NO. 91 SOLID ORGANIC FILTERS FOR 2000 A TO 3000 A*

by S. F. PELLICORI, C. A. JOHNSON,† and F. T. KING†

ABSTRACT

Earlier work on the development of organic, narrow bandpass solution filters with transmittance maxima in the 2000–3000 Å range is extended to the fabrication of solid filters using a polymethyl siloxane resin as the host material. Three transmission filters are described having maxima at 2250 Å, 2265 Å, and 2840 Å, respectively, with bandwidths ≤ 225 Å. Transmittance and spectral response curves with CsTe photocathodes are given. Results of environmental tests show that these filters are well suited for balloon and space missions.

1. Introduction

Since the introduction[1] and development of liquid organic filters for the range 2000–3000 Å a program has been underway in cooperation with the Owens-Illinois Technical Center to develop solid organic filters with similar spectral characteristics. A new silicone, Glass Resin Type 650‡ developed by Owens-Illinois, Inc., is the host material which contains the organic filter components. Glass Resins are based on an alternating silicon-oxygen system and are classed generically as silicones. However, unlike conventional silicones, they can be cured to crystal-clear thermosetting materials without the use of fillers and modifiers. As a result, some of them contain better than 75% silicon and oxygen. This leads to physical and chemical properties different from those of commercial silicones. This glass-resin is transparent through the visible and middle uv regions; the external transmittance for a sample 1 mm thick is shown in Fig. 1. The resin does not change the locations of the selective absorption bands of the organic compounds compared with their absorptions in *n*-hexane solution.

2. Filters Produced

Figure 1 also shows the transmittances of three solid filter components containing as absorbers (the detailed composition of these filters is described in Sec. IV): Curve 3—2, 4-pentanedione; Curve 4—*p*-dimethylaminobenzaldehyde; and Curve 5—2-methylpyrazine plus *p*-dimethylaminobenzaldehyde. Curve 2 shows an interference filter (special Bausch & Lomb filter for 2250 Å) [*Note added in proof:* Recently, Thin Film Products, Inc., Cambridge, Massachusetts has produced interference filters at 2200 Å with better rejection above 3000 Å, thus reducing the leak for the combination to nearly one-tenth of the value shown in Fig. 2.] that is used as a component of one of the final filters to remove the longer wavelength transmission of 2, 4-pentanedione. Addition of Schott§ filter glasses and Dow Corning 200 Silicone Fluid[1] to prevent reflection losses results in the final filters (Fig. 2). Transmittance values <0.1% are extrapolated from the Cary 14 tracings. We suspect that the Cary values below 2000 Å are low by about 0.05 transmittance.

Combination with a CsTe (solar blind) photocathode produces the spectral response to equal energy at all wavelengths, shown in Fig. 3. The superiority to other types of filters in steepness of cutoff and off-band rejection is obvious. The CsTe cathode does not respond to the transmission of the organic compounds above 3500 Å. CuI or CsI photocathodes having no response above 2600 Å would permit the use of other organic compounds described in Ref. 1. We believe that inorganic compounds could also be added to the resin to absorb the visible.

3. Environmental Stability

The transmittance of the 2250-Å filter (curve 3 in Fig. 1) was investigated at temperatures ranging from +23°C to −23°C. No detectable change was observed over this range. Two filters each of the series shown in Fig. 2 were flown twice in a balloon-borne polarimeter, which is being developed for the Voyager space mission, to a 34.6-km altitude for a total of 18 h. The temperature inside the photometer was −18°C and the pressure as 3.5 mm Hg. Another of the filters (represented by curve 1′ of Fig. 2) was located outside the photometer and was exposed to an ambient temperature of −70°C for 10 min and to −44°C for a total of

*Reprinted with permission from *Applied Optics*, Dec. 1966, 5, 1966.

†Owens-Illinois Technical Center, Toledo, Ohio.

‡This is one member of a family of resins developed by Owens-Illinois, Inc., and so named because of their glass-like appearance.

§Jena Glaswerk Schott & Gen., Mainz.

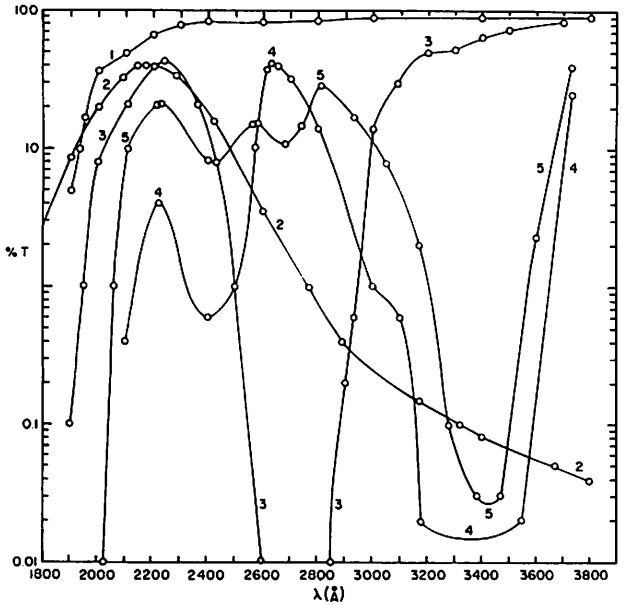

Fig. 1. External transmittance of organic compounds in Owens-Illinois Type 650 Glass Resin (curve 1, 1 mm thick) to make solid uv filter components. Curve 2 is of a special Bausch & Lomb interference filter for 2250 Å. The components of the filters represented by the remaining curves are given in Secs. II and IV.

18 h. No changes in the transmittances were detected in any of the filters after the flights.

Another set of these filters was flown in the Polariscope balloon system, and was used to obtain polarization measurements on a star and the daylight sky at a 36.1-km altitude on 27 May 1966.

A test was made to determine if the filters solarized to uv radiation. 1 h of irradiation at 23°C by 26 $\mu W/cm^2$ of the λ 2537-Å line produced no detrimental changes in the uv transmittance. Cast disks of the 650 resin (undyed) have been placed 20 cm from a 400-W uv lamp (Westinghouse H-33-1-CD), in air, and exposed for 1000 h. There was no change in the visible transmission of the castings.

A Glass Resin Type 650 casting among other materials was exposed to a simulated space radiation environment consisting of combined low energy protons (50 keV) and electromagnetic radiation, with wavelengths from 1216 Å in the extreme uv to 2 μ in the ir.[2] The casting was subjected to the equivalent of 340 h in space, during which solar flare conditions were simulated (10^{17} protons/cm^2 and 7.5 suns of solar EUV produced by hydrogen discharge). Following this radiation treatment, light transmittance dropped from 0.95 to 0.64 at 0.6 μ, a change of 0.31. Under these same conditions, fused silica (Corning No. 7940) showed a decrease of only 0.05 at 0.6 μ while all of the plastics tested degraded to near opacity. This information provides a good indication of the radiation resistance of Glass Resin Type 650 when compared with the other transparent plastics. The Glass Resin castings have been exposed to 10 Mrad of gamma radiation from a cobalt-60 source and 5 Mrad of thermal neutrons. No coloration resulted, and there was no loss of transparency. Under the same conditions, ordinary glass is discolored.

One disk containing *p*-dimethylaminobenzaldehyde to make curve 4 in Fig. 1, and one containing 2-methylpyrazine plus *p*-dimethylaminobenzaldehyde to make curve 4 in Fig. 1, were subjected to high vacua for extended periods. The test was to determine if the volatile organic absorbers would evaporate from the glass resin and degrade the filtering properties. The disks were 0.254 mm thick, and were fully exposed to the vacuum; i.e., they were not laminated with silicone fluid plus a colored glass. After one and one-half days at 1 x 10^{-8} mm Hg at about 0°C and four and three-fourths days at 1 × 10^{-6} mm Hg at +23°C, no changes in transmission could be detected. Two disks 1.27 mm thick containing 2,4-pentanedione to make curve 3 in Fig. 1 were kept at 1 × 10^{-6} mm at +23°C for four days. The transmission of one of the disks was unchanged, and the other decreased by 0.01 units. (It is uncertain whether this change was real because if some organic material evaporated, the transmission should have increased.) It is concluded that these filters are usable in the space environment for periods at least as long as above.

4. Preparation and Handling of Light Filters Using Glass Resin Type 650

The general procedure[3] used to prepare castings from glass resins was adapted to prepare the uv filters. Initially, glass resin 650 is a low molecular weight prepolymer dissolved in ethanol. First, a simple heat treatment, called a precure step, accomplishes two things: removal of the solvent, and starting the polymerization process to reduce time for postcuring.

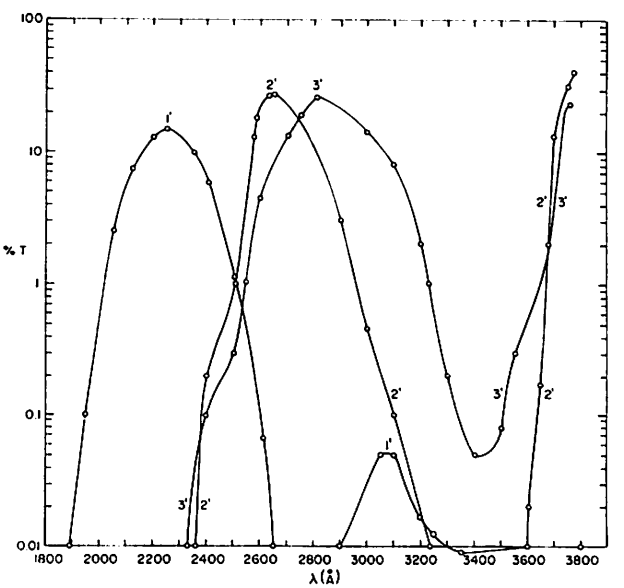

Fig. 2. External transmittances of Glass Resin filter components shown in Fig. 1 plus components to make the final filters that were used in three balloon flights: 1′ is curve 2 (Fig. 1) plus curve 3, 2′ is curve 4 plus 2 mm Schott UG-5, and 3′ is curve 5 plus 1 mm UG-11. 200 Silicone Fluid is used as a contacting agent.

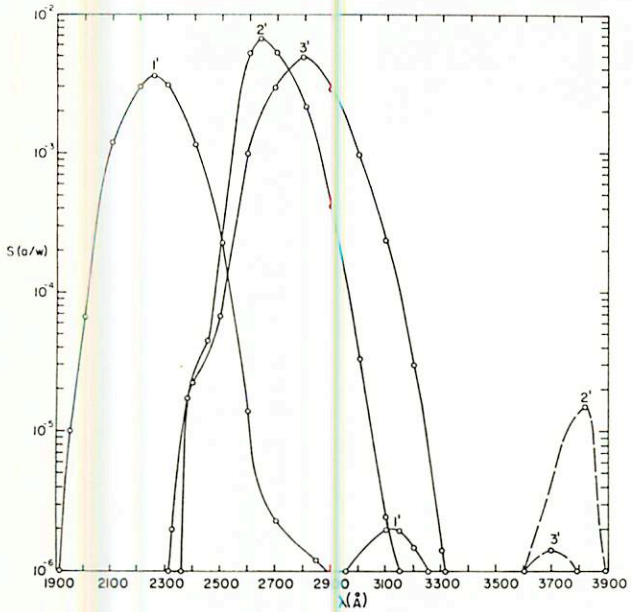

Fig. 3. Computed spectral response (cathode) to white light of filters of Fig. 2 combined with a CsTe photocathode.

Further heat treatment of the B-stage resins converts them to hard thermosetting materials. The length of time required for this final cure depends on the thickness of the casting.

The ethanol and water were boiled off from the glass resin (100 ml) as quickly as possible from a well-stirred solution in a 250-ml beaker. Within 15 min, the temperature of the low viscosity liquid (about 150 c/s) had reached 140°C. This rate of evaporation is critical for obtaining a proper precure and avoiding gellation of the resin. At this point the beaker was removed from the hot plate and the organic dye added with vigorous stirring. The solution was poured into 5.1-cm diam aluminum foil pans to make disks 3.2 mm thick; care was taken to entrap no more air bubbles than necessary. The disks, while still hot (>100°C), were placed directly into an oven maintained at 90°C. After 24 h, the disks were removed from the oven and allowed to cool to room temperature. The aluminum foil was stripped from the disks which were inverted and placed into a new foil aluminum pan. After six more days at 90°C, the disks were removed from the ovens. Then they were cut, ground, and polished to the thickness required to give the desired absorption after the light transmission of the original disk had been determined. The only precaution required during this operation was to avoid localized overheating which could cause cracking owing to thermal expansion. After the initial trial runs were finished, better estimates were made of the excess amount of volatile organic absorber that must be added at 130°C to leave the proper amount of dye in a polished disk of a convenient thickness. For example, since the boiling point of 2-methyl pyrazine was about 138°C, considerably more material was added to the glass resin being maintained at 130° C than one would add merely by calculation.

After several initial filters had been prepared in order to establish the proper technique, three types of filters were prepared as described below.

To prepare the 2250-Å filter, approximately 210 mg of 2,4-pentandione was added to 50 g of the glass resin at a temperature about 125°C to 130°C. The filter had a thickness of 1.270 ± 0.051 mm. The average deviation of the per cent transmittance at 2250-Å between the six filters was ±1%.

To prepare the 2665-Å filter, 100 g of *p*-dimethylaminobenzaldehyde was added to 50 g of the glass resin 650 at about 130°C. The filters had a thickness of 0.254 ± 0.025 mm. The average deviation of the per cent transmittance at 2665 Å between the six filters was ±2%.

To prepare the 2840-Å filter, about 200 g of 2-methylpyrazine and about 50 mg *p*-dimethylaminobenzaldehyde was added to 50 g of the glass resin 650 solution at about 130°C. The filters had a thickness of 0.254 ± 0.025 mm. The average deviation of transmittance at 2840 Å between the six filters was ±3%.

Six filters of each type were prepared for the balloon astronomical studies. The disks had uniform transmission over their area.

The glass resin is not as mar resistant as glass. Cleaning the filters must be done with soft tissue. The filters are insoluble in water. They can be soaked in pure *n*-hexane for up to 2 min with no harm. (Hexane dissolves the silicone fluid contacting agent.) Ethyl alcohol on a tissue can be used for cleaning the filters with light pressure. However, when dipped, the filters cannot survive in polar solvents because they crack.

The disks were cast by D. W. Gagnon and J. J. Tillman of the Owens-Illinois Technical Center. Appreciation is expressed to S. A. Hoenig of the Mechanical Engineering Department, University of Arizona for use of his high vacuum system. We are grateful to the Kitt Peak National Observatory for use of their Cary 14 recording spectrophotometer. This work was supported as part of the Polariscope program of the Atmospheric Sciences Section, National Science Foundation.

REFERENCES

1. S. F. Pellicori, Appl. Opt. **3**, 361 (1964).
2. C. A. Johnson and R. E. Martin, in *Proceedings of the Sixth Electrical Insulation Conference* (New York, 1965, p. 119).
3. *Combined Space Environment Effects on Typical Spacecraft Window Materials*, Final Report, Contract NAS9-2939 Avco Corporation, Tulsa Division, July, 1965.

TABLE OF CONTENTS