Report: #UW-DOES-3S

Semiannual Technical Status Report

for

A Contract Entitled

"Polymer Surface Coatings for Downconversion of UV
Radiation and Inhibition of Photodegradation"

Department of Energy Contract

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Submitted by: W. M. Yen and H. Yu
Departments of Physics and Chemistry
The University of Wisconsin
1150 University Avenue
Madison, Wisconsin 53706

695 4000

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TECHNICAL STATUS REPORT

I. CONTRACT OBJECTIVE

This is to develop and evaluate surface coatings and chemical coating methods on polymeric substrates which will downconvert the UV component of solar radiation into the visible or IR region and will simultaneously inhibit photodegradation of the plastic glazings.

I. (a) CONCEPT

Cerous ion (Ce III) and other trivalent lanthanide ions are known to downconvert UV radiation into the visible or IR owing to the large stroke's shift of their electronically excited states. Thus plastic glazing substrates overcoated with these ions in sufficient concentration are expected to be resistant to the photodegradative effect of the UV component of the solar spectrum. The central problem of plastic glazing materials has been ascribed to solarization, namely photo-oxidative degradation, with resultant deterioration of optical transmittance and of mechanical properties. The project addresses this critical issue by examining the surface screener effect of cerous and other lanthanide ion overcoatings on a variety of polymeric substrates relative to solarization.

II. SYNOPSIS OF PROGRESS

During this contract period we have begun both the chemical and the optical aspects of the evaluation. Cerous (III) polymethacrylate (CPMA), prepared by saponifying a commercial polymethyl methacrylate (PLEXIGLAS) and subsequently neutralized with cerous nitrate, were cast into film from its ethyl acetate solution. CPMA films were subjected to intense UV radiation in order to accelerate the solarization, and they were found to be substantially less susceptible to UV induced degradation than the control which was the film cast from polymethacrylic acid (PMA). A set of CPMA coated PLEXIGLAS films were then tested by the same method and the films with coating thickness of 5 μ were inhibitory to UV degradation although the surface density of cerous ion was not uniform.

A solar simulator has been installed and calibrated, and initial optical and aging measurements have been made on a series of CPMA PLEXIGLAS films. An automated solarization test system is in the process of being installed.

II. (a) TECHNICAL ACCOMPLISHMENTS

(i) Chemical

The best method of attaching cerous (III) ion on polymethyl methacrylate (PMMA; PLEXIGLAS) films so as to render them efficacious in the solarization inhibition is to coat the substrate surface with cerous salt of polymethacrylic acid (PMA). In this period, we have concentrated on this method by first preparing various films of cerous polymethacrylate (CPMA)/PMMA copolymer. Rough tests were made on the films by exposure to intense UV and affirmative results were obtained.

The film preparation scheme is depicted as follows.

- a) The chemical processes involved in the above, designated by Arabic numerals, are explained below;
- (1) room temperature dissolution of PMMA film pieces,
 - (2) a 100 to 400% excess of KOH in pellet form was added and the reaction mixture was heated to boiling for 3 to 5 days, replacing ethyl acetate as needed. Subsequently, the mixture was allowed to cool to room temperature and the excess hydroxide was neutralized by extraction with 1M HCl and the aqueous layer separated from the organic layer was discarded.
 - (3) cerium(III)nitrate hexahydrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ dissolved in ethyl acetate was added to the above organic layer or as a crystalline solid to the ethyl acetate solution, and stirred vigorously. Amount of Ce(III) added was 1/3 mole per mole of PMMA monomer in the solution.
 - (4) to remove unbound Ce(III) ion and excess hydroxide, the solution was washed with deionized water. The extracted Ce ion by this process was determined as 21% of the amount added in (3) by UV absorption.
 - (5) a similar step as (4) except that we used 1M HCl instead of water, the extracted Ce(III) ion was estimated as 6% by fluorescence analysis.
 - (6) water wash was effected after casting into film.
- b) Film casting was carried out in a Petri dish by pouring the solution at respective stages and allowing solvent to evaporate at room temperature in a fume hood. Films were optically clear and bubble free. Films II and III were about 50 μ thick, and IV, V, VI and VII were roughly 20 μ thick. Film V was soft and had a strong odor of acetic acid. This was repeatedly rinsed with water to make VII.
- c) These films were placed 7.5 cm from a UV source (Mineralight, Ultraviolet Products, Model R-52) and covered with a Pyrex petri dish to act as a cutoff filter for wavelengths less than 300nm. After 97 hours of irradiation the Pyrex filter was removed and exposure continued for an additional 90 hours. Films V and VII yellowed under the Pyrex filter. After removal of the filter only Film I showed any yellowing, and this is to a small extent. All other films appeared colorless and undistinguished to the eye.
- d) In order to quantify the irradiation effect in determining solarization extent without any artifact due to the thickness variation of the films, solutions of the exposed films were prepared by dissolving the films in ethyl acetate to give all samples at the same concentration of starting PMMA, 0.16% by weight. A Cary 14 spectrophotometer was used to obtain the absorption spectra. All samples were virtually transparent to 400nm. The visually identical films were easily distinguished on the basis of their absorption spectra at wavelengths shorter than 400nm. The table below lists cutoff wavelengths, chosen as λ where the absorbance is equal to 0.10, and the values of absorbance at 310nm as a measure of solarization.

Table

Cutoff wavelengths and absorbance value of 310nm for 0.16% ethyl acetate solutions of UV irradiated films.

Film	λ (nm) at A=0.10	A ₃₁₀
I	332	0.177
II	359.2	0.214
III	319	0.137
IV	314	0.112
V	346.6	0.446
VII	330	0.234

As can be seen from the table, expected efficacy of cerous ion coating is best reckoned by comparing III and IV since III is the most appropriate blank as opposed to I or II which has undergone a slightly different chemical processing. Purpose in testing V, VI and VII is to assess how deleterious an effect the residual alkali should impart to the coated films relative to solarization. The results show that the residual alkali has a much worse effect toward solarization than not having the cerous ion coating. Purpose of the above experiments is to determine the optimum coating process, and is not directed to find the best possible inhibitory effect of cerous ions with least possible decrease in optical transmittance of the original substrates. In our earlier study with cerium nitrate solution as the screener we could effect the inhibition by an order of magnitude better than the difference in III and IV suggests. With the experiment described above, we have begun to establish the methodology of coating and testing of the coated substrates.

(ii) Physical

In the area of physical measurements of the optical properties of the cerated films, this period has been devoted to developing the experimental capability to conduct testing in an accurate and routine fashion. Measurements to be made include standard optical absorption and emission characterizations of the substrates with and without the coating as well as exposure and aging tests to solar radiation.

For this purpose and in order to handle a volume of prepared samples we have acquired a commercial solar simulator (Schoeffel Instruments, LH 152, 2.5kW lamp system) and have assembled the automated solarization test system depicted in the block diagram (Fig. 1). The various components have only been delivered recently. We have devoted this period to various phases of checking and debugging programs in the system. The system is now almost fully operational and some initial runs have been made.

II. (b) FUTURE ACTIVITIES

Contract activities. We have embarked upon coating of cerous polymethacrylate/polymethyl methacrylate copolymers with gradual compositional change whereby the refractive index gradient is smoothly profiled so as to minimize the transmittance loss by reflectance. The next step is to determine routinely the amount of coated cerous ions. It appears that air oxidation of cerous (III) ion to ceric (IV) renders the coated film less efficacious in inhibiting solarization. Hence, we might resort to another coatant through which oxygen is less permeable to react with the coated cerous layer. In this regard we are exploring other lanthanides and nickel ions in lieu of cerous as the downconverter. Other substrate materials are being tested, specifically polycarbonates although the coating technique is yet to be developed fully. Optical characteristics of variously coated films are now being examined, and once this phase comes to a conclusive stage, we will settle on the substrate and attending coating procedure.

The mechanical property measurements in conjunction with the solarization test will be performed, and possible rain water induced leaching of coated ions must be examined. A cost effectiveness analysis will be performed at this stage to identify the most effective combination of coatants, coating methods and substrates. Field testing of pilot-plant scale products will be carried out at different DOE installations.

III. TECHNICAL PUBLICATIONS

None at this time.

Figure 1

AUTOMATED SOLARIZATION TEST SYSTEM