The Alexandrite Effect of the Tavernier Diamond Caused by Fluorescence under Daylight

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Abstract: The 56.07-carat Tavernier pear-shaped gem diamond not only has an important historical provenance, but also shows a substantial color change between incandescent light and daylight. This famous diamond exhibits a very strong blue fluorescence when exposed to longwavelength ultraviolet (UV) radiation. It appears light brown (an orange hue) under incandescent light, and light pink (a purple hue) under daylight. This change in color, or "alexandrite effect," is caused by its very strong blue fluorescence resulting from the long-wavelength ultraviolet component present in daylight. © 1998 John Wiley & Sons, Inc. Col Res Appl, 23, 323–327, 1998

Key words: alexandrite effect; fluorescence; diamond; daylight; ultraviolet; N3 center

INTRODUCTION

The important gem diamond that is the subject of this study is referred to as one of the "Tavernier" diamonds. It is thought to have been brought back from India in the 17th century by the noted French traveler and gem dealer, Jean–Baptiste Tavernier (1605–1689). During a period of almost 40 years (1631–1668), this individual made six journeys from Europe to India. At that time, India was the source of most all gem diamonds, with many being found in the region of Golconda in the central part of the country. During these visits, Tavernier was able to see and often purchase a number of spectacular diamonds. The report of his travels, first published in 1676, gives one of the more important descriptions of early diamond mining in that country.

In his report, Tavernier described a diamond locality called the Gani mine. A number of rough diamonds were found there, many ranging in weight from 10-40 carats, with the largest weighing 900 carats (1 carat = 0.2 gram). He mentioned that the colorless to light yellow diamonds from this area as having a "greasy" appearance in daylight. This kind of diamond has since been described as being of "false color," in that the appearance is due to the lighting conditions, and is not the true bodycolor. Wade discussed the kind of "greasy" diamond reported by Tavernier, and pointed out that this "false color" is caused by a blue fluorescence under daylight. 2 Light yellow diamonds from the Premier Mine in South Africa also show both blue fluorescence under daylight³ and an oily appearance. In extreme cases, the unusual "milky" appearance of these "false color" diamonds is also due to reduced transparency resulting from their UV fluorescence reaction. Whether or not the 56.07-carat diamond described here is from the Gani mine is uncertain, but it is thought to be of Indian origin, and it does fall into the category of diamonds with a strong blue fluorescence to long-wavelength UV with a slightly greasy appearance.

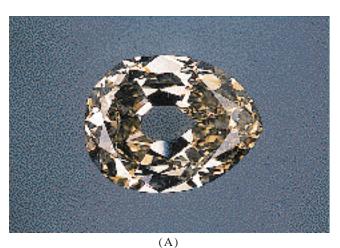
Diamond is carbon crystallized in the cubic system. The colors of diamonds are caused by the trace-element impurities (mainly nitrogen), irradiation-damage centers, or atomic dislocations in the diamond crystal structure. ⁴ The fluorescence of most diamonds is caused by the nitrogen impurity. ^{5,6}

The color measurement of diamonds began in the early 1930s when the Guild trichromatic colorimeter was used to measure the color of gemstones. Robert Shipley and his son Robert Shigley, Jr., the founders of the GIA, developed two instruments for measuring the color of colorless to light yellow diamonds. 8,9 The first instrument

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was a visual color comparator for comparing the color of a diamond with that of a wedge-shaped piece of glass that displayed a colorless to yellow appearance. The second one was a colorimeter with two detectors: one yellow and one blue. The color was determined by the ratio between the values measured by the two detectors. The Okuda Diamond Colour Checker used the same principle as the Shipley colorimeter. The major improvement of this instrument was that the diamond was placed at the center of an integrating sphere. 10 At the present time, several colorimeters and spectrophotometers have been developed for color measurement of diamonds and other gemstones, such as the Kalnew Gemcolour 2 spectrophotometer, the Zeiss-Gübelin spectrophotometer, the Gran colorimeter, the Austron diamond colorimeter, the LamdaSpec imaging spectrophotometer, and an imaging spectrograph CCD system being constructed by GIA Research. All current instruments utilize an integrating sphere. Liu and Shigley 11 found that color measurement results obtained by the 0/d geometry for reflectance measurement agree more closely with the visual color observations of faceted gemstones than other geometries.



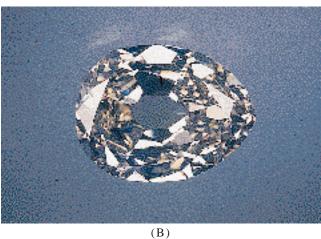


FIG. 1. The color appearances of the Tavernier diamond under incandescent light and daylight: (A) a light brown (a orange hue) under incandescent light; (B) a light pink (a purple hue) under daylight. (Photo by Shane McClure.)

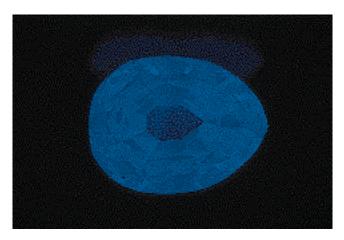


FIG. 2. The Tavernier diamond shows a very strong blue fluorescence under long wavelength UV radiation. (Photo by Shane McClure.)

The ''alexandrite effect'' refers to a distinctive color change of a material when viewed under different light sources. ^{12,13} Only a few gemstones display different colors between different light sources. The alexandrite effect is seen most notably in its namesake, the alexandrite variety of chrysoberyl, which can appear bluish-green under daylight and reddish-purple under incandescent light. In alexandrite, the hue-angle differences between these two colors can be almost 180° (i.e., they are opponent colors), when viewed between these two light sources. The alexandrite effect is a non-color-constancy phenomenon.

Recently we had an opportunity to study one of the notable Tavernier diamonds. This particular diamond shows very strong blue fluorescence under long wavelength UV radiation, and a weaker reaction to short wavelength UV. It changes color from light brown under incandescent light to light pink under daylight. This diamond demonstrates that very strong UV fluorescence, excited by natural daylight, can produce an alexandrite effect. A xenon D65 daylight simulator was used for measuring the spectrum of this diamond. This spectrum includes both spectral reflection and UV fluorescence components. Colorimetric calculation results and visual color appearances on this diamond are compared here.

SAMPLE DESCRIPTION

The Tavernier diamond is faceted as a pear-shaped brilliant, and weighs 56.07 carats. Its color change from incandescent light to daylight is shown in Figs. 1(A) and (B). The very strong blue fluorescence under long wavelength UV radiation is shown in Fig. 2. When viewed with a gemological microscope at 10× magnification, the bodycolor appears evenly distributed, even though some of the brown coloration seems to be concentrated along parallel bands. These can also be seen as a similar-appearing strain pattern when the diamond is viewed between crossed polarizing filters.

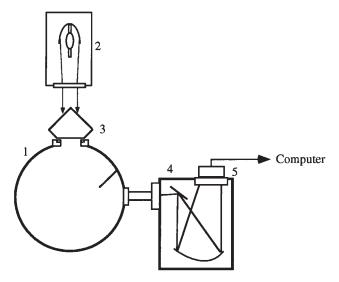


FIG. 3. A diagram of the imaging spectrograph CCD spectrometric system for measuring color of gemstones: (1) integrating sphere; (2) xenon D65 light source; (3) gemstone; (4) imaging spectrograph; (5) cooled CCD detector.

CAUSES OF COLOR AND FLUORESCENCE

The infrared spectrum identifies this diamond as a type IaA < B. From the absorption features present, the major trace-element impurity in this diamond is nitrogen, in the form of several states of atomic aggregation. These include both A and B defects, N3 centers, and larger, microscopic "platelets" that are possibly nitrogen-related defects. ¹⁴ The N3 center causes the blue fluorescence, ⁶ and contributes to the color of this diamond. The brown color is also thought to be the result in part of an atomic-level defect resulting from plastic deformation, ⁴ which took place while the diamond was still in the earth.

COLOR MEASUREMENT INSTRUMENTATION

A Hitachi U-4001 spectrophotometer was used to measure the spectral transmittance curve of the diamond without UV fluorescence. An imaging spectrograph CCD system, designed for measuring the face-up color of faceted gemstones, was used to measure the spectral transmittance curve with fluorescence under a xenon D65 daylight simulator. The CCD detector has a thermoelectric air cooling system to suppress the inherent dark current and to make the whole system stable. Both measurements were made with the diamond at room temperature. Figure 3 shows the optical arrangement of the system for measuring the spectral transmittance curve with fluorescence. The xenon D65 daylight simulator has two filters in the front; one is a colored glass filter and another is a diffuser. The colored glass filter has three functions: (1) it increases the color temperature of the light from about 5500-6500 K; (2) it removes the ultraviolet radiation below 300 nm; and (3) it absorbs heat. The diffuser, which was located far from the focal point of the xenon light, makes the light

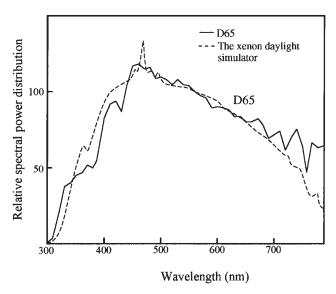


FIG. 4. The relative spectral power distribution of the xenon D65 daylight simulator compared with CIE standard Illuminant D65.

distribution more uniform. Figure 4 shows the relative spectral power distribution of the xenon D65 daylight simulator compared with CIE standard Illuminant D65. It has a similar relative spectral power distribution, in both the ultraviolet and visible regions, to that of the CIE standard Illuminator D65.

RESULTS

Figure 5 shows the spectral transmittance curve of the diamond measured by the Hitachi spectrophotometer at

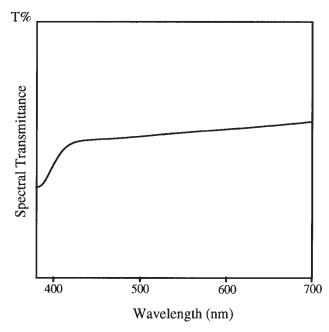


FIG. 5. The spectral transmittance curve of the diamond without fluorescence.

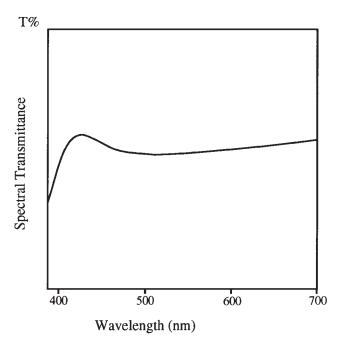


FIG. 6. The spectral transmittance curve of the diamond with fluorescence.

a 5-nm interval. This curve is typical for a diamond with the N3 center. Since the blue fluorescence of the N3 center is predominantly, if not all, caused by ultraviolet radiation below 400 nm, any fluorescence caused by incident visible light can be ignored for this study. Figure 6 shows the spectral transmittance curve measured by the imaging spectrograph CCD system under the D65 daylight simulator. This spectrum consists of two parts: one is the transmittance curve similar to the curve in Fig. 5, and the another is the fluorescence caused by the UV radiation from the D65 daylight simulator.

Figure 7 shows a comparison between spectral transmittance curves of this diamond with and without fluorescence. The spectral transmittance curve with fluorescence is normalized to the curve without fluorescence at 560 nm. The relative fluorescence intensity of this diamond under the D65 daylight can be obtained by subtracting the transmittance curve without fluorescence from the spectral transmittance curve with fluorescence (after normalization). Figure 8 shows the relative fluorescence intensity calculated in this way, with the peak of the emission centered in the blue. This curve is the typical blue fluorescence spectrum caused by the N3 center, without the sharp emission spectral lines (which are absent because the spectrum was recorded at room temperature, and to the wide bandwidth of UV radiation in the D65 daylight illumination).

Table I tabulates the calculated chromaticity coordinates of the spectral transmittance curve in Fig. 5. The calculated hue-angle is 67.2° under Illuminant A, 86.2° under Illuminant D65, and 90.2° under Illuminant F7. The hue change between Illuminants A and F7 is 23.0°, which is larger than 20°, the calculated criterion we use for

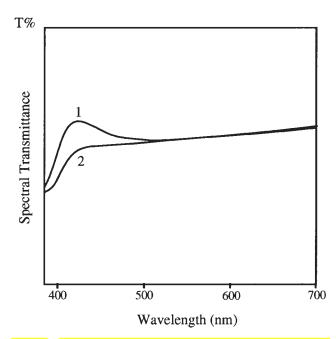


FIG. 7. A comparison of the spectral transmittance curves of the diamond with and without fluorescence: (1) the spectral transmittance curve with fluorescence; (2) the spectral transmittance curve without fluorescence.

judging whether a gemstone shows the alexandrite effect. ¹³ Under these lighting conditions, this diamond is a "type 4" alexandrite-effect stone according to our classification. This type of color change is very small in terms of the difference in color appearance.

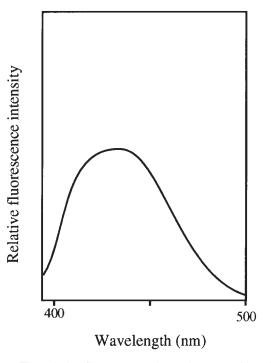


FIG. 8. The relative fluorescence intensity caused by ultraviolet component in the xenon D65 daylight simulator.

Table II tabulates the calculated chromaticity coordinates of the spectral transmittance curve in Fig. 6 under Illuminant D65. Since the light source used for the measurement is a xenon D65 daylight simulator, the calculated data under Illuminants A and F7 are not listed in this table. The hue-angle is 346.3° under this D65 daylight simulator. Comparing data in Tables I and II, the hue-angle change of this diamond between Illuminant A without fluorescence, and Illuminant D65 with fluorescence, is about 80.9°. This corresponds to the observed color change mentioned above.

DISCUSSION

Without fluorescence, this diamond shows only a very weak alexandrite effect. The spectral transmittance curve in Fig. 5 can be thought of as a "one transmittance band" spectrum, with a single broad region of transmittance starting from about 425 nm out to 700 nm. In addition to the three patterns of transmittance bands that cause the alexandrite effect, ¹³ we suggest a "one-band" spectrum can also cause the alexandrite effect.

The blue fluorescence exhibited by many yellow diamonds under daylight causes little if any change in their color appearance. However, a few colorless to light yellow diamonds have a very strong blue fluorescence, which can change their appearance between light sources with and without a UV component. The blue fluorescence can make a light yellow diamond appear less saturated (or more colorless). In the case of the light brown Tavernier diamond, the stone appears more pink.

The Tavernier diamond shows very strong fluorescence under daylight. Although diamonds that change color under different light sources are known, this is the first gemstone we have found so far that displays an alexandrite effect mainly caused by fluorescence.

CONCLUSION

Although diamonds that change from brown to pink color have been reported, this study suggests that at least some

TABLE I. Chromaticity coordinates of the spectral curve in Fig. 5.

Illuminanta	L*	a*	b*	С	Н
A	73.74	2.50	5.95	6.45	67.2
D65 F7	73.35 73.35	$0.39 \\ -0.02$	5.88 6.04	5.89 6.04	86.2 90.2

^a The hue-angle change between Illuminants A and D65 is 19.0°, between D65 and F7 is 4.0°, and between A and F7 is 23.0°.

TABLE II. Chromaticity coordinates of the spectral curve in Fig. 6 under Illuminant D65.

Illuminant ^a	L*	a*	<i>b</i> *	С	Н
D65	69.3	3.41	-0.83	3.51	346.3

^a Since Illuminants A and F7 cannot cause the strong fluorescence shown in Fig. 7, the chromaticity coordinates under the two illuminants are not listed in this table.

of color change of this diamond is caused by blue fluorescence that contributes to a more pink appearance.

The Tavernier diamond also shows very weak alexandrite effect between Illuminants A and F7. This diamond has only one transmittance band in the visible spectrum. In addition to two transmittance band spectra, multiband spectra, and step-band spectra, one band spectra can also cause the alexandrite effect.

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