AD/A-003 631

INVESTIGATION OF ADVANCED PROTECTIVE AND ANTIREFLECTION COATINGS FOR HALIDE OPTICS

Bernard L. Weigand

Rockwell International Corporation

Prepared for:

Air Force Cambridge Research Laboratories
Defense Advanced Research Projects Agency

14 June 1974

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFCRL-TR-74-0551	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD/A 003 631
4. TITLE (and Subtitle) INVESTIGATION OF ADVANCED PROTECTIVE AND ANTIREFLECTION COATINGS FOR HALIDE OPTICS		5. TYPE OF REPORT & PERIOD COVERED Scientific - Final 1 June 1973 - 19 April 1974
		6. PERFORMING ORG. REPORT NUMBER C73-892.4/201
7. AUTHOR(s) Bernard L. Weigand		8. CONTRACT OR GRANT NUMBER(s) F19628-73-C-0275
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Autonetics Division 3370 Miraloma Avenue Anaheim, California 92803		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2415 Task WU - N/A 61101E
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Cambridge Research Laboratories Hanscom AFB, Massachusetts 01731 Contract Monitor: A. Golubovic/LQP		12. REPORT DATE 14 June 1974
		13. NUMBER OF PAGES 17
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

This research was sponsored by Defense Advanced Research Projects Agency. ARPA Order No. 2415

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

RF polymerization
UV polymerication
IR coatings

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Surface Finishing

A chemical etch procedure utilizing a solution of 91 parts of glacial acetic acid to 9 parts of concentrated hydrochloric acid was developed for polishing the potassium chloride. This solution gave a dissolution rate of about 220Å/sec. and yielded a surface free of scratches with a smoothness close to 100Å.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Surface Coating

Thin film polymeric coatings were prepared by radio frequency glow discharge and ultraviolet techniques and proper equipment has been a signed and assembled.

Hexachlorobutadiene - 1.3 was used as monomer for preparation of polymeric coatings. Glow discharge polymerization was occuring primarily in the vapor phase rather than on the substrate surface thereby establishing the proper mathematical relationship between the monomer vapor pressure, flow rate, substrate temperature, power, inert gas pressure, flow substrate-to-power source spacing and deposition rate. The thin film polymeric coating showed a slight absorption at 10.6 micrometers and little or no absorption at 3 to 5 micometers. The coating demonstrated good adhesion to the substrate. The very low coating deposition rates obtained by ultraviolet photolytic polymerization of low pressure materials make this process unattractive for this type of materials.

A. WORK ACCOMPLISHED - 28 February 1974 to 19 April 1974

1.0 POLISHING OF POTASSIUM CHLORIDE

Although isopropyl alcohol etching was found to provide a controllable method for dissolving surface layers of potassium chloride windows, it was too slow to adequately remove all scratches polished into the soft material. Increasing the reaction rate with faster dissolving lower alcohols did not help the surface. Utilization of the standard procedure of concentrated hydrochloric acid etching did indeed improve the rate of scratch removal, but the dissolution rate was too fast for easy control. To improve this etching procedure and slow down the reaction rate, increasing amounts of glacial acetic acid were added to concentrated hydrochloric acid. The dissolution rates were measured for etch solutions ranging from 50% acetic (+50% concentrated hydrochloric) to 91% acetic (+9% concentrated hydrochloric). The latter, with a dissolution rate of about 220 A/sec., appears to remove scratches easily in two to five minutes. The latter etch has been shown to yield a surface free of scratches with a Talysurf profilometer smoothness close to 100 A, even though the surface originally had many 1200 A deep scratches in it.

Scatter measurements at 6328A using a He-Ne laser and measuring at a series of scatter angles were beginning to indicate excellent improvement in KCl surfaces using the acetic-hydrochloric mixed acids. Highest accuracy in determination of transmission, absorption, reflection and scatter at 6328A should be measured using 13 mm thick KCl samples and compared with data measured at 10.6 microns. The complete polish-etch procedure still requires some additional verification and process time optimization.

2.0 POLYMER DEPOSITION

2.1 Glow Discharge Deposition of Hexachlorobutadiene -1,3

In an attempt to eliminate sputtering of the glass tube under the induction coil described in the last quarterly report,[1] capacitive electrodes as described by Hollahan[2] and Wydeven were used in place of the induction coil. The electrodes were copper strips 26 mm in width by 0.3 mm thick which were formed around the glass tube with a 10 cm spacing between the electrodes. Sputtering of the glass tube still occurred at the edges of the rf input electrode. A Model 250-22-13.56 "Matchbox" coupling unit (Wm. Nye Co., Inc., Bellevue, Washington) was ordered to replace the coupling unit supplied with the Model SP430, A. D. Mathis Company, power supply. The "Matchbox" coupling unit eliminates the need for holding the second electrode at ground potential and should prevent sputtering of the glass under the input electrode. The order for this unit was cancelled when the contract was terminated so no data is available on its performance.

The thermocouple guage used for monitoring the pressure of hexachlorobutadiene -1,3 (HCB -1,3) in the glow discharge system was calibrated using an MKS Boratron Capacitance Manometer. The resultant calibration curve is shown in Figure 1.

Eight additional deposition runs of HCB -1,3 were made during this period as shown in Table I. The substrate in all cases was sapphire on which approximately 2000 A of palladium had been vapor deposited. An aluminum strip approximately 2 mm wide was placed on the substrate to act as a mask and permit Talysurf thickness measurements. The monomer pressures shown in

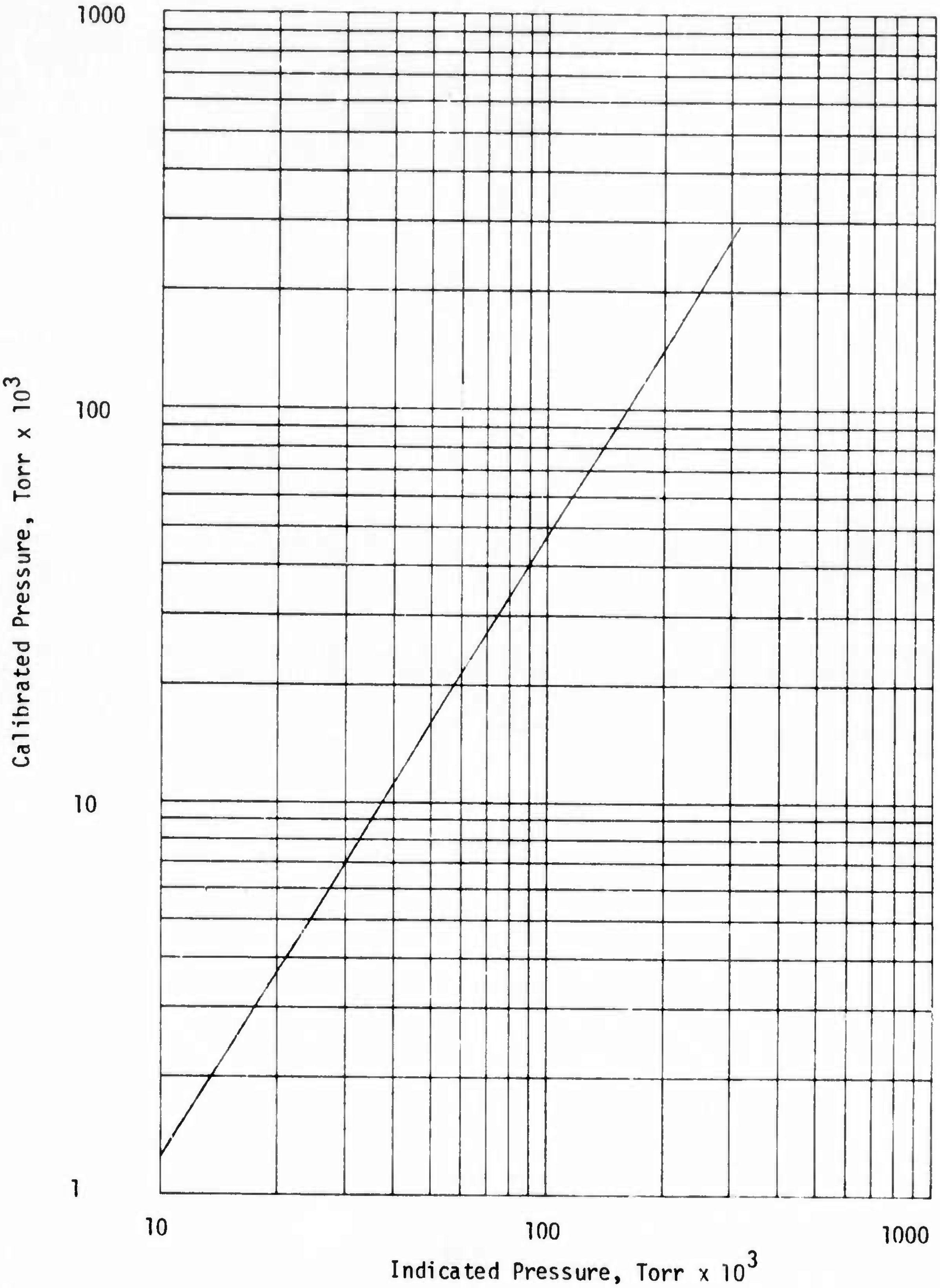

FIGURE 1. PRESSURE CALIBRATION CURVE FOR HEXACHLOROBUTADIENE -1,3

TABLE I. GLOW DISCHARGE POLYMERIZATION OF HEXACHLOROBUTADIENE -1,3

Run	Pressure Torr (Corr.)	Bath Temp °C	Substrate Temp °C	Power Watts	Time Min.	Substrate Height, cm	Electrode[a] Height, cm	Weight mg/cm^2	Thickness Angstroms	Rate x 10^4 $mg/cm^2/min$
N11191-23	0.041	22-3	12.5-13.5	50	30	16	22	0.076	3,240	25.3
N11191-30	0.046	22.5-3	13-14	50	90	16	22	-	11,430	-
N11191-31	0.041	22.5-3	14.5	60	90	16	22	-	12,450	-
N11191-34	0.041	23-4	15	60	90	16	22	-	6,650	-
N11191-37	0.065	75	13.5-14	60	11	16	22	7.127	-[b]	6480
N11191-38	0.005	24	13.5-14	60	90	16	22	0.157	8,340	17.4
N11191-39	0.016	38	13.5	60	40	16	22	0.295	14,090	73.7
N11191-40	0.028	49	14	60	30	16	22	2.020	-[b]	573

a - Capacitive electrodes with 10 cm spacing

b - Tacky, very viscous coating

Table I are the equilibrium pressures established in the system prior to striking the glow discharge. Upon initiation of the discharge the pressure immediately dropped to less than 0.004 Torr (corrected), indicating vapor phase polymerization was occurring.

The first four runs (Table I) show the variability of the deposition rate under approximately identical conditions of pressure, substrate temperature and power. The uncontrolled variables are monomer flow rate and pumping speed.

Yosuda and Lamaze[3] have shown the rate of polymer deposition in an electrodeless glow discharge to be:

$$R = a\, p_M^2 [1 + b\, p_X] \quad (1)$$

where p_M is the monomer vapor pressure, p_X is the inert gas pressure, and a and b are constants characteristic of the monomer and gas and the geometry of the system. If monomer vapor only is used, the rate equation reduces to:

$$R_o = a\, p_M^2 \quad (2)$$

where a is a constant in units of g/cm^2 · min · Torr^2.

The flow characteristics of monomer vapor are also given by a similar expression:

$$F_v \equiv [\text{flow rate in cc (S.T.P.)/min}] = \alpha_v\, p_M^2 \quad (3)$$

where α_v is a constant in units of cc (S.T.P.)/min. Torr^2.

The flow rate F_w, based on the weight of monomer, is given by:

$$F_w \equiv [\text{flow rate in g/min}] = \frac{\alpha_v M p_M^2}{2.24 \times 10^4} = \alpha_w p_M^2 \qquad (4)$$

where M is the molecular weight of the monomer and α_w is a constant in units of g/min. Torr^2.

The pressure of a vapor is dependent on the number of molecules. The rate of polymer deposition, on the other hand, is dependent on the weight of polymer (and weight of the vapor molecules). Therefore, the characteristic rate constant of vapor phase polymerization should be given by:

$$R_o = k F_w \qquad (5)$$

From equations (2), (4) and (5) the characteristic rate constant is given by:

$$k = \frac{a}{\alpha_w} \qquad (6)$$

The rate constant k is not a rate constant of the chemical reaction in a strict sense, since the polymer deposition rate by plasma polymerization is dependent on certain geometric factors of a reaction vessel such as the ratio of surface area to volume, shape of the vessel, the distance from the rf antenna, etc. The constant k has the unit of cm^{-2}.

The last four runs in Table I were made in an attempt to verify the above equations of Yosuda and Lamaze. The pump valve was opened fully to maintain as constant a pumping speed on the system as possible. The pressure and flow rate was adjusted by controlling the temperature of the monomer bath.

The value of the constant a calculated for each run using equation (2) is shown in Table II.

TABLE II. POLYMERIZATION DATA FOR GLOW DISCHARGE POLYMERIZATION OF HEXACHLOROBUTADIENE -1,3

Run	p_M Torr	$p_M^2 \times 10^5$ Torr^2	$R_0 \times 10^5$ g/cm^2/min	$a \times 10^2$ g/cm$^2 \cdot$ min $\cdot$ Torr^2
N11191-38	0.005	2.5	0.174	6.96
N11191-39	0.016	25.6	0.737	2.88
N11191-40	0.028	78.4	6.73	8.52
N11191-37	0.065	422.5	64.80	15.3

The values of the constant a found are approximately two orders of magnitude greater than those reported by Yosuda and Lamaze[3] for any of the materials they investigated and indicates the high reactivity of HCB -1,3 to glow discharge polymerization. In the case of runs N11191-40 and N11191-37 the vapor phase polymerization was so rapid that the polymer deposited as a low molecular weight very viscous coating. The variation in the values of the constant can also be attributed to this extremely high deposition rate. It is apparent that a flow meter must be installed to better control the monomer flow rate and the pumping speed must be reduced to lower the flow rate and the resultant deposition rate.

The reactivity of the HCB -1,3 to glow discharge polymerization can be attributed to its high molecular weight, the constant a being dependent[3] on $M^{2.5}$, the presence of two reactive double bonds in the molecule, and the susceptibility of the carbon to chlorine bond to plasma decomposition.

In summary, prior to determination of the absorption coefficient of the polymer films it is essential that any sputtering of the glass tube be eliminated to prevent incorporation of strongly absorbing silicon oxides in the film. It is believed that the use of a coupling "Matchbox" will alleviate this problem. The monomer flow rate and pressure must be accurately controlled in order to establish a controllable coating deposition rate which will yield a high molecular weight, high density coating with good adhesion to the polished KCl window.

1.2 Ultraviolet Photolytic Polymerization of Hexachlorobutadiene -1,3

Four runs were conducted during this period as shown in Table III. The first two runs were conducted under almost identical conditions to determine the repeatability of the deposition rate. The deposition rate was repeatable within experimental error as shown.

In the second two runs the substrate holder was moved closer to the quartz window and the iris on the Electro Powerpaks Corporation Model 371

TABLE III. ULTRAVIOLET POLYMERIZATION OF HEXACHLOROBUTADIENE -1,3

Run	Pressure Torr (Corr)	Substrate Temp °C	Time Min.	Substrate to Window, cm	Weight mg/cm^2	Thickness, Angstroms	Rate x 10^4 mg/cm^2/min
N11191-25	0.11-0.23	64-78	360	30	0.007	250	0.2
N11191-29	0.11-0.23	79-81	270	30	0.006	300	0.2
N11191-32	0.038-0.042	81.5-83	300	20.4	0.006	-[a]	0.2
N11191-33	0.036-0.083	80-82	300	20.4	0.007	-[b]	0.2

a - Crazed partially detached film, thickness not measurable

b - Very rough film, thickness not measurable housing for the 2500 watt mercury-xenon lamp was changed from a fully open position to the maximum closure position in order to determine the effect of increased ultraviolet intensity. As shown in Table III the deposition rate remained essentially the same while the deposited film became rough or crazed and embrittled.

Based on the low deposition rates obtained for the photolytic polymerization of HCB -1,3 and the limitation imposed on increasing the rate because of its low vapor pressure, additional investigations of HCB -1,3 polymer films resulting from this process are not recommended.

B. SUMMARY OF WORK PERFORMED - 1 June 1973 to 19 April 1974

The overall program is approximately 59 percent complete based on both the cost and physical projection. It was anticipated that the program would be completed on schedule with no cost overrun.

1.0 MATERIALS SELECTION

This phase of the program was completed as scheduled in accordance with the estimated cost and duration.

A total of fifteen halogenated compounds containing varying percentages of fluorine, chlorine, and bromine combined with saturated, unsaturated (single and conjugated double bonds), and cyclic structures were selected as potential candidates for evaluation. The selection resulted from a review of over 200 published papers and texts on the optical, physical and chemical properties of polymeric materials obtained by glow discharge and radiation techniques. The results of this literature survey were published in the first quarterly technical report[4].

2.0 SURFACE FINISHING

This phase of the program is 42 percent complete based on the cost estimate and approximately 53 percent complete based on the physical projection.

A chemical etch procedure utilizing a solution of 91 parts of glacial acetic acid to 9 part of concentrated hydrochloric acid was developed for polishing the potassium chloride. This solution gave a dissolution rate of about 220 A/sec. and yielded a surface free of scratches with a Talysurf profilometer smoothness close to 100 A.

Preliminary scatter measurements at 6328 A using a He-Ne laser indicated excellent improvement in the KCl surfaces.

3.0 SURFACE COATING

This phase of the program is 79 percent complete based on the cost projection and approximately 71 percent complete based on the physical projection.

Assembled ultraviolet and rf electrodeless glow discharge apparatus.

Used hexachlorobutadiene -1,3 as monomer to establish deposition characteristics and parameters of the apparatus. Made necessary modifications to equipment to permit introduction of both high and low vapor pressure monomers. Determined that rf electrodeless glow discharge polymerization was occurring primarily in the vapor phase rather than on the substrate surface thereby establishing the proper mathematical relationships between the monomer vapor pressure, flow rate, and deposition rate. Determined that rf apparatus must be modified to prevent contamination of the coatings by silicon oxides sputtered from the chamber walls. Modifications initiated but not completed. The very low coating deposition rates obtained by ultraviolet photolytic polymerization of low vapor pressure materials make this process unattractive for this type of material.

Conducted approximately 50 depositions of polymer coatings using the rf and UV equipment to establish the importance and the effect of the variables: monomer pressure, monomer flow rate, substrate temperature, power, deposition time, inert gas pressure, inert gas flow rate, and substrate-to-power source spacing. In the case of the rf electrodeless glow discharge, the coating deposition mechanism was found to be in agreement with that proposed by Yasuda and Lamaze[3]. This information will permit the selection of the optimum deposition parameters for a new monomer with a minimum expenditure of time and material.

Deposition of coatings from selected monomers on chemically polished KCl windows prepared as described in 2.0 were planned for immediate initiation in the case of UV equipment. The rf depositions were planned for initiation upon receival and checkout of the "Matchbox" coupling unit scheduled for receival on May 10, 1974. The order for this unit was cancelled upon notification of contract termination.

4.0 TEST AND EVALUATION

This phase of the program was scheduled to begin on 3 June 1974. After discussions with A. Golubovic, A. Armington and H. Posen of AFCRL on February 13, 1974, it was rescheduled to begin on April 29, 1974. Due to termination of the contract on April 17, 1974, no effort was expended. This effort involved the detailed characterization of the optical, chemical and physical properties of the coatings.

5.0 REPORTS

This phase of the program is 31 percent complete based on both the estimated cost and accomplishment.

Two quarterly technical and management reports and one semiannual technical and management report were prepared and submitted to AFCRL. All of the reports were approved and accepted by AFCRL.