Infrared Antireflection Coatings Without Thorium Fluoride

F.C. Sulzbach, Texas Instruments, Inc., Dallas, TX

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ABSTRACT

Improvements in vacuum technology and availability of Ion Beam Guns have enabled development of durable antireflection coatings for internal optics of infrared systems without using ThF_4. “Test until failure” data shows that the new coatings far surpass environmental durability requirements normally specified for internal optics and even for many external window surface coatings. The systems are usually intended to be sealed and purged with dry gas or to be desiccated. This benign operating environment deteriorates due to field conditions and to system repair in relatively unclean areas. Continual improvement of durability of internal optics coatings above the minimum acceptance criteria specified is vital for reducing the “Cost of Ownership” of Military systems. Elimination of ThF_4 further lowers maintenance costs since there is no longer a need to contain and dispose of mildly radioactive waste or to train personnel to do so.

INTRODUCTION

Passive infrared (IR) optical systems have been in use since 1965 for reconnaissance and weapon delivery. Lenses gather energy emitted by objects in the system field of view. System electronics discriminate based on slight differences in temperature of objects compared to the background temperature and convert this data into TV images. Antireflection coatings for the IR lenses often use layers of ThF_4, a mildly radioactive substance. This paper explores the impact on the optical performance and the durability of IR antireflection coatings if ThF_4 is NOT used.

The thin coating layers have imperfect microstructure and may not adhere well to the lens surface. A lens or sample coated in the same run which shows no visible damage after a series of brief tests qualifies the entire lot. The secondary theme of this paper explores how repetitive testing until the coated item does fail has aided continuous improvement of long-term costing durability. A third theme discusses whether there are other tests which are more relevant to product usage.

The atmosphere limits detectable energy emitted by objects close to room temperature to the 8-12µm range. Table I shows elements, compounds and non-oxide glasses suitable for making IR lenses. The water soluble alkali halides, such as NaCl and KBr, transmit well but are extremely fragile and too water soluble to be practical. The high refractive index of the practical materials causes high surface reflectance, which would result in low transmittance for each lens. An uncoated four lens system would transmit between 4.9 and 32.4%, depending on the material used for each lens.

With suitable coatings, the transmittance of a four lens system can exceed 96% for a single wavelength application. It nearly always requires at least two layers of practical materials to achieve zero reflectance at even one wavelength[1]. If the application uses a range of wavelengths as wide as 2.5 octaves, the transmittance of our four lens system can be as high as 70%.

Table I. TYPICAL LENS MATERIALS FOR 8—12µm SYSTEMS

Elements	Si (thin)		Ge
Compounds	ZnS	ZnSe	GaAs
Chalcogenide Glasses	Ge-As-Se		Ge-Sb-Se
High Refractive Index	2.2	- - - >	4.0
High Surface Reflectance	14%	- - - >	36%
Low Transmittance 2 Surfaces	70%	- - - >	47%
Transmittance of 4 Lens system:			
Uncoated	32%	- - - >	5%
Coated - Depends on Bandwidth	96%	- - - >	70%

The range of wavelengths for most systems is actually 7.6 to 11.9µm. A four layer coating for germanium lenses using the constant indices of refraction and layer sequence in Table II will produce very low reflectance over this wavelength range. With suitable adjustment of the four layer thicknesses, Table II shows the average reflectance (R$_{avg}$) attainable for several bandwidths.

Assume that the thicknesses of the four layers will vary in a random fashion and that the indices of refraction never vary. Table III shows predicted yield of 1000 coating runs when the requirement is R$_{avg}$ ≤0.6% over the range 7.6 to 11.9µm. Theoretical yield is 99.9% with 6% random error in layer thickness. The relative insensitivity to thickness errors of this design type allows high production yields even when using quartz crystal monitors with 4% random error.

Table II. Reflectance vs Bandwidth using 4 layers on Germanium

Germanium / 2.2 / 4.0 / 2.2 / 1.4 / AIR

|-Optimize four thicknesses for each bandwidth-|

Bandwidth %	Ravg %	λ1 --- λ2 µm	
20	.007	9 - 11	
40	.066	8 - 12	(1/2 octave)
60	.247	7 - 13	
80	.471	6 - 14	
100	.659	4.7 - 14	
120	1.931	3.5 - 14	(2 octaves)
140	5.002	2.5 - 14	

THE LOW INDEX MATERIAL PROBLEM

The design of Table II assumed the refractive index 1.4 is constant over the calculated wavelength ranges. There is no practical material with this index value and profile. Chlorides and bromides are too soluble in water. Most iodides also have higher index values and are usually soft. Though the layers needed are less than 2µm thick, most oxides absorb too much IR light to be used. Only the fluorides show promise as candidates for the outer layer in this coating. As the low index value increases, the lowest attainable average reflectance also increases. Results of the calculation “Derby” published several years ago [2] indicate that 0.66% R$_{avg}$ is the lowest value achievable if 2.2 and 4.0 are the only two indices used, regardless of the number of layers used. Effects of random error on predicted yield of these various designs were not reported.

Table III. Predicted Yield vs Random Thickness Error

Specification:

R$_{avg}$ ≤0.6% for 7.6 ≤ λ ≤ 11.9µm

Random Error	Yield %
±2%	100
4	100
6	99.9
8	96.6
10	89.4
12	85.5

DOMINANCE OF ThF$_4$

The low index material of choice for IR coatings for over 25 years has been ThF$_4$. This material easily forms cohesive layers many µm thick. It adheres well to most other materials and is nearly insoluble in water. Though its refractive index is nearly constant from 1 to 7µm there is considerable change of index in the 7 to 14µm range. Its low absorptance at 10.6µm delights the manufacturers of CO$_2$ laser optics. Its only serious flaw is low level radioactivity. Though it takes 10000 pounds of this material to register enough disintegrations to equal a Curie, inexpensive sensors easily detect the α or ß radiation of the typical 2µm thick film. The levels of radiation hazard to users of lenses containing these thin layers of ThF$_4$ is comparable solar and cosmic radiation at an altitude of 2500 feet above sea level [3]. Las Vegas is 2000 feet above sea level. Colorado Springs is 6000 feet above sea level.

The low level radiation of ThF$_4$ requires those who make or repair lens systems to have licenses, and to comply with regulations from state and federal agencies regarding containment, storage and disposal of radioactive waste. A license with stricter regulations is required if you change the form of the radioactive material from random sized lumps in a jar to 2µm thick layers on IR lenses.

Recent changes in the Federal laws require a state to dispose of its own low level radioactive waste at approved dump sites within its own borders. State governments had a grace period in which to form an alliance with a state having an approved dump site. If your state did not have an approved dump site or did not form an alliance within the grace period, then you must store your low level waste AT YOUR FACTORY until your state establishes an approved dump site. Texas thought it had a suitable site. Shortly after the end of the grace period, the neighbors of the site protested so loudly that there is now a second search for a new site. Therefore, in several states including Texas, it is no longer a good idea to use ThF_4 for IR coatings. Containment and storage of low level radioactive waste requires considerable isolated, secured volume. New regulations could be imposed at any time reducing the amount you may store or upgrading the safeguards required. Disposal cost will probably increase dramatically after the site is located, built and approved.

LIVING WITHOUT ThF_4

18 years ago the Night Vision Laboratory at Ft. Belvoir sponsored development work at another company [4] to find a replacement for ThF_4. The principal message of the final report agreed with our work done that year [5]. The internal stress generated during the condensation of films of various metal fluorides caused microscopic cracks to form in the layers. In most cases, this cracking leads to rapid delamination. We found that films of NdF_3 could be made hard, adherent, insoluble and IR transparent with an index of about 1.6. They also showed fine microcracks. These otherwise useful films were rejected for having cosmetic defects. The cracks could be eliminated by extraordinary effort involving codeposition with other materials. As customer support diminished, and ThF_4 was grudgingly tolerated, work to find replacements stopped across the Industry. To date, there has been no report of a naturally occurring replacement material which will easily form usable thick films of low absorptance in the IR and low scatter in the visible spectrum. Some workers have made mixtures of fluorides with limited success in environmental tests[6].

Though there is no single material which can replace ThF_4 in every coating design, there are ways to avoid its use. In most filter coatings, it can be removed at a penalty of only 1% average transmittance. Texas Instruments once had 84 IR processes using it. By the end of 1989, we had fully tested designs applicable to over 80% of our product [7]. By mid-1992, over 95% of our product was radiation-free. We have cleaned the coating facility and support areas. We disposed of all low-level radioactive debris' and unused coating material. A Third Party has verified our cleanup and so advised the Texas Regulatory Agency.

Our remaining involvement with the material is repair of lenses returned from the field, or installing unique purchased components containing the material.

The second generic problem with replacement materials is failure in harsh environments. Typical test environments applied to internal surface coatings are listed in Table IV. These tests were copied verbatim from the oldest Military Specifications for simple coatings about 0.1µm thick on common glass. The coating materials involved, MgF_2 and Si_xO_y, have very low solubility. The tests were intended to weed out poorly coated batches and set minimum acceptance criteria with the phrase "no visible change" as a result of exposure to the test. Since the only detector widely used at the time was the human eye, the criteria were valid. Further, these optics were usually sealed in hollow volumes with relatively little other material nearby. The risk of exposure to the environments listed was usually limited to the outer surface of a system. In most cases the internal optics merely had to survive the environment of the storage and assembly areas.

The specifications for Military systems usually include the tests of MIL-STD-810 listed in Table VI. The classic visible coatings on glass nearly always survive exposure to these test conditions with no visible change. When this STD was written, the only widely used IR optic was the solid MgF_2 dome for the 3 to 5µm Sidewinder Missile. This dome is still used today without coatings.

Table IV. Military Specifications for Internal Surface Optical Coatings

MIL-F-48616: Filter Coatings, Infrared Interference
MIL-C-48497: Coating, Single or Multilayer Interference

Compulsory Tests:
Sequentially on one sample: Adherence (weak adhesive tape)
24 hour constant humidity
Moderate Abrasion (cheesecloth)
On other samples: Thermal - 4 hrs hot / 4 hrs cold 2°c/min ramp
Solubility: Chlorothane — immerse and wipe
Acetone
Ethanol
Optional Tests: one test per sample cited on component drawings
Severe abrasion (eraser)
Distilled water solubility - 24 hours
Salt water solubility - 24 hours
Salt fog - 24 hours

Table V. Military Standard for System Performance in Harsh Environments

MIL-STD-810: Environmental Test Methods

10 day cyclic temperature/humidity - Method 507 Procedure I
48 hour Salt Fog - Method 509

Coatings containing ThF_4 survive the additional system level tests only when preceded by "adequate" coater engineering and strict process discipline. These are the tests which coatings with replacement materials fail most often. After initial development, transition to production can be slow due to several related technological hurdles including diversity of coating chamber configurations, degree of cleanliness of the vacuum attained, and imprecise measurements of vital parameters. A method successfully developed in one machine may work poorly or not at all in another, even in the same company.

Table VI shows the 1991 optical performance parameters for all production runs of a Th-free coating for germanium lenses. The design is optimized for the two narrow bands. The customer can't tell this coating from one using ThF_4 without a radiation detector.

Table VI. Th-Free Coating for Germanium - 1991 Production Summary

Bandwidth µm	R_{avg} per Surface	T_{avg} Both Sides Coated
8.0 — 11.5	0.18 %	98.66 %
7.6 — 11.9	0.22 %	98.45 %
7.6 — 13.5	0.42 %	97.45 %

Not all component drawings require the 10 day cyclic humidity test and the salt fog test. We believe that scheduling will always be imprecise and that the coater and process must always be capable of producing the most durable coating at any time. We subject samples from most runs to repeated test cycles until the coating "fails". The criterion is appearance of a defect which no longer meets 80-50 surface quality. Table VII shows the summary of "Test-To-Failure" data for Germanium coatings for 1991. The design with ThF_4 has had 20 years of refinement to attain its durability level. The Th-free design is only 3 years old. In either case, the coatings provide resistance to harsh environments far in excess of the (minimum) specified requirements of MIL-STD-810. Test data for 1992 is not yet complete. Similar Thorium-free coatings are in use for the other common IR materials, including ZnS, ZnSe, GaAs, and the Chalcogenide glasses.

Improvements in coating durability are partly due to advances in vacuum technology. Deposition in a "cleaner" residual atmosphere results in better adhesion of films to the existing surface. Traces of pump oils can result in either poor adhesion or in absorptance within the coating. Work long ago in poorly trapped coaters showed as much as 10% absorptance in the 8 to 12µm range per coated surface! Cryogenic and turbomolecular pumps more easily create clean vacuums but there can be unusual problems when converting from diffusion pumps. Leak detection becomes a bit more difficult since Helium is not pumped as well by these newer techniques as by diffusion pumps.

ION BEAM GUN BENEFITS

The Ion Beam Gun has provided a means for dramatic improvement in several areas. Brief exposure to a beam of energetic gas ions will dislodge adsorbed water vapor and loosely bound hydroxyl radicals. The gun provides streams of controlled ions which remove material from the existing surface. Most substrates have been mechanically and/or chemically damaged to

Table VII. Test-Until-Failure Data for Germanium lens coatings in 1991

Test	SPEC	OLD-with ThF_4	NEW-No ThF_4
Cyclic Temperature/Humidity	10 days	209 days	74 days
Salt Fog	1 day	82 days	44 days
Salt Water Immersion	1 day	103 days	49 days

some depth during the operations prior to coating. The ion beam removes damaged material, exposes a clean surface and promotes adhesion.

The second benefit of Ion Beam Guns is reduction of tensile film stress. Bombarding films of fluorides during deposition [8] reduces tensile stress enabling thicknesses sufficient for use in IR antireflection coatings. There will be ranges of ion flux, substrate temperature and deposition rate leading to usable films. Straying from these ranges will result in various problems such as; microcracks, haze, failure of abrasion tests, and ultimately loss of adherence. There is no "free lunch". Avoiding use of ThF_4 simplifies some aspects of IR coating while it complicates others.

TEST IT THE WAY YOU USE IT

The optics used in IR systems face environments harsher than those of the storage and assembly areas. Airborne systems fly higher and change altitude more rapidly than envisioned many years ago. The optics are no longer isolated in hollow volumes. The system is densely packed with diverse electro-mechanical devices. The efforts to seal out the environment are usually at odds with the needed turret rotation. Rapid changes in altitude cause condensation on everything within the system. The Finite solubility of various surface treatments creates condensations with unpredictable chemical properties. These unexpected solutions drip onto lenses and impose acidic or basic conditions not covered by any specification.

Though many land based systems have been built with seals, purge gas fittings and desiccant containers, few systems return to repair facilities in purged or dry condition. The reasons the systems are no longer sealed are numerous, and they suggest the axiom: "No system will remain sealed." All optics within the system will eventually see wide fluctuations in temperature, altitude, humidity and the chemical activity of condensation dripping from nearby surfaces.

About 1986, there were failures of lenses common to several unsealed systems after a few months at sea. The coating design had been used since 1971. Most of the failures were traceable to their coating batches. All batches had passed the Minimum Tests as well as the MIL-STD-810 tests. Test-To-Failure data indicated a long probable lifetime. Most of our lenses have been potted in place with elastomers. The lenses failing were mechanically clamped in steel housings. When we tested both mounting methods for only two days of the 10 day humidity test, the clamped samples failed from the edge toward the center. This indicated undercutting of layers sensitive to condensation byproducts. A simpler design used in another machine did not use the material suspected of being most vulnerable. Multiple test cycles showed that this design would not fail in either mounting condition. Though we had a mountain of data showing longevity, the clamping method promoted premature failure. We were not testing the product as it would be used. The newer design made use of the effects of ion beam cleaning, used fewer layers and fewer coating materials. The older design was permanently retired. We continue the long term testing of most IR product runs.

In another case we bought a large batch of mirrors which we normally manufactured. The purchased items met the MIL-STD-810 Humidity test requirements and also the 24 hour salt fog test requirement. We confirmed these results in our own test chambers with extra samples furnished by the vendor. We mounted the mirrors as usual with a one-part elastomer and put most of the assemblies into stock. A few months later, units from stock showed deterioration spreading from the mounting bond lines. The overcoating layer had survived all the specified tests, but could not resist mildly acidic attack of outgassing from the elastomer in moderate humidity. Tests showed that the overcoating material was one we had abandoned for this very reason 15 years earlier. Since the product met all requirements, we reluctantly removed, stripped, recoated and remounted the mirrors. We took finished systems off the shipping dock, refitted the assemblies and reran final acceptance tests. Again, results of unmounted test samples lulled us into false security.

These two horror stories elicit a reaction to specify the mounting method for testing coated samples. This is a great idea on a "first article" basis. The minimum tests of unmounted samples ensure that optics <u>will</u> survive long enough to be assembled into sealed systems. Additional tests in repeatable single purpose conditions suggest that coated optics <u>can</u> survive a long time. Lens mounting conditions can drastically reduce the life span. We must make these conditions a part of the approval cycle when qualifying a new vendor.

CONCLUSIONS

IR Coatings with low reflectance and high transmittance can be made without using ThF_4. Manufacturers and customers benefit since costs associated with containment and disposal of low level radioactive debris' may be eliminated.

The durability of the coatings far exceeds stated requirements for system usage. Sample mounting methods can drastically accelerate chemical attack and shorten the perceived life span. This "TEST IT THE WAY YOU USE IT" method is realistic and should be mandatory.

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