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A Novel Approach to the Artificial UV Weathering of Coatings,
Plastics and Composites**

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INTEGRATING SPHERE SOURCES FOR UV EXPOSURE:

**A Novel Approach to the Artificial UV Weathering of
Coatings, Plastics and Composites**

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The primary method for obtaining laboratory weathering data for a wide range of commercial polymer products including coatings, textiles, elastomers, plastics and polymeric composites is through the use of ultraviolet radiation exposure chambers (UV chambers). Although numerous improvements have been made in the design of UV chambers over the last 80 years, the repeatability and reproducibility of the exposure results from these chambers have remained elusive. This lack of reproducibility and repeatability is attributed to systematic errors in their design, operation, and control which, in turn, have prevented comparisons of the performance of materials exposed in the same environment, comparisons of the performance of the same material exposed in different laboratories, and the comparison of field and laboratory results. This paper describes an innovative UV chamber design having a basis in integrating sphere technology that greatly reduces the magnitude of these errors, as well as provides additional experimental capabilities.

Introduction

Ultraviolet radiation exposure chambers (UV chambers) are the primary means for generating laboratory weathering data for a wide range of commercial products including coatings, elastomers, plastics and polymeric composites (collectively termed *construction materials*) (1). Over the years, numerous technical improvements have been implemented in the design, construction, and control of these UV chambers. However, the repeatability and reproducibility of the exposure results obtained from these chambers have remained elusive (2,3,4,5,6).

The repeatability and reproducibility of exposure results are affected not only by variability in material response, but also by *experimental* and *systematic* errors. Experimental errors and material variability, which are present in all experiments, are random in nature and can be compensated for through the use of proper experimental designs.

Systematic errors, on the other hand, are uncompensated, non-random sources of error which bias experimental results. Common sources of systematic errors associated with existing UV chambers include human/machine interactions, high specimen temperatures, non-uniform irradiance over the surface of a specimen, and temporal changes in exposure conditions. These errors can be minimized by standardizing test procedures, making changes in existing exposure equipment, or circumventing them through the use of alternate UV chamber designs. In this paper, known sources of systematic errors are discussed and an innovative UV chamber, based on integrating sphere technology, which may be capable of reducing the magnitude of these systematic errors, is presented. In addition, it will be shown that the use of an integrating sphere-based UV chamber allows for greater experimental capability in terms of testing conditions.

Current Laboratory UV Weathering Instrumentation

Commercially available UV chambers began to appear circa 1920. Atlas Electric Devices[†] introduced its carbon arc “Fade-O-Meter” in 1918; several years later, Nelson (7) published preliminary exposure results for a UV chamber design using a mercury arc lamp in 1922, and Buttolph (8) patented several

[†] Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

modifications to Nelson's UV chamber in 1924. UV chambers containing fluorescent lamps were introduced at a later date.

Numerous modifications in the early UV chamber designs have been made over the last 80 years. These modifications have been aimed at improving the repeatability and reproducibility of exposure results and include:

- The identification of a more temporally stable ultraviolet light source
- The identification of spectral radiant power distribution which more closely approximates the maximum solar ultraviolet radiant power (9,10,11,12), and
- The re-design of the exposure racks within a chamber to improve the spatial irradiance uniformity over the dimensions of a specimen and among specimens.

Specific examples of improvements include:

- Identification of cut-off filter combinations to remove radiation below 290 nm
- The introduction of photopic sensors and feedback-control devices for minimizing temporal changes in the radiant power (13,14,15), and
- The introduction of the three-tier exposure racks in xenon arc UV chambers.

These changes have greatly reduced the variability in exposure results, but they have not fully resolved issues related to the lack of repeatability or reproducibility (5,6).

Factors Affecting Reproducibility and Repeatability of Current UV Chambers

Common sources of systematic error found in current UV chambers include human/machine interactions, unnatural exposure conditions, non-uniform irradiance over the dimensions of a specimen and among specimens, the inability to accurately and precisely measure ultraviolet radiation dose, and temporal changes in exposure conditions. Of these sources of error, unnatural exposure conditions, non-uniform irradiance and temporal changes in exposure conditions have been targeted by NIST researchers as those which could be mitigated by the use of a novel integrating sphere-based UV chamber.

Unnatural Exposure Conditions

Xenon arc lamps are almost always operated at a higher current density than mercury arc lamps because of the smaller cross-sectional area of the xenon atom relative to that of the mercury atom (16). This high current density makes the xenon arc a very “hot source” (17,18); that is, xenon arcs emit a substantial amount of energy in the visible and infrared regions. As such, the temperature of exposed specimens has been observed to approach 60 °C (19,20).

Improved temperature control of UV chambers can be achieved by removing the primary source of thermal energy, visible and infrared radiation, while maintaining the photolytically effective ultraviolet radiation. This can be accomplished by introducing a heat controlling optical element (e.g., a dichroic mirror) between the light source and the specimen. Dichroic mirrors or filters are designed to transmit (or reflect) ultraviolet radiation through (or off of) the dichroic mirror and onto the specimens while reflecting (or transmitting) the visible and infrared portions to a heat sink.

Ultraviolet radiation with a wavelength less than 290 nm does not reach the earth’s surface (21,22); thus the presence of radiation with wavelengths below 290 nm may induce “unnatural” chemistry in materials. Efforts have been made by UV chamber manufacturers to eliminate these wavelengths by carefully researching light sources and utilizing cut-off filters. Although not a perfect match, certain grades of fluorescent lamps or xenon arc lamps equipped with borosilicate/borosilicate filters appear to be a close approximation to the solar spectrum (12).

Temporal Variation

The radiant power output from an arc source is known to be unstable over time. This temporal instability can be attributed to both equipment variables and changes in the light source as it ages (light source plus the filters).

The major equipment variable affecting radiant power output is a change in the electrical current density over time. The higher the current density, the higher the temperature of the plasma and, thus, the greater the radiant power. Also, the higher the current density, the higher the proportion of the total radiant power emitted in the ultraviolet region (23,24). Thus, temporal stability of a lamp depends heavily on the stability of the lamp power supply.

The optical properties of the arc lamps, filters (in the case of xenon arc lamps), and phosphors (in the case of fluorescent lamps) change with time through an aging process. The tungsten electrodes operate near the melting temperature of tungsten when the lamp is on, thus causing tungsten to be sputtered off the electrodes and deposited onto the interior walls of the glass

cylinder (16,25). These deposits reduce the spectral transmittance properties and eventually cause the glass envelope to devitrify and crack (23). In commercial xenon arc chambers, efforts have been made to minimize this effect by placing a metallic sleeve around the anode.

The glass enclosure surrounding the arc also ages. This can occur whenever the arc plasma touches the enclosure, causing it to melt and to deposit silicon onto the interior surface of the glass. The quartz and other glass filters surrounding a xenon arc also age through a process called solarization (26). Solarization is the reduction in transmittance of a filter resulting from the exposure to short wavelength UV radiation and to high temperatures.

Spatial Irradiance Uniformity

Ensuring spatial irradiance uniformity over the dimensions of a specimen and between specimens is a prime consideration in designing any optical system. Spatial uniformity is needed to determine the spectral ultraviolet radiation dosage received by a specimen. Spectral ultraviolet radiation dosage must be known in order to compare the performance of materials exposed in the laboratory and those exposed in the field (27,28).

Spatial irradiance uniformity is difficult to attain in current UV chambers due, in part, to the larger surface area over which uniformity must be controlled. Factors affecting irradiance uniformity include reflectance from the specimen and walls of the chamber and physical limitations imposed by the optical system (e.g., the geometry of the light source and the dimensions of the specimens). The remainder of this paper addresses a proposed solution to the problem of spatial irradiance uniformity in conventional UV chambers, through the use of an integrating sphere as a UV source.

Integrating Sphere Theory

The theory of integrating spheres, as well as their uses in a wide variety of applications, is well-established (29,30,31). An integrating sphere is a hollow spherical chamber with an inner surface coated with a diffuse reflecting, or *Lambertian*, coating. Light entering an integrating sphere undergoes multiple diffuse reflections at the interior surface, resulting in a uniform field of light within the sphere. This collected light can then serve as a means of measurement or as a source of uniform illumination. This latter function will be utilized in the novel UV weathering device.

Integrating sphere theory has its origin in the theory of radiation exchange between diffuse surfaces (32). Although the general theory can be complex, the

symmetry of the sphere simplifies the analysis. Consider the exchange of radiation between two differential elements of diffuse Lambertian surfaces A_1 and A_2 , with areas dA_1 and dA_2 as shown in Figure 1. The fraction of the total flux leaving A_1 (Φ_{A_1}) and arriving at A_2 (Φ_{A_2}) is given by:

$$\frac{\Phi_{A_2}}{\Phi_{A_1}} = dF_{1-2} = \frac{\cos \theta_1 \cos \theta_2}{\pi S^2} dA_2 \quad (1)$$

where dF_{1-2} is the exchange factor. If these two surface elements are contained inside a diffuse sphere surface, and $S = 2R \cos \theta_1 = 2R \cos \theta_2$, as shown in Figure 2, then equation 1 becomes:

$$dF_{1-2} = \frac{dA_2}{4\pi R^2} \quad (2)$$

Equation 2 is independent of the locations of the two elements and as well as the distance between the elements. This result is significant because it states that the fraction of flux received by A_2 is the same for every other point on the sphere surface.

If the differential areas dA_1 and dA_2 become finite areas A_1 and A_2 , then Equation 2 becomes:

$$dF_{1-2} = \frac{1}{4\pi R^2} \int_{A_2} dA_2 = \frac{A_2}{4\pi R^2} \quad (3)$$

Equation 3 is also independent of dA_1 , allowing it to be expressed as:

$$dF_{1-2} = \frac{A_2}{4\pi R^2} = \frac{A_2}{A_s} \quad (4)$$

where A_s is the total surface area of the sphere. Thus, the fraction of energy received by A_2 is equal to the fraction of surface area that it takes up within the sphere.

The physical significance of the previous analysis is that every point on a sphere is equally illuminated by reflections from every other point. This leads to the conclusion that theoretically, not only should the output intensity be uniform across the plane of an exit port, but every exit port should have the same spectral output as every other exit port. This property of integrating

spheres will be exploited to produce a artificial UV weathering device with improved spatial irradiance uniformity. Thus, it can be seen that the use of an integrating sphere as a uniform UV source can potentially resolve one of the major problems in current UV chamber design; that is, non-uniform irradiance across the dimensions of a specimen and from specimen to specimen.

The throughput, at a given port, of an integrating sphere with multiple ports is given by:

$$\frac{\Phi_o}{\Phi_i} = \frac{\rho f_e}{1 - \rho(1 - f_{tot})} \quad (5)$$

where Φ_i is the input flux, Φ_o is the output flux, ρ is the average sphere wall reflectance, f_e is the fraction of the sphere surface area taken up by the exit port of interest, and f_{tot} is the total fraction of the sphere surface area taken up by all of the exit ports. This equation assumes that no portion of the input flux is directly incident on any of the exit ports. It is generally recommended that f_{tot} be less than 5% if sphere output uniformity is critical. If a known input flux is known, the output flux of an actual sphere can be calculated via equation 5.

In order for the above-mentioned equations to be correct and for the successful use of an integrating sphere as an optical device, it is critical that the sphere interior surface scatter light in a perfectly Lambertian fashion over the wavelength region of interest. If the scattering is non-Lambertian, then the basic assumptions for the standard integrating sphere analysis are violated. The effects of non-Lambertian reflectance on integrating sphere measurements are presented by Hanssen (33).

In the wavelength regions of interest, namely 290 nm to 400 nm, materials which provide the greatest degree of Lambertian reflectance are based on barium sulfate powder or polytetrafluoro-ethylene (PTFE). The reflectance of pressed PTFE powder has been studied by Weidner and Hsia (34), and was measured to be > 0.98 in the region from 250 nm to 2000 nm. In recent years, a solid, machinable PTFE material has been developed with the high reflectance of the powder, but with greater durability and resistance to temperature, moisture and corrosive chemicals. PTFE maintains its reflectance indefinitely under normal laboratory conditions if not contaminated and does not need to be repacked or recoated (35). In the event that reflectance does decrease over time due to surface contamination, the material can be sanded or vacuum baked (36) to regenerate its original reflectance.

Integrating Sphere Based UV Chamber

NIST researchers are currently developing a novel integrating sphere-based UV chamber, and have procured a 2 m diameter integrating sphere. A photograph and schematic representation of the NIST 2 m sphere are shown in Figures 3 and 4, respectively. The sphere construction is based on a modular panel design, which allows individual panels to be removed for modification or repair. The interior of the sphere is lined with PTFE panels, and currently contains thirty-two 11.2 cm diameter ports, and a 61 cm diameter top port to accommodate a high intensity UV light source.

The proposed lamp system for the 2 m sphere is a microwave-powered, electrodeless lamp system with an output which is rich in the region between 290 nm and 400 nm. A multiple lamp system will be utilized, which has been calculated to provide an output greater than 50 equivalent suns (where a “sun” is defined as the integrated irradiance between 305 nm and 400 nm taken from the direct normal spectral solar irradiance distribution in ASTM G159). A multiple lamp system, in contrast to a one lamp system, allows the response of a material to various irradiance levels to be evaluated, thus providing opportunities to test the law of reciprocity.

Dichroic reflectors in the lamp housings will remove (80 to 90) % of the infrared and visible output from the lamps. In the event that wavelengths > 400 nm are predicted to be instrumental in the photodegradation of certain materials, the dichroic reflectors can be replaced with conventional reflectors, thus retaining a greater proportion of the visible spectrum. Figure 5 shows the output spectrum for the lamp system with the dichroic reflectors in place.

As was discussed earlier, due to the fact that every point on the sphere surface is theoretically equivalent to every other point, the monitoring of UV spectral intensity is quite simple. For instance, a fiber optic probe could be inserted at an arbitrary point in the sphere wall (away from the “first strike” region of the light source) and connected to a spectroradiometer to provide a measure of the spectral radiance within the sphere. Through photofeedback processing, lamp power can be continually adjusted to compensate for temporal instabilities in, and diminishment of lamp output, over time.

This design appears to be capable of mitigating most, if not all, of the systematic errors from unnatural exposure conditions and spatial irradiance non-uniformity discussed earlier. Prior to the design and fabrication of the 2 m integrating sphere, a prototype 50.8 cm sphere was utilized to determine the suitability of integrating spheres for use in artificial weathering devices. Spectral UV measurements were made in the center of two 12.7 cm diameter apertures of this sphere, a schematic of which is shown in Figure 6. Spectral output from the two exit ports for a 1000 W xenon arc source are overlaid in

Figure 7. It should be pointed out that no discernible difference in the spectral output is apparent.

In order to study the environmental durability of materials used in building and construction applications, it would be advantageous to uniformly irradiate specimens under a variety of conditions. This could be accomplished by equipping each port with a specimen chamber in which temperature, relative humidity, mechanical loading and other factors can be independently controlled.

Because each chamber is independent of the others, a multiplicity of environmental conditions can be evaluated in a given experiment. While the UV irradiance would be identical between the ports, narrow band-pass filters or neutral density filters can be installed at the exit port to study the effect of a narrow wavelength region or to adjust the intensity, respectively. For instance, it would be possible to expose a specimen at one exit port to 60 °C, 95 % relative humidity, polychromatic light; whereas, at another exit port, the specimen could be exposed to 50 °C, 95 % relative humidity, and 290 nm radiation. The capability to apply mechanical stresses to the specimens while they are undergoing UV exposure can also be achieved, as shown in Figure 8. Other unique exposure environments can also be created, including freeze/thaw cycling and acid rain.

It will be necessary to situate the specimen chamber at some distance from the integrating sphere exit port to accommodate specimens which need to undergo mechanical loading, due to the physical space taken up by the loading frame and specimen grips. In order to convey the highly uniform radiation from the sphere exit port to the above-described specimen chambers without loss of uniformity and with minimal loss in intensity, non-imaging optical devices will be utilized. Such non-imaging optical devices are also known as compound parabolic concentrators, Winston cones, and cone concentrators, and are considered to be more efficient than conventional image-forming optics in concentrating and collecting light. These devices date back to the 1960's and were once used for solar collection; a detailed treatment of this subject is given by Welford and Winston (37). A typical cone concentrator is shown in Figure 9. In the application at hand, they will be used to collimate the diffuse output from the sphere exit port to within 20° and transfer it to the specimen surface.

Summary

UV chambers play an important role in comparing or predicting the performance of construction materials and determining the effect of different weathering factors on the performance of a construction material. Although significant modifications have been made in current UV chamber designs,

controlling the systematic errors and thus the repeatability and reproducibility of these chambers has remained elusive. An integrating sphere UV chamber design is being developed which appears to be capable of mitigating known sources of systematic errors. Assuming that the sphere is properly designed and that the UV lamps are correctly integrated, uniform irradiance across the dimensions of a specimen and from specimen to specimen is assured by integrating sphere physics.

The improvements offered by an integrating sphere UV chamber over conventional weathering instrumentation are summarized as follows:

- Simplicity in design and easy accessibility to the light source, exposure cells and specimens.

The light source, exposure cells, and specimens are located on the exterior of the integrating sphere and, thus, they are readily accessible even while an experiment is in progress.

- Removal of visible and infrared radiation from the radiant flux

High specimen exposure temperatures can be minimized by removing most of the visible and infrared portions of the radiant energy flux emitted by the light source prior to entering the sphere. By removing most of the visible and infrared radiation emitted by the light, the temperature within the chamber can easily be maintained at slightly above room temperature.

- Removal of radiation below 290 nm.

By positioning a cut-off filter after the dichroic mirror, radiation below 290 nm can be removed from the radiant flux. Moreover, interference or cut-off filters can be positioned in front of each specimen so that each specimen can be uniquely irradiated using any combination of wavelengths.

- Spatial irradiance uniformity.

As a uniform radiation source, an integrating sphere is capable of minimizing errors due to non-uniform irradiance over the dimensions of a specimen and from specimen-to-specimen. Spatial irradiance uniformity does not depend on the light source, the age of the light source, or batch to batch variability, but, instead, it is controlled by the physics of integrating spheres.

- Temporal irradiance monitoring and control.

Temporal changes in the spectral radiant intensity of the light source can not be controlled. Through the use of the integrating sphere, however, temporal variations can be easily spectroradiometrically monitored. This is

possible because the radiant power within the integrating sphere remains uniform and, thus, changes in the radiant power can be easily monitored.

- Experimental Flexibility
Finally, use of an integrating sphere provides the opportunity to simultaneously and independently expose a multiplicity of specimens each to its own exposure environment. This can be achieved by positioning specimens in individual exposure cells and uniformly irradiating the specimens by projecting the output from the exit ports with the use of non-imaging optical devices. The environmental and operating conditions within each exposure cell can be uniquely selected.

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