STABILITY AND IMPROVEMENT OF HOSHINO-YOSHIDA FILTERS

by

WILLIAM HOWARD TOBEY

B. S., Kansas State University, 1960

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1962

TABLE OF CONTENTS

INTRODUCTION

In recent years, a need has developed for a low-cost, easily-produced filter capable of transmitting radiation in the 2500-2700A range, particularly for isolation of the mercury (Hg) 2537A line in the output of a low-pressure Hg lamp. Specifically, such a filter is desired in the areas of sensitized fluorescence, shock front radiation, ultraviolet (uv) exposure, and information transmission through the use of uv radiation.

Hoshino and Yoshida (1) published the first information concerning the filter to be discussed in this paper. The method of construction was tedious but resulted in a polyvinyl alcohol film which was dipped in a water-base iodine dye to achieve the finished form. Later work by investigators (4) at Kansas State University produced improvements in the production techniques and filter quality. Soon after the publication of these results, a group (3) at Bowdoin College found that the transmission characteristics of these filters were not stable over a period of time when exposed to the radiation from a low-pressure Hg lamp. They found that the filters broke down and transmitted unwanted radiation in the visible range.

With this information, the project to be discussed herein was initiated with two goals in mind. First, a study of the time-varying characteristics was to be made and, second, attempts were to be made to improve the stability and transmission characteristics of the filter.

APPARATUS AND PROCEDURE

Sylvania type G4T4/1, 4 watt low-pressure Hg germicidal lamps producing the Hg line spectrum were used in all measurements. A study of the intensities of the spectral lines in the 2500-7000A range indicated that the major lines were located at 2537A, 3132A, 3650A, 4047A, 4358A, and 5460A. Therefore, only those six lines were used in the transmission analysis of the filters.

The laboratory apparatus was designed to satisfy two basic requirements. First, the amount of radiation received by every filter in a given time had to be a constant to make comparison of the time-varying characteristics possible. Second, the transmission measuring system had to be set up so that every time a filter was placed in the system, the same filter area would be exposed to the measuring beam in the same position.

The following method was used to accomplish constant irradiation. To obtain uniform radiation sources, the G4T4/1 lamps were used for irradiating only after they had been operated at full power for twenty hours to insure stability in outputs. These lamps were then enclosed in shields having $\frac{1}{2}$" by 1" light ports in the middle of each side as shown in Plate I, Fig. 1.

To insure constant filter position with respect to a light port, several identical filter holders were made to receive the filter samples in the form of $1\frac{1}{4}$" diameter disks. The filter holders were made from two 1.5 cm. lengths of 1/8" wall, $1\frac{1}{4}$" outside diameter brass tubing. The filter sample was placed between the ends of the two cylinders and an external bracket made from $1\frac{1}{4}$" inside diameter brass tubing held them together as shown in Plate I, Fig. 2. When assembled, the holder and filter formed a solid unit which permitted safe, easy handling of the filter.

Brackets were placed next to the lamps so that each exit port lined up with the center of the end opening in the adjacent filter holder. The holder

EXPLANATION OF PLATE I

Fig. 1. G4T4/1 Hg lamp in shield showing position of light ports

Fig. 2. Filter holder assembly

PLATE I

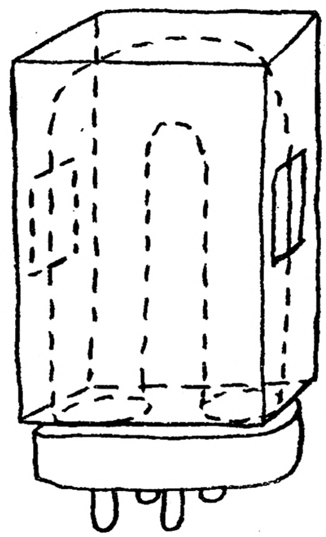


Fig. 1

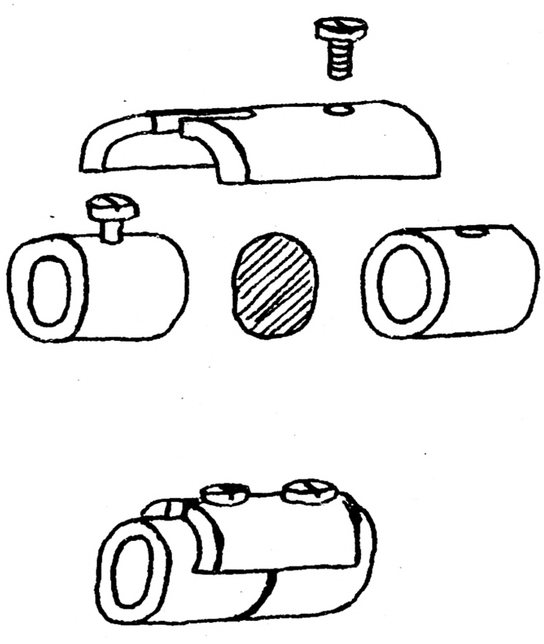


Fig. 2

supporting bracket was a $1\frac{1}{4}$" inside diameter half-cylinder which, with the $1\frac{1}{4}$" inside diameter half-cylinder on the holder, completed the cylinder surrounding the $1\frac{1}{4}$" outside diameter cylinders in the holder. This insured reproducible positioning of each holder every time it was placed in its support bracket. Marks were used on the holders to indicate which ends were to be placed toward the lamps.

The lamps were supplied with power from identical commercial ballasts. A fine adjustment, 10 ohm potentiometer was placed in the current-carrying leads in every lamp circuit to compensate for minor differences between individual power supplies. Meters were used to determine the operating voltage and current which were held at 40 volts and 250 milliamperes respectively.

The transmission measuring system operated in the following manner. A beam of light from a G4T4/1 lamp was alined to fall on the entrance slit of a Bausch and Lomb 500 mm. grating monochromator which was used to separate the different wavelengths of radiation in the beam. A detector consisting of a 1P28 photomultiplier tube was placed in a fixed position at the exit slit of the monochromator. The 1P28 was connected to a Photovolt model 520M photometer which supplied power to the 1P28 and gave metered readings of the 1P28's output.

To obtain a percent transmission reading for a filter at a given wavelength, the monochromator was first set at this wavelength. An intensity reading, I_1, was taken with no filter in the input beam. The filter was then placed in the beam and a second intensity, I_2, was read. Then I_2/I_1 times 100 gave the percent transmission for the filter at the given wavelength. A determination of the linearity and reproducibility of transmission percentages derived from the photometer data indicated that all percentages had uncertainties of less than 0.5 percent.

A rigid bracket held both the source of the measuring beam and the filter holder such that the same area of the filter was always placed in the same position in the measuring beam.

RESULTS

Initially, the earlier work at Kansas State University was successfully reproduced. The filters were made by dissolving 5 gm. of commercially available polyvinyl alcohol powder in 50 ml. of distilled water at room temperature. This produced a milky solution. To dissolve the powder completely, it was necessary to warm the solution to 60-65°C. This clear solution was then poured on a clean, level glass plate and allowed to dry, the drying taking approximately 24 hours. A dye solution was prepared by dissolving 2 gm. of potassium iodide (KI) and 1 gm. of iodine (I) in 100 ml. of distilled water at room temperature, the KI being necessary to produce a solution in which the I was soluble.

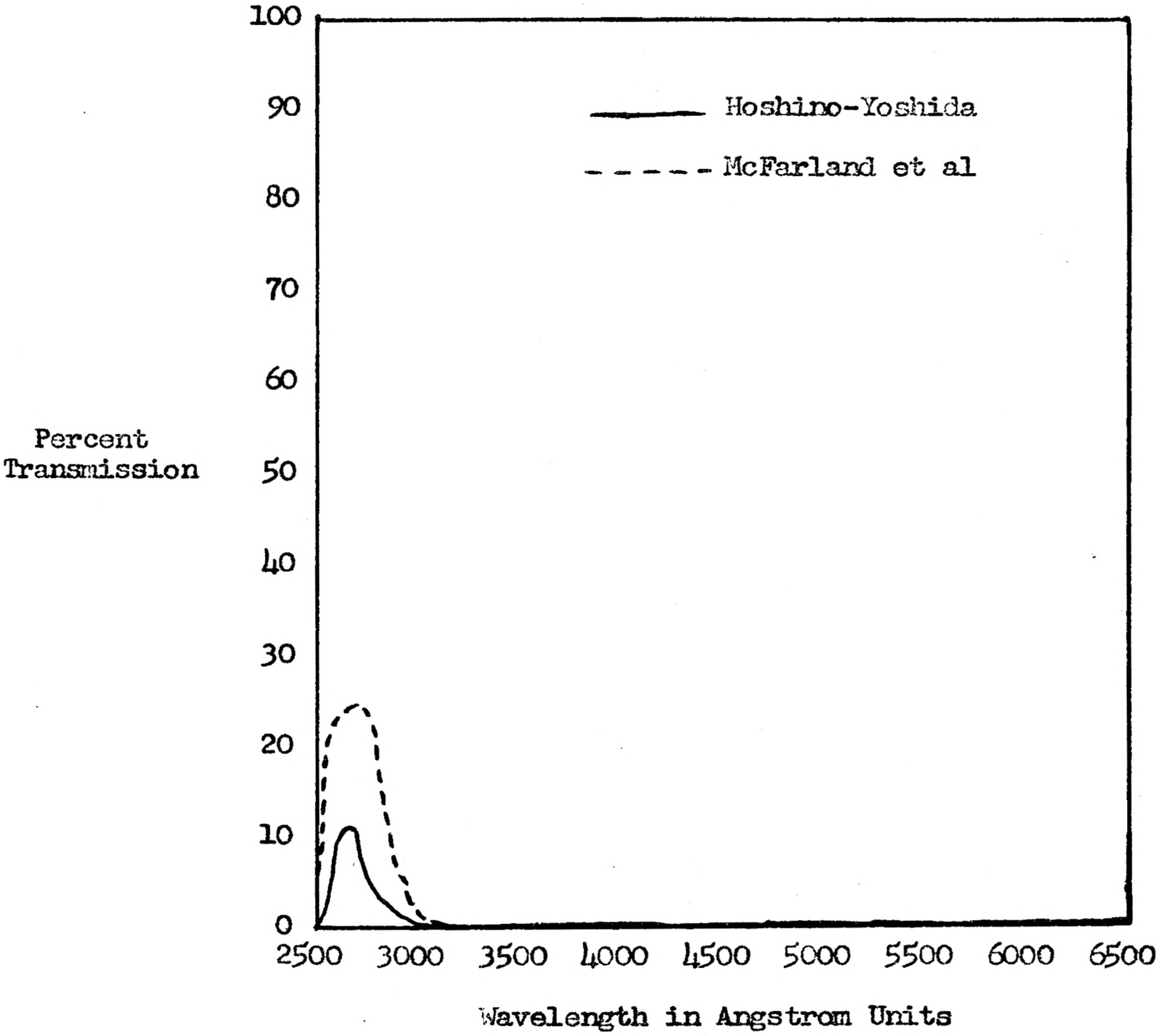
When the film, about 0.25 mm. thick, was dry, it was peeled off the glass. A piece of the film was then dipped in the dye for a few seconds, then hung up to dry. Due to the method of dyeing, uniform filter quality was difficult to achieve. However, these filters did have better transmission characteristics than the earlier Hoshino-Yoshida filters, as seen in Plate II, primarily as a result of the use of the purer commercial polyvinyl alcohol powder.

The Bowdoin College group used these newer filters and exposed them to G4T4/1 radiation long enough to obtain data of the type shown in Plate III.

EXPLANATION OF PLATE II

Initial transmission characteristics of Hoshino-Yoshida type filters

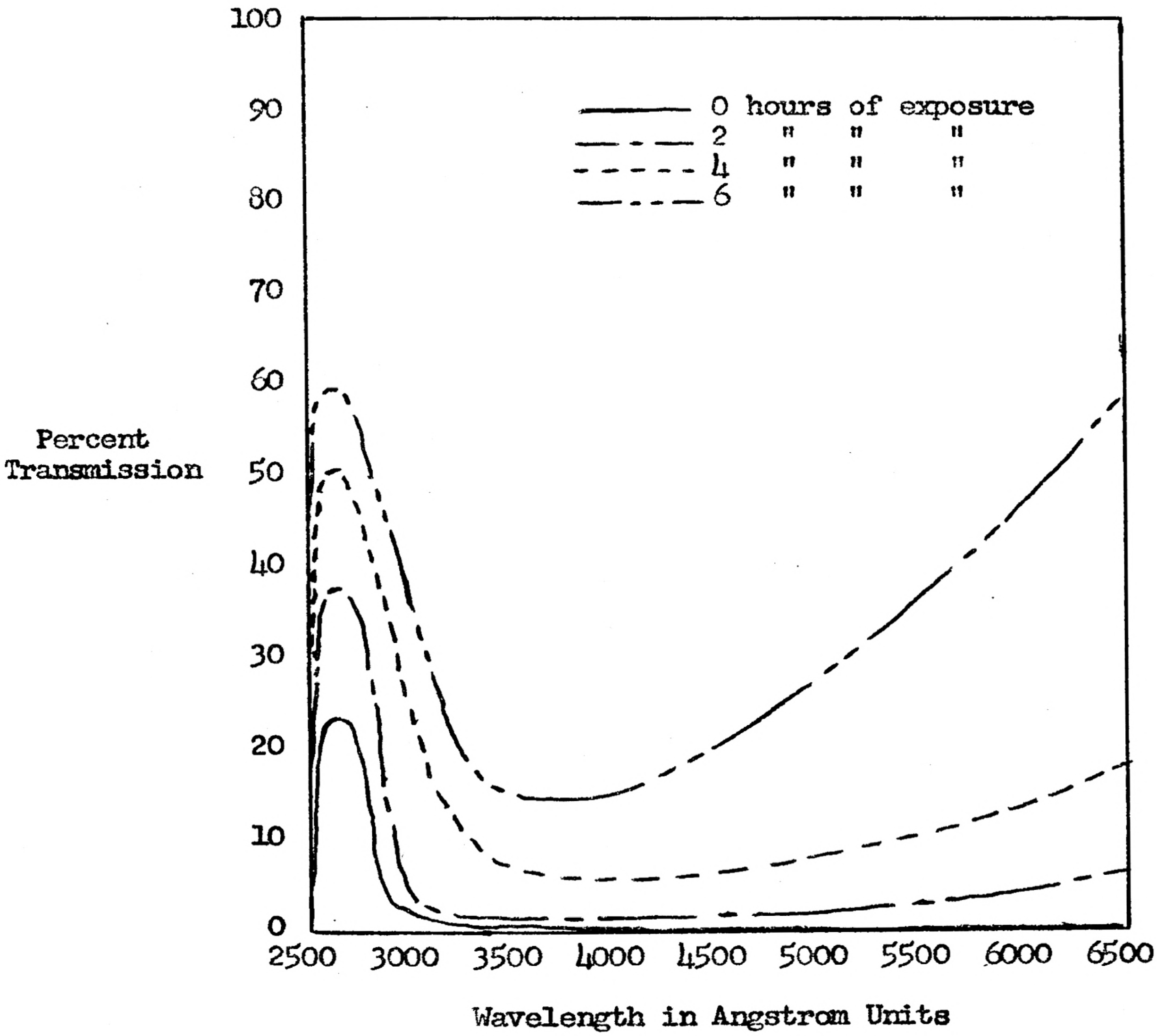
PLATE II


Hoshino-Yoshida
McFarland et al
Percent
Transmission
100
90
80
70
60
50
40
30
20
10
0
2500 3000 3500 4000 4500 5000 5500 6000 6500
Wavelength in Angstrom Units

EXPLANATION OF PLATE III

Time-varying filter characteristics of the type reported by the Bowdoin College investigators

PLATE III



100
90
80
70
60
50
40
30
20
10
0
Percent Transmission
0 hours of exposure
2 " " "
4 " " "
6 " " "
2500
3000
3500
4000
4500
5000
5500
6000
6500
Wavelength in Angstrom Units

The initial transmission increase was in the uv range but later the visible transmission increased rapidly. These observations were duplicated in work on this project.

At this point, a different method of plotting the data was adopted in which the percent transmission was plotted versus time for the various wavelengths. This produced graphs of the type shown in Plate IV.

Since use of the filters was being planned for future projects, a standard plan of filter classification was necessary. A good dip-dyed filter had initial 2537A transmission of 20-25 percent while the transmission of the other major lines ranged from 0.1 to 2.0 percent. In this group of undesirable lines, the 5460A transmission was not the largest initially but it was always observed that exposure to G4T4/1 radiation brought about more rapid change in the 5460A transmission than in the transmission of the other undesirable lines. This effect can be seen in Plate III. Thus irradiation produced rearrangement in the undesirable lines with respect to percent transmission in such a manner that the 5460A line eventually had the greatest percent transmission in this group. Therefore, the 2537A line and the 5460A line were chosen as the key lines for filter comparison.

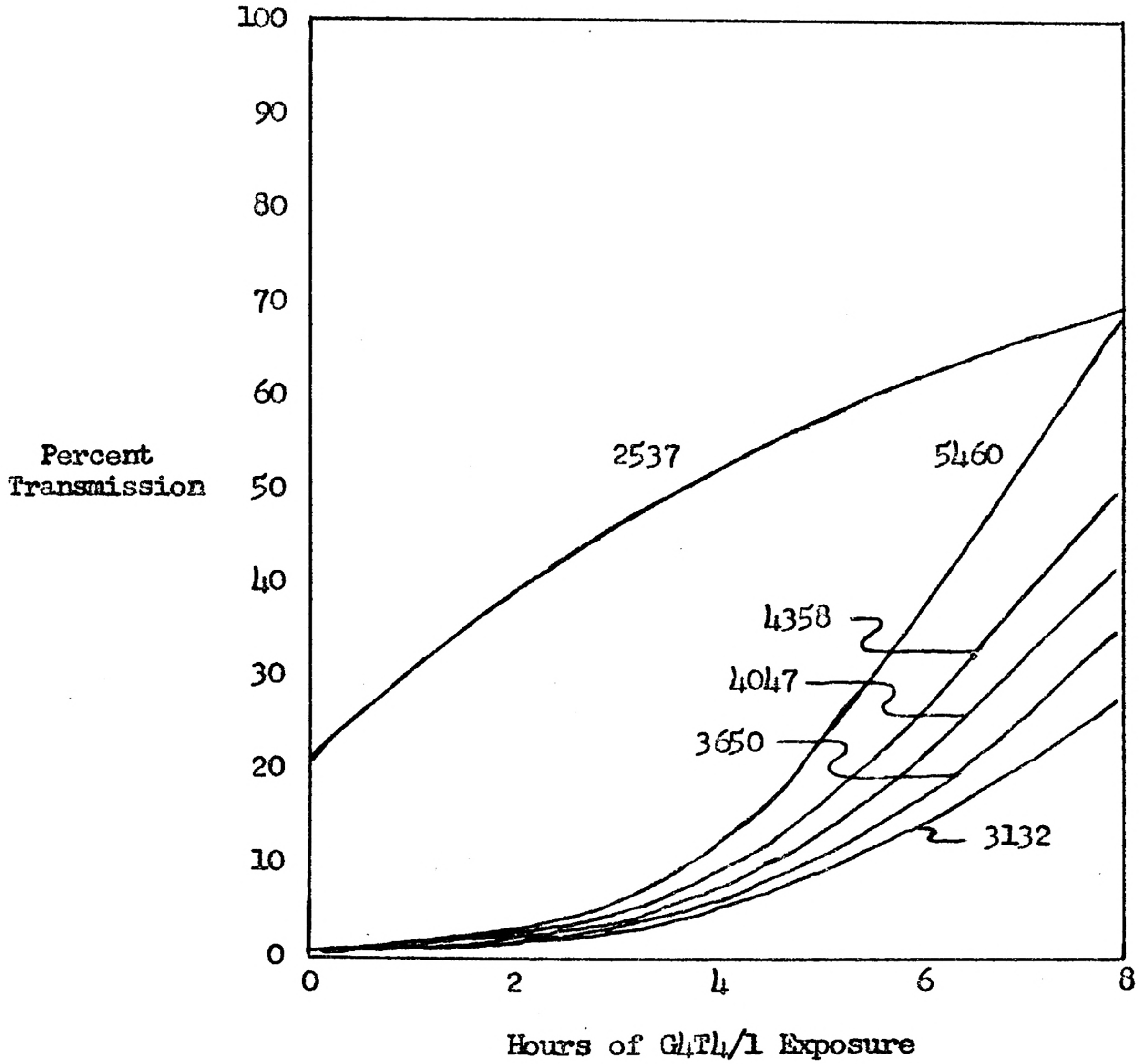
It was decided that an effective filter should transmit no more than 1.0 percent of the 5460A radiation. The transmission of the other unwanted lines ranged from 0.2 to 2.0 percent, depending on initial dye density, when the 5460 transmission reached 1.0 percent. With this filter comparison method, it was sufficient to plot only the 2537A and 5460A transmissions versus time.

Many filters of the dip-dyed type were made with varying degrees of dyeing, the density of dyeing being controlled by the duration of the dyeing time. These filters were irradiated as described previously and their trans-

EXPLANATION OF PLATE IV

Typical filter instability data

PLATE IV


Percent Transmission
100
90
80
70
60
50
40
30
20
10
0
2537
5460
4358
4047
3650
3132
0
2
4
6
8
Hours of G4T4/1 Exposure

mission percentages were measured hourly. 2537A and 5460A transmission curves from several typical filters are illustrated in Plate V. It was observed that the greater the dye density in the filter, the lower the percent transmission of all lines. Also, greater dye density resulted in slower rates of change in the transmission characteristics. There were apparent upper limits to the transmission of the 2537A and 5460A radiations of about 70 percent and 90 percent respectively.

In all of the filters tested, the rim portion which was shielded from the radiation by the filter holder did not alter its appearance along with the rest of the filter. During the irradiations depicted in Plate V, the filters changed from deep purple to light brown in color.

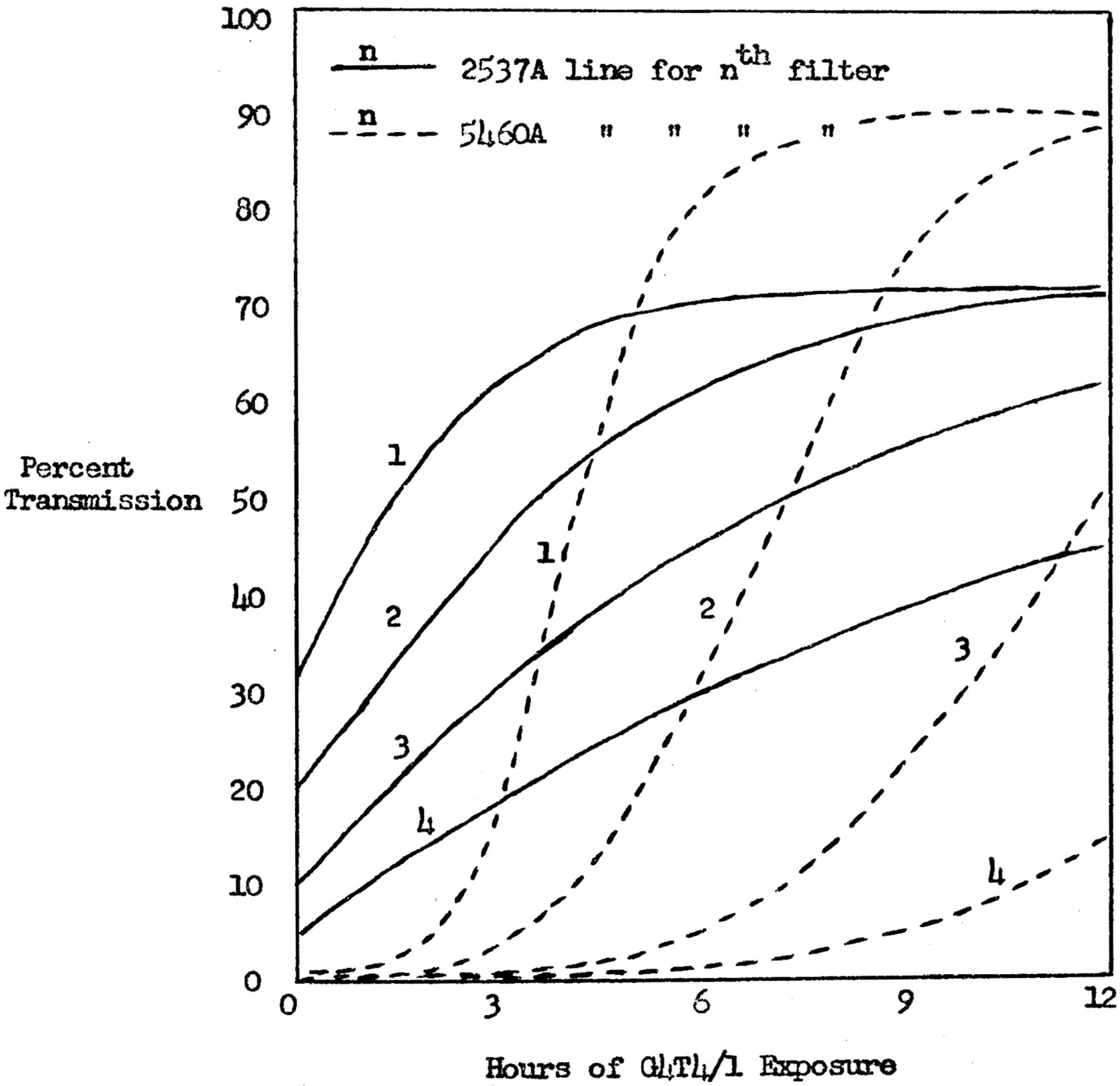
Knowing that the characteristics of the polyvinyl alcohol film itself must be included in the total filter effect, a study was made of the effects of the G4T4/1 radiation on the clear film. Plate VI illustrates the short term and long term effects of such irradiation. It was seen that the G4T4/1 radiation produced a sharp initial increase in the percent transmission of 2537A radiation by the clear film alone. The long term decrease in 2537A transmission will be discussed later but it can be noted that much longer irradiation times than those used with the filters so far were necessary to produce the decrease.

The difference between upper transmission limits for the two lines in Plate VI helped to explain the difference in these limits for a dyed filter. The rapid initial change in 2537A transmission by the clear film under G4T4/1 radiation also provided insight into why the 2537A transmission of a dyed filter increased much more rapidly initially than did the 5460A transmission of the dyed film. It was apparent that this disparity was due to a change in

EXPLANATION OF PLATE V

Transmission curves for the 2537A and 5460A lines for four different dip-dyed filters

PLATE V



100
90
80
70
60
50
40
30
20
10
0
Percent Transmission
n 2537A line for n^th filter
n 5460A " " " "
1
2
3
4
1
2
3
4
0
3
6
9
12
Hours of G4T4/1 Exposure

EXPLANATION OF PLATE VI

Fig. 1. Short term effects of G4T4/1 radiation on clear polyvinyl alcohol film

Fig. 2. Long term effects of G4T4/1 radiation on clear polyvinyl alcohol film

PLATE VI

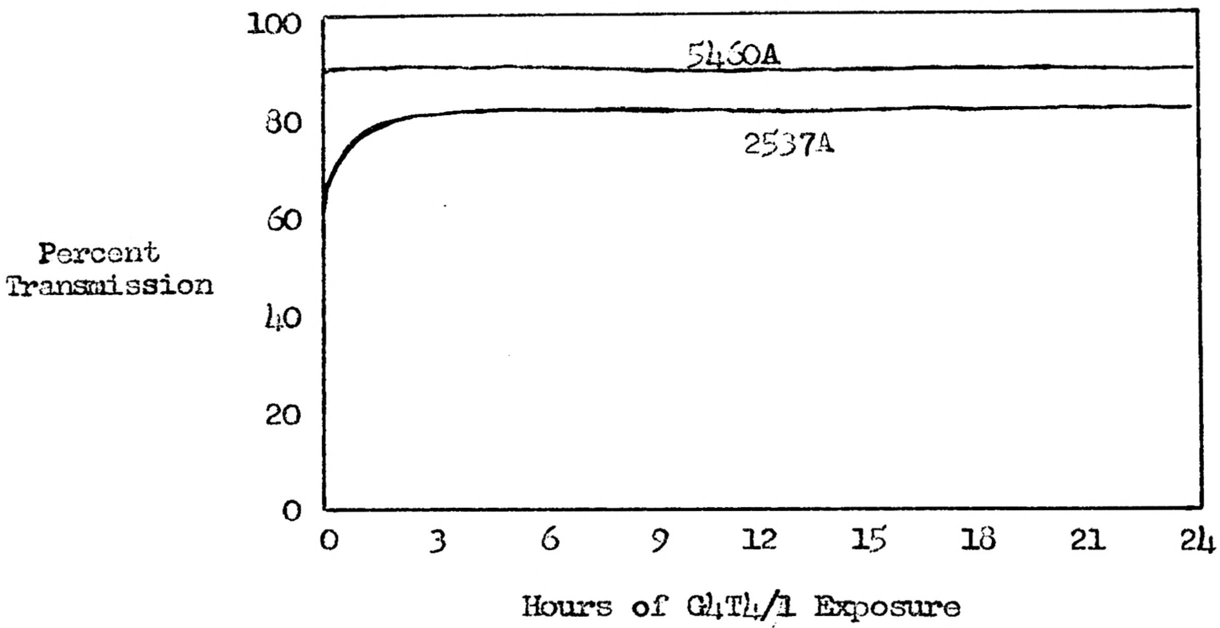


Fig. 1

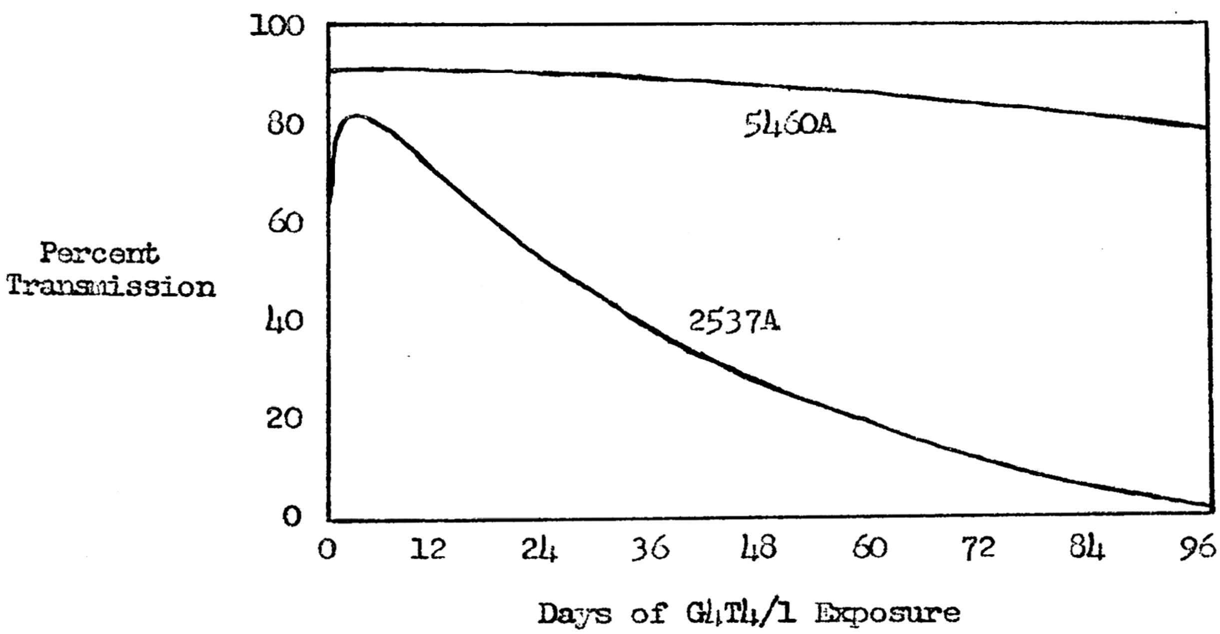


Fig. 2

the basic film itself.

Thus far, the radiation effects had been studied only under total radiation from G4T4/1 lamps. It was found that if ordinary glass was placed between the lamp and the filter, the filter showed no appreciable change over a period of hours. Since the glass effectively did not transmit wavelengths shorter than 3800A, it was established that the uv radiation was responsible for major changes in the filter.

Next, the effect of heat on the filters and clear film was examined. The exposure was accomplished by standing the filter holder, with filter or clear film inside, on end for one minute on a hotplate at 180°C. The holder was allowed to cool to room temperature and transmission measurements were made, followed by another heat exposure. The results of the heat treatment on a filter and clear film are given in Plate VII. This data indicated that heat absorption plays a significant role in the changes observed in the filters. In particular, the 2537A transmission plotted in Plate VII, Fig. 1 showed that the long term 2537A transmission decrease under lamp irradiation shown in Plate VI, Fig. 2 was a heat effect.

It was noted that a G4T4/1 lamp supplied heat to a filter being irradiated. In addition, the lamp furnished uv radiation which was capable of producing important initial changes in the 2537A transmission of the film itself. When this uv effect on the 2537A transmission was combined with the heat effect shown in Plate VII, Fig. 2 with due compensation for the slower rate of heat transfer from a lamp as compared with the rate from a hotplate, it was found that the result was in good agreement with the result obtained by lamp irradiation alone.

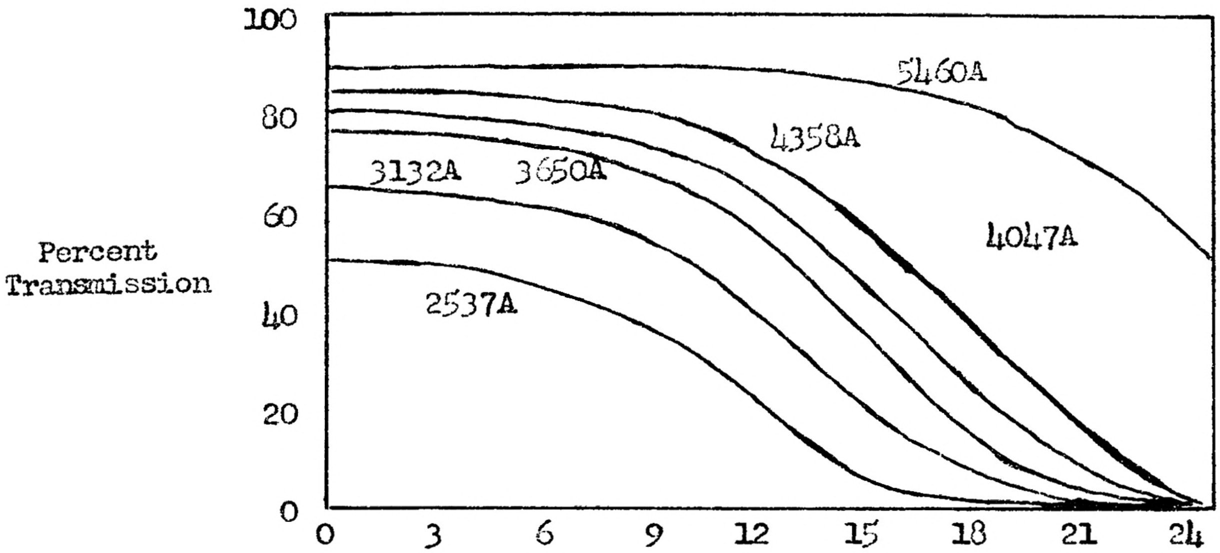
The color changes observed in the filter during heat treatment agreed

EXPLANATION OF PLATE VII

Fig. 1. Effect of heat on clear polyvinyl alcohol film

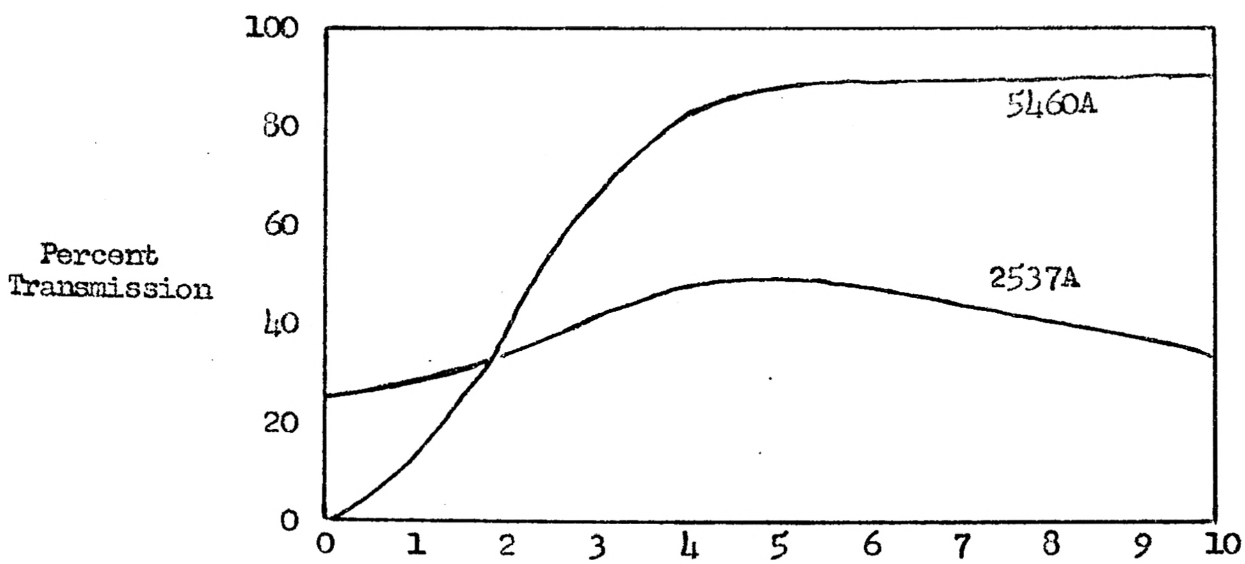
Fig. 2. Effect of heat on dip-dyed filter

PLATE VII



Number of One-minute Exposures at
1.5 cm. from 180°C. Hotplate

Fig. 1



Number of One-minute Exposures at
1.5 cm. from 180°C. Hotplate

Fig. 2

with the color changes observed during lamp irradiation.

Therefore, the conclusion was reached that the net effect of lamp irradiation was due to the uv effects on the film base combined with heat effects on the dye and film base.

With the data accumulated up to this point, it had become possible to predict accurately the behavior of the dip-dyed filters when exposed to lamp radiation. All of the filters behaved in the manner shown for any of the four filters in Plate V. The magnitudes of the transmission percentages varied with the dye density but the general form was always the same.

At this stage of the project, it was decided attempts should be made to make the filter more stable while using the same materials. In examining the filter construction method, attention was centered on the dyeing process. The dip-dyeing took a matter of a few seconds and the conclusion was reached that the dye could be expected to be concentrated on the surfaces of the filter. Therefore, a more uniform dye distribution was sought.

The attempt led to a pre-dyed filter which had greater stability but similar characteristics when compared with the dip-dyed filter. The method for making the pre-dyed filters was as follows. To insure maximum clarity in the finished filter, the polyvinyl alcohol was sifted through a 50-mesh screen to remove lumps. Five grams of this powder was then mixed in a beaker with 50 ml. of distilled water, forming a milky solution. This solution was stirred constantly and warmed in a thermostatically controlled water bath to 60°C. to achieve a clear solution. Dye was prepared by completely dissolving 2 gm. of KI and 1 gm. of I in 200 ml. of distilled water at room temperature. 50 ml. of this dye was added to the 50 ml. of warm water-polyvinyl alcohol solution with stirring utilized to achieve a uniform solution.

The 100 ml. of solution, then at 40°C. due to the addition of the 20°C. dye, was then poured onto two 14" by 14" squares of level plate glass at room temperature and allowed to spread freely. The solution became more viscous as it cooled on the glass and hence the two squares furnished sufficient area. At the time of pouring, the solution had a light yellowish-green color. As the material cooled on the glass, it passed through shades of green and blue and arrived at its final shade of deep purple in a few minutes.

The wet filters were not moved for 24 hours while they dried in the laboratory atmosphere which was reasonably dust-free. Any tilting during drying would result in wrinkles in the finished filter. After two days, the filters were peeled from the glass and analysis began in the same manner as used on the dip-dyed filters.

Many combinations of the above ingredients were tried before the given formula was reached. It should be noted that a finished filter's transmission characteristics are very sensitive to minor changes in the above formula. However, each combination produced a filter having a different dye density and this seemed to correspond to changing the dyeing time in the dip-dyed filters. Thus there was an abundance of pre-dyed filters to compare with the earlier filters.

The first improvement noted in the pre-dyed filters was that, for any given initial dye density, i.e. for any given level of initial 2537A transmission, the time rate of change of a pre-dyed filter was about one-half the rate observed in a dip-dyed filter exposed to the same rate of irradiation. Thus better dye distribution resulted in greater stability.

In the dip-dyed filters, it was observed that all filters having initial 2537A transmission at or below 23 percent had 5460A transmission at or below

1.0 percent. In the pre-dyed filters, all filters with 2537A transmission at or below 28 percent initially satisfied the 1.0 percent maximum limit on 5460A transmission. Thus the pre-dyed filters had a better initial characteristic in the ratio of 2537A transmission to 5460A transmission.

In all lamp-irradiated filters, both dip- and pre-dyed, the very slow initial change in 5460A transmission was observed. Thus if this transmission was below 1.0 percent initially, it would stay there for a period of time while the 2537A transmission increased. A comparison was made between the dip- and pre-dyed filters in which the initial 2537A transmission percentage was plotted versus the 2537A transmission percentage at the time when the 5460A transmission reached 1.0 percent. The latter 2537A percentage was called the maximum effective limit for the filter in that further irradiation would lift the 5460A transmission above 1.0 percent and the filter would fall into the ineffective category. The above comparison is illustrated in Plate VIII. Due to initial 5460A transmission greater than 1.0 percent in the dip- and pre-dyed filters, the curves have cutoffs at 23 percent and 28 percent respectively on the abscissa. This comparison pointed out another advantage of the pre-dyed filters which was their ability to achieve higher 2537A transmission before 5460A transmission reached 1.0 percent.

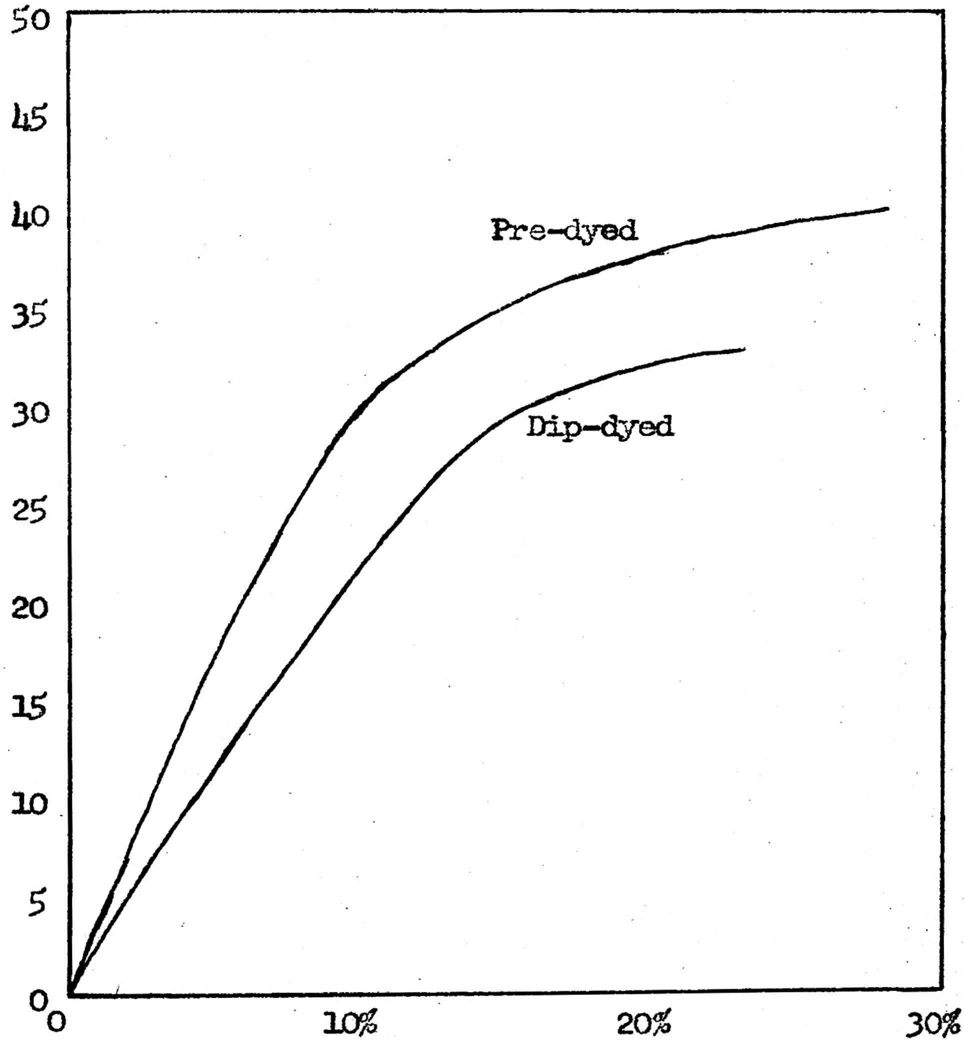
Since heat had been identified as a major agent in the filter changes, attempts were made to irradiate the filter at reduced temperatures. The first arrangement involved operation of the irradiating system and filter at room temperature and at -20°C. for alternate three hour intervals. The rate of change of the filter proceeded normally with no observable slowing during the periods of cooling.

A filter was then irradiated alternately at room temperature and in air

EXPLANATION OF PLATE VIII

Comparison of maximum effective limits of dip- and pre-dyed filters

PLATE VIII



Percent Transmission of 2537A radiation when 5460A transmission reaches 1.0 percent

Initial 2537A Transmission

cooled to the temperature of liquid nitrogen, approximately -190°C. The rate of change of characteristics when chilled was roughly one-half the rate observed at room temperature.

It has been reported (2) that polarizers could be made by iodine-dyeing a stretched polyvinyl alcohol film. This method was confirmed and two other alternate techniques were used on this project to make polarizing films, the other methods involving stretching dip- and pre-dyed filters. Stretching was accomplished by clamping a strip of the filter at both ends and drawing the strip back and forth over a ¼" diameter smooth cylinder until a section in the center of the strip had doubled its length and reduced its width to one-half of the original width.

No study was made of the time-varying characteristics of these polarizers although polarizers made from a sheet of pre-dyed filter were analyzed for initial transmission properties. The results are shown in Table 1 along with the characteristics for the unstretched filter from which the polarizers were made.

Table 1. Polarizer characteristics

Wavelength in Angstrom units	Basic Filter	Stretched to form polarizer: one layer	two parallel layers	two perpendicular layers	Polarization
	Percent transmission				
2537	25.2	37.8	20.4	10.4	32.5%
3132	.57	3.95	.43	.14	51%
3650	.23	3.01	.19	.07	46%
4047	.30	11.3	2.27	.04	97%
4358	.17	21.3	8.76	.01	99.8%
5460	.17	24.0	15.6	.12	98.5%

The "Polarization" in Table 1 is defined as

$$P = \frac{\%\ \text{transmission parallel} - \%\ \text{transmission perpendicular}}{\%\ \text{transmission parallel} + \%\ \text{transmission perpendicular}} \times 100\%$$

where P is the polarization. Many commercial polarizing films are available whose polarizations equal or exceed the polarizations in the visible range given in Table 1. However, attempts in 1961 by the author and others to locate a commercial polarizing film in this country having a polarization response in the 2500A range were unsuccessful. Therefore, the stretched polarizers tested on this project are useful in that they furnish a low-cost, easily produced polarizer with response in the 2500A range.

DISCUSSION AND CONCLUSIONS

All of the objectives of the project were successfully met. A thorough study of the time-varying characteristics of the filters was made and the causes of the changes, heat and uv radiation, were explored. This resulted in sufficient understanding to enable prediction of filter behavior under exposure to radiation from a G4T4/1 lamp which was the source of the 2537A radiation which the filter was designed to isolate.

Innovations in the method of filter construction led to the pre-dyed filter which possessed greater stability and a higher ratio of 2537A to 5460A radiation transmission than the dip-dyed filters.

It was also shown that a much lower filter temperature led to greater stability but this was an environmental improvement rather than a basic filter improvement. Also, the inconvenient liquid nitrogen cooling could not be justified when even greater stability could be achieved by slowly changing the location of the exposed area on a strip of filter material in a beam-type experiment.

In addition to satisfying the original goals, it was confirmed that polarizers could be made with the filter materials, these polarizers being significant because of their response in the 2500A range.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Robert H. McFarland for his guidance and encouragement given on this experimental investigation and to Dr. Basil Curnutte, Jr. for his valuable assistance in the preparation of the thesis. The author also wishes to thank James E. Swain for assistance and the entire physics department staff for advice and encouragement.

LITERATURE CITED

(1) Hoshino, Y., and S. Yoshida.
Ultra-violet filter for isolation of the 2537A line of a mercury quartz lamp. J. Electrochem. Soc. (Japan) 17:221-223. 1949.

(2) Jenkins, Francis A., and Harvey E. White.
Fundamentals of optics. New York: McGraw-Hill, 1957.

(3) Jeppesen, M. A.
Effect of ultraviolet radiation on Hoshino-Yoshida filters. J. Opt. Soc. Am. 49:489. 1959.

(4) McFarland, R. H., R. A. Anderson, M. Nasim, and D. G. McDonald.
Improved uv filter for isolation of the 2537-A line of a mercury low-pressure lamp. Rev. Sci. Instr. 29:738-739. 1958.

STABILITY AND IMPROVEMENT OF HOSHINO-YOSHIDA FILTERS

by

WILLIAM HOWARD TOBEY

B. S., Kansas State University, 1960

ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1962

Earlier work has shown that it is possible to construct a filter suitable for isolation of the Hg 2537A line in the output of a low-pressure Hg lamp by dip-dyeing a clear polyvinyl alcohol film in an iodine dye. Further investigation has uncovered detrimental instabilities in the transmission characteristics of these filters when exposed to total radiation from a low-pressure Hg lamp.

This project was conceived with the intent of thoroughly studying these instabilities and, if possible, improving production techniques to provide a more stable filter.

Exploration of the time-varying transmission properties led to the isolation of heat and ultraviolet radiation as the principal causes of the changes. Ultraviolet radiation acted beneficially by increasing the 2537A transmission of the polyvinyl alcohol film base. Heat absorption, on the other hand, brought about dye changes which led to greatly increased transmission of radiation other than the 2537A line.

Attention was then directed toward stabilizing the filter. The effort was centered around achieving a uniform dye distribution throughout the filter rather than the surface effect which could be expected with short duration dip-dyeing. The experimentation led to a pre-dyed filter in which the dye solution was added to the warm polyvinyl alcohol-water solution before the liquid was poured to form the filter.

These filters behaved in the same general way as the dip-dyed filters but differed from the dip-dyed filters in two important aspects. First, the pre-dyed filters showed only one-half the rate of change observed in the dip-dyed filters when exposed to equal Hg lamp radiation. Second, it was possible, with proper construction and irradiation, to produce a filter having 40 percent 2537A transmission with 5460A transmission at 1.0 percent. This compared with a maximum of 33 percent 2537A transmission and 1.0 percent 5460A transmission in an equally carefully prepared dip-dyed filter. The 1.0 percent limit on 5460A transmission had been established as a common measure of filter quality.

Reduction in the detrimental heat absorption effects by cooling was found to be impractical.

An outgrowth of the project was the construction of polarizers through stretching any of the filters described above. These polarizers are significant because of their ability to provide 30 percent polarization at 2537A, a shorter wavelength than is covered by commercial polarizing films available in this country.