General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE
The School of Science and Engineering
Department of Physics
P. O. Box 1247
Huntsville, Alabama 35807

F I N A L   R E P O R T

MEASUREMENTS OF MATERIAL PROPERTIES FOR SOLAR CELLS

Contract NAS8-32398

February 7, 1977 - March 6, 1978

by

J. G. Castle, Jr.
Principal Investigator
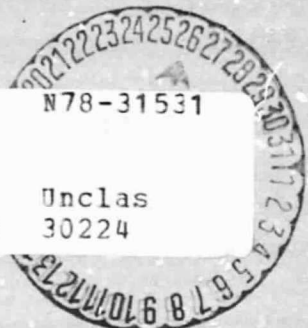
Prepared for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama   35812

July 1978

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE
The School of Science and Engineering
Department of Physics
P. O. Box 1247
Huntsville, Alabama 35807

F I N A L   R E P O R T

MEASUREMENTS OF MATERIAL PROPERTIES FOR SOLAR CELLS

Contract NAS8-32398

February 7, 1977 - March 6, 1978

by

J. G. Castle, Jr.
Principal Investigator

Prepared for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama   35812

July 1978

A B S T R A C T

Measurements on two candidate materials for space flight
are reported. The observed optical transmittance of aluminum
films vapor deposited on fused quartz shows anomalously high
transmittance thru 400 Å and 600 Å and shows an effective
skin depth of 110 Å in the latter part of the 1000 Å thick-
ness. KAPTON* films are shown by their optical transmission
spectra to have an energy gap for electron excitation of
approximately 2.5 eV, which value depends on the thickness
as manufactured. The resistance of KAPTON film to ionizing
radiation is described by their optical spectra and their
electron spin resonance spectra; the former show that traps
are formed by proton irradiation just below the energy gap
and the latter indicates three different kinds of electron
traps are formed, each growing in number in direct propor-
tion to the proton fluence.

*KAPTON is a registered trademark of the EI du Pont de Nemours Co.,
Inc., Delaware. See Reference 1.

ACKNOWLEDGEMENTS

Table of Contents

I.   INTRODUCTION

Extended space flights are being plan..ed for which the "aging"
of the materials during space flight due to ionizing radiation pre-
sents effective limits to the flight duration. The rationale for the
materials measurements of the kind made during the present study is
that nondestructive measurements of sufficient precision should permit
interpretation in terms of a microscopic model of the radiation damage.
The model should in turn, serve to estimate the aging in materials
properties to be found during extended space flight.

A similar need and rationale apply to NASA's plans for devel-
oping large space structures. Because of their size, these structures
will use the thinnest materials available by current manufacturing
methods. Therefore, NASA needs to know how the materials properties
depend on the thickness and/or the manufacturing process in the range
of very thin materials.

The emphasis here was materials which were and are candidates
for use in our solar arrays for space flights being planned, with the
expectation of effective service for several years in space. Optical
and microwave properties were measured with the aim of correlating
the results so as to form the basis for a microscopic model for the
aging of the functional properties needed during space flight. Two
materials were selected: vapor deposited aluminum films and KAPTON
polyimide sheet. Our results for each are presented in detail in
Section II.

I.   A.   Optical Transmittance of Aluminum Films

Aluminum films offer a reasonable measure of protection from

the sun's ultraviolet radiation for the thin plastic sheets which serve as structural support in NASA's solar arrays. The large size makes weight of the essence. However, the optical properties of thin films of aluminum do not correspond directly with those of bulk aluminum. Therefore, it is important to know how the transmission of thin $A\ell$ films depends on thickness and mode of manufacture, at least into the near uv region.

The optical absorption process (Ref. 2,3) in bulk aluminum is not describable by the classical skin depth (Ref. 4), δ_c. Therefore, it is further necessary to measure the <u>absolute</u> transmittance into the near uv for the purpose of planning and detailed design of the large solar arrays to be flown in earth orbit.

Measurements we have made of the optical transmittance of a series of aluminum films over the wavelength range from 600 nm to 350 nm yield values of absolute transmittance as low as 1/3000. The results of these measurements on a series of sample $A\ell$ films formed at NASA by vapor deposition are presented in Section II A below and interpreted in terms of oxidation during the early stages of the $A\ell$ vapor deposition.

1.   B.   Transmittance of KAPTON Films versus Manufactured Thickness

KAPTON polyimide film as manufactured (Ref. 1) in the thickness range of 0.5 to 2 mil (12 to 50 micron) has excellent radiation re-sistance of its high mechanical strength, making it the likely material of choice for support in large space arrays. Attempts to produce thinner KAPTON sheet are underway. Measurements of the optical transmittance for several thicknesses are reported below which show that KAPTON has an absorption edge in the near uv whose

position depends on the manufacturing process. An interpretation is offered in terms of polymerization, specifically a dependence of crosslinking on thickness.

These results were reported in a paper presented at the Third Southeastern Conference on Application of Solar Energy, at UAH in April 1978. In that paper (Appendix A of this report) we suggest the use of the sharp absorption edge in the blue as protection against the uv of sunlight. We propose in this report that the electronic excitation which leads to the absorption edge also gives KAPTON its superior radiation resistance.

I. C. Effect of Ultraviolet Irradiation of KAPTON Sheet

Irradiation of KAPTON films held at low oxygen pressure with the ultraviolet radiation from discharge lamps - simulating sun spectrum in space - is known from recent NASA measurements to produce slight darkening at 600 nm wavelength. Our measurements of this darkening show it to be rather uniform across the visible region to the absorption edge, which appears to be unchanged in value after exposure equivalent to more than a month of sunlight. This was reported as indicated in Appendix A.

Caution should be exercised in using these results or any others that do not include the likely synergistic effects of concurrent exposures to the several kinds of ionizing radiation present in the solar wind. We propose no improvement in the uv resistance of KAPTON, but rather the likelihood of synergistic improvement in the resistance to damage from energetic particles (protons and electrons) due to coincident uv radiation.

1.   D.   Effects of Proton Irradiation on KAPTON Sheet

The deterioration of the mechanical properties of KAPTON sheet due to irradiation from fast protons is not well understood. As a preliminary step toward a useful understanding of the damage process, we report in Section II. D. below, our measurements of optical transmittance T_s, and electron spin resonance (ESR) absorption on several series of KAPTON films. We find a strong dependence of the rate of damage by protons of 2-Mev on the thickness of KAPTON and a direct proportion between the number of paramagnetic traps formed and the proton fluence. Discussion of the microscopic model of the damage process is brief. Caution is again urged because we expect a synergistic effect from concurrent exposure to uv and fast protons.

These results were reported in a seminar given to Organization 2300, Sandia Laboratories, NM, in December 1977. The information presented in that seminar forms Appendix B of this report.

II.   Results

A.   Optical Transmittance of Aluminum Films

Aluminum is known to have an absorption resonance centered near 800 nm wavelength and to have reasonably constant reflectance, about 92%, from 600 nm into the ultraviolet beyond 300 nm. Furthermore, the mean free path, ℓ_c, of the carriers in solid aluminum (Ref. 2) at 300K is given by the Drude theory to be slightly more than 100 Å. This value is many times larger than the classical skin depth (Ref. 4) $\delta_c = 16$Å at 400 nm wavelength. Therefore, a thick Al film is expected to have an anomalous skin depth, δ_f, even when the deposited film is sufficiently thick and dense to have bulk electrical properties. That is, we expect $\delta_f > \delta_c$ because $\ell_c > \delta_c$ in the

visible and near uv regions. Therefore, direct measurements of the optical transmittance over the spectral range significant for space flight service are needed to verify the utility of any particular technique of Al film deposition.

Al films vapor deposited on fused quartz were chosen for this study of the thickness dependence of optical transmittance. Fused quartz has the advantage of a known index of refraction and an essentially zero absorption over the visible and near uv region. The thickness range of steps of 200Å up to 1000Å total thickness includes sufficient attenuation to reduce the transmitted light intensity to less than 1/3000 of the incident intensity.

Absolute transmittance values, T_s, of four sample films were obtained on a double beam spectrophotometer (Cary Model #14) by observing recording the relative optical transmission of the films in pairs and the two thinnest ones relative to air in the reference beam. In that way, together with sufficient reduction of stray light, the normal Cary 14 range of X100 was extended to a range of X3000. Selected values read from the Cary 14 output charts for the four Al films are listed in Table 1. Redundant pairing of the films as shown in the table, gives a direct measure of the experimental uncertainty of the readings of relative transmittance; it appears to be within the white noise seen on the chart record and listed in the table as $\pm$ 0.005 to $\pm$ 0.01 in $logT_s$. In a more complete study, several sample films of each value of the nominal thickness should be used in order to establish the reproducibility of deposition and handling.

The precision of the Cary 14 chart was checked once on each of

Table 1. Measured Optical Transmittance of Evaporated Aℓ Films, as Log (T_r/T_s).

Relative transmittance values (T_r/T_s) were read from the output chart of the double beam Cary Model 14 Spectrometer, whose beams were passed thru test films as indicated. The pk-pk white noise on the chart is indicated by the ± values. The test films were all at room temperature on fused quartz substrates.

Sample Beam	Reference Beam	650	600	550	500	450	400	350
Fused Quartz	MT	.032 ±.002			.036 ±.002			.054 ±.002
400A	MT	.968 ±.004	.918	.862	.792	.708	.622	.534
600A	MT	2.02 ±.01	1.973 ±.005	1.917 ±.005	1.842 ±.007	1.75 ±.01	1.65 ±.01	1.524 ±.005
600A	400A	--	1.060 ±.005	1.060	1.058	1.048	1.032	.994
800A	400A	1.884 ±.005	1.892	1.904	1.898	1.874	1.84 ±.01	1.800 ±.005
1000A	800A	--	.700 ±.007	--	.755 ±.005	--	.775 ±.005	.755 ±.005
800A	600A	.84 ±.02	.846 ±.005	.852	.858	.852	.848	.830
Fused Quartz	MT					.036 ±.002		.036 ±.002
Balzer 16.6%	MT		.756 ±.004		.756 ±.004		.740 ±.004	
Balzer 5.9%	MT		1.286 ±.004		1.294 ±.004		1.270 ±.004	

Table 2. Values of Absolute Optical Transmittance, as $\log T_s^{-1}$ Calculated from Data in Table 1, versus Nominal Thickness of Aluminum Vapor Deposited on Fused Quartz.

nm	Nominal Thickness of Deposited Aℓ						
	400A		600A		800A		1000A
650	0.968	±.005	2.02	.01	2.845	±.01	—
600	.918	±.005	1.975	±.005	2.82	±.01	3.52*
550	.862	±.005	1.920	±.005	2.77	±.01	--
500	.792	±.005	1.845	±.007	2.70	±.01	3.45
450	.708	±.005	1.753	±.01	2.60	±.01	·--
400	.622	±.005	1.652	±.01	2.48	±.02	3.25
350	.534	±.005	1.526	±.005	2.35	±.02	3.10

* Apparently increased as much as 0.1 by light leakage in the Cary 14.

the two ranges, 0 to 0.1 and 0.1 to 0.01, by using calibrated Balzer filters. The transmittance of the 16.6% Balzer filter was read on the Cary 14 chart as 17.5% and that of the 5.9% Balzer filter, as 5.2%. For a more complete study, the two scales on the Cary 14 would have been readjusted to conform more closely to the standard filters than even these small discrepancies of 0.8%.

Table 1 also contains the transmittance of the clear fused quartz blank relative to air as log T_q = 0.035 $\pm$ 0.002. This value corresponds to an index of refraction of n = 1.49 $\pm$ 0.03 assuming zero losses within the quartz, obviously in excellent agreement with the known values of the index for fused quartz, e.g., 1.496 @ 275 nm and 1.460 @ 550 nm.

The measured values of log (T_r/T_s) in Table 1 have been used to calculate the absolute T_s for each of the four sample films listed in Table 2 as log T_s^{-1}. A few of these values of log T_s have been plotted on the graph in Fig. 1 to show that the decrease in log T_s with increasing thickness is closely linear in the range from -2.2 to -3.5. The slope versus thickness is meaningful if one assumes the same process goes on in the first 400 Å of deposition of each of the thicker films. The slope in Fig. 2 is closely the same for each wavelength, namely 260Å $\pm$ 20Å per decade. This corresponds to a skin depth in the last few hundred Angstroms of thickness of δ_f = 110 $\pm$ 10 Å, a value comparable to the expected mean free path for the carriers in dense aluminum. Therefore, the skin depth is expected to have no variation with wavelength.

Interpretation of the values of T_s in Table 2 and in Fig. 1 should consider the high reflectance of 0.92 expected from each surface of
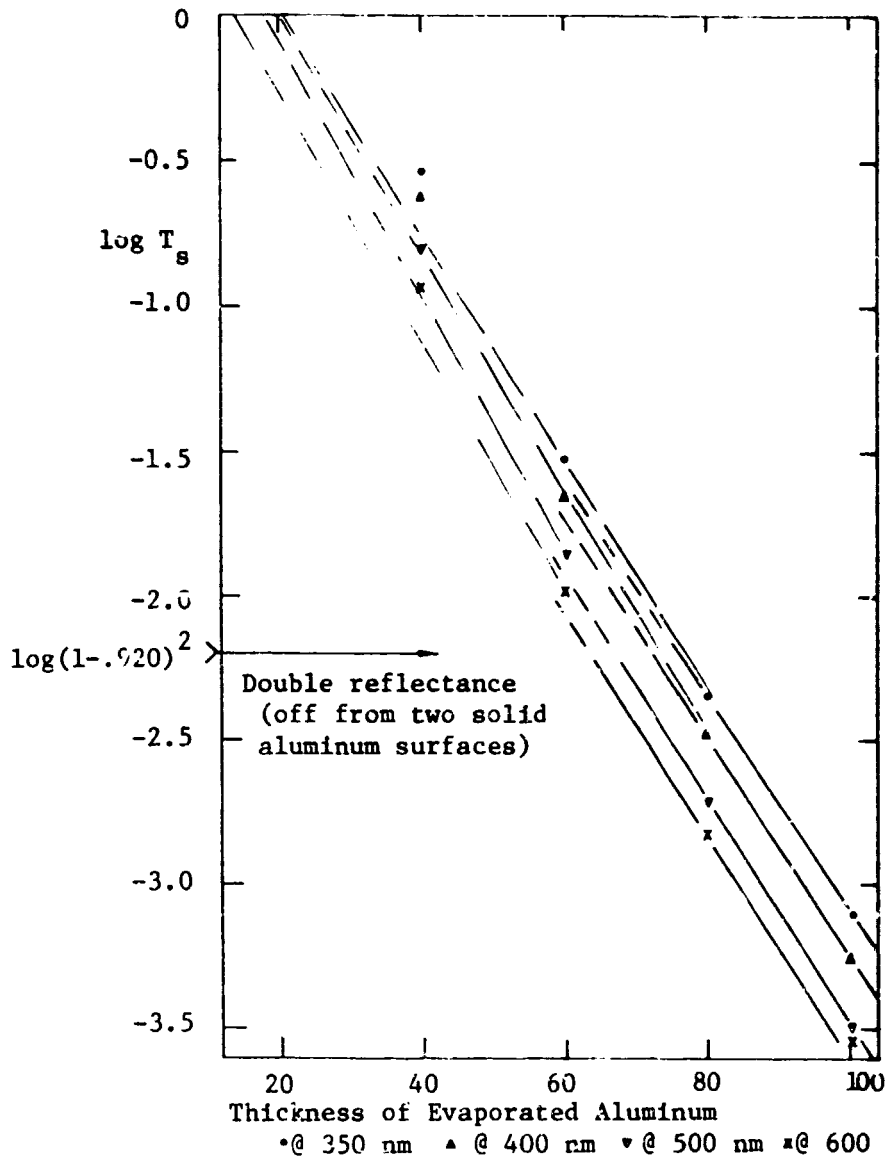
Figure 1. Absolute optical transmittance T_s on log scale versus nominal thickness of aluminum films evaporated on fused quartz. Values from Table 2 are plotted for four wavelengths: ● @ 350 nm, ▲ @ 400 nm, ▼ @ 500 nm and x @ 600 nm.

of smooth dense films of aluminum in this wavelength region. The corresponding value of log T_8 is -2.20 to which the absorption within the Al must be added to get the final T_8. Therefore, these four films appear to have at least one surface with low reflectance and the curvature in Fig. 1 suggests that the 400 Å film may well have pinholes in it. The log reflectance may be due to oxidization of the Al during the initial stages of deposition. The increase in transmittance as the wavelength changes toward the ultraviolet is real for these four films, but may depend strongly on the same process producing the low reflectance. Until a series of experiments is carried out to ascertain the reflectance and its dependence on deposition conditions, one is forced to conclude tentatively that a thickness of 1000Å of vapor deposited is needed to reduce the optical transmittance below 1/1000 in the near uv and below 1/3000 in the red.

By comparison with these real films which appear to be either poorly reflective or weakly absorptive in the first few hundred Angstroms of thickness or both, we expect a dense film of aluminum could produce an attenuation of 32 dB by having the bulk reflectance of 0.92 at each surface, and the same effective skin depth we observe in the last few hundred Angstroms (δ_c = 100Å) in a total thickness of only 260Å. This would reduce the weight of aluminum needed by a factor of almost four, probably unduly optimistic.

We further know that KAPTON substrates may behave different than quartz, so that this type of double beam measurement of optical transmittance should be applied to Al films deposited on KAPTON to see what thickness is required on KAPTON to get the transmittance down below 30 dB.

II. B.   Optical Transmittance of KAPTON film versus Thickness

The optical transmittance of KAPTON films at room temperature was measured using the double-beam Cary Model 14 Spectrophotometer.   One example of the data is given in Table 1 of Appendix A, for three thicknesses, 0.1 mil, 0.5 mil, and 2.0 mil. The consistent features of every optical transmission spectrum of an unirradiated KAPTON film that we have seen are:

1.   high transmittance (circa 85%) from 800 nm to almost 550 nm, and 2.   sharply falling transmission near 500 nm.

These features can be seen clearly in Fig. 2, which is a plot of the data in columns three and four in Table 1 of Appendix A, transmission for one of the 0.5 mil film, and a 0.1 mil film. The high transmission can be interpreted as showing zero absorption within the film and a reflection coefficient at each of the two surfaces corresponding to the square of the index of refraction being 2.95 ± 0.12. This value is lower, and therefore consistent with the listed (Ref. 1) dielectric constant of 3.5 at power frequencies. We conclude, as in Appendix A, that an antireflection coating on each side of the KAPTON would raise the transmission close to 100%.

The sharply falling transmission is undoubtedly due to strongly increasing absorption as the wavelength is changed toward the ultraviolet. The simplest interpretation is to use the straight line fit on the log plot in Fig. 2 to get the intercept, called the absorption edge, and associated with an energy gap in the electronic excitation spectrum of the KAPTON polyimide polymer. The straight lines on Fig. 2 show the absorption edge for 0.5 mil film to be 490 ± 5 nm, slightly
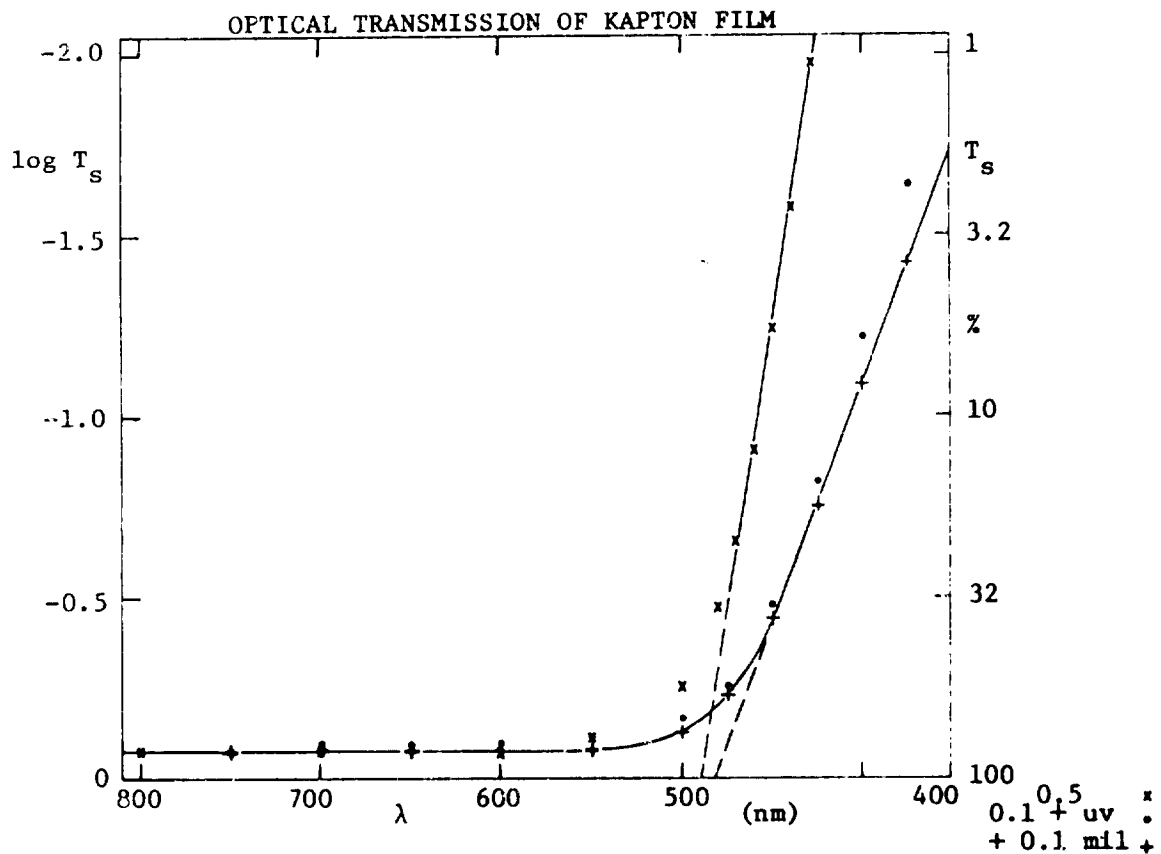
Figure 2. Optical Transmittance of KAPTON Films versus Incident Wavelength. The reference beam in the Cary Model 14 Spectrophotometer had only air. The data for three sample films in Table 1 of Appendix A correspond as follows: x 0.5 mil, + 0.1 mil and ● 0.1 mil after uv irradiation equivalent to more than one month in earth orbit.

above the 480 $\pm$ 5 nm value for 0.1 mil film. For 2.0 mil KAPTON, we
find 520 nm. In Appendix A, the absorption edge is related to the
length L of a box (potential well with steep sides a distance L apart).
For these values the "box" in which these excited electrons in KAPTON
find themselves free has L = 7Å. The difference of nearly 10% between
the absorption edge in 0.1 mil and the 2.0 mil film is to be attributed
to an increase of 5% in the effective length of the excursion of these
excited electrons, excited by light with wavelength less than the ab-
sorption edge. Relating this length L to specific manufacturing pro-
cedures would seem useful for UASA's goal of maximum properties for
minimum thickness.

II. C.   Effect of Ultraviolet Irradiation of KAPTON Film

The slight darkening for incident wavelengths from 800 nm to the
absorption edge shown in Fig. 2 is typical of the spectrum seen follow-
ing irradiation with simulated sun ultraviolet in low pressure air.
The increase in absorption at wavelengths beyond the absorption edge
is noticeably larger, tho for a months equivalent irradiation, there
is no change in the effective absorption edge.

One can conclude in terms of our model of electron excitation into
boxes of uniform length (ring structures measuring about 7Å long) in
the KAPTON that the direct excitation by ultraviolet photons appears
to do no permanent damage. The slight rise in absorption could be
due to absorption in one of those few sensitive bonds that are loca-
ted away from one of these extended ring structures, so that the ion
pair formed may result in permanent damage to that bond; the damage
may require the presence of oxygen gas, or water vapor. Clearly more

extensive measurements are needed to refine the relation between ultra-violet irradiation dose and the darkening. It may even be a dirt effect, as mentioned in Appendix A.

II. D. Effects of Proton Irradiation of KAPTON Film

Protons of 2.0 MeV pass thru 1.0 mil KAPTON; about 50% of them are stopped in 1.2 mil thick KAPTON, and almost all of them are stopped in 2.0 mil KAPTON. The rates of darkening in the 2.0 mil KAPTON are observed to be much higher than for the thinner films; the optical transmittance versus wavelength from 800 nm to about 500 nm for a 0.5 mil film after a proton fluence of 1×10^{16} per cm^2 is almost identical to that for a 2 mil film after a proton fluence of 10^{15} per cm^2.

As an aid to thinking about the microstructure of these films, the repeating molecular structure given by J. Kreuz in Ref. 1 was repeated twice and is shown in Fig. 1 of Appendix B. Crosslinking is likely to be the source of those uniform sized ring aggregates leading to the optical absorption edge of 2.5 eV.

1. Optical Transmittance

The first effect of increasing proton fluence is to reduce optical transmission slightly, more near the absorption edge than in the red, but leave the value of the absorption edge unchanged. With further increases in proton fluence, the darkening spreads rapidly across the visible, indicating many ring aggregates are being formed of various sizes larger than the 7Å long structures in the polymerized unirradiated film. Both of these stages can be seen in Fig. 2 of Appendix B, for 0.5 mil KAPTON film.

The ionization, due to the dose from the fluence of 2.6×10^{15} protons/cm^2 escaping the back of the 0.5 mil KAPTON, produces slightly

more darkening than a few months of solar uv but also begins the
increased ring formation because a proton fluence of 4 times larger
produces a much lower energy (~ 600 nm) band edge in the 0.5 mil
KAPTON. On the other hand, Fig. 3 in Appendix B shows that the
damage rate in the 2 mil KAPTON is much higher per proton than in the
0.5 mil films; at 1×10^{14} protons/cm^2, the darkening is severe all
across the visible to wavelengths of nearly 800 nm. This extra
damage is probably produced near the end of the proton range as they
are stopping within the 2 mil KAPTON.

   2. Electron Spin Resonance

   When a KAPTON film has been darkened by irradiation, we can
find electron spin resonance absorption. The ESR spectra from 2 mil
KAPTON films show only one line located near the free spin value at
g = 2.0305. With increased proton fluence, the line narrows and
appears to shift away from the free spin value, to g = 2.0325. The
number of unpaired spin centers giving rise to this ESR line is closely
proportional to the proton fluence. These features are listed in
Table 1 of Appendix B.

   The ESR spectra of 0.5 mil KAPTON films, on the other hand, show
two resolved absorption lines, one at the same g = 2.033 and another
somewhat weaker line even farther away at g = 2.037. Increasing the
fluence of fast protons to 10^{16} per cm^2 increases the number of elec-
tron traps giving rise to each of these lines in approximately a
direct proportion to the proton fluence, but these ESR lines do not
shift. Table 1 lists these data too, in Appendix B.

   The saturation characteristics are observed to be very similar

amongst all these ESR lines. An attempt was made to obtain absolute center densities from the ESR spectra but the ESR equipment failed.

3. Tentative Model for the Radiation Damage from Protons

Our tentative model for radiation damage rests on the "semi-conductor model" for the unirradiated KAPTON polymer discussed briefly above. In that model, the absorption edge corresponds to an energy gap, above which the excited electron has considerably more room to move in – roughly 7 Å. Damage from ionizing irradiation appears to be at first ameliorated well (compared to MYLAR) and we attribute that to the ability of the excited electrons to spread the excitation around over more atoms in the polymer structure. Some damage will appear at the edges of these ring structures as unsaturated bonds are left behind, following energetic ionizing collisions. These show up in ESR whenever the bond is single and left unsaturated, in the presence of room air as handled in this study. They also show up as a steeper optical absorption edge of the same intercept.

The damage centers that are formed in the KAPTON structure at atom sites removed from the aggregate ring structures can give rise to the general darkening across the spectrum. ESR data indicate that if there are such centers that are paramagnetic, they are remarkably similar, producing only one more ESR line. Clearly more extensive ESR measurements are in order at higher sensitivities and at lower proton fluences so as to establish the buildup of damage centers in more detail.

III. Summary

The results presented in this report show strong positive correla-
tion with other aging effects on KAPTON films due to ionizing radia-
tion. It seems clear that the specific details obtained from the
optical and ESR spectra show promise of leading to a sufficiently
detailed understanding of the damage processes to permit estimates of
aging rates for several materials properties critical to space flight
performance. The simple energy gap model for KAPTON proposed above
appears to explain many of the observed facts and is therefore a
useful step in that direction. In addition, that model suggests that
there may be a synergistic effect of giving KAPTON more resistance to
aging from fast protons when uv is also present; concurrent ex-
posures are therefore desired.

The correlations in this study of optical properties with manu-
facturing process - both for evaporated aluminum film and for KAPTON
polymer thin films - offer NASA an opportunity to monitor the quality
of the product being produced in a nondestructive way. Perhaps quality
control of this kind can be crucial to the success of large space
structures for which materials properties such as mechanical strength
or optical transmittance need to be held closely to their optimal
values during manufacture and subsequent handling.

REFERENCES

1. J. A. Kreuz, "KAPTON[R] Polyimide Film in Flexible Printed Circuits," Technical paper, 1976. Copies available from Plastic Products and Resins Department, E. I. duPont de Nemours and Co., Circleville, Ohio, 43113.

2. N. W. Ashcroft and N. D. Mermin, "Solid State Physics," Holt, Rinehart and Winston, New York, 1976, p 52, and p 301ff.

3. H. E. Bennet, M. Silver, and E. J. Asnley, J. Opt. Soc. AM. 53, 1089 (1963).

4. cf. J. Stratton, "Theory of Static and Dynamic Electromagnetism," McGraw Hill Book Co., NYC, 2nd Edition.

APPENDIX A

Final Technical Report, Contract NAS8-32398

/

April 1978

Appendix A contains the manuscript submitted to the Proceedings

of the Third Southeastern Conference on Application of Solar Energy,

held at UAH, April 17-19, 1978, S. T. Wu, Chairman. As indicated by

the coauthors, the study was a cooperative one.

TITLE: PROTECTION OF SOLAR COLLECTOR MATERIALS FROM UV.

AUTHORS: J. G. Castle, Jr., Physics Department, University of Alabama in Huntsville, and

R. L. Gause and Ann Whitaker, Materials and Processes Laboratory, NASA/MSFC

SUMMARY:

Certain plastic films, such as KAPTON*, are known to be stable with excellent long-term aging characteristics under intense uv radiation. Our recent measurements of the optical transmission spectra of KAPTON films show an absorption edge in the blue and are interpreted in terms of an electronic excitation mechanism. The application of this type of film as covering for solar collectors is discussed in regard to the protection this strong uv absorption offers to the materials underneath.

INTRODUCTION:

Application of solar energy technology frequently requires the use of materials whose special performance degrades under long exposure to the ultraviolet component of sunlight. Yet in most applications the investment in the solar energy collecting system is sufficiently high to require long life in service. In this paper, we point out that certain polyimide films have optical transmission characteristics which allow them to serve as useful covers, passing the visible sunlight and protecting the materials underneath from ionization by the uv sunlight.

Applications of solar collectors in space flight encounter the most severe requirements for protection from uv radiation. The present studies of radiation damage are aimed principally at the space flight applications with the hope of extending the solar collector's useful life to several years. Applications on the ground require less uv protection, but many of us are familiar with the bleaching effects of sunlight in the Southeast. For example, a coat of flat "black paint" should stay black much longer with protection from the ultraviolet in the sunlight reaching the ground.

It is the specific purpose of this paper to present some of our data on optical transmission of KAPTON films showing a sharp absorption edge in the blue region and to suggest that use of one of these thin polyimide films as a cover in a solar collector system may well extend the performance life of the collecting system.

KAPTON POLYIMIDE FILMS

The history of the development of KAPTON polyimide film has been described in a report by J. A. Kreuz[1] in which he lists many of KAPTON's properties. KAPTON film is polymerized from pyromellitic dianhydride and 4,4'-diaminodiphenylether. The microstructure of the film is apparently chains of the repeating unit which measures some 20 Å long. The film is available commercially in thicknesses from several thousandths of an inch (mils) to recent production of 0.1 mil thick sheets. The strength – both mechanical and electrical strengths – of KAPTON film is remarkably high, considerably higher than MYLAR. The dielectric constant observed at low frequencies is 3.5, and the yellow color of light transmitted thru KAPTON is due to absorption in the blue region of the visible spectrum.

MEASURED CHARACTERISTICS OF KAPTON FILM

The optical transmittance of a variety of KAPTON films was measured as part of a NASA supported study of the radiation resistance of solar array materials. Two consistent features of these preliminary data taken at low light levels over the wavelength range of 800 nm to 400 nm are a high transmittance value of 86 ± 1% from the infrared across the visible to the blue, and a sharp absorption "edge" in the blue which reduces the transmittance in the uv to well below 1%.

The transmittance of 86 ± 1% in the red and near infrared regions is consistent with the reflection expected from the two flat surfaces of the film at normal incidence provided the dielectric constant has the value of 2.95 ± 0.12. This is below the low frequency value of 3.5, as expected from being at frequencies above those of infrared absorption bands of KAPTON. Therefore, there is zero absorption in the 800 to 550 nm range and the 0.1 mil KAPTON film could be brought toward 98% transmittance for normal incidence by an appropriate antireflection coating[2] on each surface.

The shape of the absorption edge observed in the blue for each of these KAPTON films is consistent with a simple model[3] of the polyimide polymer behaving as a semiconducting medium to the incoming sunlight. For wavelengths longer than the band edge near 500 nm, corresponding to the semiconductor energy gap, E_g, of 2.4 eV, there is no absorption of the sunlight in the film. For wavelengths shorter than the band edge, i.e., for photon energies greater than E_g, each sunlight photon absorbed excites an electron from a polymer bond into a conduction band where the electron can wander thru some limited length, L, of the polymer structure as a "free" carrier. The model considers this excited electron to be moving in a potential well with very steep sides separated by a distance L. The activation energy can be associated with the energies allowed for a particle in a box[4], namely

$$E_g = 1.1/L^2,$$

where E_g is in electron volts and L in nanometers.

Table 1. Optical Transmission Observed for KAPTON Films

The transmission coefficient, T_f of KAPTON films vs wavelength was recorded at room temperature using a double-beam Cary Model 14 Spectrophotometer. The values of optical density (OD $\equiv -\log_{10}T_f$) listed here are the deflections from zero on Cary charts for normal incidence on the KAPTON and air in the reference beam. The spread indicated by the $\pm$ tolerance represent approximately peak to peak noise.

Wavelength (nm)	Film Thickness (inches/1000)				
	2.0	0.5	0.3	0.1	0.1 after uv irradiation
800	.070 ±.005	.077 ±.005	.070 ±.005	.070 ±.004	.077 ±.004
750	.090	.077	.070	.072	.079
700	.090	.077	.070	.074	.084
650	.095	.080	.067	.074	.089
600	.110 ±.005	.085	.075	.074	.094
550	.20 ±.02	.110 ±.005	.110 ±.005	.077	.112
525	.36 ±.02				
510	.60 ±.03	.195 ±.01⁻	.190 ±.01⁻		
500	.90 ±.04	.255 ±.01⁻	.245 ±.01	.122 ±.005	.167 ±.005
490	1.3 ±.05	.33 ±.01			
480	1.7 ±.05	.47 ±.01	.47 ±.01		
475				.227 ±.01⁻	.24 ±.01⁻
470	1.95 ±.05	.65	.66		
460	>2	.90	.91		
450	>>2	1.21 ±.01	1.23	.44 ±.01	.47 ±.01
440		1.58 ±.02	1.57		
430		2.01 ±.02	1.96		
425		>2	>2	.75 ±.01	.82 ±.01
400		>>2	>>2	1.09 ±.02	1.22 ±.02
375		>>2	>>2	1.42 ±.03	1.64 ±.03
λ(@ Eg) (in nm)	520 ± 5	490 ± 5	490 ± 5	480 ± 5nm	480 ± 5nm

Typical values we have observed for the optical transmission coeffi-
cient at normal incidence for KAPTON films at room temperature are listed
in Table 1. These data show, in addition to the high transmittance in
the red & yellow, a significant shift in values of E_g with thickness,
from 2.3 eV for 2 mil to 2.5 eV for the 0.1 mil films. These values of
the band edge correspond, on the semiconductor model of the polymer, to
L values near 7 Å.

The resistance of KAPTON to aging under uv radiation is indicated
by the transmittance values in the last column in Table 1, observed for a
0.1 mil film after exposure in an evacuated solar simulator to the equiv-
alent of longer than one month in space. The value of the absorption
edge is unchanged and there is a slight decrease in the transmittance in
the yellow. The latter is due to a small absorption which may not be due
to the KAPTON but rather to the impurities remaining on the 0.1 mil film
after the manufacturing etch. Further experiments will be required to
identify the source of this small absorption in the yellow.

INTERPRETATION AND CONCLUSIONS

The data presented here show that the use of thin KAPTON film as a
cover for a solar collector will shield the materials underneath effec-
tively from the uv in sunlight due to the strong absorption edge, found
for example at 480 nm in the 0.1 mil thick films. Such a cover should
extend the useful life of critical materials such as paint and semicon-
ductors. The high transmittance observed from 800 nm to 550 nm indicates
no absorption there and suggests the feasibility of raising the transmit-
tance significantly by antireflection coatings on the KAPTON surfaces. A
slight absorption will remain near the band edge due probably to the ran-
dom component of bonds formed during the polymerization of the film.

The desirability of a thin KAPTON cover for a solar collector will
be affected by the lifetime of the KAPT itself. Our preliminary data
on uv irradiated films indicate that the thin (0.1 mil) film has a
reasonably long life under uv radiation.

*KAPTON is a registered trademark of E. I. duPont de Nemours Co., Inc. of
Delaware.

ACKNOWLEDGEMENTS

REFERENCES

1. J. A. Kreuz, "KAPTON Polyimide Film in Flexible Printed Circuits," dated after 1975. Copies available from the Industrial Films Division, E. I. duPont de Nemours Co., Inc., Circleville, Ohio, 43113.

2. Robert Hahn and R. Winegarner, "The Solar Key Word is Coatings," Optical Spectra, April 1978, p. 36-39, The Optical Publishing Co., Pittsfield, Mass. 01201.

3. A similar model has, for example, been used to relate the absorption edge in pyrolyzed hydrocarbon films with the optical excitation of electrons into conduction bands which extend across the small aggregates of hexagonal carbon rings. cf. E. A. Kmetko, Phys. Rev. 82 456 (1951) and B. D. McMichael, and E. A. Kmetko, J. Optical Soc. Am. 44 26 (1954).

4. cf. L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw Hill Book Company, New York, 1935, p95ff.

APPENDIX B

These pages contain most of the information presented in the
invited seminar, entitled "Radiation Damage in KAPTON" at Sandia
Laboratories in December 1977. Credit was given for NASA support
of this study.

FIGURE 1 — Molecular Structure of
KAPTON® Polyimide Film
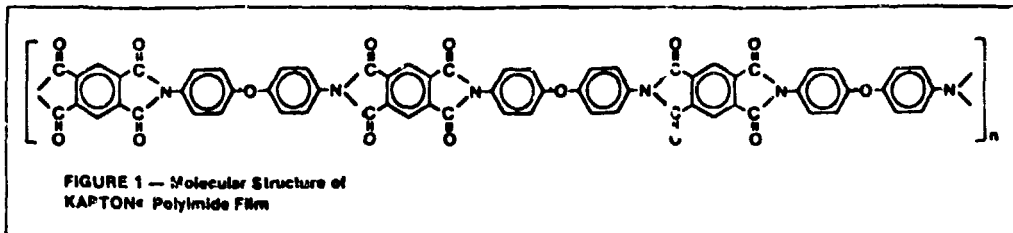
Figure 1.   Molecular Structure of KAPTON Polyimide Film.   The structure
           shown is three of the basic repeating units given for KAPTON
           by J. Kreuz in Reference 1 of the Final Technical Report.
           Cross linking patterns are not yet available, but are likely
           the source of the ring aggregates which give rise to the
           absorption edge near 500 nm.

OPTICAL TRANSMISSION of 0.5 mil KAPTON
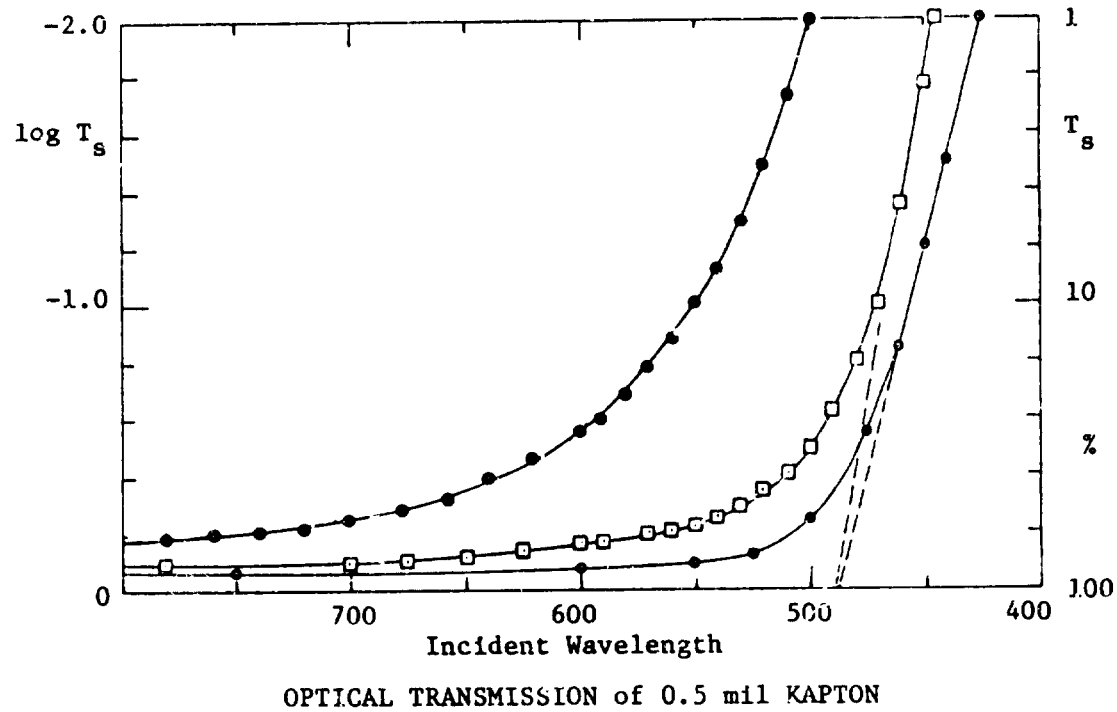
Fluence of 1.78 MeV protons/cm^2:   ●-1.0 x 10^{16} ▫-2.6 x 10^{15} ●-none

Figure 2. Optical transmission of 0.5 mil KAPTON filter versus incident wavelength. Fluence of 1.78 MeV protons was: none for o, 2.6 x 10^{15}cm^{-2} for ▫ and 1.0 x 10^{16}cm^{-2} for ●.
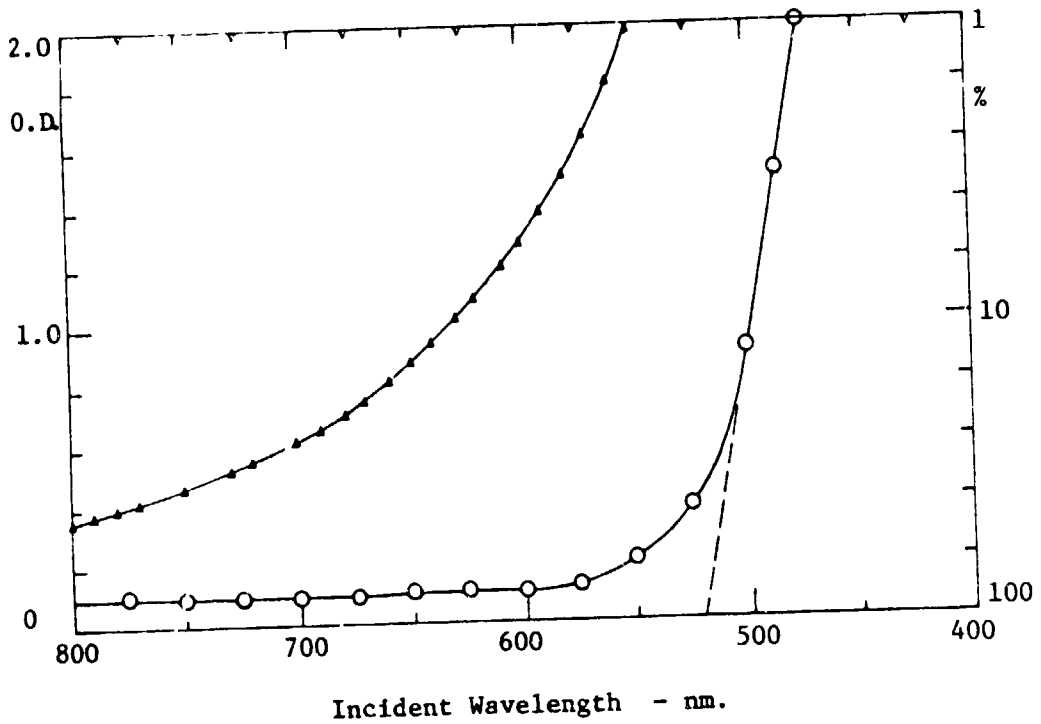
OPTICAL TRANSMISSION OF 2-mil KAPTON

Fluence of 2-MeV   O None $\blacktriangle$ - 1 x 10^{14} $\blacktriangledown$ - 1 x 10^{15} cm^{-2}
    Protons:

Figure 3. Optical Transmission of 2.0 mil KAPTON Film versus Incident
          Wavelength. Fluence of 2 MeV protons was: none for $\bullet$,
          1 x 10^{14} per cm for $\blacktriangle$, and 1 x 10^{15} per cm^2 for $\blacktriangledown$.

Table 1 of Appendix B

ESR ABSORPTION LINES IN KAPTON

At Room Temperature, following Irradiation by 2 MeV Protons

Film Thickness	Proton Fluence	g-value	ΔB_{pp}	Relative # of Spins per cm^2
(mil)	(cm^{-2})		(gauss)	
2	1×10^{14}	2.0305	24	1.0
2	1×10^{15}	2.0325	16	9.2
0.5	2.6×10^{15}	2.0373	16	0.57
		2.0331	21	1.5
0.5	1.0×10^{16}	2.0376	16	1.6
		2.0330	20	3.9
Nominal Thickness	Aℓ side exposed	$^+_-.0005$	$\pm$ 2G	$\pm20\%$