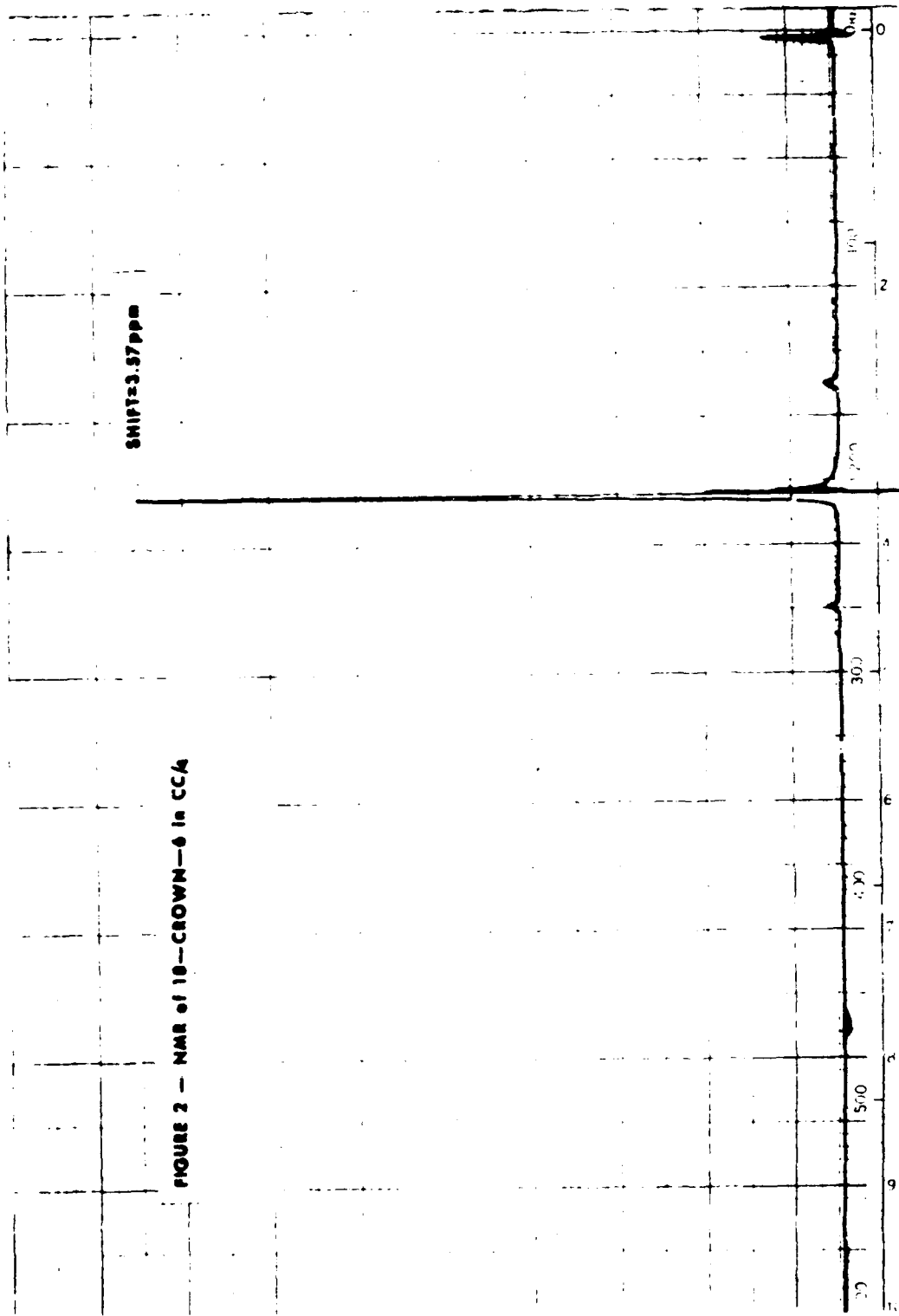


FIGURE 2 - NMR of 18-CROWN-6 in CCl₄

Figure 2. NMR of 18-CROWN-6 in CCl₄

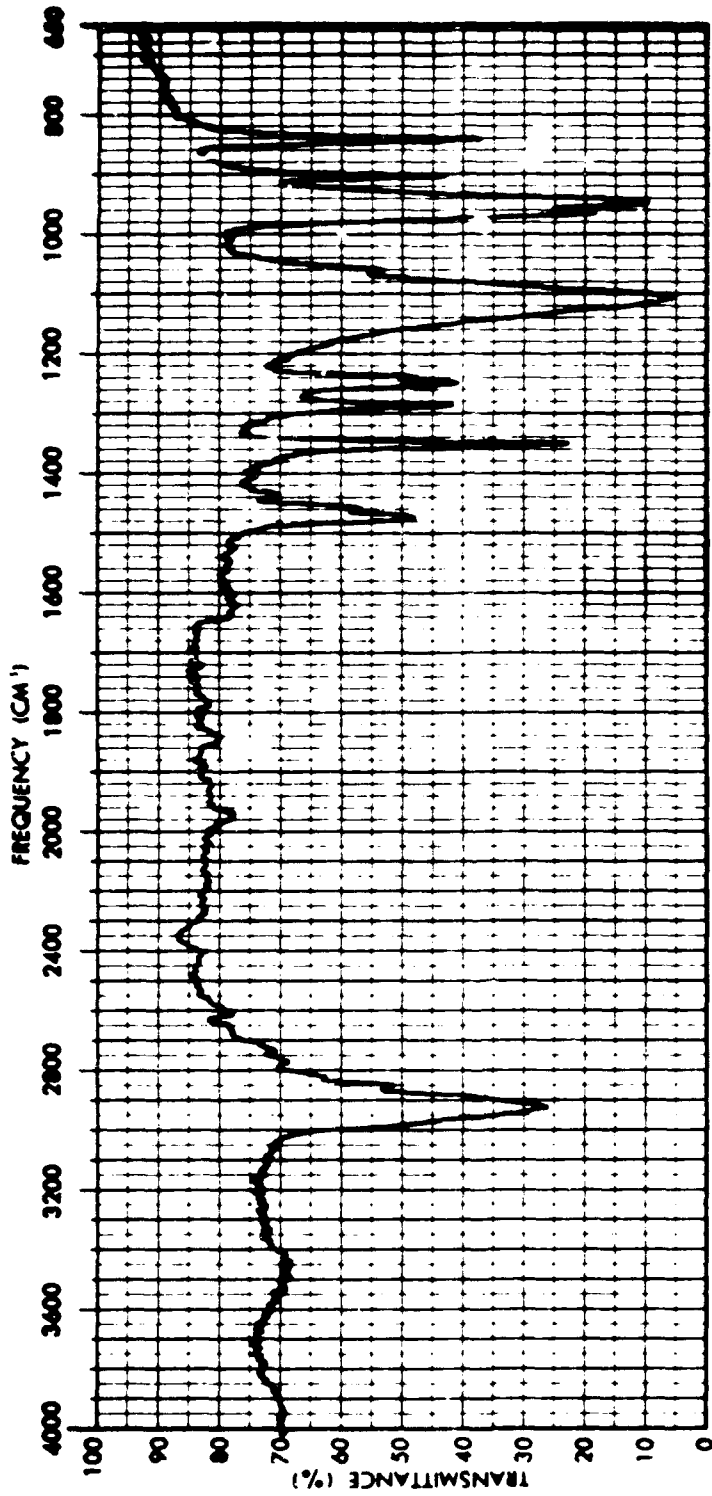


FIGURE 3 — IR of POTASSIUM CHLOROCHROMATE COMPLEX of 18-CROWN-6.

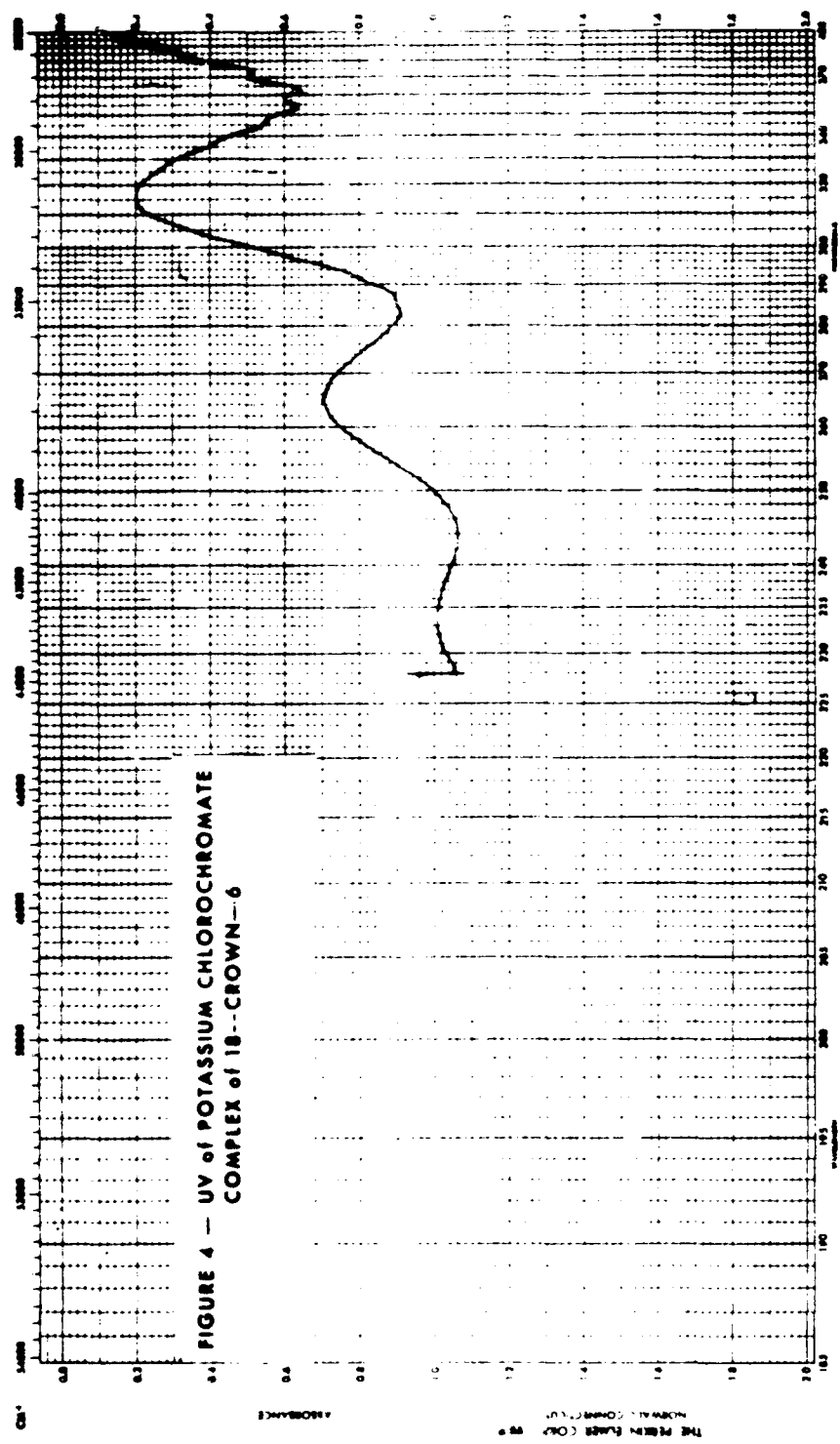


Figure 4. UV of Potassium Chlorochromate Complex of 18-CROWN-6

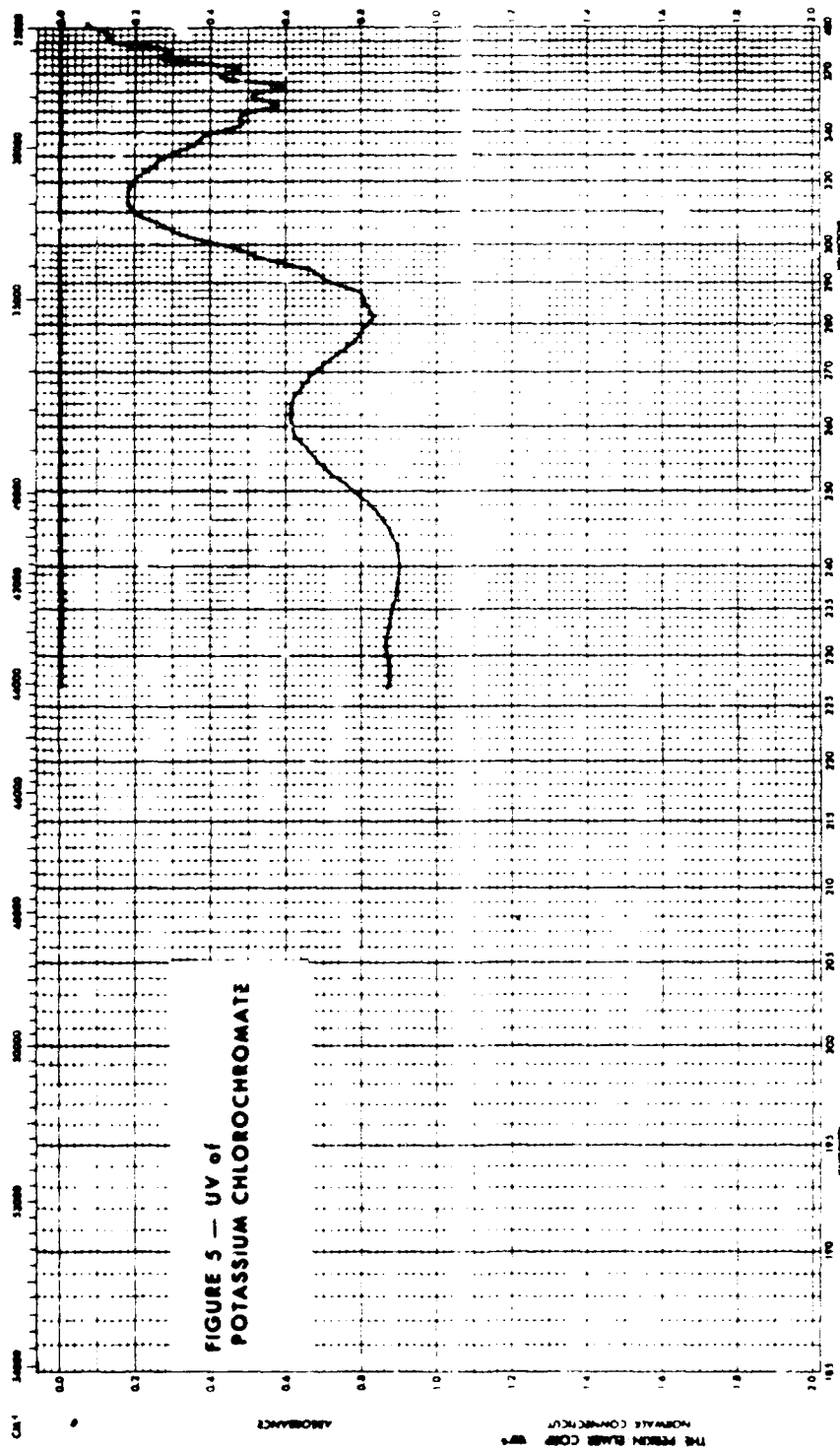


Figure 5. UV of Potassium Chlorochromate

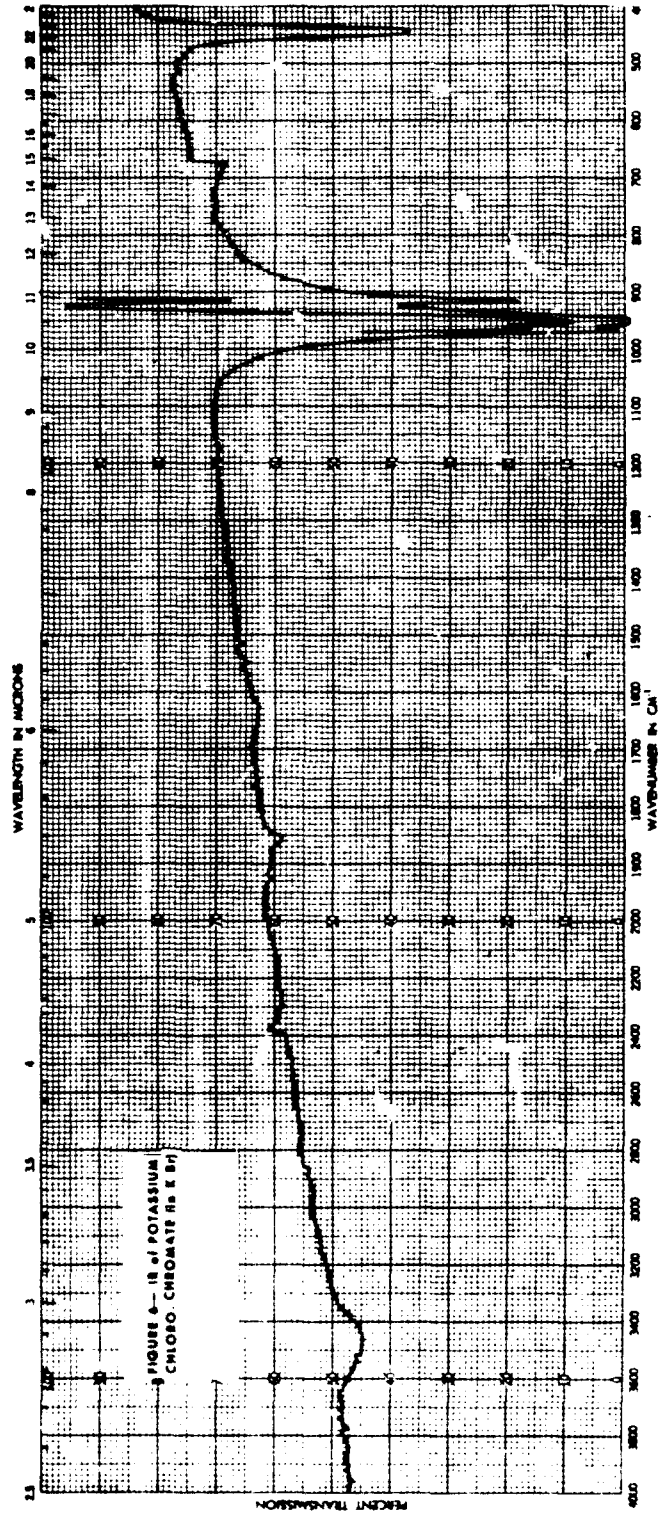


Figure 6. IR of Potassium Chlorochromate (in K Br)

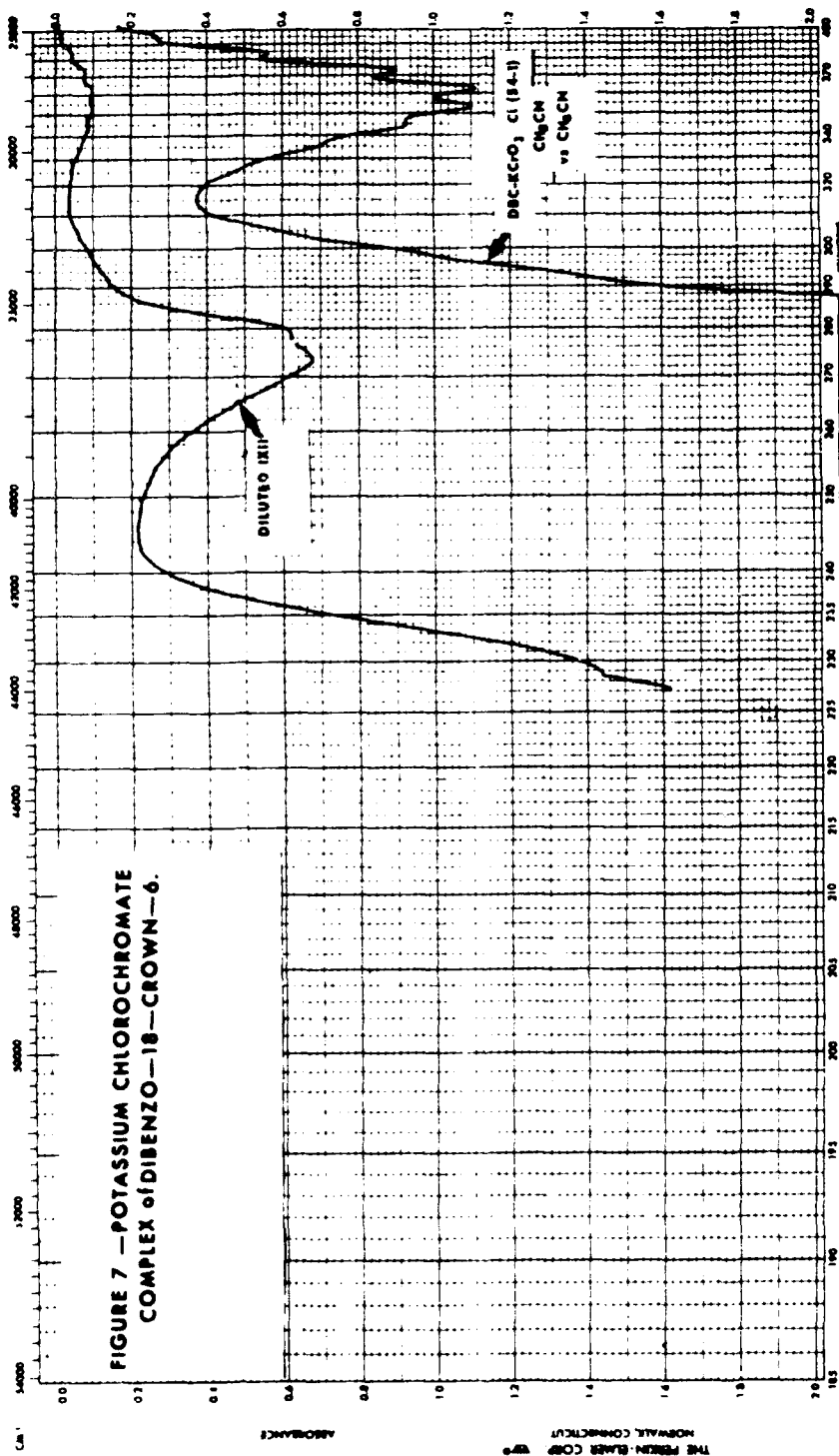


Figure 7. Potassium Chlorochromate Complex of Dibenzo-18 CROWN-6

R E S U L T S

1. The 18-crown-6 and dibenzo-18-crown-6 complex systems when prepared according to reference (g) produced chlorochromate, CrO_3Cl^- (reference (k)) as anionic partner to the complexed potassium cation as illustrated in Figure 1. Such hexavalent chromium systems we choose to designate as AMLchrome.
2. The 18-crown-6 was synthesized according to reference (h) in an overall yield of 18%.
3. The 18-crown-6 AMLchrome exhibited rapid deterioration at room temperature, even under nitrogen, so that after a few weeks the clear AMLchrome had changed to a deep brown viscous mass. Presumably, the product is a polymer resembling a polyether since no significant changes appeared in the infrared for the before and after situations. The product is completely insoluble in methylene chloride, the best solvent for the AMLchromes. Moreover, gases are produced during the oxidation which could be a fire hazard if stored in large enough quantity.

C O N C L U S I O N S

1. The AMLchromes when prepared according to reference (g) consist of a complexed potassium cation with chlorochromate, CrO_3Cl^- , as the anionic partner.
2. Even though the AMLchromes are effective corrosion inhibiting agents for paint coatings, they have poor shelf lives and hence are impractical (and even hazardous) for Fleet use at this time.

R E C O M M E N D A T I O N S

1. It is recommended that this research be terminated on the basis that further work for increasing the shelf life of the AMLchromes does not appear promising. Accordingly, this is considered to be a final report on the AMLchrome research.

R E F E R E N C E S

- (a) C. J. Pedersen, J. Am. Chem. Soc., 89, 2495 (1967)
- (b) C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967)
- (c) C. J. Pedersen, J. Am. Chem. Soc., 92, 386 (1970)
- (d) C. J. Pedersen, J. Am. Chem. Soc., 92, 381 (1970)
- (e) C. J. Pedersen, Fed. Proc. 27, 1305 (1968)
- (f) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Ed.*, Vol. 2, No. 1, pp 16-25 (1972); and references therein.
- (g) U. S. Patent Application Serial No. 511328 (allowed) by Ohr and Clark.
- (h) Private communication from Professor Charles L. Liotta, Chemistry Department, Georgia Institute of Technology, Atlanta, Georgia 30332.
- (i) R. M. Greene, *Tetrahedron Letters*, 1993 (1972)
- (j) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 11, London, Longmans, 1931
- (k) F. A. Cotton and G. Wilkenson, *Advanced Inorganic Chemistry*, 3rd Ed., p 841, Interscience (1972)