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MOISTURE PROTECTIVE COATINGS FOR ALKALI HALIDE IR OPTICS

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3011 Malibu Canyon Road
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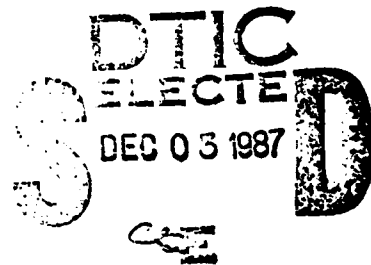
1 November 1979 through 30 June 1981
ARPA Order No. 3833

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cont'd → KBr flats and press-forged KBr lenses. Polycrystalline KBr formed localized grains on polishing that could not be removed by chemical etching with HBr. Since the hygroscopic nature of alkali halides is due to the presence of surface hydroxyl groups, passivation methods were developed to minimize the effect of these groups. Several methods were developed: (1) chemical etching with HBr which repairs grinding defects and partially removes hydroxyl groups; (2) plasma decomposition of CF_3Br or CF_2Cl_2 , creating halogen species that substitute and remove surface hydroxyls; (3) coating with surfactants such as Quilon-C or octadecylamine; (4) surface cleaning with an argon plasma; and (5) coating with a thin layer of SiO_2 . Methods 1, 2, and 3 were all useful passivating methods, with methods 4 and 5 being only marginally successful. Method 3 showed the best reproducibility. Several methods to quench residual free radicals in the freshly prepared films were developed: (1) allowing the radicals to act as initiators for the polymerization of ethylene; (2) exposing the film to a hydrogen plasma; (3) exposing the film to a CF_2Cl_2 plasma to increase the surface crosslink density; and (4) preparing the film by pulse-mode deposition. All methods were successful, but Method 1 was used routinely in this study. The refractive index of our films was 1.67 in the IR. Films $\sim 5 \mu\text{m}$ thick adequately covered surface defects while retaining a transmission of $>90\%$. The absolute absorption of PPE was 0.4% per micrometer thickness. Lifetimes of PPE-coated KBr flats exposed to 85 to 100% RH approached 100 hr. The films passed moderate abrasion, adhesion, and 24-hr humidity tests, but did not pass exposure to salt spray for 48 hr. The film showed sufficient fungus resistance.

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FOREWORD

This contract was administered by the Defense Advanced Research Projects Agency, Materials Sciences Office. Maj. Harry V. Winsor, and later Dr. E.J. Friebele, served as the DARPA project engineer. Mr. Robert Dockery was the contract monitor for the Night Vision and Electro-Optics Laboratories, Ft. Belvoir, VA.

The program manager was Dr. Frederick G. Yamagishi, head of the Plasma Chemistry Group of the Device Materials Section headed by Dr. Leroy Miller. Professional assistance was provided by Ms. Diana D. Granger. Technical assistance was provided by Mr. S. Thomas Taylor and Mr. Willis H. Smith, Jr.

Work was performed in the Exploratory Studies Department of Hughes Research Laboratories under the management of Dr. Donald H. Close, and later, Dr. Jan Grinberg.

The authors gratefully acknowledge the participation, consultation, and advice of Dr. Arthur Adamson of the Department of Chemistry, University of Southern California, for his input into the direction of our approach in this project. We are also indebted to Dr. Joe Friebele for his concern and capable persistence that allowed this program to be completed.



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SECTION 1

INTRODUCTION

For the past five years, Hughes Research Laboratories (HRL) has been carrying out an internally funded program on IR protective coatings. HRL has an extensive background in IR materials, antireflection coatings, polishing, surface analysis, and, more recently, in protective coatings for alkali halide windows. Much of this expertise was used during the extent of this contract.

Alkali halides are attractive materials for IR detector and laser systems, particularly for use in the far-IR (8- to 12- μ m) range, because of their transmissivity and relatively low cost. However, these materials are highly sensitive to moisture, which rapidly attacks the surface and degrades the optical quality. Furthermore, since the materials are soft and fragile, the optical components must be handled and cleaned carefully. Thus, there is a need to protect the surface of alkali halide optical elements from damage caused by exposure to uncontrolled environments and to increase their durability so that they can be conveniently handled during installation and maintenance.

During our internally funded program in IR protective coatings, we investigated the use of polymeric materials prepared in a low-pressure, rf-generated glow discharge. This process is commonly called plasma polymerization. Polymers can be prepared conveniently in a plasma as thin, pinhole-free, adherent, and conforming films. Their utility is enhanced by their hydrophobicity and their high crosslink density, which minimizes their permeability to water. A plasma polymer derived from ethane, which cannot be polymerized by any other method, is highly transparent in the 8- to 12- μ m range. Thus, this material is a likely candidate for a low-absorption, moisture-protective coating.

Our investigation showed that the nature of the substrate surface is of paramount importance to enable plasma-polymerized films to act as effective protective coatings. For NaCl, extended lifetimes under high-humidity conditions required preparing a smooth, passivated surface by chemically etching with hydrochloric acid before depositing the polymer

film. On an internally funded program, we developed an effective in situ surface-passivation method that uses the active species formed in a plasma derived from chlorofluorocarbon gases. We believe that the chlorine and/or fluorine atoms replace hydroxyl groups on the crystal surface, and that these OH groups, if not replaced, are responsible for binding to the surface and accelerating its attack by moisture. Since we carry out both the passivation and the coating deposition in the same reactor, the passivated surface is not exposed to ambient conditions before the film is deposited. A plasma-polymerized ethane (PPE) protective coating deposited on a passivated NaCl window provided protection from damage by water vapor at 98% relative humidity (RH) for at least 100 hr, at which point the testing was arbitrarily stopped. The demonstration of tremendously increased lifetimes provided by the approaches taken in our IR&D research shows the promise of plasma-polymerized films as protective coatings for alkali halide lenses and windows.

Under a DARPA/NVEOL contract, Honeywell recently demonstrated the feasibility of producing low-cost, press-forged KBr optical elements. These optics, should they meet the proper specifications, are being considered as replacements for the internal ZnSe color-corrector elements in FLIR systems being developed by the Night Vision and Electro-Optics Laboratories. The objective of our program was to develop plasma-polymerized films that are transparent and moisture protective, and to use these films to increase the lifetime and durability of press-forged KBr IR optical elements. It is anticipated that these optical elements will be enclosed in military FLIR systems under partially controlled atmospheric conditions, but will be occasionally exposed to uncontrolled conditions during maintenance operations. Plasma-polymerized films will protect these elements from damage when the FLIR system is opened to humid environments.

SECTION 2

SUMMARY

This final report details the results obtained on a contract entitled "Moisture Protective Coatings for Alkali Halide Infrared Optics" under DARPA sponsorship, with technical monitorship by the Night Vision and Electro-Optics Laboratories. The objective was to develop plasma-polymerized films that are transparent and moisture-protective, and to use these to increase the lifetime and durability of press-forged KBr IR optical elements. This section summarizes the results by task. More detailed methods, results, and discussions are presented in Section 3.

A. TASK 1: SURFACE PREPARATION AND REACTION CONDITIONS

Reaction conditions were optimized to yield uniform films of PPE on polished and passivated single-crystal KBr flats and press-forged KBr with a deposition rate of $\sim 0.25 \mu\text{m/hr}$. We found that commercially available polycrystalline KBr flats could not be polished without localized grains forming that could not be removed by chemical etching with HBr.

B. TASK 2: SURFACE PASSIVATION

The hygroscopic nature of alkali halides is due to the presence of surface hydroxyl groups. Surface passivation by removing or converting these groups to nonpolar species is needed to allow plasma polymerized films to act as effective moisture barriers. We developed several methods to passivate KBr surfaces: (1) chemical etching with hydrobromic acid, which repairs grinding defects and partially removes hydroxyl groups; (2) in situ methods using active halogen species from Freon plasmas to displace and substitute for the surface hydroxyls; and (3) thin layer surfactants to either effectively hide hydroxyls, or chemically convert them to less polar groups. All of these methods were successful in passivating KBr. Lifetimes of PPE coated windows versus passivation

methods are shown in Table 1. Other methods, such as etching with an argon plasma, or using a SiO_2 layer were marginally successful.

C. TASK 3: EXPANSIVE STRESS RELIEF

Expansive stress is commonly manifested by cracks in the film. This was not a problem with PPE on KBr flats.

D. TASK 4: QUENCHING FREE RADICALS

We investigated several methods to quench residual free radicals following the deposition of PPE: (1) allowing the free radicals to act as radical initiators for the free radical polymerization of ethylene; (2) exposing the polymer to a hydrogen plasma for 5 min or 30 min; (3) exposing the polymer to a CF_2Cl_2 plasma to generate more surface radicals which would promote a higher degree of crosslinking at the surface; and (4) preparing the polymer by pulse-mode deposition. All methods were successful, but Method 1 was used routinely in this study.

E. TASK 5: THICKNESS EFFECTS

Thickness effects on moisture protection and transmission were evaluated with each sample. A refractive index of 1.67 (in the IR) was determined for films obtained under the reaction conditions used in this study. Films ~5- μm thick were adequate to completely cover non-jagged surface defects, while retaining a transmission of >90%.

F. TASK 6: IR ABSORPTION MINIMIZATION

IR spectra were taken routinely on each sample. The absolute absorption of PPE was found to be 0.4% per micrometer thickness by laser calorimetry. Progress in this task can be correlated with progress in Task 4 since the problem here is directly related to the concentration of residual free radicals.

G. TASK 7: MOISTURE RESISTANCE OF COATED SAMPLES

A water-tight sealing method was developed so that only one side of a window would need to be coated for high humidity testing. Moisture resistance was dependent upon the method and degree of surface passivation and the degree of free radical quenching. Lifetimes approaching 100 hr at 88% RH at 25°C were obtained.

H. TASK 8: ENVIRONMENTAL AND DURABILITY TESTS

PPE films on passivated KBr flats passed the moderate abrasion (cheesecloth rub), adhesion (cellophane tape pull), and 24 hr humidity tests, administered according to MIL-C-675B. The film failed, however, when it was subjected to salt water spray according to MIL-STD-810B. It was found that PPE possessed sufficient fungus resistance when tested in accordance to MIL-STD-810B.

SECTION 3

TECHNICAL DISCUSSION

This section discusses, task by task, the problems and solutions encountered during the extent of this contract, which includes the dates 1 November 1979 through 16 October 1980 when the Night Vision and Electro-Optics Laboratories removed their support to this technology development program. Work was resumed on 1 March 1981 under the sole sponsorship of DARPA.

A. SURFACE PREPARATION AND REACTION CONDITIONS

Task 1. Establish reaction conditions to prepare plasma-polymerized ethane on polished and passivated KBr windows and press-forged KBr optics.

In prior work, we used sodium chloride substrates to develop our technique for using plasma-polymerized films as moisture-protective coatings. Unfortunately, this technology on the surface preparation of polycrystalline NaCl was not entirely applicable to polycrystalline KBr without large-grain domains forming. After grinding by standard methods, various methods of polishing were used on a total of 17 samples:

- (1) polishing on Polytex Supreme with Linde A in isopropyl alcohol;
- (2) polishing on pitch with Linde A in ethylene glycol; and (3) polishing with black or red rouge on a variety of backing cloths. In no case were the domains eliminated. Furthermore, chemical etching with 48% HBr, which is a method described in the literature for repairing grinding damage at the surface,¹ proceeded at different rates in these domains and the remaining area. The etching did not completely remove the grains ($\sim 0.5 \mu\text{m}$ in diameter), and the optical flatness was degraded severely. A film of PPE on these surfaces, which were passivated with plasma-generated halogen atoms, afforded protection at 88% RH for no more than 3 hr.

We have eliminated the problem by using single-crystal KBr (Harshaw, crystallographic face unknown). No grain boundaries were found on

grinding, and chemical etching with 48% HBr for ~30 sec yielded a smooth, wet-looking surface.

Reaction conditions for the deposition of uniform films of PPE on these smooth surfaces have been established, although the deposition rate was fairly low (~0.25 $\mu\text{m/hr}$). Twenty six experiments were carried out in which pressure and flow rate were varied while rf power was held constant. The deposition rate was calculated by measuring the thickness of the film (Dektak FLM surface profile measuring system). Although higher deposition rates would obviously be desirable, we found that an oily film was obtained at rates above ~0.3 $\mu\text{m/hr}$. Those PPE films that were of high quality visually were studied spectrophotometrically. The reaction conditions that produced the highest quality films were chosen for this work. Periodically, we made calibration runs on glass slides to verify the reproducibility of film quality under a given set of conditions. A PPE-coated KBr window is shown in Figure 1.

A typical experiment was carried out as follows: A polished and chemically etched KBr flat was passivated using one of the methods described in Section 3.B (Task 2) and placed in an appropriate reactor, such as the Tegal PR-100 shown in Figure 2. The reactor was pumped to a background pressure of ~0.06 Torr, at which time ethane was introduced into the system at ~100 ml/min for at least 15 min. The flow rate was then reduced to 10 ml/min and the pressure was increased to 1.00 Torr by a throttle valve. A Datametrics Baracel pressure regulating system kept the pressure constant throughout the run. Following equilibration of the initial conditions, a plasma was struck using a Tegal P-300 rf generator (13.56 MHz) at 200 W through an impedance matching network. Since the deposition rate was calibrated under these conditions, desired thicknesses could be obtained by running the experiment for a predetermined time. During the first hour of the experiment, the reaction conditions had to be adjusted slightly due to thermal changes. The final temperature of the system was 100 to 120°C after a 20 hr run. Following the deposition of PPE, the system was evacuated to 0.06 Torr and then flushed with ethylene for 15 min. Approximately 11 to 20 Torr of ethylene was admitted into the system which was then closed off. The coated KBr window was allowed to stand in the ethylene atmosphere at least until the system cooled to room

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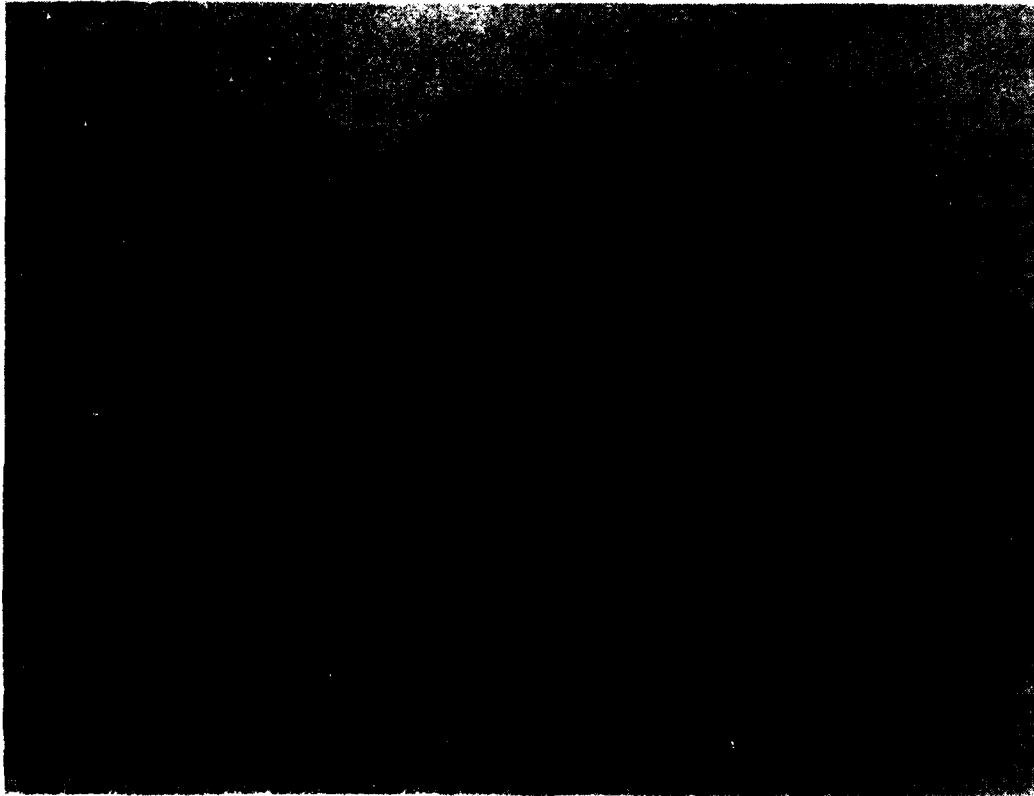


Figure 1. A typical example of PPE on KBr.

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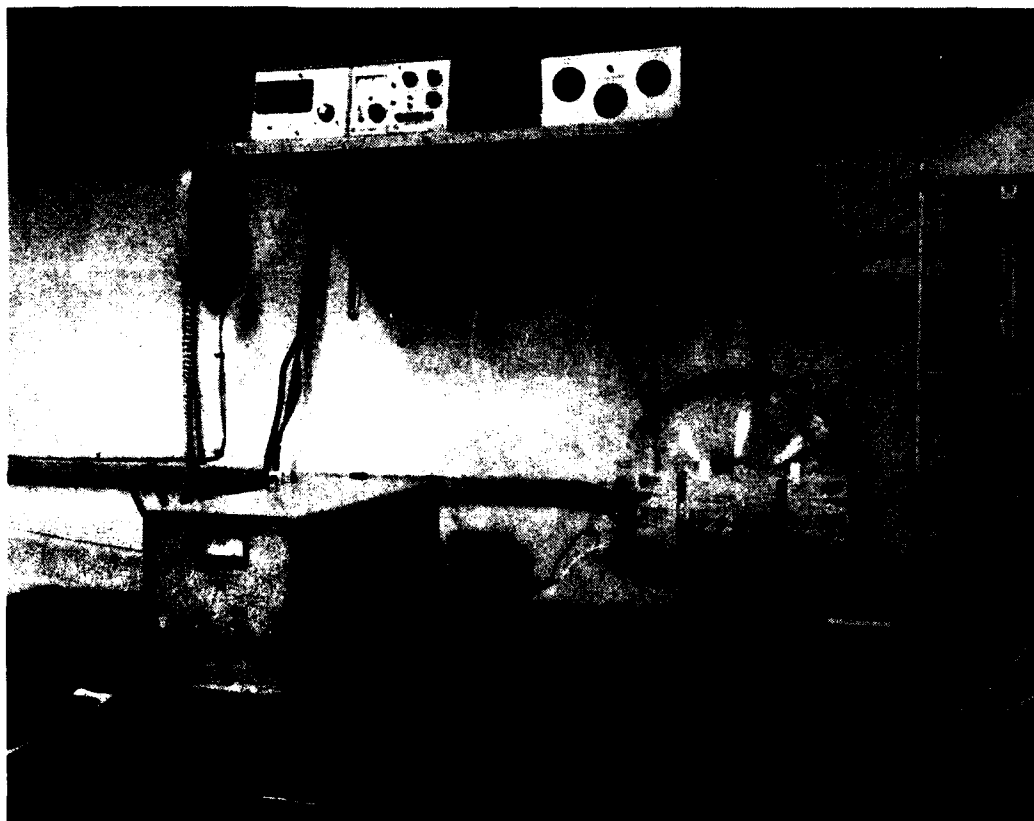


Figure 2. A capacitively coupled plasma polymerization reactor (Tegal PR-100), rf generator (Tegal P-300), and related support equipment.

temperature or, more commonly, overnight. The system was backfilled with air and the window removed. IR spectra were taken, and the window was then further tested, e.g., exposed to high RH.

At a recent program review, we learned that the group at Honeywell was studying the use of PPE as a protective outer layer on an AR stack on KBr. Their reaction conditions were significantly different from ours. Therefore, at the suggestion of our DARPA project engineer, we attempted to prepare PPE films under conditions similar to those devised by the Honeywell investigators. We used a flow rate of 10 ml/min at STP of ethane for the preparation of PPE films throughout this project. Honeywell reported that they were able to obtain films that were nearly colorless (ours are a pale yellow) by using flow rates of ~50 ml/min. We prepared two films: (1) flow rate = 50 ml/min, pressure = 1.00 Torr, power = 50 W; and (2) flow rate = 43 ml/min, pressure = 1.00 Torr, power = 200 W. In both cases, the resulting film was only very slightly yellow, and the index of refraction in the IR of each was 1.24 and 1.33, respectively, which was lower than the index of 1.67 found for the films prepared at a flow rate of 10 ml/min.

These results serve to point out that the resulting polymer can have different properties, and most likely different structures, depending upon the reaction conditions used in its preparation. The characterization of a reactor for each monomer is necessary to define the reaction condition limits in which the desired polymer form, i.e., film, oil, or powder, can be prepared. However, within those limits a material can have different properties. The conditions should be established for optimizing those desired properties while retaining the highest possible deposition rate. Although the films obtained in this case at high flow rates had a lower refractive index and were slightly less colored, they did not have superior transmission properties in the 8- to 12- μ m region, nor was the moisture protecting quality superior to the films that we prepared at lower flow rates. Furthermore, at lower flow rates, the deposition rate was greater than a factor of 2 higher. Since ethane polymerizes slowly, this is a practical consideration that should not be overlooked.

Two press-forged, plano-concave KBr windows (Lens No. KBO-0138-003 and KBO-0138-008), supplied from Honeywell through NVEOL, were coated on

both sides with PPE. Prior to coating, both windows were nearly clear in the center, but the edges were cloudy with subsurface cracks. Window -003 received no pre-treatment or surface passivation, but window -008 was chemically etched in 48% HBr for 90 sec. The surface of this etched window was slightly foggy due to grain formation. Etching an additional 30 sec did not improve its appearance. This window was also passivated by our in situ method using CF_2Cl_2 (see Section 3.B). Each side of the windows was coated separately under the reaction conditions found to give uniform coatings in the experiments above. A PPE film was applied to the flat side and the concave side, 5.3- μm and 5.5- μm thick, respectively, on window -003, and 4.6- μm and 5.1- μm thick, respectively, on window -008. Very uniform films were obtained on each side; the concave side showed no signs of strain or bubbles. These coated windows were tested for their resistance to high humidity. The results are discussed in Part G of this section.

B. SURFACE PASSIVATION

Task 2. Optimize our in situ surface-passivation method for KBr using a variety of halocarbon reactants, and study their effectiveness; and investigate other novel passivation techniques, which may not be in situ methods, such as thin layer surfactants.

Plasma-polymerized ethane shows tremendous promise as a protective coating. There are, however, substrate surface factors that must be considered before PPE can be practically utilized as a moisture barrier on alkali halide surfaces. Pastor and Pastor² have reported that the major impurity on NaCl, KCl, and KBr surfaces is the corresponding hydroxide. A plot of Mulliken electronegativity and hydration energy of the halide and hydroxide ions versus their ionic radii, shown in Figure 3, illustrates that the hydroxide ion falls naturally onto the curve for the halides and can be considered a pseudohalide. Since the alkali metal hydroxides are deliquescent, and since pure, powdered NaCl and KCl are not inherently hygroscopic,³ it is reasonable to assume that the hygroscopic nature of NaCl, KCl, and KBr windows is due to the presence of hydroxide ions.

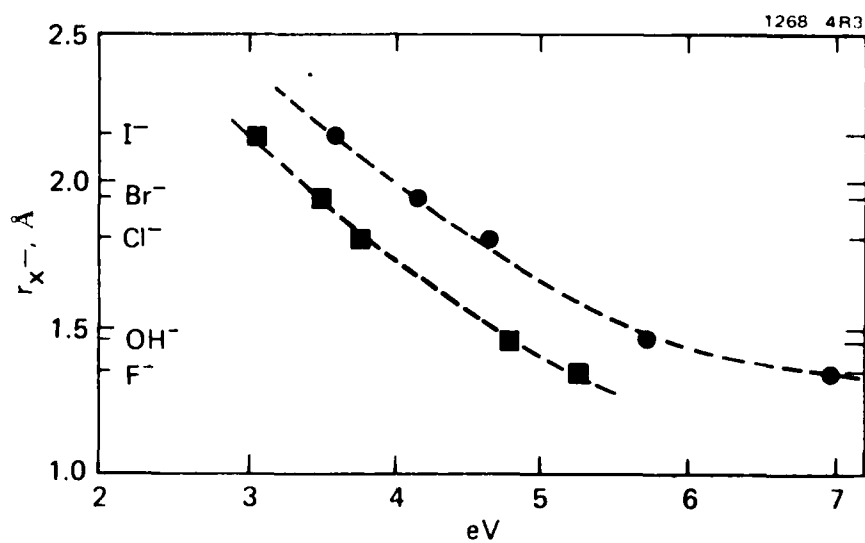


Figure 3. Anion size versus Mulliken electro-
negativity (●) and the hydration
energy (■).

This would create a polar, high-energy surface, and hydration of the hydroxide groups would tend to lower the surface free energy. This process could provide a driving force to pull water through a plasma-polymerized film matrix to lower the energy difference at the substrate-film interface. Removing surface hydroxide groups will effectively passivate the surface of alkali halides.

We concentrated our efforts to achieve effective surface passivation on KBr in three main areas: (1) chemical etching with hydrobromic acid; (2) in situ plasma decomposition of Freon gases; and (3) thin-film surfactants. The use of hydrobromic acid was discussed in Section 3.A. Table 1 summarizes the moisture protection of PPE on KBr as a function of the surface passivation method. The effectiveness of the method was evaluated empirically based on the protective ability of the film on a passivated surface after exposure to high RH.

Along with the smoothing of the KBr surface, HBr partially passivates the surface by replacing some of the surface hydroxyl groups with bromide. However, even though the process is carried out in a nearly dry atmosphere, it is done in a water solution. Thus, it is nearly impossible to remove all of the residual water, and the etched window is ultimately exposed to ambient conditions following the etching, allowing water to adsorb onto the surface. Nevertheless, this method was used in all experiments dealing with the passivation of KBr windows.

We had found previously that halogen atoms generated from inert Freon gases passivated the surface of NaCl. We believe that halogen atoms replace surface hydroxide groups, although the process may remove surface layers of KOH as well. One advantage of this method is that it is done under vacuum in the reactor just before the plasma-polymerized film is deposited, thus avoiding contamination problems. On this program, we initially tested CF_3Br for the surface passivation of KBr. However, we found that this material caused electrode corrosion. The PPE films deposited hereafter were inferior, as evidenced by their cloudy appearance and large refractive index change. The corrosion problem was traced to a small airleak in the reactor system. After the leak was repaired, we found that CF_3Br could indeed be a useful starting material for passivation. Although we did not investigate the specific role of air,

Table 1. Moisture Protection of PPE Coated KBr Flats with Surface Passivation Method at 25°C

Method	Thickness of PPE, μm	Relative Humidity, (%)	Lifetime, ^a Hr	Comments
HBr	~5	88	3	
CF ₃ Br	~5	83	95	5 min treatment
Q/C ^b	6.5	88	80	1 layer
Q/C	4.8	88	50-100	3 layers
Q/C	5.5	85	52	Baked at 65° for 65 hr
Q/C	4.0	88	18	Baked at 129° for 17.5 hr
ODA ^c	~5	88	48	Slow salt formation over 5 days
ODA	5.5	85	52	Baked at 65° for 65 hr
ODA	4.0	88	18	Baked at 129° for 17.5 hr
CF Cl ₂ (Plasma)	5.1	86	15	3 hr treatment
Argon (Plasma)	7.4	88	30-80	Non Reproducible
SiO ₂ (50 Å)	5.4	88	38	

^aLifetime = salt deposition on the surface after drying.

^bQ/C = Quilon-C (DuPont), diluted 1 part in 200 parts of 2-ethoxyethanol.

^cODA = octadecylamine.

we speculate that excited oxygen and nitrogen molecules or atoms interacted with the excited species in the plasma. Bromine may be an ultimate product of this interaction, which would account for the electrode corrosion. Also, excited nitrogen and/or oxygen could interact with CF_3 radicals to form a species that may be polymerizable in a plasma. A polar film of this type would be expected to have a significantly different index than PPE. Therefore, the deposition of PPE would actually yield a composite having an index different from that expected.

In this program, the in situ passivation method emphasized the use of two Freon gases, CF_3Br , and CF_2Cl_2 . The gas CF_3Br was chosen, since the weakest bond in this material is the carbon-bromine bond; thus, bromine atoms and ions would be preferentially formed in the plasma. The gas CF_2Cl_2 was a successful passivating agent on NaCl. We wanted to test its effectiveness on KBr and see if chlorine could be substituted for the hydroxyls without affecting the physical or optical properties of the window. However, although CF_2Cl_2 was useful in the passivation of NaCl (5 min plasma exposure), it did not yield comparable results with KBr. Short exposures of KBr (5 min) to a CF_2Cl_2 plasma did not significantly increase the lifetime of the coated window over other passivation techniques (vide infra). A longer exposure (3 hr) tended to etch the window and leave a fogged surface. Lifetimes of ~15 hr at 86% RH were obtained in this case. The gas CF_3Br was found to be a useful passivating agent. Lifetimes approaching 100 hr were obtained.

On a concurrent internally funded program, we developed another surface-passivation technique, which was incorporated into this program. This technique used a surfactant called Quilon-C (DuPont), which was applied as a very thin-film, and was therefore transparent in the IR. Treating the surface of NaCl with this surfactant and then depositing PPE afforded protection from damage by 98% RH for 11 days. During this period, no cracks or bubbles in the film were observed. No spectral data were obtained on this sample because the film was torn when it was removed from its holder. Methods to eliminate this holder are discussed below in Section 3.G (Task 7).

We used an O-ring cylinder, piston-type holder (see Figure 4) for RH testing so that only one side of the alkali halide window would need to

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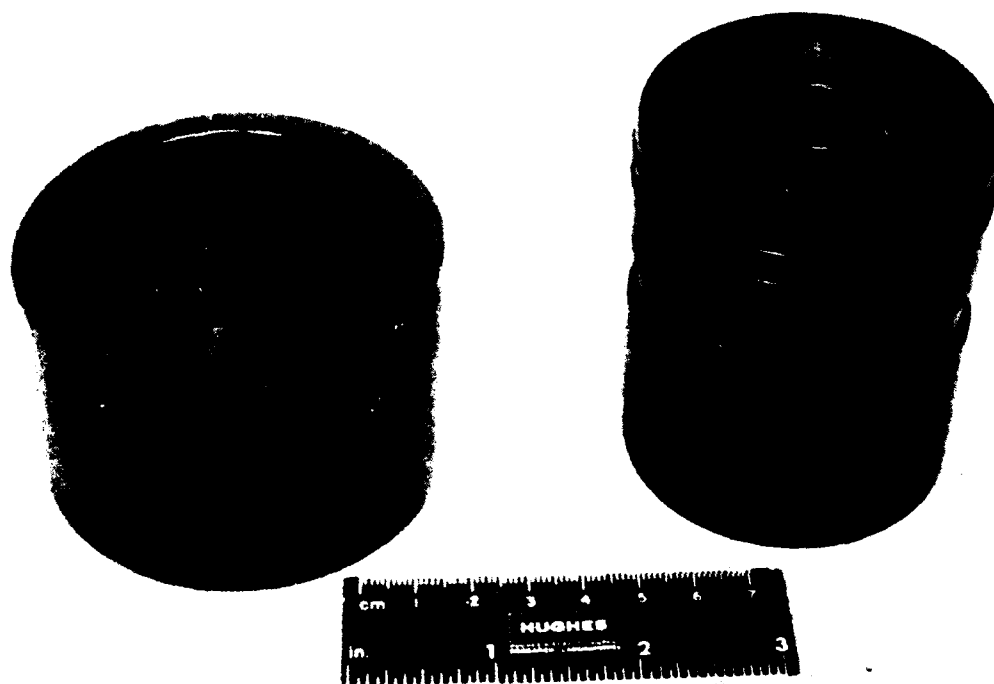


Figure 4. O-ring holder for humidity testing.

be coated. The coated window was placed at the bottom of the cylinder, and the film was exposed to high RH through a hole in the piston. A seal at the hole was provided by a Buna rubber O-ring, which was compressed against the coated alkali halide window. When the holder was disassembled, the film was often torn by this O-ring, either because of sticking or because of a twisting at the interface. Another explanation could be that water diffused through the film and reduced the adhesion at the film-surface interface, which would promote the tearing of an effectively free standing film. An example of the damage caused by this O-ring holder is shown in Figure 5.

We investigated three surfactants as passivating agents. The effectiveness of octadecylamine and its hydrobromide salt were studied. Long-chain alkylammonium salts are used in the saturated solution separation of potassium and sodium salts.⁴ The -NH_3^+ group is approximately the same size as the potassium ion which can be replaced by the alkylammonium ion in a cluster of potassium chloride molecules in a potassium chloride-sodium chloride mixture. The potassium-alkylammonium chloride complex becomes hydrophobic due to the long-chain alkyl group on the surfactant and floats to the top of the solution. We felt that a similar complexation could occur with an alkylammonium salt applied to a KBr surface. This process would allow the alkyl group of the long-chain amine to extend away from the surface, which would not only create a non-polar surface (possibly useful for increasing the adhesion of the nonpolar PPE film), but effectively hide or mask the surface hydroxyl groups. However, we were unable to identify a practical technique to apply octadecylammonium bromide to the surface of KBr uniformly, or thin enough so that its presence did not interfere with the optical transmission of the window in the IR. Octadecylamine was only slightly soluble in concentrated HBr, and dipping a KBr window into this solution following etching with HBr was not effective. The surface of the KBr window was noticeably streaked from the nonuniform application of the alkylammonium salt.

We tried several methods for coating KBr with thin-films of octadecylamine. Solvent casting (from hexane or ethoxyethanol solution), and spreading by rubbing the melt were attempted. In both cases, it was

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Figure 5. Typical damage to PPE-coated KBr after humidity testing in the O-ring holder.

found that the contact angle of CH_2I_2 on the coated surface was greater than the surface itself and approached a value of 61 deg, the contact angle of CH_2I_2 on paraffin.⁵ The contact angle, measured goniometrically, is proportional to the surface tension and, therefore, to the surface energy. A large contact angle implies a low energy, or a non-wettable (to water) surface such as paraffin. However, upon deposition of PPE it was evident that the octadecylamine was coated unevenly. Lifetimes of these coated windows was limited by the uniformity of the surfactant; the longest lifetime obtained was 48 hr at 88% RH. Baking the coatings at 65°C for 65 hr increased the lifetime slightly, although changing the conditions to 129°C for 17.5 hr reduced the lifetime to 18 hr. This was probably due either to desorption, or to the migration of the surfactant into domains, or to the thermal decomposition of the octadecylamine.

The other surfactant that we investigated is a reactive, chromium-fatty acid complex, Quilon-C (DuPont). The chemical structure of Quilon-C is shown in Figure 6. This material reacts with hydroxyl groups creating an oxygen-chromium bond while eliminating HCl. Thus, the hydrophilic hydroxyl groups are converted into chromate groups which are relatively nonpolar. Enhancement of the adhesion of PPE would be expected with this surfactant as well, possibly by the interaction of the surface alkyl groups with the plasma to create free radicals, which can be used to chemically bind the resulting polymer film to the surface. Again, the long chain alkyl group is oriented normal to the surface so that it has been effectively changed from a polar to a nonpolar one. As pointed out earlier, Quilon-C was a very effective passivating agent on NaCl. As it turned out, however, PPE-coated KBr, spin-coated with Quilon-C identically to the NaCl, did not produce similar extended lifetimes after exposure to high humidity; the NaCl window survived longer by at least a factor of 24.

We found that lightly etching the surface of KBr with an argon plasma was somewhat effective in passivating the surface. Although this increased the lifetime over a non-treated surface, the results were not reproducible and this technique was not vigorously pursued. We also investigated using a thin layer of SiO_2 (50-Å thick) as a passivating and sticking layer. An absorption of 1.5% at 9.5 μm resulted from this layer due to the Si-O stretching vibration. After deposition of PPE onto this

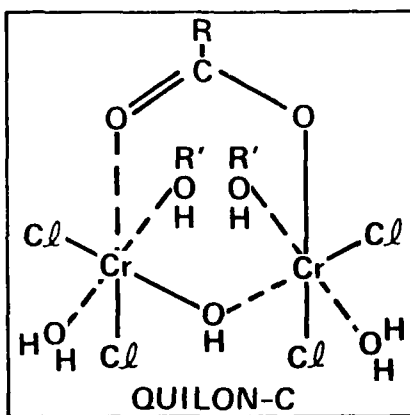


Figure 6.
Chemical structure of
Quilon-C (DuPont) where
 $R = C_{14}H_{29}$, and R' is
derived from the solvent
alcohol.

surface and exposure to high humidity, the resulting lifetime was 38 hr. This technique was also not pursued further.

Typical results of lifetimes of PPE-coated KBr discs as a function of the surface passivation method are shown in Table 1. The lifetimes are the longest achieved for each method, although reproducibility was usually within 10 hr of the listed values.

In all cases, the surface passivation methods investigated increased the lifetimes of PPE on KBr when exposed to high humidity. However, the results were less impressive than those obtained on NaCl in earlier IR&D work. Whereas our in situ passivation method with CF_2Cl_2 resulted in routine lifetimes of >100 hr at 98% RH with NaCl, this gas and CF_3Br resulted in a maximum lifetime of 95 hr, with lifetimes of ~50 hr commonly seen on KBr at 85 to 88% RH.

The most reproducible results in this study were obtained with the surfactants, especially with Quilon-C. This material is obtained as a dark green solution in isopropyl alcohol. We diluted this stock solution by evaporating one part under a stream of nitrogen and dissolving the residue in 200 parts of 2-ethoxyethanol. The HBr-etched, KBr disks were spin-coated with this diluted solution at 2000 rpm for 2 min. When more than one layer was desired, the spin-coating process was repeated for each layer. It was found that this technique dried the sample sufficiently so that the window could be coated without further treatment. However, a few samples were heated to investigate the effect of temperature on the reaction of the Quilon-C with the surface hydroxyl groups, as discussed above. The resulting PPE films on Quilon-C-treated KBr were uniform. Furthermore, the quality of the underlying surface can often be evaluated visually after the PPE is applied due to refractive index differences. In one case, Quilon-C appeared to have been coated evenly across the entire surface. More careful examination under a microscope showed that, in one case, there appeared to be a slight build-up of surfactant along the edges of the window. Although the thickness of the resulting layer was not known, there was no loss of transmission in the 8-to 12- μm region, even with three layers of surfactant on the surface. Lifetimes approaching 80 hr at 88% RH were obtained routinely on KBr with one layer of Quilon-C, and 100 hr with three layers. The extra layers of surfactant apparently

coat voids or pinholes in the first layer, and may account for the added lifetime. This method had the disadvantage that it was not done in situ, so there was the possibility that water vapor could adsorb on the surface during transfer. This, however, did not appear to be a major problem, particularly in view of the results on NaCl where lifetimes of up to 11 days exposure to 98% RH were achieved.

The difference in results between NaCl and KBr is perplexing, to say the least. Like NaCl, the hygroscopic nature of KBr must certainly be related to the concentration of surface hydroxyl groups. Yet methods to reduce or eliminate these groups, which were successful on NaCl, showed only limited effectiveness on KBr. Several explanations may be expounded upon, although none has been identified as the major cause of this difference. In the case of the in situ passivation method, the surface hydroxyl groups need to be exchanged at the surface with active halogen species. Since we were using single crystal KBr windows, the reactivity of the hydroxyl groups could be different than the reactivity of hydroxyl groups bound to polycrystalline NaCl. It is well known that the surface reactivity can vary significantly with crystal plane. Furthermore, the lattice energy of KBr (see Table 2) is lower than that for NaCl, and the lattice energy difference between KOH and KBr is higher than that for NaCl and NaOH. This suggests that substitution of a species at the surface favors the removal of the bromine moiety rather than the hydroxyl. A similar argument can be stated for the NaCl case, although the energy difference is smaller, and therefore, a significant number of hydroxyl groups are replaced along with surface chlorines. Further, the grinding and polishing steps for KBr can cause surface defects in the form of peaks and valleys. This process actually exposes other crystal planes to the surface so that the reactivity can vary along the surface. It seems possible that these other crystal planes may contain an increased concentration of hydroxyl groups, although at the same time they may be less labile to substitution by impinging halogen species from the plasma. Also, if the grinding is not exactly parallel to the desired crystal plane, the surface of the KBr will rearrange back to that crystal plane, but in the process, form steps whose walls will be oriented along another plane. A difference in reactivity would be expected in this case as well.

Table 2. Lattice Energy of Selected Compounds, Kcal/mol.
Data taken from M.C. Ball and A.H. Norbury,
Physical Data for Inorganic Chemists (William
Clowes and Sons, Ltd., London, England, 1974)
p. 96.

	Na ⁺	K ⁺
Cl ⁻	185	168
Br ⁻	176	161
OH ⁻	211	189
E _{NaOH} - E _{NaCl} = 26 Kcal/mol.		
W _{KOH} - E _{KBr} = 28 Kcal/mol.		

The practical problem in the case of the surfactants was lack of a reproducible method for applying them as very thin, uniform films. However, when NaCl and KBr were coated with the same concentration of Quilon-C by spin coating under identical conditions, the PPE coated NaCl window had a significantly longer lifetime than the coated KBr window after exposure to high humidity. We suggest that the difference in reactivity between the two materials may also be related to the difference in the crystallinity. The crystal face will determine the degree of exposure to the surface that can be obtained by a surface hydroxyl group since the arrangement of potassium and bromine ions, which also controls the arrangement of hydroxyl groups, will vary. Figure 7 shows the arrangement of potassium and bromine ions on three possible crystal faces. Thus, a face that has a higher concentration of bromine atoms will also have a higher concentration of hydroxyl groups. Further, bromide has a larger ionic radius than chloride. Since Quilon-C must approach the hydroxyl groups unimpeded, the bromide groups may provide enough steric hindrance so that the reaction is inefficient. In polycrystalline NaCl there are, in effect, several faces exposed and several arrangements of chlorides and hydroxyls. Also, the chloride is a smaller species and may not provide enough steric hindrance to prevent the reaction with surface hydroxyl groups and the Quilon-C.

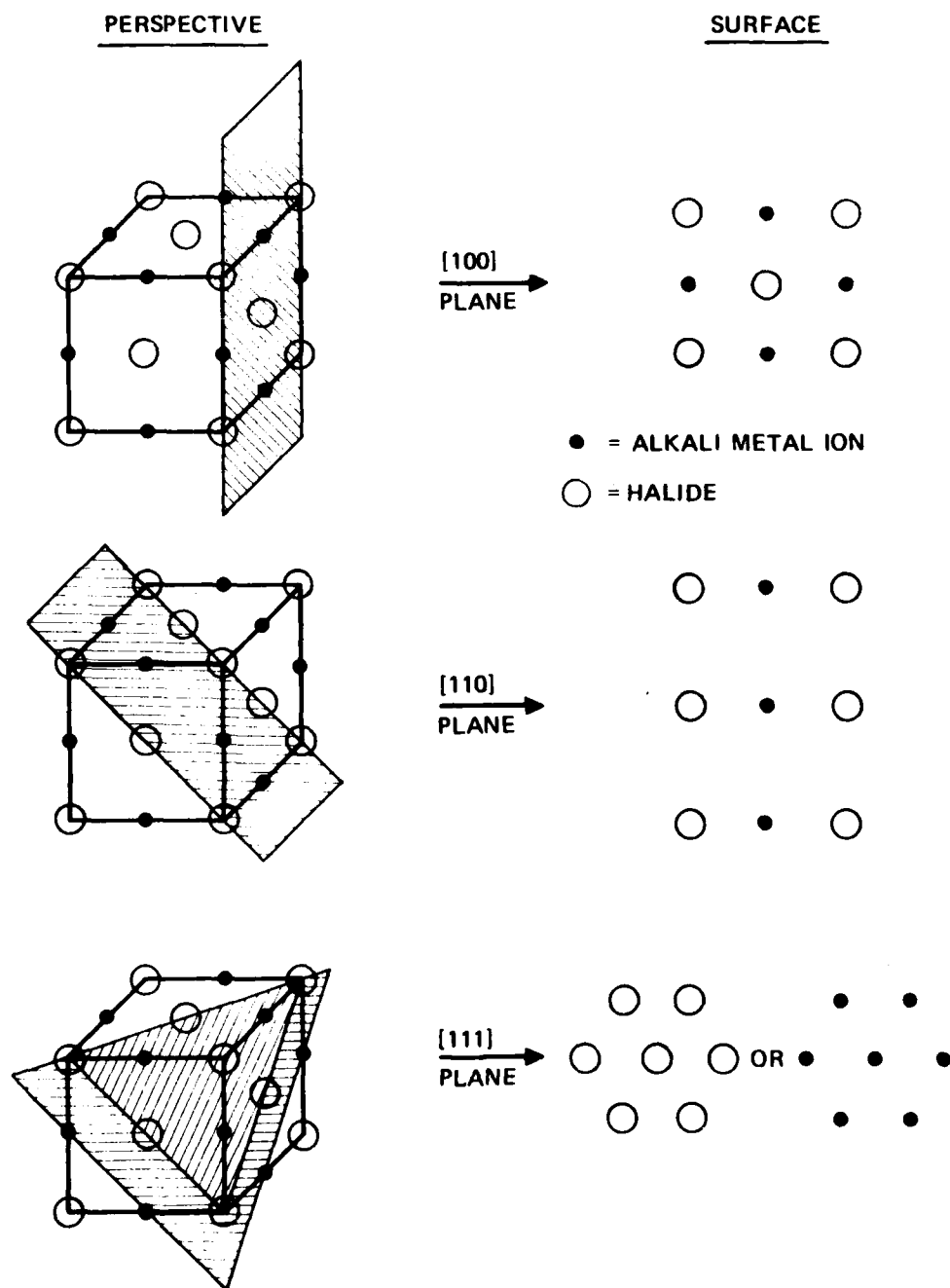


Figure 7. Arrangement of atoms on the surface of various crystal faces for a face-centered cubic crystal.

C. EXPANSIVE STRESS

Task 3. Study the relief of expansive stress in the films by annealing and by decreasing the deposition rate using pulse-mode operation.

In the past, film failure from exposure to high humidity caused by expansive stress was manifested by large cracks in the film. This has not been seen in films on KBr flats, which implies that expansive stress is not a problem in this case.

D. QUENCHING FREE RADICALS

Task 4. Investigate the quenching of trapped free radicals with hydrogen atoms derived from a hydrogen plasma as well as from other hydrogen atom sources not necessarily derived from a plasma; study the decrease of free-radical concentration by pulse-mode deposition and post-heating.

It is known that long-lived free radicals are trapped in plasma polymerized films.⁶ For the film to retain maximum hydrophobicity, the free radicals must be efficiently quenched so that no polar oxygenated sites can form on the surface or in the bulk by exposure to the atmosphere. In earlier work we allowed the residual free radicals in PPE to act as initiating agents for the chain-reaction polymerization of ethylene. Although this method works reasonably well, it is, as expected, neither efficient nor completely effective, as shown by the data in Table 3. Treating PPE with ethylene and then exposing the film to dry air resulted in the reaction of oxygen with remaining trapped radicals after 56 days, as shown by the formation of a carbonyl group which was observed in the IR spectrum. A chain reaction polymerization generates a new free radical in each step as the chain grows, and eventually the polymeric radical must be quenched by reaction with another radical or a chain transfer agent. With plasma-polymerized films, termination can only occur by the radicals of two growing chains coming into contact with each other. This is not a very efficient process since the polymeric radicals are trapped within a solid matrix, where they are often isolated.

Furthermore, ethylene can permeate the polymer matrix and partially react with radicals below the surface, causing disclinations in the polymer structure, localized swelling, and increased expansive stress.

We treated PPE with hydrogen atoms derived from a hydrogen plasma, but only for 5 min. Comparison of the effectiveness of this method with that of storing the film under an ethylene atmosphere is shown in Table 3. Three KBr flats were coated with PPE and treated as shown. Each was removed from the reactor and stored in dry air. They were monitored periodically for the formation of a carbonyl group, which shows a strong absorption at $\sim 5.8 \mu\text{m}$ in the IR. We found that treating PPE with a hydrogen plasma for 5 min did quench free radicals, but the method was no more effective than storing under ethylene. Storing under a hydrogen atmosphere was not effective.

Table 3. A Comparison of Free Radical
Quenching Methods

Treatment	Time for C=O Appearance, Days
Stored under O_2	37
Stored under ethylene	56
H_2 plasma/stored under H_2	52

During the last half of this program, we investigated three methods to reduce the free radical content of the newly deposited PPE film: (1) hydrogen plasma for 30 min; (2) CF_2Cl_2 plasma (a modified crosslinking by activated species of inert gases, or CASING); and (3) pulse-mode deposition of PPE, followed by quenching with ethylene. We monitored the effectiveness of each technique by evaluating the eventual lifetime of a PPE coated KBr window upon exposure to high humidity, rather than by observing the formation of a carbonyl group by IR spectroscopy, which would have taken nearly two months. Two polished and chemically etched KBr windows were each treated with Quilon-C; one with one layer, the other with three layers. PPE was deposited onto this surface and treated by a particular free radical quenching method. The results of the lifetimes of these windows are shown in Table 4.

The six windows were all tested simultaneously at 85% RH at 25°C. After 23 hr, the samples were removed and all showed some sign of failure, i.e., small salt deposits along the face of the window at "pinhole" sites. Nevertheless, because a salt rosette is observed at a point on the film surface, that does not necessarily prove that the failure at that point was due to a pinhole defect. Water could diffuse through the film through an indirect route controlled by defects in the matrix structure of the highly crosslinked polymer network. Thus, salt may appear on the polymer surface at a point removed from the place where the water was actually in contact with the alkali halide surface. In this test the least damage to the surface occurred using CF_2Cl_2 in the modified CASING experiment.

CASING is usually done with an inert gas plasma, e.g., Ar^+ ions, which impinge on a polymer causing bond breakage and forming free radicals at the surface. These radicals can interact with each other, assuming enough proximity to form a crosslinked network at the surface. It was felt that in this case argon ions would provide too much energy at the surface and might lead to film erosion. In this experiment with a CF_2Cl_2 plasma we tried to create more radicals than were present in the freshly deposited polymer to decrease the overall concentration of radicals by promoting crosslinking reactions to occur. Although this appeared to be the case, the overall lifetime of the resulting coated window was not enhanced greatly.

Table 4. Lifetimes of PPE-Coated KBr Flats with Free Radical Quenching Methods at 85% RH at 25°C. All Samples Were Tested Simultaneously.

Quench Method	Quench Time, min	Lifetime, hr	Comment
H ₂ Plasma	30	23	Modified casing ^a Least damage of the lot
CF ₂ Cl ₂ Plasma	10	23	
Pulse-Mode Deposition	--	23	Stored overnight under ethylene
^a Casing means crosslinking by activated species of inert gases.			

It has been reported that the concentration of free radicals is greatly reduced by depositing the film under pulse-mode conditions.⁷ Using a low duty cycle allows active species to form in the plasma during a short pulse, after which they can interact to form a polymer during a longer time period. Thus, a polymer can form without being constantly bombarded by newly formed active species or electrons, which would form new free radicals around the growing film. We used a duty cycle of 0.6 msec on and 2.4 msec off. The deposition rate under these conditions was 0.06 $\mu\text{m/hr}$, around 1/4 the deposition rate of continuous-mode deposition. In our case this method did not enhance the lifetime of a coated KBr window and was considered to be too slow a process to merit further refinement.

It is difficult to compare the results of the 30 min hydrogen plasma method to the earlier work when the polymer was treated for 5 min, since the monitoring methods were different. Nevertheless, it would appear that the longer treatment was no more effective than the 5 min treatment.

Although these methods were successful in quenching residual free radicals, we judged that they were not superior to the use of ethylene for that purpose. Therefore, all films, unless otherwise noted, were treated by this latter method.

E. THICKNESS EFFECTS

Task 5. Determine the optimum thickness for adequately coating surface irregularities while having minimum interference with the optical performance of the window. Establish conditions for uniform deposition on both surfaces and edges of a plano-concave structure.

The effect of thickness on moisture protection and transmission was evaluated with each sample. The index of refraction in the IR was calculated by measuring the optical thickness of PPE on ZnS. A value of 1.67 was determined for films obtained under the reaction conditions used for preparation of coatings throughout this study. We found that a thickness of $\sim 5 \mu\text{m}$, which corresponds to $\sim 3/4$ of a wavelength at

10 μm , and which, therefore, should provide a maximum in transmission at that wavelength, was adequate to completely cover non-jagged surface defects while retaining the transmission in the 8- to 12- μm region at >90%.

Due to the lack of supply of press-forged KBr, thickness evaluations were made on KBr flats. Uniform deposition of PPE on press-forged KBr was obtained in two cases, as described in Task 1.

F. IR ABSORPTION MINIMIZATION

Task 6. Evaluate methods for minimizing absorption in the 8- to 12- μm range by employing reaction conditions that minimize carbon-carbon double bond formation and by removing residual free radicals to prevent the formation of carbon-oxygen functions in the film. Monitor the absorption by IR and ATR spectroscopy and by laser calorimetry at 10.6 μm .

IR spectra were obtained routinely on each sample. A typical example of the IR spectrum of PPE on KBr is shown in Figure 8. The absolute absorption of PPE on KBr at 10.6 μm was found to be 0.4% per micrometer in thickness, as measured by laser calorimetry. Progress in this task can be correlated with progress in Task 4 since the problem here is directly related to the concentration of residual free radicals.

G. MOISTURE RESISTANCE OF COATED SAMPLES

Task 7. Measure moisture resistance of plasma-polymerized films on KBr by exposure to relative humidities ranging from 84 to 100% (specifically 84, 88, 92, 98, 100% RH), with concurrent temperature cycling between -54 and 95°C. Our goal is a lifetime of at least 200 hr in 88% relative humidity at 20°C.

An RH chamber was purchased with company funds. We previously had used saturated salt solutions for 98% RH (cupric sulfate pentahydrate) and 88% RH (potassium chromate). Both solutions are rated at 20°C. The temperature in the laboratory was usually higher than that and was rarely constant. This chamber is capable of controlling the temperature to $\pm 0.5^\circ\text{C}$ and the RH to $\pm 2\%$. All routine testing was done in this chamber.

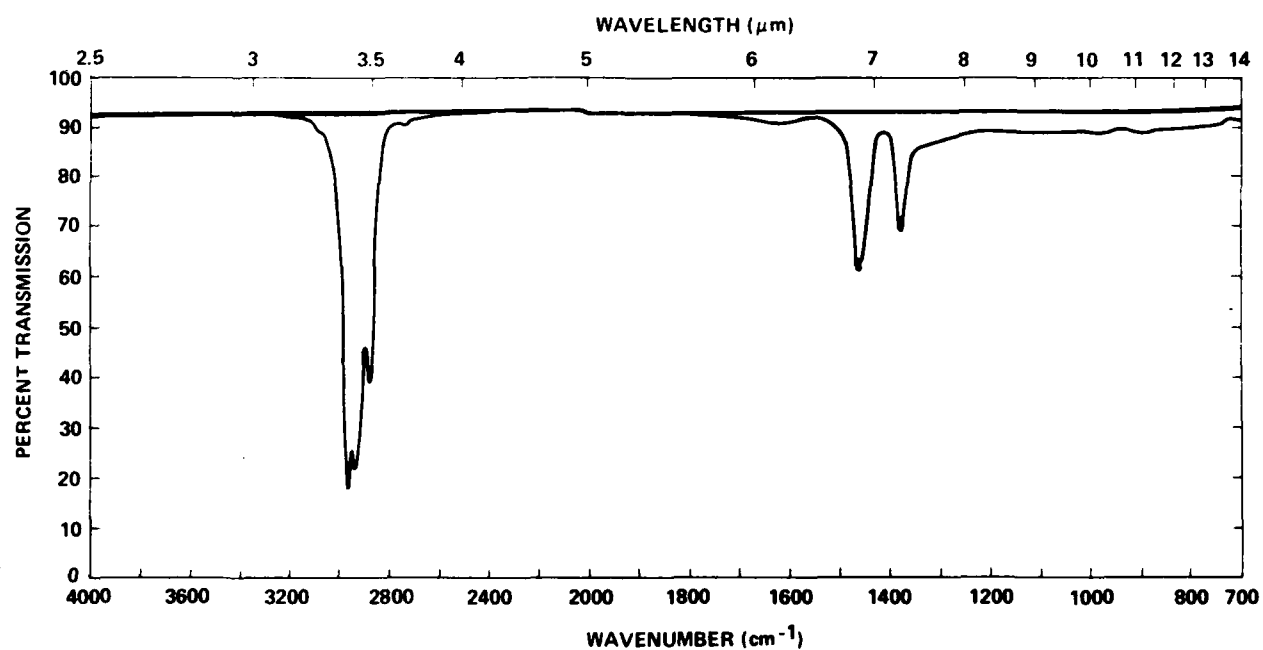


Figure 8. Infrared spectrum of PPE (4.8-μm thick) on KBr.

We tested a variety of water-tight sealants to replace the O-ring holder described in Section 3.B (Task 2). The sealant must not only be impervious to moisture penetration for extended periods, but must also be easily removed without the optical quality of the surface being affected. Seven experiments using collodion, paraffin, clear fingernail polish, and two types of stop-off lacquers (used in electropolishing) all met with only marginal success. The most promising material was a plastic coating called PDS (Plasti-Dip International). After six experiments, this material met the requirements mentioned above. We also investigated the use of RTV-60 (General Electric), which is used to mount the color corrector lens into the holder of the imager, for its sealing capability and compatibility with PPE on KBr. This sealant was also useful, although it was found to be much more tedious to use for routine experiments than the PDS. Therefore, the latter sealant was used in routine RH testing.

A summary of our results in the moisture resistance of PPE-coated, KBr windows can be seen in Tables 1 and 4. These results were discussed earlier.

As described in Section 3.A, we coated both sides of two press-forged KBr lenses with PPE. The edges of window -003 were sealed with RTV-60 which was allowed to dry for 24 hr at 25°C. The coated sample was subjected to 88% RH at 25°, and after 8 hr water had penetrated the film on the concave side; the flat side showed no signs of damage. The appearance of the sample remained unchanged after 97 hr, at which time it was removed from the humidity chamber and allowed to dry at room temperature. The sample had a large crack on the concave side that followed the circumference; the center portion was essentially unblemished. The flat side showed no cracks and only a few small salt rosettes. An IR spectrum of this window after RH testing showed ~10% loss in transmission in the 8- to 12- μ m region over the transmission of the window before testing.

The crack on the concave side of this window can be attributed to stress of film at the edge of the substrate, water penetration through a defect in the RTV-60 at the edge, or a thinner film coating at the edge than at the center. Although the reason cannot be defined at this time, it would appear that the film was under stress, as exemplified by the

pattern of the crack along only the edge of the window. This stress along the edge was compounded by the absorption of water vapor and was ultimately relieved through the cracking of the film.

Window -008, which had been chemically etched and passivated in a CF_2Cl_2 plasma, was sealed around the edges with PDS and subjected to 89% RH at 26°C. After 5.4 hr the sample was removed and salt formations, in the form of small rosettes, were visible on both sides. An IR spectrum after RH testing showed a 13% loss in transmission at 10 μm from the original value of the untested film. Although there were no cracks on the film surface, there were several subsurface cracks emanating from the edges of the window. Salt deposits were present on the outer surface of the PPE film at points where several of the subsurface cracks intersected. Water apparently crept under the film at the edges or penetrated the film near the edges. The moisture then collected and channeled through the KBr at the film-KBr interface until a defect in the polymer matrix was met. When a series of channels intersected at that point there was sufficient water to penetrate the film from the inside to the outside. Thus, in this case, the problem may not necessarily be the permeability of the bulk film to moisture but rather an adhesion or uniformity problem at the edges.

H. ENVIRONMENTAL AND DURABILITY TESTS

Task 8. Test and evaluate the adherence of plasma polymerized ethane films on press-forged KBr for compliance with the environmental and durability specification requirements according to the Development Specification for Alkali Halide Lens Elements with Moisture Protective Coatings. Specifically:

- a. Moderate Abrasion - according to MIL-C-675B
- b. Adhesion - according to MIL-C-675B
- c. Humidity - according to MIL-C-675B
- d. Salt Sea Atmosphere - according to MIL-STD-810B, Method 509, Procedure I for 48 hr
- e. Severe Humidity - according to MIL-STD-810B, Method 507, Procedure I
- f. Fungus - according to MIL-STD-810B, Method 508, Procedure I.

The environmental and physical durability tests on the coated optical element according to the pertinent methods and procedures of MIL-STD-810B and MIL-C-675B as listed in the Development Specification for the Optical Imager (Spec. No. B2-28A050104A) were carried out within Hughes Aircraft Company (HAC) facilities, with the exception of fungus testing. Fungus resistance testing was carried out by Truesdail Laboratories, Inc., Los Angeles, California.

Five samples of PPE (5- μ m thick) on Quilon-C-passivated KBr were submitted to the HAC Coating Evaluation Laboratory in Culver City, California for environmental and durability testing. All samples passed the moderate abrasion (cheesecloth rub) and adhesion (cellophane tape pull) tests. The windows were then sealed onto a glass slide with PDS along the edges so that only the coated side of the window was subjected to humidity testing. This particular test was improperly carried out for >72 hr rather than the prescribed 24 hr; the film failed to protect the surface under these conditions.

Another five samples were prepared under similar conditions yielding a 6.1- μ m thick PPE film on KBr flats. The report of these tests is shown in Figure 9. The substrate material in this report was mistakenly stated as "NaCl" by the Coating Evaluation Laboratory and should actually be "KBr." The handwritten changes on the report were made by F.G. Yamagishi after the report was issued. Of these samples, all passed the moderate abrasion test, but one sample failed the adhesion test. The failure occurred at a defect in the substrate at an edge, since a chip of KBr was removed by the cellophane tape, along with a portion of the film. The four remaining samples were subjected to 24-hr humidity testing and all samples passed. However, upon 48-hr salt spray testing, all four samples failed. Severe degradation was seen in these samples. Moisture penetrated the film in localized areas and, it appeared, at the edges. Some samples showed large cracks across the surface emanating from the edges.

Fungus resistance test samples were prepared on both glass slides and on a KBr flat. Glass substrates were chosen so that the inherent resistance of PPE to fungus growth could be observed, rather than a potential extrinsic influence of the KBr substrate by altering the salt

INTERDEPARTMENTAL CORRESPONDENCE



TO: Fred Yamagishi
ORG:

CC: D. Granger

DATE: 7/22/81
REF.

SUBJECT: Coating Evaluation

FROM: D. S. Lund
ORG. 77-45-23

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LOC. 1451

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EXT. 7365 CC

Certain environmental tests were performed on coating samples supplied by Malibu Research. The results of these tests are given in the table below:

Program name: _____ Vendor: _____
Parts coated per HAC drawing number: _____ Number of parts: 5
Substrate material: NaCl K13000 Wavelength region: _____
Size: Diameter: 1" Thickness: .25" Length: _____ Width: _____
Type of coating: Mirror Antireflection Filter
Silver _____ Multilayer _____ NBP _____
Alum _____ Single layer _____ WBP _____
Gold _____ "V" coat _____ LWP _____
Overcoat _____ Type _____ SWP _____
Other _____ Other _____

Remarks: _____

Sample No.	Moderate Abrasion Mil-C-675B	Adhesion Mil-C-675B	24-hour Humidity Mil-C-675B	Salt Spray Mil-STD-810B 48-hour	Severe Humidity Mil-STD-810B
1	<u>passed</u>	<u>passed</u>	<u>passed</u>	<u>failed</u>	_____
2	<u>passed</u>	<u>passed</u>	<u>passed</u>	<u>failed</u>	_____
3	<u>passed</u>	<u>passed</u>	<u>passed</u>	<u>failed</u>	_____
4	<u>passed</u>	<u>passed</u>	<u>passed</u>	<u>failed</u>	_____
5	<u>passed</u>	<u>failed</u>	_____	_____	_____

Remarks: _____

Test performed by: Deborah S. Lund

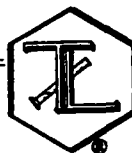
Approved: Deborah S. Lund

Figure 9. Results of environmental and durability testing.

content of the test culture. There was also the possibility that the KBr would be completely dissolved under the conditions and duration of the test. Figure 10 is the report submitted by Truesdail Laboratories, Inc. In the case of both substrates, PPE was found to possess sufficient fungus resistance when tested in accordance with MIL-STD-810B.

REPORT

TRUESDAIL LABORATORIES, INC.



CHEMISTS - MICROBIOLOGISTS - ENGINEERS
RESEARCH - DEVELOPMENT - TESTING

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CLIENT Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265
Attention: Mr. Fred Yamagishi

DATE July 8, 1981

RECEIVED May 20, 1931

SAMPLE Three (3) materials
P. O. No: SI-102040-9

LABORATORY NO. 38088

INVESTIGATION

Fungus Resistance Testing (MIL-STD-810B)

RESULTS

Fifteen day cultures of the following pure culture fungi were harvested, washed and their spore counts adjusted to 1,000,000 (+200,000) per ml.

<u>Organism</u>	<u>ATCC Number</u>
Aspergillus niger	9642
Aspergillus flavus	9643
Aspergillus versicolor	11730
Penicillium funiculosum	9644
Chaetomium globosum	6205

The samples were placed in a preconditioned chamber along with controls and sprayed with the combined spore suspension. The test items were examined for growth weekly. The results are given below:

<u>Sample Designation</u>	<u>Observations (Rating*) After</u>			
	<u>7 Days</u>	<u>14 Days</u>	<u>21 Days</u>	<u>28 Days</u>
1. PPE on glass, K1515-55L, 2 samples	0	0	0	0
2. PPE on glass, K1515-55R, 2 samples	0	0	0	0
3. PPE on KBR, K1515-59, 1 sample	0	0	0	0
4. Controls	4	4	4	4

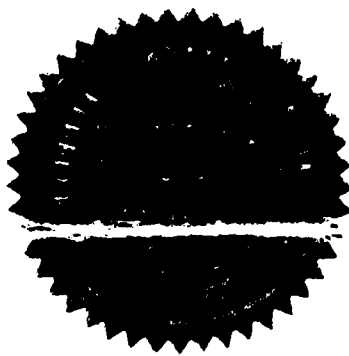
*Rating: 0 = no growth; 1 = traces; 2 = light; 3 = moderate; 4 = heavy growth

Figure 10. Results of fungus resistance testing.

This report applies only to the sample, or samples, investigated and is not necessarily indicative of the quality or condition of apparently identical or similar products. As a mutual protection to clients, the public and these Laboratories, this report is submitted and accepted for the exclusive use of the client to whom it is addressed and upon the condition that it is not to be used, in whole or in part, in any advertising or publicity matter without prior written authorization from these Laboratories.

Conclusion

The materials submitted were found to possess sufficient fungus resistance when tested in accordance to MIL-STD-810B.



Respectfully submitted,

TRUESDAIL LABORATORIES, INC.

Karl W. Schiller

Karl W. Schiller, M. S.
Chief Microbiologist

Figure 10. Continued.

SECTION 4

CONCLUSIONS

We have shown that plasma polymerized ethane can provide moisture protection to KBr optical windows, provided that the surface of that window has been adequately passivated by converting the surface hydroxyl groups to nonpolar moieties, or by removing them and substituting nascent halogen species in their vacant locations in the crystal lattice. The beginning surface quality, i.e., smoothness, flatness, grain domains, and hydroxyl concentration, cannot be overemphasized regarding its importance in allowing plasma polymerized films to act as effective moisture barriers. All materials are inherently porous to water, with polymers being relatively high on the porosity scale. However, polymers can be prepared as very hydrophobic films and their porosity can be decreased by increasing the degree of crystallinity, or by increasing the degree of crosslinking, which is the technique used in plasma polymerization. Nevertheless, the porosity of plasma polymerized films cannot be eliminated completely so that any extrinsic influence, i.e., large energy gradients, must be minimized. In the case of alkali halide substrates, this requires an adequate surface passivation method.

We developed a number of passivation methods in this program that have increased greatly the lifetime of PPE coated KBr windows over nonpassivated windows. Furthermore, methods to quench trapped free radicals, which will react with atmospheric oxygen to form polar, IR-absorbing groups on the surface, were developed. These methods were all useful in increasing the desired properties of the PPE films while not affecting the advantage of PPE, i.e., its high transmission in the 8- to 12- μ m region. PPE films of ~ 5 μ m in thickness generally had transmissions of $>90\%$.

Although we were unable to attain our goal of a 200 hr lifetime at 88% RH, we have shown that lifetimes approaching 100 hr can be expected at 88 to 98% RH in some cases. Since it was anticipated that the KBr optical elements would be enclosed in FLIR systems under partially controlled atmospheric conditions and would be exposed only occasionally to

uncontrolled conditions during maintenance operations, the coated window would not be subjected constantly to high humidity conditions. Therefore, from a practical point of view, PPE, deposited on a passivated surface as developed in this program, would adequately protect KBr optical elements from damage by short-term exposure to high humidity while the FLIR system undergoes maintenance. Thus, PPE can be useful in extending the lifetime of KBr optical windows in deployed FLIR systems in most environmental situations.

FUTURE RESEARCH AREAS

We have emphasized the importance of surface considerations that allow plasma polymerized films to be effective moisture barriers on alkali halide optical windows. Since we did not achieve lifetimes with KBr equivalent to those obtained with NaCl, it would be useful to correlate the difference between the two surfaces. Surface analysis techniques, particularly XPS (also called ESCA), could not only distinguish the chemical state of the parent species, but also the degree of coverage of hydroxyl groups. Passivation techniques, such as those discussed in this report, could be monitored by surface analysis methods, and their effectiveness could be compared to conditions used in the passivation step. The effect of crystallinity, crystal plane, surface roughness, etc. could be measured also.

Transmission in the 8- to 12- μ m region could probably be improved by reducing even further the carbon-carbon double bond content which arises by the formation of ethylene in the plasma. This could be accomplished by adjusting the reaction conditions or preparing the film in the presence of a reducing agent, e.g., hydrogen. Preparations of this type have been reported, although the specific properties of the films were not described. This would probably reduce the ultimate free radical content of the resulting film while concurrently increasing the long-range atmospheric stability.

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APPENDIX

PUBLICATIONS AND PRESENTATIONS

1. "Plasma Polymerized Films as Moisture Barriers for Alkali Halide Optics," presented at the International Conference on Metallurgical Coatings, San Francisco, CA, April 6-10, 1981.
2. "Plasma Polymerized Films as IR Protective Coatings," presented at the 1981 American Vacuum Society Meeting Symposium on Plasma Processing and Related Technologies, Anaheim, CA, April 21-22, 1981.
3. F.G. Yamagishi, D.D. Granger, A.E. Schmitz, and L.J. Miller, "Plasma Polymerized Films as Moisture Barriers for Alkali Halide Optics," Thin Solid Films, accepted for publication.