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THE STRATEGIC TECHNOLOGIES FOR AUTOMATION AND ROBOTICS (STEAR) PROGRAM
PROTECTION OF MATERIALS IN THE SPACE ENVIRONMENT SUBPROGRAM

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SUMMARY

Three projects are currently underway for the development of new coatings for the protection of materials in the space environment. These coatings are based on vacuum deposition technologies. The projects will go as far as the proof-of-concept stage when the commercial potential for the technology will be demonstrated on pilot-scale fabrication facilities in 1996. These projects are part of a subprogram to develop supporting technologies for automation and robotics technologies being developed under the Canadian Space Agency's STEAR Program, part of the Canadian Space Station Program.

1.0 INTRODUCTION

The Protection of Materials in the Space Environment subprogram is part of a larger Canadian Space Agency (CSA) program called STEAR (Strategic Technologies for Automation and Robotics). The STEAR Program was established to encourage the participation of Canadian companies, universities and research organizations in automation and robotic technologies which will have the potential to be used on advanced versions of the Mobile Servicing System (MSS). Canada is responsible for the development of the MSS for the international Space Station. "Protection of Materials in the Space Environment" was initiated as a supporting technology development for the automation and robotics technologies. It aims to identify, develop and demonstrate through detailed testing and evaluation, effective means of protecting structural materials and finishes used for the MSS, which will maintain their physical and functional integrity in the Low Earth Orbit (LEO) environment for 10 to 30 years. Three protection of materials research and development projects have commenced and will proceed over the next two years through to proof-of-concept and prototype development. This paper discusses the objectives and status of the Protection of Materials in the Space Environment subprogram and introduces the work being done by the three participating companies.

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[1] Addresses and phone numbers are provided in footnotes throughout the paper.

2.0 PROTECTION OF MATERIALS IN THE SPACE ENVIRONMENT SUBPROGRAM

2.1 STEAR Program Objectives

2.1.1 Specific STEAR Program Objectives

The STEAR Program's specific objectives are to:

- identify for development advanced strategic technologies which offer potential for incorporation into advanced versions of the MSS;
- support research and development of selected technologies in the private sector, until proof-of-concept is demonstrated;
- encourage the collaboration and networking of industries, universities and nonprofit research organizations;
- promote commercial exploitation of the strategic technologies developed within the Program by joining STEAR contractors to the MSS prime contractor/team and to government programs which support future product development and marketing; and
- ensure the regional distribution of STEAR developed activities across Canada.

2.1.2 STEAR Program Technology Emphasis

Emphasis is placed on strategic technologies which support the technical and operational advancement of the MSS and, in particular, its capability to:

- maximize the productivity of the Space Station's resources;
- minimize the operating costs;
- minimize extra-vehicular activities by the Space Station's flight crew; and
- maximize the service life of the MSS materials and structures.

2.1.3 The Need for the Protection of Materials on the MSS

The LEO environment in which the MSS will operate has proven to be very hostile. Recent experience has shown that many important materials used on the exterior of spacecraft, such as thermal control blankets, are rapidly attacked and eroded by atomic oxygen. Some of the features of the LEO environment which could prove hazardous to the MSS include: atomic oxygen, ultraviolet radiation, charged particle radiation, temperature extremes, thermal cycling, micrometeoroids, long term exposure to vacuum, and combined effects.

The flight segment of the Space Station MSS (see Figure 1) consists of three main elements: the Mobile Servicing Centre (MSC) - which includes the Space Station Remote Manipulator System (SSRMS) and the Mobile Base System (MBS); the Special Purpose Dextrous Manipulator (SPDM); and the MSS Maintenance Depot. The SSRMS is a versatile, 17 metre long manipulator arm, capable of moving more than 100,000 kilograms in space. It is an enhancement of the Shuttle's highly successful Remote Manipulator System (the "Canadarm"). A seventh joint will allow the SSRMS to mimic most of the movements of the human arm as it sweeps through space to grasp, place or move objects, or to manoeuvre astronauts. The SSRMS is a symmetrical design with either end being capable of acting as the shoulder or the wrist. The shoulder joint is attached to a rigid base through Power Data Grapple Fixtures (PDGFs) which also provide the electrical power, data and video interfaces. The wrist's end effector will be able to grasp tools, payloads, the SPDM or even the Shuttle Orbiter. The SPDM is equipped with two manipulator arms and will incorporate innovative technologies such as machine vision and force feedback to handle delicate work such as replacing components and working on the Space Station's electrical connections. The robotic manipulators will access specially designed tools and spare parts from the MSS Maintenance Depot.

The MSS will be constructed of standard space-rated materials as well as advanced composite materials such as graphite/epoxy and PEEK/graphite (poly ether ether ketone). Multi-layer thermal blankets will be used in some areas of the MSS and other areas of the Space Station to protect composite, aluminum and other metallic and non-metallic components. Thermal blankets are typically thick and heavy; for example, the blankets used on the Canadarm have an outer layer of Beta cloth, two layers of single-goldized Kapton[2], and two layers of double-goldized Kapton with each layer separated by a Dacron scrim cloth.

The protective coatings being developed on the STEAR Program offer the potential of being able to provide at least the same amount of protection as thermal blankets currently planned for use on the MSS and other areas of the Space Station at a significantly lower weight and thickness. These coatings also have potential for the protection of other space hardware systems such as Canada's RADARSAT which is an advanced Earth observation satellite project to monitor environmental change and to support resource sustainability.

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[2] Kapton is a registered trademark of DuPont.

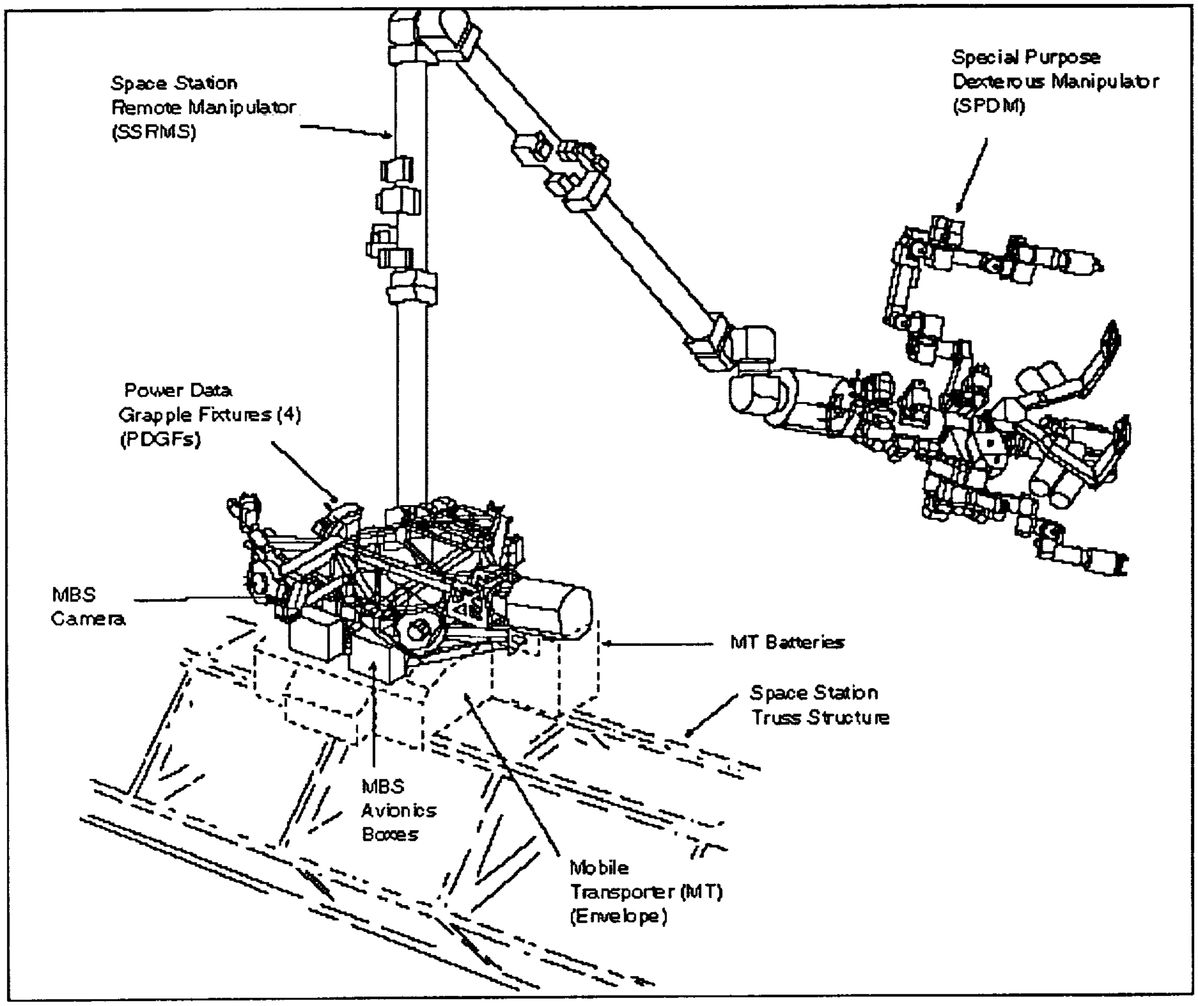

Figure 1.
The Mobile Servicing System

Some of the advantages being sought from the development of new protective coatings include:

- light weight
- strong adherence to the substrate
- resistance to attack by atomic oxygen
- tolerance to ultraviolet radiation while not changing the optical or thermal properties of the underlying substrate material
- antistatic properties, to prevent the build-up of harmful potential gradients
- ability to minimize the thermal cycling effects within the substrate
- ability to withstand temperature extremes

2.2 Protection of Materials in the Space Environment Subprogram

2.2.1 Subprogram Overview

The Protection of Materials in the Space Environment Subprogram is being conducted in two phases. During Phase I (July 1991 to May 1992), six companies won competitive bids to conduct feasibility studies to identify, develop and demonstrate through test and evaluation, effective means of protecting structural materials and finishes used for the MSS in the LEO Environment for 10 to 30 years. At the end of Phase I, each of these companies submitted a feasibility study report and a proposal for a Phase II development. Phase II projects (November 1992 to April 1996) will further develop the technology to the proof-of-concept stage including a demonstration of a prototype fabrication capability.

2.2.2 Phase I - Feasibility Study

The companies selected in a competitive bid process for the six, one-year, $100,000 Phase I projects were:

- Aastra Aerospace Incorporated of Downsview, Ontario
- Cametoid Advanced Technologies Incorporated of Whitby, Ontario
- Ceramics Kingston Incorporated of Kingston, Ontario
- Datco Technology Limited of Mississauga, Ontario
- FRE Composites Incorporated of Saint-André, Québec
- MPB Technologies Incorporated of Pointe Claire, Québec

During Phase I, the contractors investigated the deposition of a number of different coatings, by various methods, on a number of substrates and then characterized the performance of the system using a standardized mandatory test plan set by CSA, and non-mandatory tests as selected by each of the contractors for their own unique processes. Substrates for the standardized testing were supplied to the contractors, including Aluminized Kapton, Aluminized Teflon, Beta Cloth, Carbon/Epoxy and Carbon/PEEK. The mandatory tests included:

- High Energy Atomic Oxygen and Ultraviolet Radiation
- Thermal Cycling
- Outgassing
- Solar Absorptivity and Emissivity
- Scanning Electron Microscope: Topography
- Scanning Electron Microscope: Defect Density
- Adhesion: Peel Tape Test
- Flexibility

2.2.3 Phase II - Technology Development

Three of the Phase I feasibility study contractors were selected to proceed to three-year, $900,000 Phase II development projects based upon:

- the performance of their specimens on the Phase I mandatory tests;
- an understanding of the effects of the LEO environment on materials and the requirements of a protective coating;
- the technical merit of the Phase II proposals;
- the management abilities of the project team; and
- the potential to commercialize the technology in both space and terrestrial applications.

The companies selected for Phase II contracts include:

Cametoid Limited:	Development of Novel Composite Coatings for Material Protection in LEO Environment
FRE Composites:	Plasma-Deposited Protective Coatings for Spacecraft Applications
MPB Technologies:	ECR-Plasma Deposition of Silicon Dioxide

Specimens from Phase I contractors were also provided for the CANadian EXperiment (CANEX-2), Materials Exposure in Low Earth Orbit (MELEO) experiment which was part of the STS-52 shuttle mission in October,1992. Since this mission occurred several months after the completion of Phase I, the results were not available or used for the selection of Phase II contractors.

The primary objectives of Phase II of the Protection of Materials in the Space Environment Subprogram is to demonstrate a prototype fabrication capability using a full scale component for a commercially viable process for the protection of materials from the space environment, and to demonstrate compliance with a set of performance requirements. Each of the three projects is well underway with positive results beginning to show promise for the new coating technologies. The remainder of this paper provides brief summaries of the three specific projects (in alphabetical order by company) with some discussion of the preliminary results of testing. The full results of scale-up capabilities for each coating technology will not be known until the end of the subprogram in 1996.

Further information on the STEAR Program or the Protection of Materials in the Space Environment Subprogram can be obtained by contacting the Canadian Space Agency[3]. Further information on the individual projects described below can be obtained directly from the companies involved.[4]

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[3] Contact Lorne Schmidt at the Canadian Space Agency, Space Station Program Office, STEAR Program, 6767 Route de l'Aéroport, St. Hubert, Québec, Canada, J3Y 8Y9, Tel: 514-926-4462, Fax: 514-926-4448.

[4] See the relevant sections for contact names and addresses.

3.0 CAMETOID ADVANCED TECHNOLOGIES INCORPORATED PROJECT[5]

3.1 Development of Novel Composite Coatings for Material Protection in LEO Environment

Cametoid Advanced Technologies Inc. has developed a composite coating for the protection of Kapton from the Low Earth Orbit (LEO) environment. The coating is deposited by simultaneous electron beam (EB) evaporation of two materials. Extensive testing has been carried out according to CSA, NASA and ESA specifications, and the results have indicated excellent performance as presented in the next paragraphs.

Adhesion. The coating was subjected to the tape peel test, and optical microscopy at 400X magnification showed no sign of cracking or delamination.

Flexibility. Strips of coated Kapton were bent around a 0.125" mandrel without cracking or delamination as determined by optical microscopy at 400X magnification.

Thermal Shock. Coated Kapton specimens were submerged into liquid nitrogen for 1 minute, then into boiling water immediately after for another minute and finally back into liquid nitrogen for 1 minute. Optical microscopy evidenced no cracks or delamination at 400X magnification.

Optical Properties. Table 1 shows that the absorptivity (α) and emissivity (ε) of the coating are very close to the α and ε values of aluminized Kapton.

	α	ε	α/ε
Cametoid LEO Coating	0.37	0.62	0.59
Kapton	0.37	0.68	0.54

Table 1
Optical Properties of Cametoid LEO Coating

Defect Density. A scanning electron micrograph at 5000X magnification is presented in Figure 2. No evidence of cracks or pin hole defects was found.

Thermal Cycling. Coated Kapton samples were subjected to thermal cycling between +100°C and -100°C and for 10 cycles with 1-2 minute dwell at each temperature; the heating and cooling rates were 10°C/min and 13.8°C/min, respectively. No evidence of cracking was observed by SEM at 10,000X magnification. The tested samples were subjected to and passed the adhesion test (see above).

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[5] For further information on Cametoid's technology, contact Dr. Alina Agüero or Dr. Kam Yan, Cametoid Advanced Technologies Inc., 1449 Hopkins Street, Whitby, Ontario, Canada, L1N 2C2, Phone: 905-666-3400, Fax: 905-666-3413.

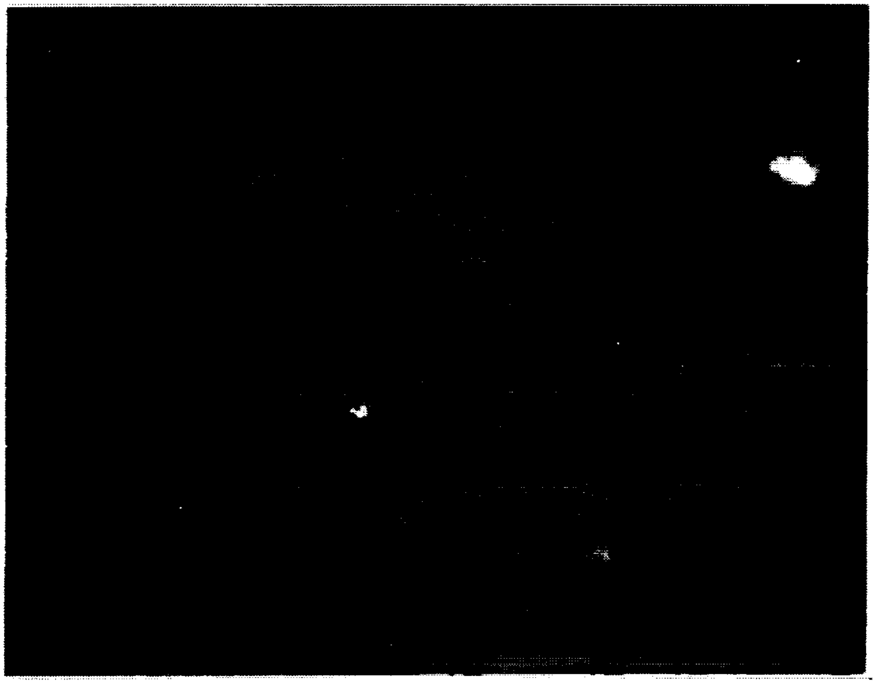

Figure 2
SEM image of the surface of the coating (5,000X)

Atomic Oxygen (AO) and Ultraviolet Erosion Resistance. The coating was tested at the AO beam facility of the University of Toronto Institute for Aerospace Studies (UTIAS). Real time mass loss data was collected with a dual quartz crystal microbalance (QCM) system. Some of the characteristics of the system are summarized below:

Atomic Oxygen:	energy	2.3eV	
	flux	> 10^{17} atoms/cm^{2}s	
	angle	0-90^0	
Vacuum Ultraviolet:	flux	10 ES (120-200 nm)	(ES: Equivalent Sun)
	angle	0-90^0	

The reaction efficiency (RE) was calculated by the formula:

$$RE = \frac{\text{mass loss rate}}{\text{flux x area x coating density}}$$

Table 2 shows the results as well as the minimum thickness required for 30 years in orbit. The test was also performed employing coated Kapton specimens and no weight loss could be detected on a microbalance (with a sensitivity of 10^{-6}g) for the same fluence. Further, no signs of under-cutting could be observed by SEM.

	Coating Mass (μg)	Coating Density (g/cc)	Mass Calibration (ng/Hz)	Time Exposed (sec)	Mass Loss Rate (ng/sec)	Reaction Efficiency (cc/atom)	Thickness (30 yrs) (μm)
Cametoid LEO Coating	90	3.59	707	21000	0.013	1.1E-28	0.2

Table 2
Atomic Oxygen & UV Test Results

The coating has been analyzed and characterised by a number of techniques including Electron Energy Loss Spectroscopy/Transmission Electron Microscopy (EELS/TEM), X-rays Photo-electron Spectroscopy (XPS), Electron Probe Micro-Analysis (EPMA), Energy Dispersion Spectroscopy (EDS) and Auger Electron Spectroscopy (AES). A TEM image of the coating cross-section is shown in Figure 3. The sectioning process required for sample preparation caused fracturing normal to the sectioning direction (a common artefact in the sectioning of brittle materials). The coating is amorphous, uniform and very dense.

Another interesting feature offered by Cametoid's coating process lies in the fact that by varying the composition of the coating, different optical properties can be obtained. Further, the composition can be varied as a function of the coating depth allowing a large range of values for both absorptivity and emissivity to be obtained. An example of such variations is presented in Table 3 where the α/ε values are shown as a function of the composition for homogeneous coating formulations on Kapton. Since both components (A and B) are essentially atomic oxygen resistant, it is possible to produce LEO resistant coatings for other substrates and applications requiring specific thermal and solar characteristics.

A (at. %)	09	13	19	30	32	38	40	50	60	76
B (at. %)	91	87	91	70	68	62	60	50	40	24
α/ε	0.50	0.50	0.50	0.54	0.53	1.0	1.1	1.4	2.3	6.6

Table 3
Optical Properties of Coated Kapton as a Function of the Coating Composition

Presently, a pilot scale coater for deposition on Kapton rolls is being built. The coating will be deposited by electron beam evaporation and a proprietary masking design and implementation process have been developed to ensure thickness and composition uniformity. An example of the masking effects on the thickness uniformity is illustrated in Figure 4.

In conclusion, Cametoid has developed a new, proprietary coating material for the protection of Kapton in the LEO environment. Preliminary observations indicate that this film outperforms any existing commercially available coatings, specifically in flexibility and resistance to cracking and delamination [1]. Further, the process can be employed to produce different coatings formulations, expanding its potential space applications.

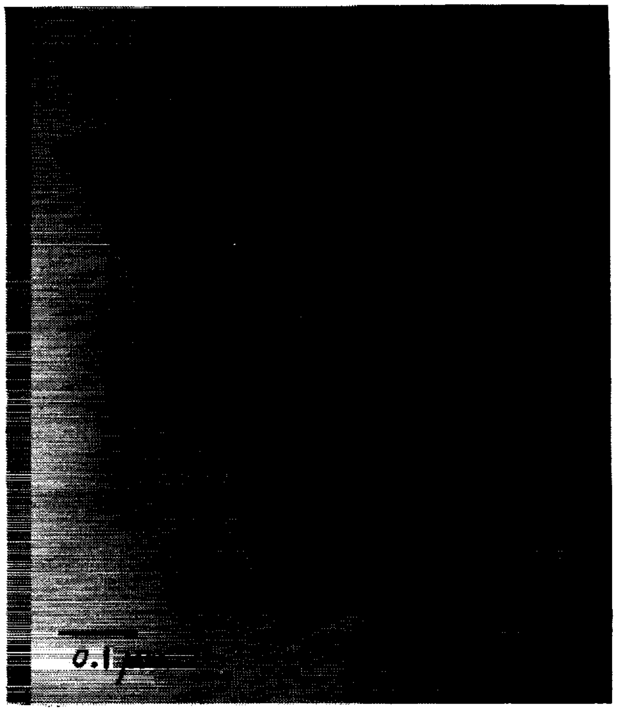

Figure 3
Transmission Electron Microscopy image of the cross-section of the coating

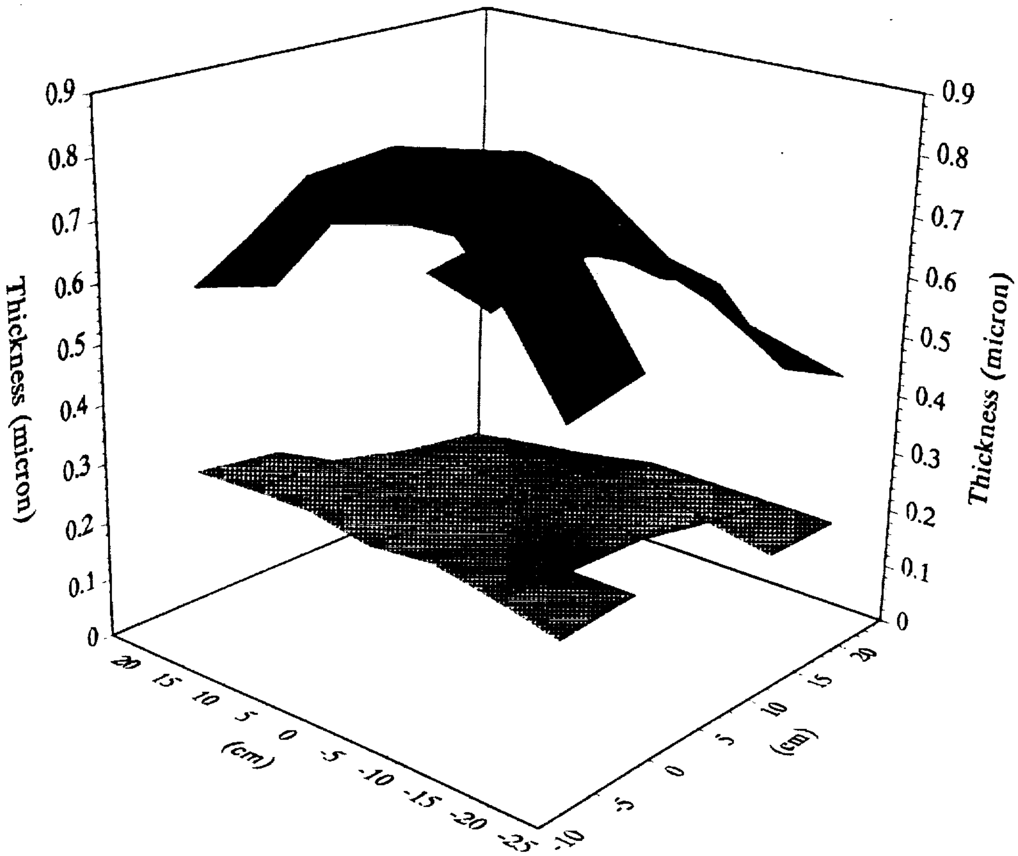

Figure 4
3-D plot of the coating thickness distribution with (grey) and without (black) masking

4.0 FRE COMPOSITES INCORPORATED PROJECT[6]

4.1 Plasma-Deposited Protective Coatings for Spacecraft Applications

In 1987, we commenced work in this laboratory (École Polytechnique, Département de génie physique) on the project "Multipurpose Protective Coatings for Spacecraft Materials", a theme which is still being pursued diligently to this day [2-5]. The objective is to coat both rigid (e.g. carbon/epoxy or carbon/PEEK composites) and flexible (e.g. polyimide) polymeric materials commonly employed in space technology with thin protective layers, using plasma enhanced chemical vapour deposition (PECVD) processes [6]. Our particular PECVD technique, dual-frequency plasma deposition, uses proprietary large area microwave (MW, 2.45 GHz) excitation combined with radio frequency (RF, 13.56 MHz) bias applied to the substrate. This MW/RF process allows one to deposit dense, flawless films onto substrates maintained at ambient temperature, a key feature when dealing with polymeric substrates [7,8].

The protective layers we have examined are the following: plasma-polymerized hexamethyldisiloxane (PP-HMDSO), amorphous hydrogenated silicon (a-Si:H), and inorganic silicon compounds (silicon dioxide p-SiO_2, nitride p-SiN, and oxynitride p-SiON), typical coating thicknesses being between 0.3 μm and 1.5 μm. Current work is focussed on p-SiO_2 which can be obtained both from inorganic or organic volatile Si compounds (SiH_4 and HMDSO).

The performances of coated substrates have been studied in depth with regard to the following criteria:

- resistance to atomic oxygen/vacuum ultraviolet (AO/VUV) exposure;
- charging and discharging characteristics;
- "other" characteristics, such as thermal radiative properties, ageing under thermal cycling and other mechanical stressing...

So far, coated specimens have flown on several Shuttle missions:

- STS 32 (December 1989)
- STS 40 (November 1991)
- STS 46 (July 1992, EOIM III)
- STS 52 (October 1992, MELEO)

Far more detailed evaluations have been conducted in laboratory simulations, as discussed below.

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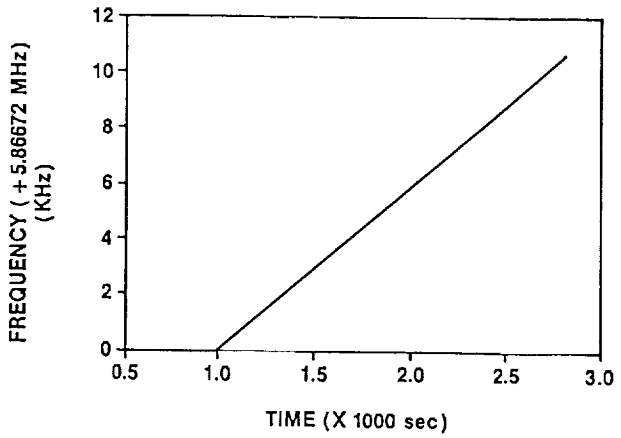
[6] For further information on FRE Composite's Project, contact Rhéal Comte, FRE Composites Inc., 75 Rue Wales, St-Andre-Est, Québec, Canada, J0V 1X0, Tel: (514) 537-3311, Fax: (514) 537-3415 or Dr. Michael Wertheimer at École Polytechnique, Département de génie physique, 2900 Blvd. Édouard-Montpetit, C.P. 6079, succ. Centre-Ville, Montréal, Québec, Canada, H3C 3A7 Tel: (514) 340-4749, Fax: (514) 340-3218.

Protection of organic substrates against AO/VUV exposure is probably the most important among the above-cited criteria for low Earth orbital (LEO) applications; it is routinely tested in this laboratory by subjecting samples for long durations to dual-frequency MW/RF oxygen plasma, following which the samples are examined for mass loss, and for possible undercutting erosion under defects such as pinholes or cracks [9]. The latter test is accomplished by peeling away the coating over undercut areas; this can reveal the number density and spatial distribution even of microscopic (sub-μm) coating defects by optical microscopy. The advantage of MW/RF plasma is that it combines a very efficient AO/VUV source with energetic particle bombardment, simulating the reactive particle flux in the ram direction during LEO space flight.

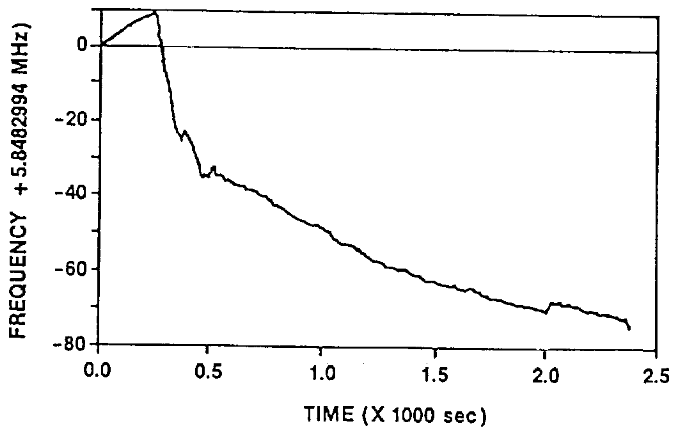
Even more realistic LEO simulation can be achieved in the well-known UTIAS beam facility [10], since there a well-characterized AO flux with 2.5 eV of kinetic energy can be directed at a VUV-illuminated sample surface at 10^{-5} Torr. Figure 5 shows the results of experiments in which quartz crystal microbalances (QCMs) coated with very thin (a few μm), solution-deposited layers of polyimide (PI) are exposed to an AO flux of 5.6×10^{16} $cm^{-2} \cdot s^{-1}$: In Figure 5a, which was obtained using an unprotected PI surface, the linear rise in frequency after an induction period of about 17 minutes reflects the expected mass loss due to AO/VUV-induced erosion ("etching") of the polymer. In the case of Figures 5b and 5c, the PI has been overcoated with 0.5 μm layers of p-SiO_2 and a-Si:H, respectively. Noting the change in scales of the ordinates (in Hz, versus kHz for Fig. 5a), one first observes a brief period of mass loss (removal of absorbed water vapour and organic contaminant), followed by periods of slight mass gain (total $\Delta m \leq 10^{-8}$ g). Using Auger Electron Spectroscopy (AES) we have shown [4,5] that the surface region of the protective layer becomes fully oxidized to a depth of a few tenths of a nm, the reason for the observed mass gain, following which $dm/dt \to 0$ (i.e., the frequency response becomes time-invariant). This result strongly suggests that the protective PECVD layers are essentially defect-free over the roughly 1 cm^2 surface area of the QCM. Undercutting through microscopic defects (pinholes, microcracks), as reported by Banks [9], would give rise to a measurable positive slope on the QCM response curve.

Space limitations do not permit us to describe the other attributes of PECVD protective coatings, for example, their antistatic characteristics [4,5,11] which will be particularly advantageous in geosynchronous orbit. However, we do wish to say at least a few words about terrestrial spin-off applications and scale-up. First, regarding the latter, Figure 6 shows a pilot-scale MW/RF PECVD roll-coater now being commissioned in this laboratory. This machine will soon be able to coat 12 inch-wide (30 cm) rolls of flexible substrate materials in a "batch-continuous", roll-to-roll mode, for example, one-side metallized polyimide thermal blanket material.

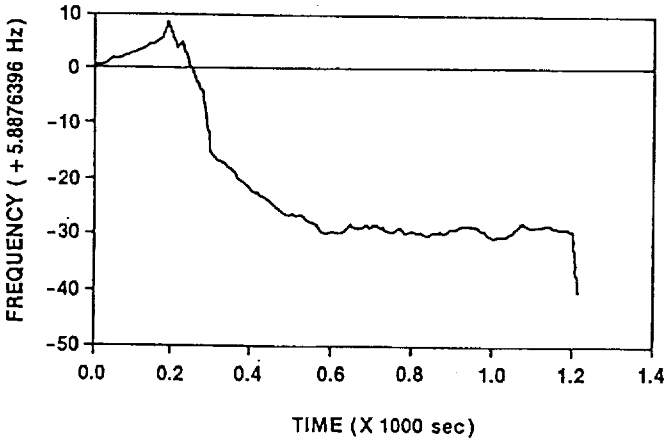
p-SiO_2 displays excellent barrier characteristics not only against the permeation of AO, but also against molecular O_2, H_2O vapour, and other gases or vapours of interest in plastic packaging applications of Earth. This technology is also being pursued vigorously in this and other laboratories [12,13].



a) POLYIMIDE



b) SiO_2 OVER POLYIMIDE



c) a-Si:H OVER POLYIMIDE

FREQUENCY SHIFT OVER TIME
FOR AO EXPOSURE OF COATINGS

Figure 5

Figure 6
Pilot-scale MW/RF PECVD roll-coater

5.0 MPB TECHNOLOGIES INCORPORATED PROJECT[7]

5.1 ECR-Plasma Deposition of Silicon Dioxide

Given the objective of protecting space structures against the Low Earth Orbit (LEO) environment for a life of 30 years, a deposition process for thin protective films of silicon dioxide is being developed.

Glass, particularly fused quartz alias silicon dioxide (SiO_2), is known for its inertness to all but the most reactive of chemical species. It is ideal for protection against Atomic Oxygen (AO), the dominant threat of LEO. The AO radical, being a stronger oxidizing agent than any chemical compound, has oxidation as its major route of attack. SiO_2, being already in its highest oxidation state, is quite unaffected by this affront. The secondary route of attack by AO in LEO is by sheer kinetic energy. SiO_2, having a bond energy of 8.3 eV [8] is equally well equipped to resist the attack of LEO AO which is typically at 5 eV, with a distribution tail up to 8 eV.

Producing a thin, adherent coating of p-SiO_2 [9] is achieved by ECR-PECVD (Electron-Cyclotron-Resonant Plasma-Enhanced Chemical-Vapour Deposition). An important aspect of depositing high-quality p-SiO_2 is the activation energy available to the reactive species. With a CVD process, that energy can be made available by heating the substrate to 400oC or more, or by impinging the reactive surface with kinetically energetic species. The plasma enhancement of the CVD process achieves the latter. Even so, the substrate must be heated to 200oC to achieve a reasonable quality. A magnetic field in the plasma activation region so as to obtain the ECR condition allows more energy to be imparted to the reagents, in turn allowing deposition of high-quality film on actively cooled room-temperature substrates. This is important for depositing on organic substrates such as Kapton or composite materials such as graphite/PEEK.

The task remained to develop a facility that could implement this process on industrial-scale substrates. It is planned on this project to manufacture an apparatus capable of depositing coatings of p-SiO_2 on 5-foot-wide rolls of Kapton at MPB Technologies. There are two basic approaches to the scale-up problem. One is to increase the size of the plasma source so as to be able to deposit simultaneously across the 5-foot-width of the substrate. It was decided that a previously developed plasma source would be used. The size of the substrate was accommodated instead by raster scanning it under the plasma beam.

The principle of raster scanning has been verified with a miniature substrate manipulating

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[7] For further information on MPB Technologies' project, contact Dr. Jeff Blezius, MPB Technologies Inc., 151 Hymus Blvd., Pointe-Claire, Québec, Canada, H9R 1E9, Tel: (514) 694-8751, Fax: (514) 695-7492.

[8] The 8.3 eV Si-O bond energy is large as compared to the 3 to 4 eV bond energy found commonly in materials.

[9] The prefix "p-" refers to the plasma source and is an acknowledgement that the material is distinguishable from natural SiO_2 upon careful study.

device that fits into the existing facility. The resulting thin film has been verified to be at least as good as that produced without the manipulating device.

The AO erosion rate of the p-SiO_2 film has been measured on the UTIAS (University of Toronto Institute of Aerospace Studies) AO facility which produces a beam of 2.3 eV [10] oxygen atoms. A total fluence of 1.4×10^{21} atoms/cm^2, combined in the latter half of the exposure with 7 equivalent sun days of UV, produced a mass loss of less than 1.1×10^{-29} cm^3/atom, as measured by the in-situ quartz crystal microbalance (QCM). The measurement was limited by the resolution of the QCM. At that rate, the erosion of the thin film due to a 30-year AO fluence in LEO of 1.5×20^{23} atoms/cm^3 would be less than 16 nm, a thickness that is easy to obtain.

The solar emissivity, ε, and absorptivity, α, of p-SiO_2 on aluminized Kapton have been tested according to ASTM-E-408-71 and ASTM-E-490-73a. Upon coating, the ratio α/ε changed from 0.45 to 0.48 [11]. Upon AO exposure of a coated QCM in the UTIAS facility, the ratio α/ε changed from 1.98 to 1.90. The same measurements were made for p-SiO_2 on Kapton before and after exposure to in-situ AO on the Canadarm, as a part of the "MELEO" experiment of the Canadian Space Agency: the changes in thermo-optical properties, as well as the resistance to LEO AO, were corroborated. Thus, the effect of the p-SiO_2 coating on the thermo-optical properties is only just measurable.

A preliminary qualitative test has been performed to verify the adhesion of the coating to the substrate. Adhesive tape 3M-610 (45 oz/in of tape width on steel) was pressed to the coating surface and removed. Examination of the coating and the tape under an optical microscope with polarized lighting revealed absolutely no removal of the film, indicating a good qualitative adhesion.

The coating flexibility has been measured based on ASTM-D-522-88. The coating on 25 μm thick Kapton flexed successfully around a 0.038" diameter mandrel. At this small diameter, it was necessary to press the specimen to the mandrel with a gloved hand to ensure complete flexure. Examination of the coating under an optical microscope with polarized lighting revealed no cracking of the film. An analysis of the tensile stress imposed on the coating by this test yielded a tensile strength of at least 240 psi. This can be compared to that of fused silica with 7.1 psi, quartz fibres with 130 psi, and a p-SiO_2 film prepared by B. Banks [14] with 205 psi. Thus, the tensile strength of p-SiO_2 and its resistance to cracking are good.

The p-SiO_2 film on Kapton withstood preliminary thermal cycling and shock tests. The temperature was cycled ten times between +155°C and -135°C. The sample was also immersed for 1 minute in liquid nitrogen followed by 1 minute in boiling water, repeated twice. Examination under optical microscope revealed no change in the film, indicating good resistance to the LEO thermal environment.

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[10] Less than the 5 eV encountered in LEO, but nonetheless one of the best Earth-based simulations.

[11] The short-term repeatability of these thermo-optical measurements is ± 2%. However. the long-term (months) repeatability seems to be double that. Thus, the variations reported here are all just above the level of resolution.

Because of the long mean free path in the plasma at the deposition pressure, the reactive gas can diffuse around a three-dimensional substrate. The result is coating on all surfaces. A preliminary deposition on a surface which did not have a direct line of sight to the plasma source has verified this principle with film of good quality.

The defects in the applied thin film were counted. There were, however, defects in the Kapton substrate before the p-SiO_2 coating was deposited. It is, therefore, difficult to distinguish between a well coated defect in the substrate and a defect in the coating. For this reason, the Substrate Undercutting Enhancement Test (SUET) was developed. This test consists of three steps. The coated substrate is first exposed to AO from a plasma source to a fluence of 10^{20} atoms/cm² at 10 eV as measured by Kapton mass loss on a simultaneously exposed uncoated sample. During this exposure, the AO penetrates any defect in the film and reacts with the Kapton underneath.

Secondly, the sample is subjected to peel tape 3M-610 (45 oz./in of tape width adherence to steel) to remove areas of coating that are unsupported due to undercutting by the AO. Thirdly, the sample is examined by SEM, looking for the characteristic pattern of eroded Kapton. This technique was taken from reference [15]. Not only does this technique distinguish between well coated defects in the substrate and defects in the coating, it also renders the defects in the coating more visible.

In a preliminary test, 0.7 cm² of a sample was completely scanned by SEM and 10 film defects were found, typically of a diameter less than 5 µm. The SEM resolution was 0.1 µm. This yields a defect density of 15/cm² which is much lower than the 1000 defects/cm² [16] of commercially available sputtered SiO_2 film. The defect density can also be compared to the debris impact rate in LEO: the 1988 impact rate for debris of 2 µm diameter is $5x10^7$/year/(5000m²), or 1/year/cm². Thus the film defect count will be overcome by debris impacts in the first 15 years of flight, without even considering the growing debris population and the factor of 5 of crater size with respect to impacting particle size, indicating that this pin-hole density is insignificant with respect to protection against LEO.

It is informative to compare the resolution of this SUET technique to an equivalent one based on a mass loss measurement of the undercut Kapton substrate. With the UTIAS facility in mind, one would need to test a coating which is 10 times thicker than the proposed coating in order to meet the quartz microbalance requirements. Such a coating gives only the minimum step resolution of 5 ng; over 6 hours one could resolve a mass loss of about 20 ng.

Based on $1.45x10^{21}$ oxygen atoms/cm², a 100% reaction efficiency with the Kapton (13% is more realistic until the undercutting becomes pronounced), and an exposed sample area of 0.75 cm², the resolution limit would be five 5-µm (diameter) defects/cm² and that is still for a film which is 10 times thicker than the one of interest. This is to be compared to the SUET resolution of about 1 defect/cm² (any defect larger than about 0.1 µm). Thus, the defect density that has been easily observed by the SUET would probably have gone unresolved by a mass-loss detection method.

Thus, a facility for the large-scale deposition of thin-film protective coatings of p-SiO_2 on three-dimensional substrates is being constructed. The resulting film has already been shown to have a very low erosion rate in atomic oxygen, to have a pin-hole (less than 5 μm diameter) density of only 15/cm², to have only a small effect on the thermo-optical properties of the substrate/coating system, to adhere well to the substrate, to be flexible to less than ⅛ inch diameter, and to be resistant to thermal cycling. In short, it is a good candidate as a protective coating for long-term protection against the LEO environment.

6.0 CONCLUSIONS

The three projects in the Protection of Materials in the Space Environment Subprogram have completed their first year of a three year development. The results from previous feasibility studies and the early experimental results from the current projects have already demonstrated that good quality coatings can be produced to address a variety of requirements for the protection of materials, not only in the space environment, but also in terrestrial applications. The development of pilot-scale fabrication facilities over the next two years will demonstrate the commercial viability of reproducing these coatings on an industrial scale.

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