Stability of the optical properties of abnormally dispersive liquids

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ABSTRACT

Abnormal dispersion is found in a large number of optical liquids. These liquids are quite useful in the design of apochromatic lens systems because they are inexpensive and are readily available compared to the expensive abnormal dispersion glasses and crystals more commonly used. Further, there is no practical upper limit on the size of a liquid optical element. However, because the use of these materials as optical elements is quite new, the long term stability of their optical properties after exposure to various environmental conditions must be determined.

In this paper, we report on a series of tests performed to determine the optical stability of several abnormal dispersion liquids. The liquids were subjected to: (1) high intensity ultraviolet radiation, (2) high temperatures, and (3) long term exposure to air. Measurements of both optical transmission and refractive index were performed before and after each exposure. The tests were performed on four abnormal dispersion liquids that have been found to be quite useful in the design of apochromatic lenses. The results indicate that long term exposure to either intense ultraviolet radiation or air, produced only negligible changes in the index of refraction. Changes in optical transmission were observed, but they were largely confined to the ultraviolet spectral region. Prolonged exposure to temperatures of 60°C did not produce any measurable change in the optical properties.

The measurements were performed at the Vavilov State Optical Institute, St. Petersburg, Russia, in collaboration with Lockheed Palo Alto Research Laboratory, Palo Alto, California.

INTRODUCTION

Optical materials with good transmission over the visible spectrum can be divided into two broad groups based on their dispersion characteristics. By tradition, materials in each group are said to posses either "normal" or "abnormal" dispersion.

The first group includes the overwhelming majority of all optical glasses. Normal dispersion materials have an essentially linear relationship between the first and second order terms of their refractive index versus wavelength polynomials (these terms are frequently referred to as the dispersion coefficients).

The second group includes those materials that have an unusual relationship between their respective dispersion coefficients. Abnormal dispersion is much more common in liquids than it is in glasses.

It is this property of liquids that has made them so useful in the design of apochromatic optical systems.

NORMAL AND ABNORMAL DISPERSION

One method of displaying the normal and abnormal dispersion characteristics of a material is with a Buchdahl dispersion plot.[1,2] In Figure 1, the primary and secondary Buchdahl dispersion coefficients are plotted for Schott optical glasses, along with a number of optical liquids and a few crystals. Those materials which lie close to a straight line known as the "Normal" line are considered to have

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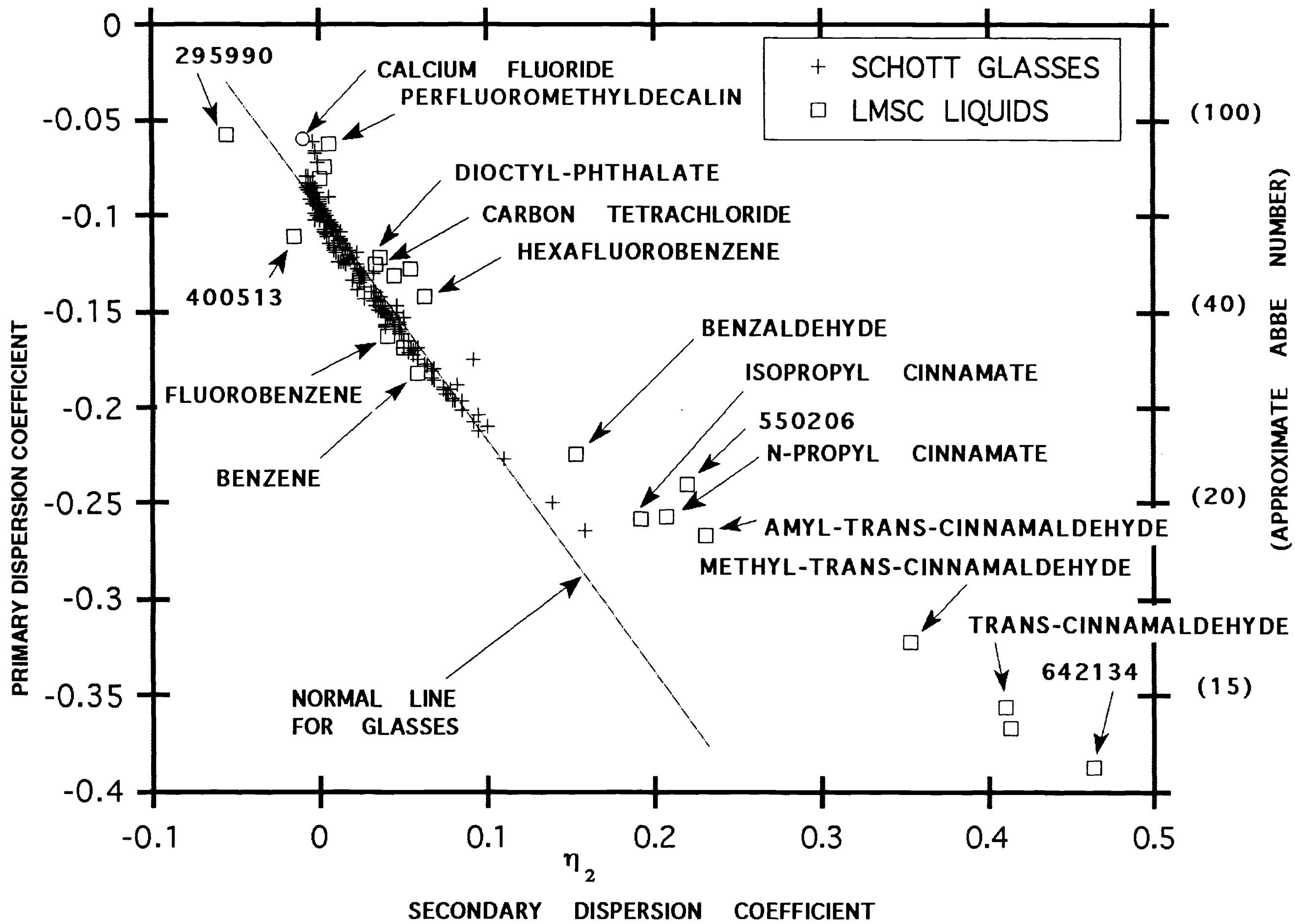


Figure 1. Buchdahl dispersion map for glasses and liquids. The primary and secondary Buchdahl dispersion coefficients for Schott optical glasses, calcium fluoride, and a number of optical liquids are plotted.

normal dispersion. Materials that lie well off this normal line are considered to be abnormal. The greater the deviation of any material from this normal line, the more abnormal the material is said to be and generally the more useful it is in the design of apochromatic lenses.

The requirement for abnormal dispersion materials in apochromatic optical systems has been known for many years, and the use of liquids in this connection has been described in a number of recent papers.[3-5] Liquids provide many advantages to the designer. They are inexpensive and readily available; there is no practical upper limit on the size of a liquid optical element; and they can sharply reduce both the cost and delivery time of an apochromatic system. However, because these are new materials, their stability after long term exposure to various environmental conditions must be investigated.

STABILITY OF THE OPTICAL PROPERTIES

The abnormal dispersion liquids studied were 550206, 400513, 642134, and 295990. As is common with glasses, these numeric names reflect both the liquid's nominal index of refraction and its Abbe number. The composition of these liquids has either been described previously,[3,4] or is considered proprietary.

EXPERIMENTAL PROCEDURE

It is well known that changes in the optical properties of materials resulting from prolonged exposure to solar irradiation are driven primarily by the ultraviolet (UV) portion of the spectrum. To determine the effect of UV irradiation on the liquids, a special instrument was assembled. This instrument consists of a high pressure 3-kilowatt DC Xenon lamp and a monochromator.

The Xenon lamp, which produces considerable UV radiation, was calibrated at various currents to determine quantitatively the intensity of UV light. The liquid being exposed to the UV-irradiation is contained in a cell made from fused silica, which transmits wavelength as short as 0.19 μm. Unless otherwise noted, cells having liquid thickness of 10 mm were used for all test.

To expose the liquids to high temperature, a thermally controlled heater was used. The liquids were contained in a tightly sealed fused silica cell and the temperature was held at 60 ± 0.5°C for 4 hours.

To investigate the effect of atmospheric exposure, each liquid was contained in fused silica cell with a top open to the atmosphere for a period of one month.

Environmentally induced degradations were measured by comparing the transmission spectra and the index of refraction versus wavelength, before and after each exposure.

The transmission of the liquids in the ultraviolet, visible, and the infrared were made by using three spectrophotometers with overlapping spectral ranges. These instruments were:

- Specord M-40 spectrophotometer. Covering the UV and visible region (UV cutoff was 0.2 μm)
- Hitachi EPS 3T spectrophotometer. Covering 0.21 to 2.6 μm.
- Specord M-82 spectrophotometer. Covering the wavelength range from 2.5 to 40 μm.

All transmission measurements were made at room temperature (approximately 20°C).

RESULTS OF UV EXPOSURE ON TRANSMISSION

We found that exposing these four liquids to the intense broad band UV light from the Xenon lamp produced significant changes in the transmission of the liquids in the UV end of the spectrum, very slight changes in the visible spectrum, and negligible changes in the near infrared. Figures 2a through 2d present the transmission spectra through a 10-mm layer of the four liquids. In all cases, the liquids were stirred during the UV irradiation. The transmission of the non-irradiated liquid in each case is shown as curve #1.

The UV exposure affects the four liquids in different ways. However, in all cases, the largest changes in the transmission spectra took place during the first hour of irradiation.

For liquids 550206, 400513, and 642134 the influence of UV-irradiation takes the form of a shift of the UV absorption edge towards longer wavelengths. The most sensitive liquid to UV-irradiation is 550206 (Figure 2a.). In this case, the edge shift was nearly 100 nm at the 50% transmission point.

For the liquid 295990 the UV-irradiation changed the shape of the UV absorption edge—it increases the transmission in the shorter wavelengths and decreases the transmission in the longer wavelengths (Figure 2d.).

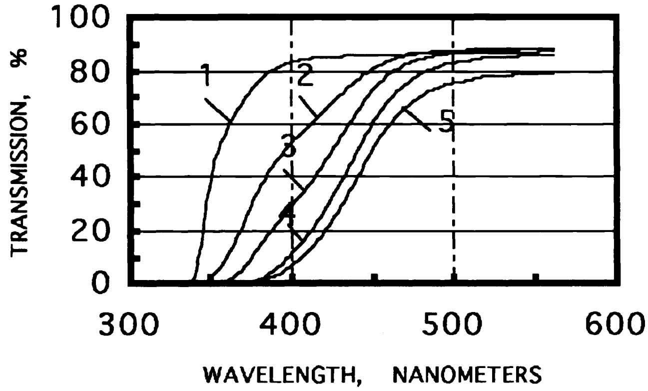
EFFECTS OF HIGH TEMPERATURE ON TRANSMISSION

We have found that holding each of the four liquids at a temperature of approximately 60°C for four hours had no effect on their transmission over the wavelength range of 0.2 to 2.5 μm. In addition to having negligible changes in transmission, changes in the refractive index or dispersion of these liquids were also negligible.

EFFECTS OF ATMOSPHERIC EXPOSURE ON TRANSMISSION

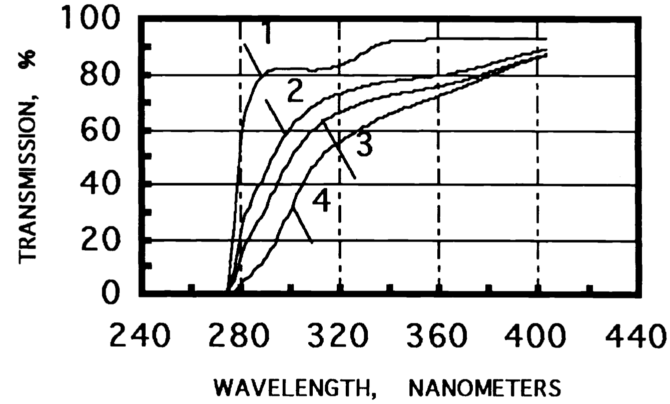
For this test, each liquid was contained in an unsealed, fused silica cell for one month. The transmission of two of these liquids, 642134, 550206, did not change. The transmission of liquids 400513 and 295990 was found to have some dependence on atmospheric exposure.

Figures 3a and 3b shows the transmission through a 10-mm layer of the liquids 400513 and 295990 before and after exposure. The transmission changes are similar in both liquids. The UV absorption edge shifts towards longer wavelengths, and the shape of the UV absorption edge changed. Liquid 295990 is the most sensitive liquid of the group to atmospheric exposure, having the 50% transmission point shifted by 50 nm.



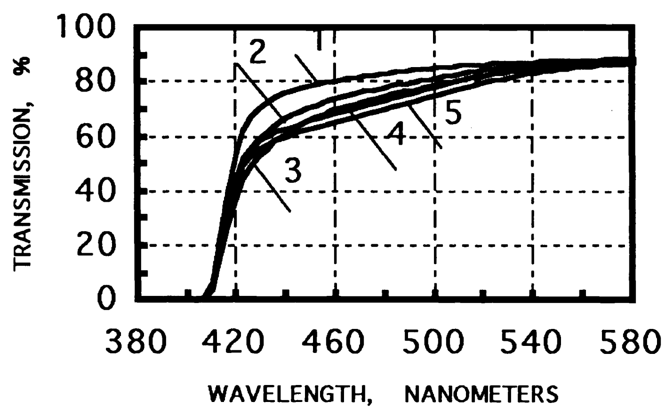
Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 1 hour.
Curve 3—transmission after irradiation for 2 hours.
Curve 4—transmission after irradiation for 4 hours.
Curve 5—transmission after irradiation for 6 hours.

Figure 2a. Liquid 550206 transmission after irradiation with broad band UV light.. Liquid thickness: 10 mm.



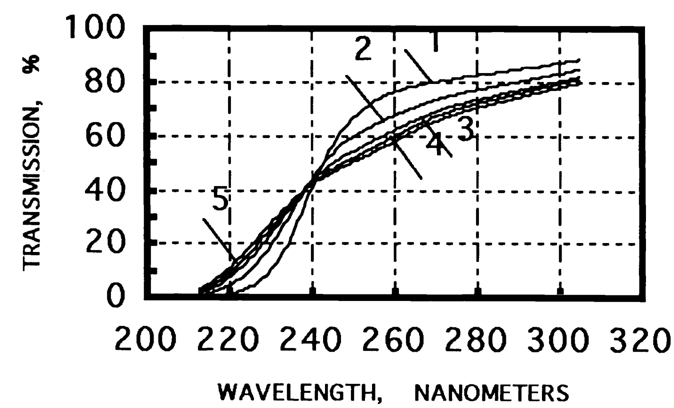
Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 1 hour.
Curve 3—transmission after irradiation for 2 hours.
Curve 4—transmission after irradiation for 4 hours.

Figure 2b. Liquid 400513 transmission after irradiation with broad band UV light. Liquid thickness: 10 mm.



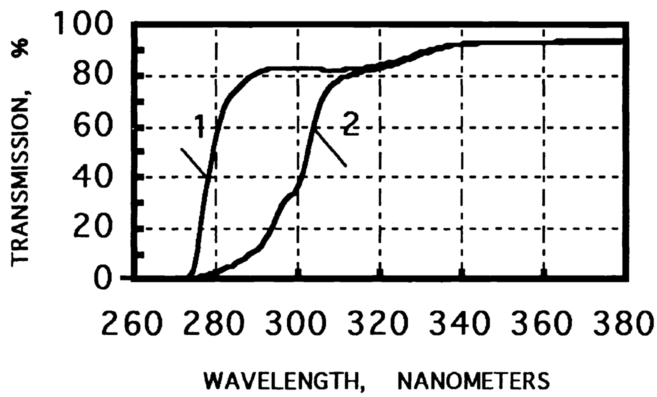
Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 1 hour.
Curve 3—transmission after irradiation for 2 hours.
Curve 4—transmission after irradiation for 4 hours.
Curve 5—transmission after irradiation for 7.5 hours.

Figure 2c. Liquid 642134 transmission after irradiation with broad band UV light. Liquid thickness: 10 mm



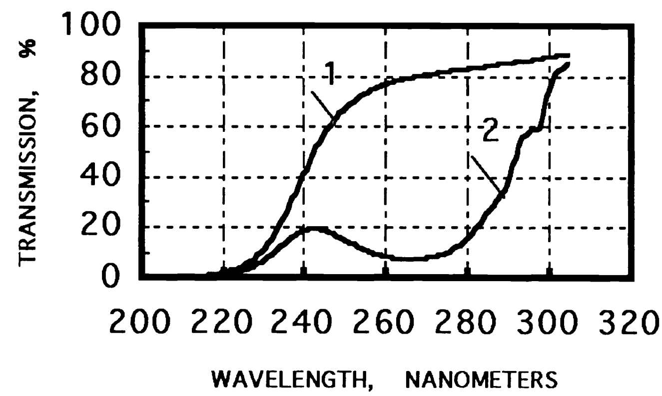
Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 1 hour.
Curve 3—transmission after irradiation for 2 hours.
Curve 4—transmission after irradiation for 3 hours.
Curve 5—transmission after irradiation for 4 hours.

Figure 2d. Liquid 295990 transmission after irradiation with broad band UV light. Liquid thickness: 10 mm.



Curve 1—transmission of non-exposed liquid.
Curve 2—transmission after exposure for one month.

Figure 3a. Liquid 400513 transmission after exposure to air for one month. Liquid thickness: 10 mm



Curve 1—transmission of non-exposed liquid.
Curve 2—transmission after exposure for one month.

Figure 3b. Liquid 295990 transmission after exposure to air for one month. Liquid thickness: 10 mm

RESULTS OF UV EXPOSURE ON DISPERSION

To better understand effects of UV irradiation on the dispersion of the liquids, we studied the properties of irradiated liquid 550206 more closely. Liquid 550206 was chosen because its transmission was the most sensitive to UV-irradiation (Figure 2a.). The UV absorption edge of this liquid was shifted towards longer wavelengths by nearly 75 nm at 50% transmission. It can reasonably be assumed that this liquid would also suffer the greatest dispersion changes.

The refractive indices were measured for 550206 over a wavelength range of 0.4047 to 1.6 μm at three different temperatures. The irradiated sample was exposed to broad-band UV irradiation for two hours. The refractometer facility was described in detail in the article cited in Reference 4. Two similar high-precision goniometer type refactometers were used. Two identical thermal stabilization cells were also used, one for the visible and the other for the IR.[4] New liquid prisms were also developed and used in these experiments.[5] These prisms were made BaF2 or fused silica windows cemented together to form a hollow prism. The chamber windows were made of the same materials as the prisms.

The accuracy of the refractive index measurements was ±0.00001 over the wavelength range from 0.4047 to 1.5 μm, and ±0.00005 at 1.6 μm. The temperature of the liquids was controlled to ±0.02°C, and measured to an accuracy of ±0.01°C.

Measurements were made at three temperatures (nominal room temperature plus and minus approximately 9°C), and the data then reduced to a temperature of 25.0°C using the derived values of dn/dt.

These results (see Table 1) show that intense broad band UV irradiation reduces the refractive indices of the liquid. However, the difference is small enough to be accommodated by a slight shift in focus if the liquid were used in a lens system. The UV irradiation also produces a slight reduction in the dispersion of the liquid, but this is so small as to be unlikely to upset the chromatic correction balance of any prospective lens.

To characterize this change in dispersion, the primary and secondary Buchdahl dispersion coefficients of the irradiated and non-irradiated 550206 were calculated. The primary and secondary Buchdahl dispersion coefficients are 0.262 and 0.201 for the non-irradiated liquid, and 0.261 and 0.202 respectively for the irradiated liquid. This amount of change in dispersion is negligible.

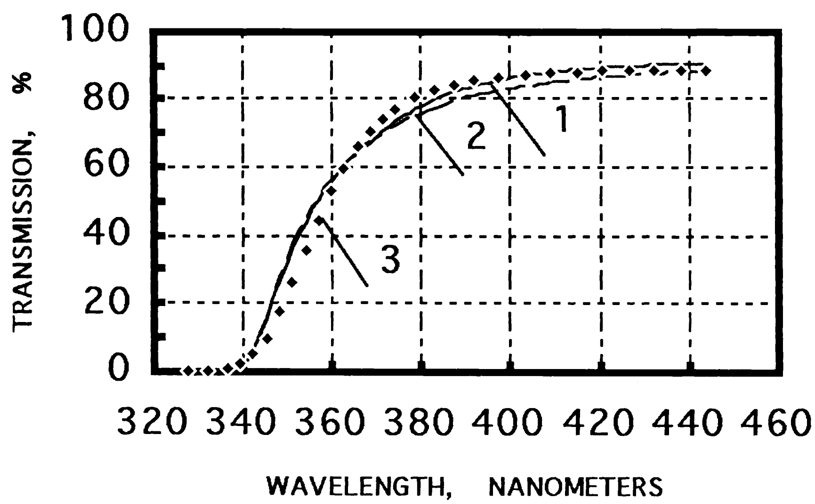
To summarize, for liquid 550206, exposure to broad band UV-irradiation for two hours causes changes in transmission of the UV-violet end of the spectrum. These absorption changes also slightly decreased the refractive index in the visible, but the visible dispersion properties were unaffected. This means that incorporating 550206 in a lens design which was exposed to intense broad band UV radiation would result in a slight change in visible transmission of the lens, but would not alter the aberration correction or spatial resolution of the system.

Table 1
Refractive indices for liquid #550206 at 25.00°C before and after exposure to broad band UV for 2 hours

Visible Region			
Wavelength, μm	Non-irradiated	Irradiated	Difference
0.4047	1.60617	1.60527	0.00090
0.4358	1.58828	1.58753	0.00075
0.4800	1.57171	1.57105	0.00066
0.4861	1.56994	1.56930	0.00064
0.5461	1.55653	1.55592	0.00061
0.5876	1.55018	1.54962	0.00056
0.5893	1.54995	1.54938	0.00057
0.6439	1.54383	1.54328	0.00055
0.6563	1.54270	1.54216	0.00054
0.7065	1.53872	1.53820	0.00052
Infrared Region			
Wavelength, μm	Non-irradiated	Irradiated	Difference
0.7	1.53923	1.53871	0.00052
0.8	1.53355	1.53297	0.00058
0.9	1.52979	1.52919	0.00060
1.0	1.52719	1.52656	0.00063
1.1	1.52519	1.52454	0.00065
1.2	1.52362	1.52293	0.00069
1.3	1.52239	1.52171	0.00068
1.5	1.52052	1.51980	0.00072
1.6	1.5197	1.5190	0.0007

To further quantify the effects of UV exposure on liquid 550206, it was irradiated with narrow-band UV light in addition to the broad-band UV irradiation described above. The broad band UV spectrum of the lamp was narrowed by using of a colored glass absorption filter. Figure 4 presents the transmission of the non-irradiated liquid, the filter, and the liquid after being irradiated through the filter.

It is interesting that the transmission through a 10-mm layer of the liquid is the same as the transmission spectrum through the 3-mm thick, BC 7 -UV absorption filter.[6] The UV filtered irradiation of 550206 for 2 hours does not cause any significant changes in the transmission (Figure 4, curves 1 and 2). Irradiation with the full spectral range of the lamp for 2 hours produced significant changes (Figure 2a, curve 3).



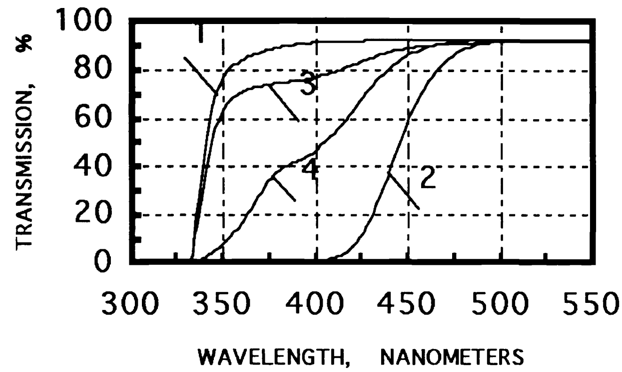
Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 2 hours trough UV filter.
Curve 3—transmission of UV filter (BC 7).
Figure 4. Liquid 55006 transmission after irradiation with narrow band UV light. Liquid thickness: 10 mm.

Subsequent irradiation of liquid 550206 with very narrow band monochromatic UV light showed that the transmission is most sensitive to a wavelength of approximately 320 nm. The spectral width of the monochromatic irradiation used for all tests was 8 nm. The cell used for each of these monochromatic tests had a liquid thickness of 1 mm.

Figure 5a presents the transmission liquid 550206 after exposure for one hour with various monochromatic UV wavelengths. The UV absorption edge after exposure to 320 nm shifted towards longer wavelength by nearly 105 nm (Figure 5a, curves 1 and 2). The total energy absorbed by the liquid at 320 nm is calculated to be 8 J over the irradiated area of 0.25 cm^2.

Irradiation at a wavelength of 400 nm for one hour had no effect on the transmission of the liquid, despite the fact that the DC Xenon lamp has a total power of 3.4 mW at this wavelength.

Irradiation with 350 nm light (curve 3 in Figure 5) influences on the transmission of the liquid only slightly. The shape of the absorption edge changes slightly and an additional absorption dip appeared at approximately 380 nm. Approximately 9.7 J was absorbed at this wavelength.



Curve 1—transmission of non-irradiated liquid.
Curve 2—transmission after irradiation for 1 hour, l = 320 nm.
Curve 3—transmission after irradiation for 1 hour, l = 350 nm.
Curve 4—transmission after irradiation for 1 hour, l = 300 nm.

Figure 5a. Liquid 550206 transmission after irradiation with monochromatic UV light. Liquid thickness: 1 mm.

Surprisingly the changes in transmission due to 300 nm irradiation (Figure 5a, curve 4) were less than that at 320 nm. However, the character of the changes is similar. At 300 nm the liquid absorbed 5.4 J.

Thus, liquid 550206 is affected primarily by wavelengths of 320 nm and shorter.

CALCULATING THE EFFECT OF SOLAR EXPOSURE

The irradiation of 550206 with 320 nm light resulted in an energy density of approximately 9 mW/cm^2 over a 315 to 325 nm bandwidth.

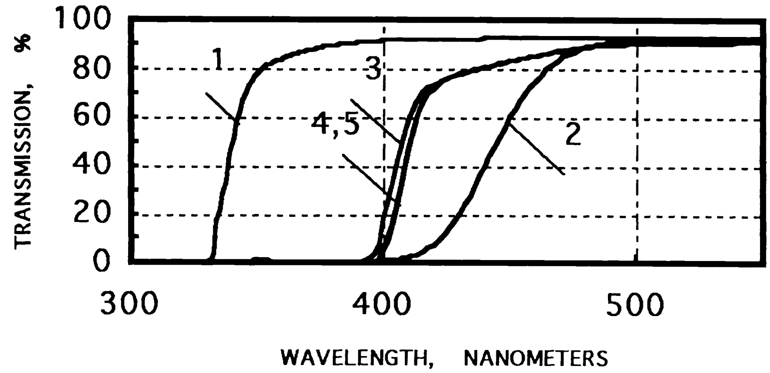
The spectrum of the sun is approximately that of a black body with a temperature of 5700 K. The energy in the spectrum between 315 and 325 nm is about 0.01 of the energy in the whole solar spectrum.

It is well known that the energy density of sunlight above the Earth's atmosphere is about 100 mw/cm^2. So our irradiation in the UV is nearly 10 times greater than natural sunlight irradiation. This means that a one-hour exposure with the DC Xenon lamp is equivalent to about 10 hours of unprotected exoatmospheric solar exposure.

Naturally the atmosphere and the glass lenses that surround and contain the liquids in a typical lens will reduce the available solar flux at 320 nm considerably. A conservative estimate (based on Schott BK7 glass elements) is that more than 60 hours of unprotected solar exposure would be required to equal one hour exposure with the lamp. It would be a small matter to use only glasses that transmit poorly below 350 nm or to use liquids other than 550206 in lens designs (if the loss of UV-violet transmission is considered a problem).

To further investigate the UV influence on the optical properties of the liquid 550206, we need to understand what photo-chemical reactions take place in this liquid in the presence of intense UV-irradiation. The composition of the abnormal dispersion liquid 550206 is primarily ethyl cinnamate.[2] One line of investigation is to compare the UV influence on the liquid 550206 with a liquid having similar chemical structure.

Figure 5b shows a transmission comparison through a 1 mm thickness for liquid 550206 and methyl-trans-cinnamaldehyde. As can be seen in the dispersion plot of Figure 1, methyl-trans-cinnamaldehyde is even more abnormal than 550206. Methyl-trans-cinnamaldehyde was exposed to monochromatic UV-irradiation under the same condition as liquid 550206. Irradiation with 320 or 380 nm light had no affect on the UV absorption edge. The methyl-trans-cinnamaldehydehe sample absorbed 9.7J and 11.1 J respectively in this experiment.



Curve 1—transmission of non-irradiated 550206 liquid.
Curve 2—550206 transmission after irradiation for 1 hour, l = 320 nm.
Curve 3—transmission of non-irradiated methyl-trans-cinnamaldehyde.
Curve 4—methyl-trans-cinnamaldehyde transmission after irradiation for 1 hour, l = 320 nm.
Curve 5—methyl-trans-cinnamaldehyde transmission after irradiation for 1 hour, l = 380 nm.

Figure 5b. Liquid 550206 and methyl-trans-cinnamaldehyde transmission after irradiation with monochromatic UV light. Liquid thickness: 1 mm.

We believe that the photo-chemical reactions caused by intense UV irradiation substantially alter the chemical moieties responsible for the intensive UV absorption of 550206. The UV absorption band appears to become less intense and broader resulting in a shift of the UV absorption edge toward longer wavelengths. The effect of this appears to be sufficient to decrease the absolute refractive index but insufficient to change the Buchdahl dispersion coefficients and therefore, the abnormal dispersion properties of the liquid.

Methyl-trans-cinnamaldehyde is a more abnormal dispersion liquid than 550206 and was found to be unaffected by the intense UV-irradiation of our experimental setup. Methyl-trans-cinnamaldehyde has an aldehyde group with double bonded oxygen. We believe that this structure is responsible for the liquid's pronounced abnormal dispersion. This structure would also appear to be more stable under UV irradiation than that of ethyl cinnimate.

CONCLUSIONS

The stability of optical properties in four abnormal dispersive liquids exposed to UV irradiation, heat, and air were investigated.

The only significant degradation observed as a result of these exposures was the UV- violet transmission of liquid 550206. This was caused exposure to intense UV irradiation at wavelength of 320 nm. The other liquids investigated (295990, 400513, and 642134) were largely unaffected.

While this investigation revealed no practical environmental limitations on the use of abnormal dispersive liquids in the design of high performance visible optical systems, prudence does suggest two simple design rules: the liquids should always be hermetically sealed in the lens assemblies and UV wavelengths shorter than about 320 nm should be absorbed by the surrounding glass optical elements.

REFERENCES

1. P. N. Robb, "Selection of Optical Glasses: 1: Two Materials," *Appl. Opt.* **24,** 1864–1877 (1985).

2. P. N. Robb and R. I. Mercado, "Calculation of Refractive Indices Using Buchdahl's Chromatic Coordinate," *Appl. Opt.*, **22,** 1198–1204 (1983).

3. R. D. Sigler, "Apochromatic Color Correction Using Liquid Lenses," *Appl. Opt.*, **29,** 2451–2459 (1990).

4. R. D. Sigler, "A new abnormal dispersion liquid for use in the design of high performance optical systems," *Passive materials for Optical Elements II*, SPIE Vol. 2018,188–199 (1993).

5. P. N. Robb, M. N. Tolstoy, and M. V. Petrova, "Refractive Indices of Liquids in the Ultraviolet and Infrared," *Passive Materials for Optical Elements II*, SPIE Vol. 2018, 200–205 (1993).

6. A. G. Plyukhin, M. V. Petrova, M. N. Tolstoy, P. N. Robb, R. D.Sigler, and D. F. Leary, "Refractive Indices of Liquids in the Infrared Spectral Region," *Current Developments in Optical Design and Optical Engineering IV*, SPIE Vol. 2263, (1994).

7. G. T. Petrovsky, ed., *Russian Colored Optical Glass Catalog*, Moscow, 1990.