Solarization of Short-Wave Filters

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INTRODUCTION

For more than 50 years short-wave (SW) ultraviolet (UV) filters have been used with germicidal lamps [low pressure mercury arc lamps] in UV light assemblies (UV lights), see Warren (1983). These UV lights are what we FMS members use to fluoresce or "lamp" our SW minerals. The amount of UV radiation that a given filter can transmit decreases with exposure time by a process called solarization. The actual chemical process of solarization is beyond the scope of this article, but see Rentschler (1945 a, b), Baynton and Moore (1954), White and Silverman (1958), and Koller (1952). A glossary of terms is included at the end of this article.

Figure A shows the spectral transmission for a "common" SW filter (dotted line). Figure A also shows the mercury wavelengths and relative intensity of the emission lines generated by a typical germicidal [low- pressure] lamp. About 80 to 90% of the energy in low pressure mercury arc lamps is at the 253.7nm wavelength. The purpose of the SW filter is to absorb all the visible light [between about 400nm to 750nm] while freely transmitting the SW UV. Even though most filters transmit red to deep red light, from 650nm to 750nm, the germicidal lamp does not produce any significant light at these wavelengths, with the exception of some lamps dull red glow of the lamp filaments [cathodes]. It should be pointed out that there are <u>at least</u> five interrelated characteristics [excluding cost] that are necessary qualities for a good SW filter: (1) high initial transmission of SW UV [at 253.7nm], (2) slow solarization rate, (3) minimum transmission of visible light, (4) good physical characteristics [it does not break easily or cloud up with humidity, etc.], and (5) the need to be producible at an commercially acceptable yield rate [if only every other glass batch was any good the yield would not be acceptable]. Technology is not advanced enough to permit the manufacture of SW filters that optimize all of these characteristics. A perfect filter might have a spectral transmission that would be zero at 220nm, reach a peak of 100% at 253.7nm, and decrease to zero at 290nm. No commercial filter comes close to that. Note that most filters do not reach their peak until 300nm or 310nm. And for most SW filters the 253.7nm transmission is only 60 to 75% when <u>new</u>!

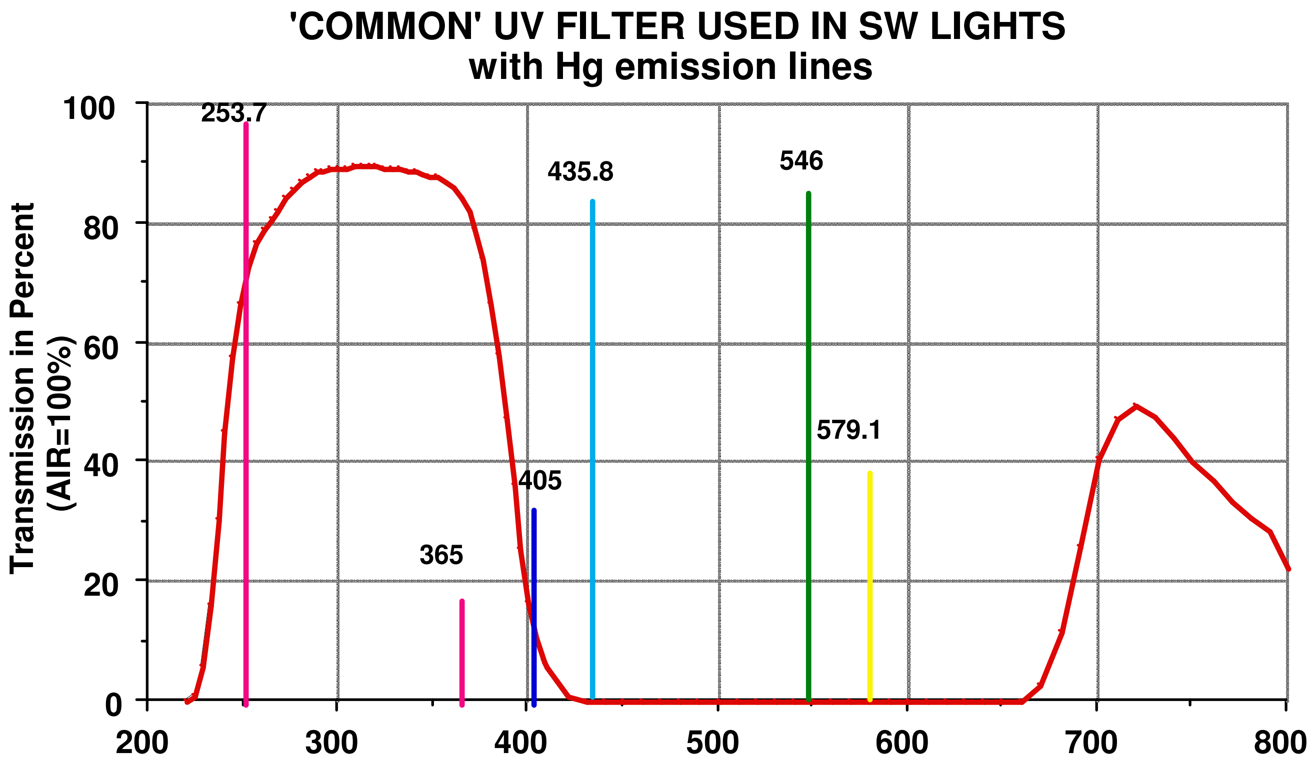


FIGURE A

In 1984 I noted that some manufacturers of UV lights advertise that their SW filters would solarize less (last longer) than "other" brands of SW filters. I thought that it might be a good idea to determine which brand of SW filter would last the longest. In 1985 a FMS Research Committee was formed to conduct "Solarization Experiment 1985". The committee members were: Mr. Richard Bostwick of Metuchen, NJ; Dr. Eugene Foord of Golden, CO; Dr. Gerhard Henkel of Baden-Baden, West Germany; Dr. Warren Miller of Neshanic Station, NJ; Dr. Peter Modreski of Littleton, CO; Mr. George Nelson of Milan, PA; Mr. Manuel Robbins of Cherry Hill, NJ; Dr. Earl Verbeek of Golden, CO; and I as the research coordinator. The committee formed a test plan, the objective which was to determine quantitatively the effects of SW UV on the transmission characteristics of SW filters currently available.

Nine manufacturers of UV light assemblies and/or filters were requested to donate at least three (preferably seven) samples of their SW filters for this experiment. Several samples were requested to increase the probability that the filters might be from different glass batches, and therefore be more representative of each company's "typical" filter. Five companies responded with samples: Corning Glass Works, with their #9863 filter; Hoya Optics, Inc. with their U-325C filter; Raytech Industries, Inc.

with their Color Blaze filter; Schott Glass Technologies, Inc. with their UG 5 filter; and UVP, Inc. with their UVG filter. After the test it was learned that both Raytech and UVP obtain their filters from Hoya Optics, Inc.; however, that does not assure that the formulation for the Color Blaze and UVG filters is exactly the same as the U-325C filter. Hoya manufacturers their filters in Japan and Schott Glass Technologies obtains their filters from Schott in Mainz, West Germany. When the test started Corning made there filters in Corning, NY, but since then they have sold their process and formulation to Kopp Glass of Swissvale, PA. Kopp is using the Corning formulation in their #9863 glass.

TEST PLAN AND TEST PROCEDURE

A solarization jig (Figure B) was constructed to expose the test filters. Two 30-Watt germicidal lamps were used as the source for the UV radiation. The 30-W lamps were operated for over 340 hours prior to the experiment so that rates of solarization of the glass tubes of the lamps would have slowed, thereby ensuring relatively constant output throughout the tests. The jig was designed so that the area where the filters were to be placed would be uniformly flooded with UV radiation. The average energy level during the tests was approximately 3.6 mW/cm^2 at 254nm, and for the majority of measurement increments ranged from 2.95 to 3.79 mW/cm^2. This is comparable to approximately half the level that a filter would be exposed to in a typical 6-Watt UV light. The jig was periodically adjusted to bring the UV lamps closer to the filters to compensate for solarization of the germicidal lamp glass and thus to keep exposure rates approximately constant. A model UVX radiometer was used to monitor the output of 254nm radiation from the lamps for adjustment of the jig.

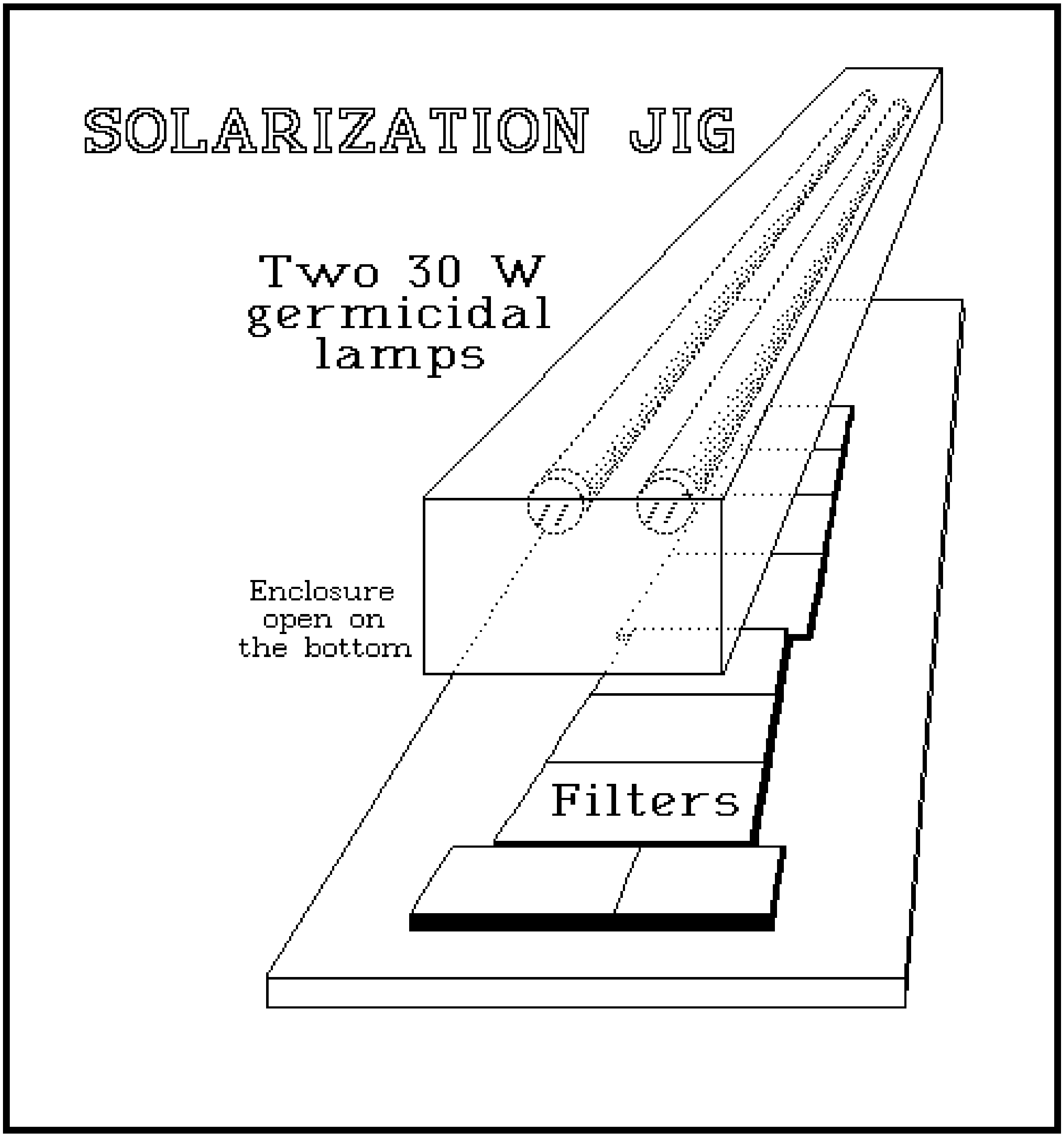


Figure B

To ensure a blind test, a neutral technician had the large samples cut into suitable sizes and inscribed a random alpha-numeric code on each filter. He then sealed the key to the filter code for the duration of the experiment [the tests were completed on Aug. 27, 1987 and the key was opened Jan. 23, 1988]. When the filter codes were revealed, it was discovered that more UVP filters had been included in the experiment than from the other companies. This was a result of the blind test selection process.

A custom-built portable carrying case was made to transport the filters from the solarization jig to the spectrophotometer lab. Each filter had its own identified padded slot in the carrying case.

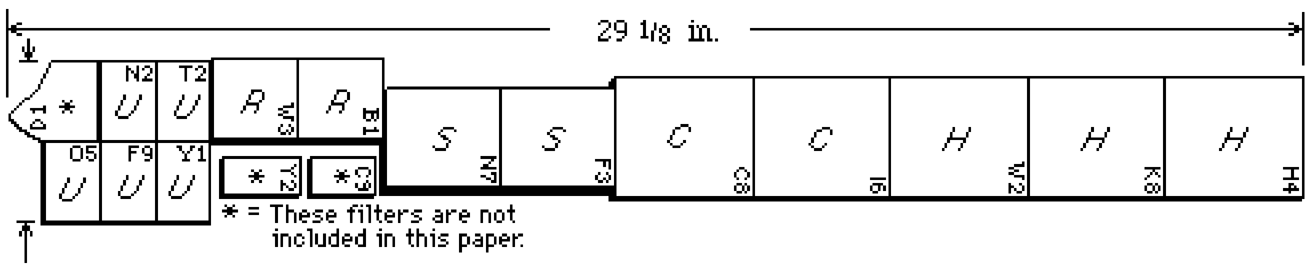
Transmission measurements were made with a Perkin-Elmer double-beam, double-monochromator, ratio recording, Lambda 9 UV/VIS/NIR spectrophotometer. This spectrophotometer is owned, operated, and calibrated by the Boeing Materials Technology department of the Boeing Commercial Airplane Group. The planned measurement intervals, in hours, of SW UV radiation at 253.7nm were: initial, 1, 2, 4, 8, 16, 24, 48, 72, 96, 120, 240, 500, 1000, 1500, 2000, and 2500. In addition, spectral transmission measurements from 200nm to 800nm were to be made at: initial, 24, 120, 500, and 2500 hours. The actual times of measurement were reduced because of restricted use of the spectrophotometer. Four elapsed-time meters were used for redundancy to record the filter exposure times.

After each filter was inscribed with the unique alpha-numeric code, its size was measured and the surfaces visually described (Table 1). A micrometer was used to measure the thickness of each filter. Then, for each filter, spectral transmission measurements were made from 200nm to 800nm, and percent transmission measurements were made at exactly 253.7nm. Throughout the tests, each filter was inserted in the spectrophotometer sample holder the same way, facing the deuterium UV energy beam. The filters were wiped clean before all measurements and were handled only with lint-free lab gloves.

During the reference measurements, tests were made to determine the magnitude of short-term variations in the measurements due to diffusion of radiation from unpolished sample surfaces and due to instrument drift of the spectrophotometer. To investigate the first effect, three different filters were repeatedly measured in the spectrophotometer at different locations and orie-ntations in the sample chamber. Since the optics of the spectrophotometer provide nearly collimated light which passes through the sample chamber, unpolished surfaces of some filters could affect the readings. As expected, the filters with unpolished rough surfaces caused the most variation in the readings, as much as ±1.95%, while the smooth or polished filters caused a variation of ±0.98% or less [usually less than ±0.5%]. These variations were considered acceptable for the type of measurements in the tests, where transmission reductions of 25% or more were to be measured over time. The short term repeatability of the spectrophotometer was determined by repeated measurements of several filters, with each filter held in a constant position and orientation. This uncertainty is ±0.09%.

For each set of transmission measurements the standard attachment on the spectrophotometer had to be removed, and the transmission attachment had to be installed. Thus, the system had to be recalibrated each time measurements were taken. Consequently, a set of five non-exposed control filters was used to check the long-term repeatability of the spectrophotometer. Transmissions at 253.7nm of the control filters were measured at five different times. The measurements indicated that the spectrophotometer's long-term variability was not a problem.

A sketch was made of the layout in the solarization jig so that the filters were placed in the same location for each exposure time interval, with the code mark facing up, towards the UV lamps (Figure 1).



First Test Set - 2016 total hours

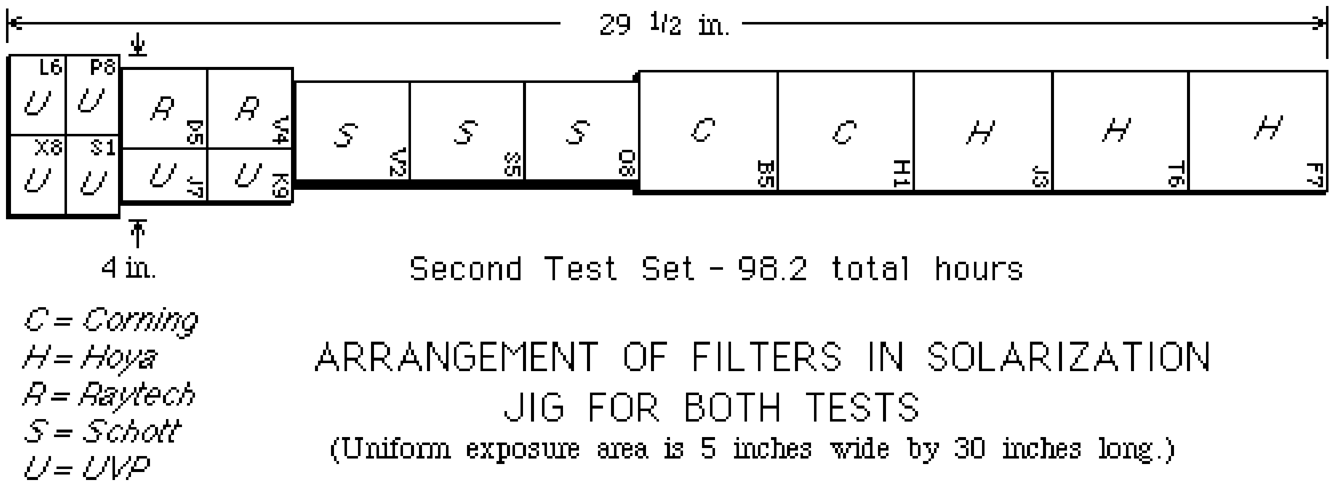


Figure 3

<u>First Test Set</u>

Forty-five samples were available for this experiment. This was more than the jig could accommodate, and testing of this many samples would have taken more spectrophotometer time than was available. Accordingly, the first test set was limited to 17 filters, the maximum that could be placed beneath the exposure area of the lamps at one time. The test results for three of the filters (those parked with an asterisk in Figure 1) are not included in this paper because no additional control samples were available, and the origin of the manufacturer was in doubt. To increase the chance that at least two samples from each company would be included in the test, it was assumed that filters of similar size and texture were from the same company (of course, this gave no indication which company the filters came from). When the sealed code was opened after the tests, it was confirmed that those of similar size and texture were indeed from the same company (Table 1).

Transmission measurements at 253.7nm were made at: initial, 1, 4, 16, 48, 98, 242, 500, 1006.7, 1510, and 2016 hours. Spectral transmission measurements from 200nm to 800nm were made at: initial, 16 and 98 hours, and from 200nm to 500nm at 500 and 2016 hours.

<u>Second Test Set</u>

In order to check the results of the first test, a second set of filters was tested. It was thought that relatively short exposure times would suffice to confirm the results; accordingly, the second set of filters was exposed for a total of 98.2 hours.

The second test set had 16 samples. As in the first set, the filters were grouped by size and texture with the intent of including at least two filters from each company. The measurement intervals were: initial, 1, 4, 16, 50, and 98.2 hours. No spectral transmission measurements from 200-800nm or 200-500nm were made on the second batch because of lack of spectrophotometer time.

RESULTS

The ideal SW filter would have a high initial transmission at 253.7nm and a low solarization rate. These two characteristics are not necessarily related. Excluding surface reflections, the thickness and the glass formulation are the two characteristics which principally determine the transmission at 253.7nm and absorption in the visible range.

This experiment did not test whether or not the different solarization rates were influenced in part by the varying thicknesses of the filter samples. Table 2 shows the calculated and measured filter transmission for both actual and calculated thicknesses, including calculated percent 253.7nm transmission at initial and end-of-test, for five thicknesses representing all five companies. Table 2 shows that even though the thicker filters had less initial transmission, the solarization is a function of the manufacturer (formulation).

The results of the experiment are displayed in the graphs of Figures 2, 3, and 4. Because of the different thicknesses of the filter samples, all the plots are based on percent transmission at 253.7nm, where the initial transmission is taken as 100%. Table 1 shows the thickness of each filter sample. Figure 2 plots the transmission vs. time of all the filters in the first test set grouped by company for a test duration of 2016 hours. Figure 3 shows the plots of all the filters in the second test set grouped by company for a test duration of 98.2 hours. Figure 4 shows the average performance for all the samples of each company.

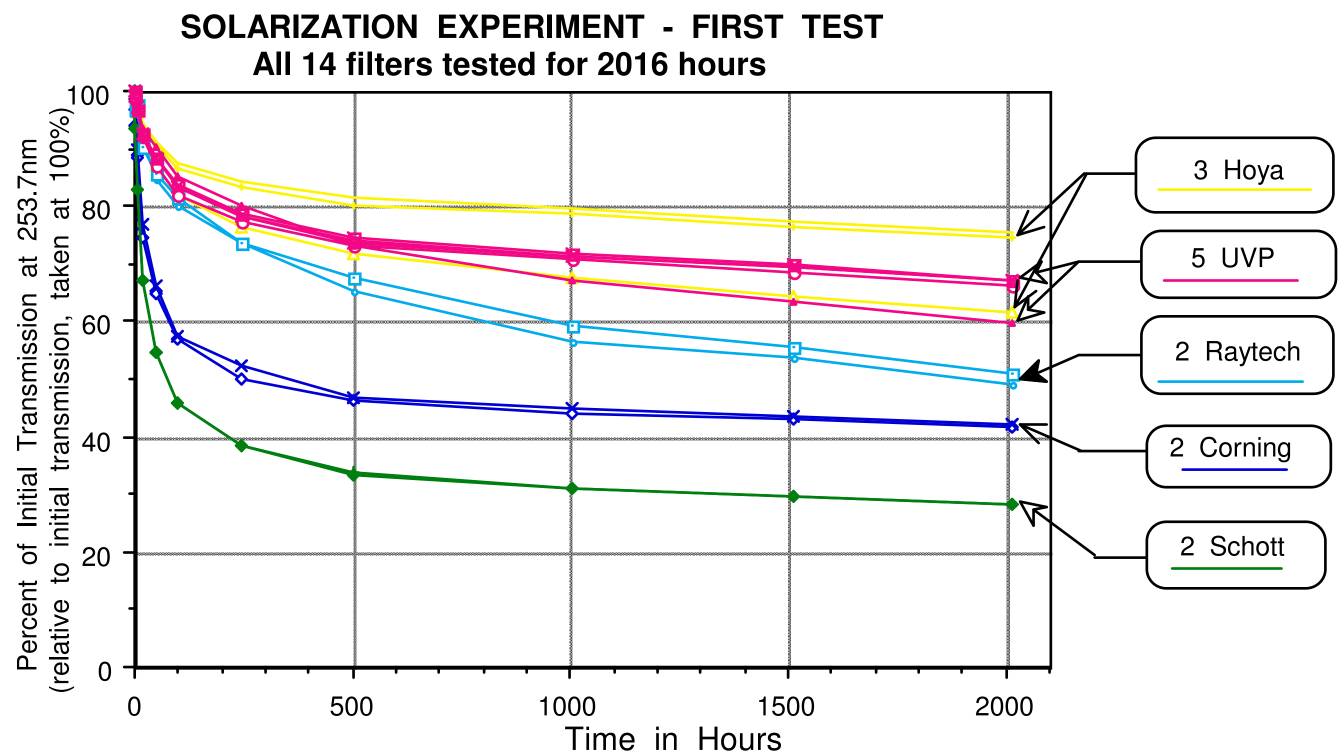


FIGURE 4

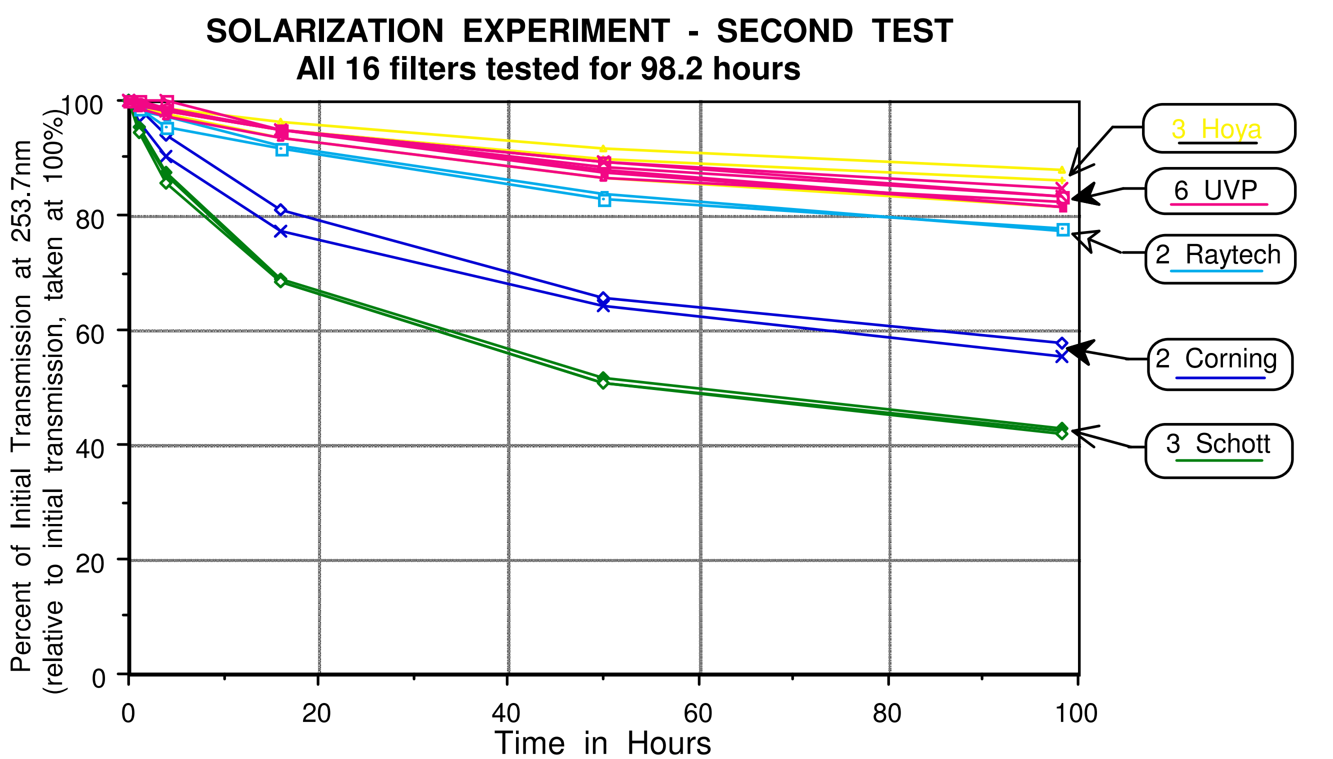


FIGURE 5

Figure 4 shows the result of thirty samples, with at least four samples from each company. Of the six samples of U-325C filters from Hoya Optics, Inc. all but two show the lowest rates of solarization in this experiment. These six U-325C filters also had the highest average transmission at 253.7nm during the entire duration of the solarization tests.

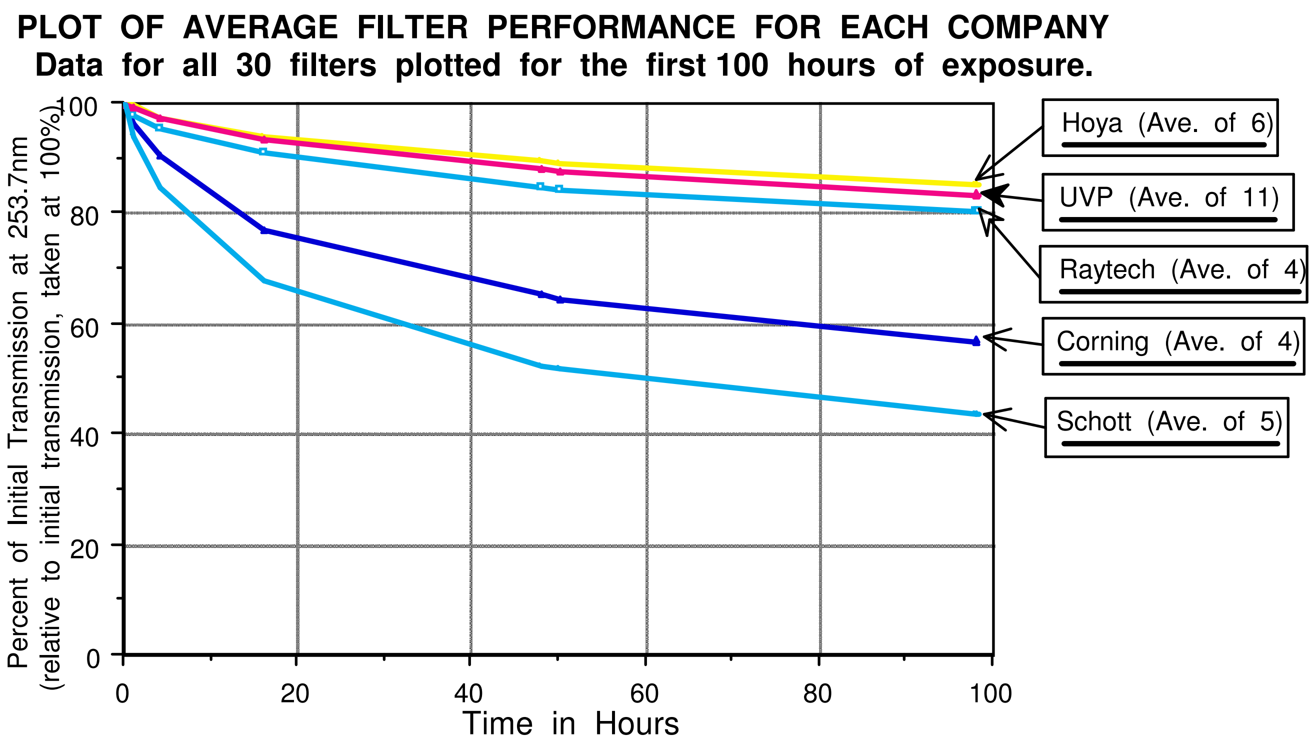


FIGURE 4

Data Sheet 1 shows the percent of initial transmission and the absolute measurements for the first test set. Data Sheet 2 shows corresponding transmission data for the second test set. The first table on each data sheet shows the percent of initial transmission relative to the initial transmission (which is equated to 100%), and the second table on each data sheet shows the absolute percent transmission (where transmission through air=100%) vs. time. The initial transmission is arbitrarily taken to be 100% for purposes of charting relative percent decrease. The data from the second test confirms the first test when both are compared for the first ninety-eight hours of exposure. Filters P8, J7 and B1 in the Data Sheets show small inconsistencies; however, they are minor and well within the tolerance limits of the spectrophotometer and the experimental procedure.

An interesting feature of this experiment was determination of the effect of solarization on the spectral transmission of the filters through the entire UV range, the LW UV included. Figures 5 through 9 show spectral transmission curves for one filter from each of the five companies. The plots show the transmission from 220nm to 405nm plotted at initial, after 98 hours, and after 2016 hours exposure. Some filters show the greatest change at the shorter wavelength, while others show a gradual change across the UV range. The fact that the solarization affects the transmission of some filters from 220nm all the way to about 400nm was not expected. All the samples exhibited negligible visible transmission from 420 to 650nm. All filters had significant transmission in the deep red to near-infrared with a peak transmission of 42% to 64% in the 715nm to 720nm range. The visible red to near-infrared transmission (660nm to 800nm) of the filters is not affected by UV solarization.

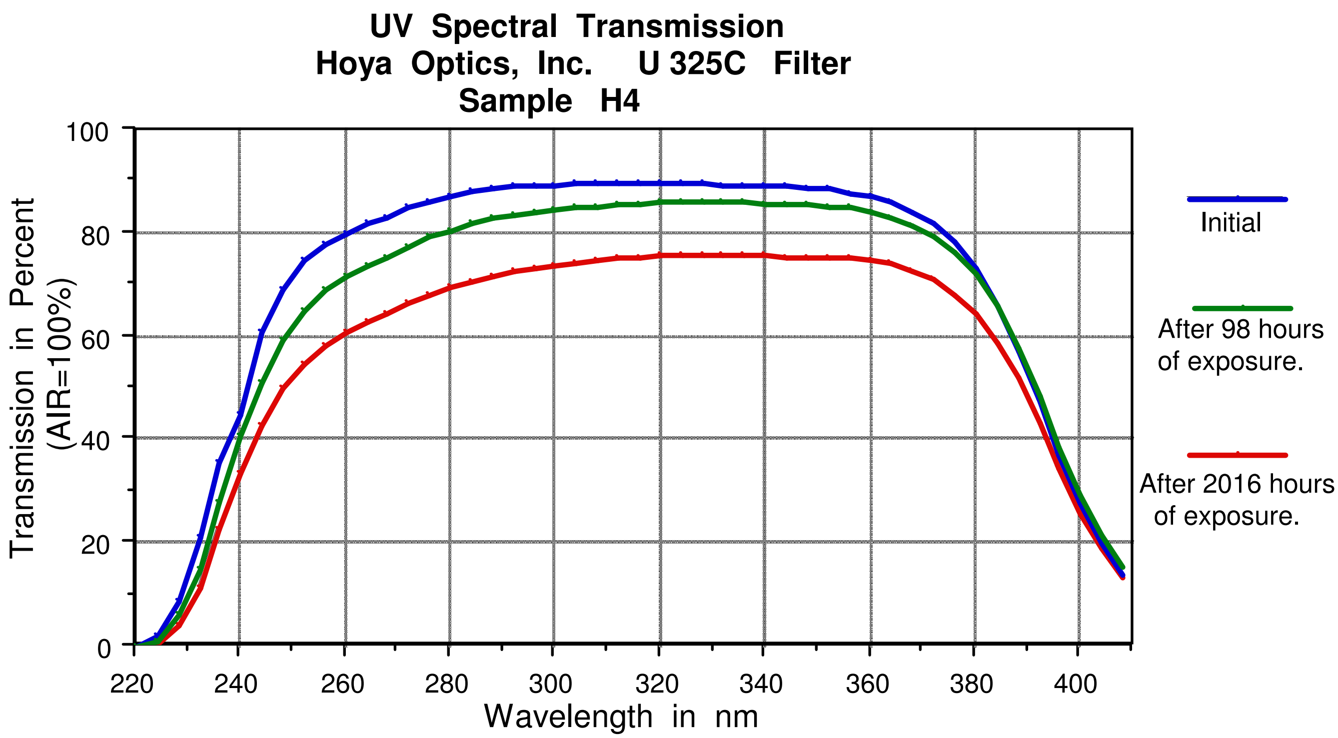


FIGURE 5

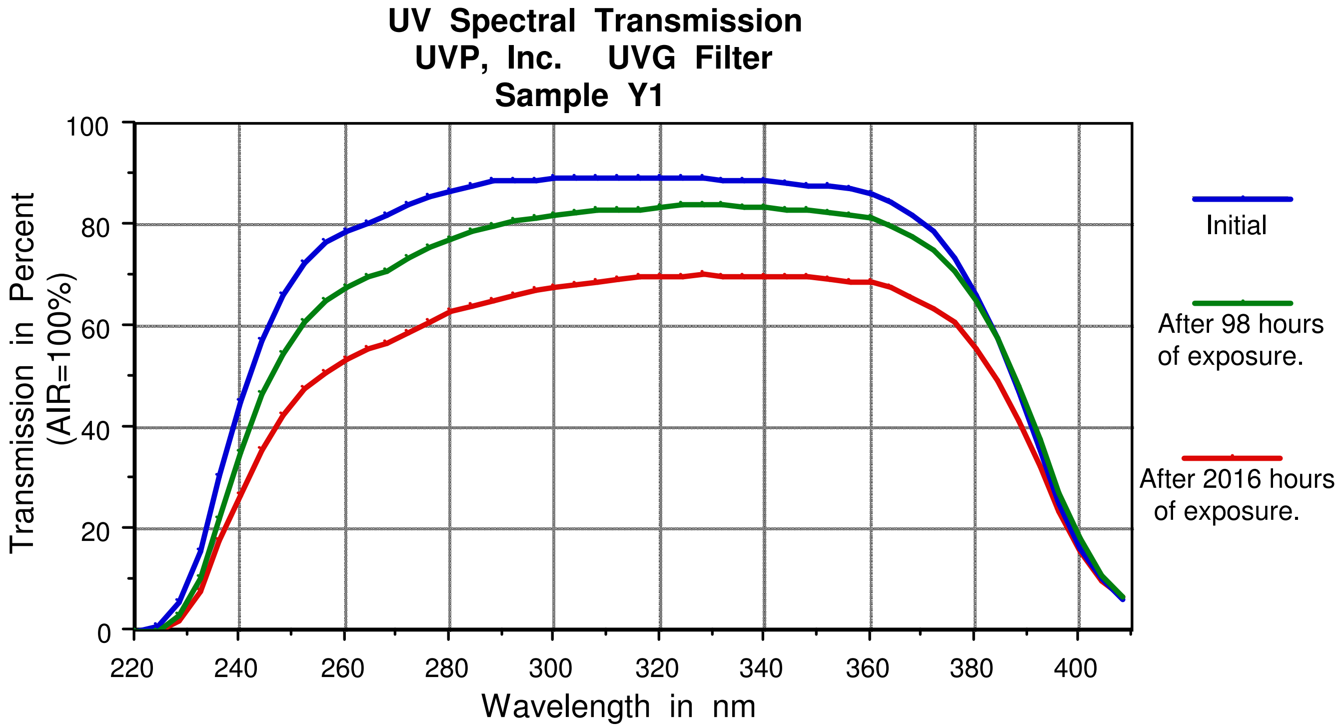


FIGURE 6

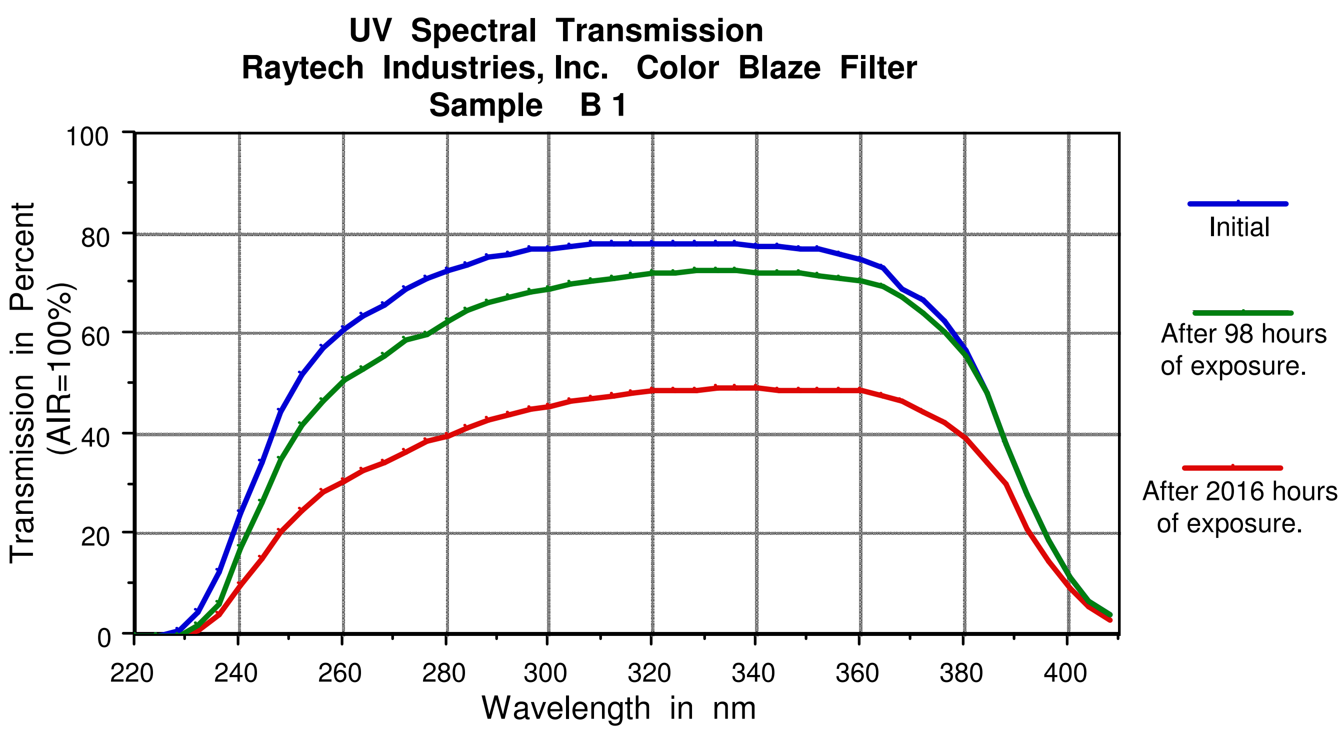


FIGURE 7

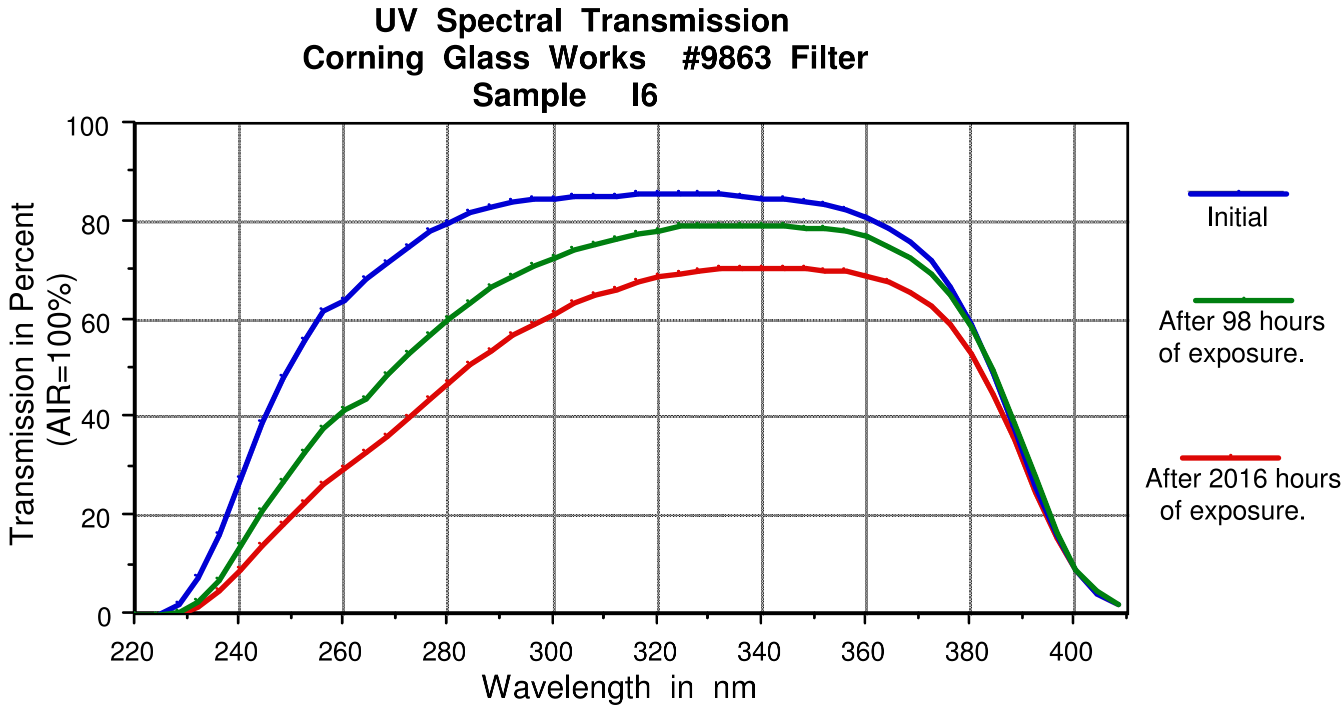


FIGURE 8

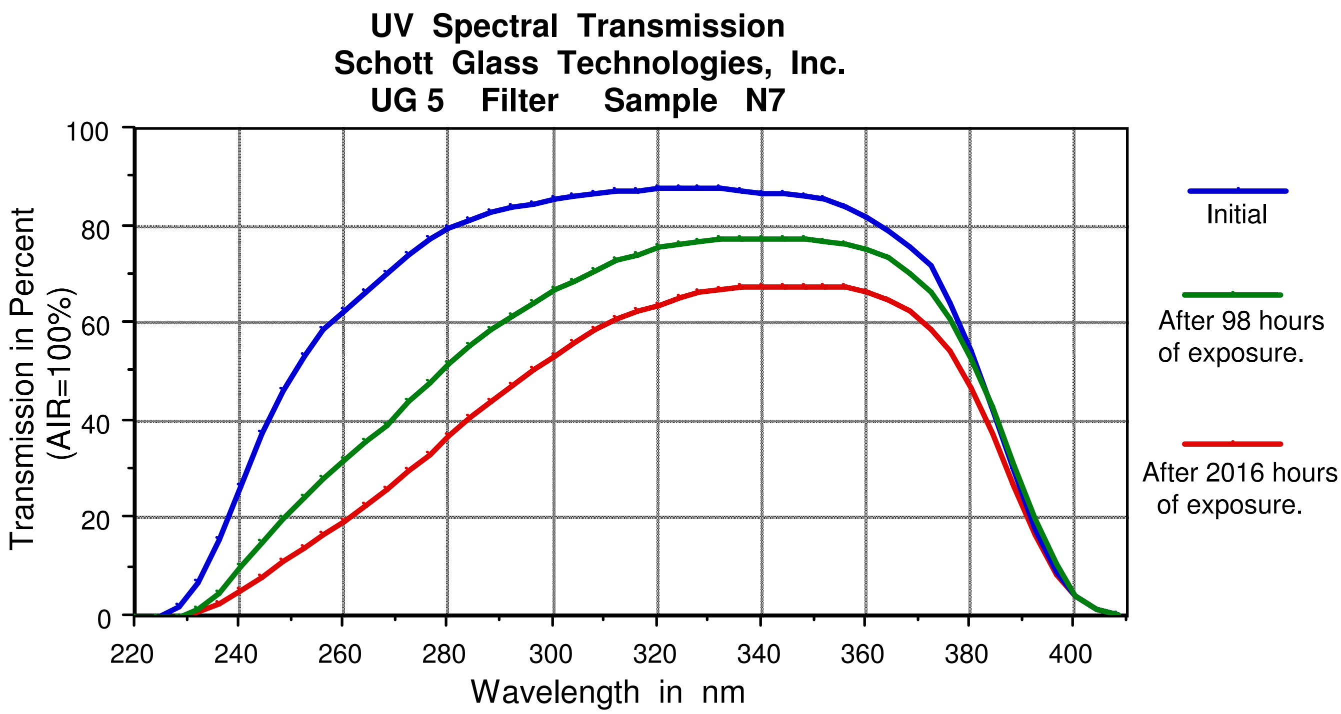


FIGURE 9

DISCUSSION

As with any experiment, there are limiting conditions that should be noted. The filter samples were obtained over a period of time from Oct. 1985 to May 1986. Variations in performance among individual filters from the same source could be caused by differences between different batches of filter glass. It would not be reasonable to expect the manufacturing process for each supplier to remain static; the formulation for a specific filter type may be modified from time to time and this could alter performance. With this in mind, one could expect that the SW filters available on the market today might solarize at a rate somewhat different from the samples tested in this experiment.

Still other areas that should be researched include how physically deep into the filter the solarization occurs (at least one source , Koller [1952], indicates that the solarization occurs only near the exposed surface) and explaining the long-term effects of thermal rejuvenation of solarized filters, (Corning Glass Works, 1948). These and other areas will have to be left to other investigators since the Boeing Lambda 9 spectrophotometer is no longer available.

CONCLUSIONS

The Hoya U-325C filters for the most part lasted longer than any of the other filters tested.

The radiation levels in this experiment, though only about half that of a typical 6-Watt light, nevertheless caused a very rapid decrease in transmission at 253.7nm. Significant solarization of some filters was evident after only one hour of exposure to 3.6 mW/cm^2 SW radiation. For these or similar filters the solarization rate could be determined in less than 100 hours of exposure to a SW UV source of at least 3 mW/cm^2.

As shown in Figures 5 through 9, the solarization causes a decease in the spectral transmission not just in the SW UV range, but in Middle and Long Wave ranges as well.

ACKNOWLEDGMENTS

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GLOSSARY

400nm - 750nm = Visible light.

200nm - 280nm = Short Wave ultraviolet light, UV-C.

280nm - 320nm = Medium Wave ultraviolet light, UV-B.

320nm - 400nm = Long Wave ultraviolet light, UV-A.

Germicidal lamp = A mercury arc lamp that produces short wave ultraviolet radiation, usually concentrated at 253.7nm wavelength.

Hg emission lines = The UV and light energy from a mercury arc. The energy from the arc does not form a continuous spectrum but instead is concentrated at discrete wavelengths; these are the emission lines of the arc.

Spectral transmission = The transmission of a material, usually a glass, over a range of wavelengths, commonly shown as a plot of wavelength along the x axis vs. percent transmission along the y axis.

Spectrophotometer = A device that measures the transmission of light through objects (the filters in this experiment) at specific wavelengths; most results are shown in this paper as plots of spectral transmission.

Solarization = A chemical process in some materials (in this case, glass filters) caused by light energy that results in a decrease in transmission.

UV radiometer = A device that measures the amount of UV radiation falling on the radiometer (similar to a light meter except it measures only UV radiation).

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