

COATED PINK DIAMOND— A CAUTIONARY TALE

David J. F. Evans, David Fisher, and Christopher J. Kelly

The Diamond Trading Company (DTC) Research Centre had the opportunity to examine a diamond that, on submission to a commercial gem laboratory, was stated to have been HPHT treated. However, spectroscopic analysis yielded data inconsistent with this statement. After further testing, it was determined that this diamond, which originally was probably pale yellow, had been coated to change its color to the equivalent of Fancy Intense purple-pink. Careful examination with a microscope revealed evidence of a coating exclusively on the pavilion facets. Elemental analysis of the coating suggests it may be calcium fluoride with a gold impurity that was added either to generate the absorption responsible for the pink color or to assist as a nucleating agent for the calcium fluoride film.

The emergence of high pressure/high temperature (HPHT) color treatment of natural diamond has brought about a marked increase in the sophistication of the spectroscopic analysis used by grading laboratories when testing diamonds (see, e.g., Fisher and Spits, 2000; Smith et al., 2000). Care must be exercised, however, that the reliance on such advanced analytical techniques does not cause the gemologist to neglect the more “traditional” means of identifying simpler forms of treatment. The case described here serves to highlight the potential consequences of such

neglect, although the net result was the gathering of interesting analytical information on a diamond treated by an older technique.

A CASE STUDY

During September 2004, scientists at the DTC Research Centre in Berkshire, United Kingdom, had the opportunity to study the 0.85 ct round brilliant cut diamond shown in figure 1. The diamond had been graded Fancy Intense purple-pink by a gemological laboratory and was said to have been color enhanced by HPHT treatment. Although pink HPHT-treated diamonds with colors as strong as Fancy Deep have been reported (see, e.g., Hall and Moses, 2000), they are extremely rare. Therefore, this identification immediately raised our suspicions.

Spectroscopic Analysis. Because the diamond had been described as HPHT treated, testing began with the advanced analytical instrumentation that is typically used to determine when the color of a diamond has been modified by exposure to HPHT treatment conditions. This involved the use of several spectrometers, including those that analyze the absorption of light throughout the ultraviolet, visible, and near-infrared regions of the spectrum (a Perkin Elmer Lambda 19 UV-Vis-NIR spectrometer, with the diamond at room temperature as well as cooled to liquid nitrogen temperature using a

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suitable cryostat) and the mid-infrared region (a Nicolet Magna IR 750 Fourier-transform infrared [FTIR] spectrometer, at room temperature only). The diamond's photoluminescence (PL) spectra were recorded under a range of different laser-excitation wavelengths: 325 and 633 nm excitation using a Jobin-Yvon Labram Infinity spectrometer; 488 and 514 nm excitation using a Spex 270M spectrometer. For the PL spectroscopy, the diamond was again cooled to liquid nitrogen temperature in a cryostat.

UV-Vis-NIR spectroscopy revealed that the pink color was caused by a broad absorption band centered at around 550 nm (figure 2). A similar absorption feature at this wavelength is responsible for the color in most natural-color pink diamonds, both (nitrogen containing) type I and (nitrogen free) type II stones (see, e.g., Collins, 1982; King et al., 2002). In natural-color pink diamonds, however, this 550 nm band typically is accompanied by a broad absorption band at 390 nm (again, see figure 2), which was not recorded in this sample. The diamond did show an absorption line at 415 nm (the N3 center), a nitrogen-related feature that is found in most type Ia diamonds.

Figure 2. The UV-Vis-NIR absorption spectra of the 0.85 ct diamond at room temperature and liquid nitrogen temperature show a broad 550 nm band and N3 absorption at 415 nm; the latter is present in most type Ia diamonds. A room-temperature absorption spectrum of a type IaAB natural-color pink diamond is provided for comparison. It shows the two broad absorption bands at 390 and 550 nm that are characteristic of such diamonds; careful examination allows the 390 nm band to be distinguished from the broad absorption associated with N3.

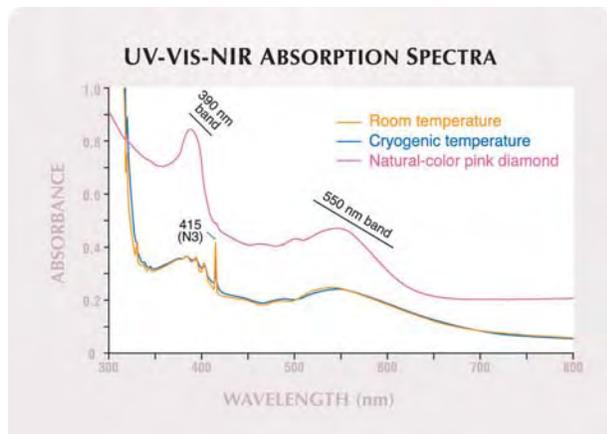
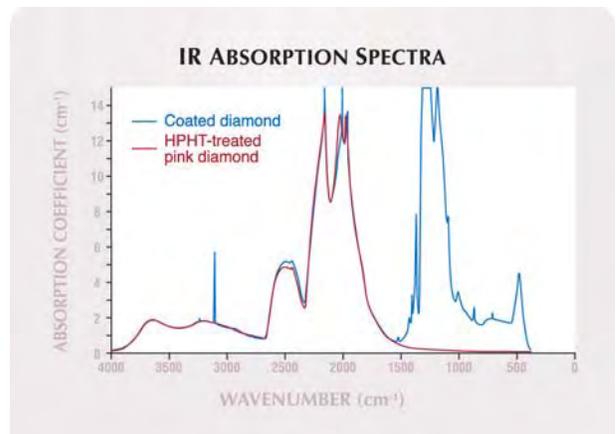


Figure 1. This 0.85 ct purple-pink diamond was examined at the DTC Research Centre to investigate the claim that it had been HPHT treated. Careful analysis and observation revealed that the color of the diamond was due to a topical coating that had been applied to the pavilion of the stone. Photo by Chris Kelly.

Using FTIR, we discovered that the diamond was a type IaAB, with the majority of the nitrogen in the A aggregate form (figure 3). (For a description of diamond types and how they relate to the various aggregation states of nitrogen impurities in diamond, refer, for example, to Fritsch and Scarratt, 1992.) Although the spectrum was saturated in the region

Figure 3. The infrared spectrum of the 0.85 ct diamond revealed that it was a type IaAB, whereas pink HPHT-treated diamonds are typically type IIa.



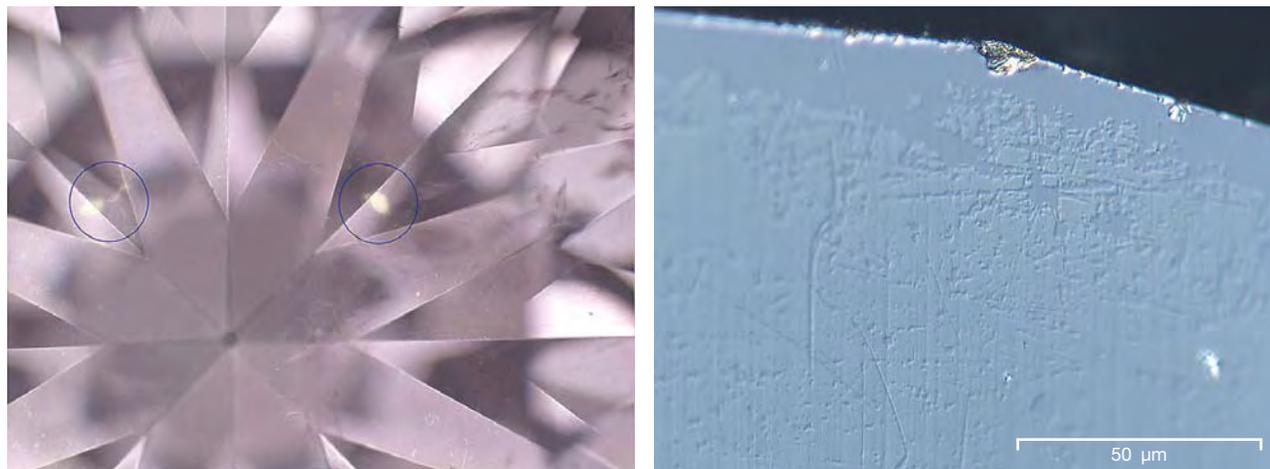


Figure 4. This photomicrograph of the 0.85 ct diamond in transmitted light (left) shows two pale yellow regions (circled) where the pink color is not visible (photomicrograph by Chris Kelly; magnified 35×). The Nomarski image (right) of the edge of one of the pavilion facets shows how the coating has worn away (photomicrograph by David Fisher).

associated with nitrogen-related absorption (approximately $1300\text{--}1100\text{ cm}^{-1}$), spectral fitting techniques developed at the DTC Research Centre provided nitrogen concentration estimates of 470 parts per million (ppm) of A-form nitrogen and 280 ppm of B-form nitrogen. Fairly strong hydrogen-related absorption also was detected in the form of the C-H stretch mode at 3107 cm^{-1} . These results contradict the stated origin of color: HPHT-treated pink diamonds are typically type IIa, and the absorption characteristics were not consistent with those one would expect to encounter in *any* type IaAB diamond that had undergone HPHT treatment at temperatures sufficiently high to generate a significant color change (Reinitz et al., 2000). Natural-color pink diamonds do show a range of nitrogen concentrations and aggregation states, but in our experience they typically do not show the very high levels measured in this case and their aggregation levels tend to be higher.

Low-temperature photoluminescence spectroscopy with 325 nm excitation revealed dominant N3 luminescence (main line at 415 nm), consistent with its observation in the absorption spectra. The spectrum taken with 488 nm excitation showed two lines at 503 nm separated by 0.2 nm. One was the frequently observed H3 center (from a nitrogen-vacancy-nitrogen impurity). The identity of the other line, at a slightly shorter wavelength, is not certain, but it may be the S1 center (for a description of luminescence centers, see Davies, 1977, and Field, 1992). Other strong luminescence features observed with 488, 514, and 633 nm excitation were lines at 701, 787, and 793 nm. All of these have been seen in natural “cape” yellow diamonds (Field,

1992), and it is the experience of the authors that they are generally encountered in untreated near-colorless to pale yellow diamonds with a nitrogen content of a few hundred parts per million and significant hydrogen-related absorption. No indication of HPHT treatment was found, and we have not seen the 701, 787, and 793 nm lines at the strength observed here in natural-color pink diamonds.

Although the diamond had been described as being HPHT treated, the data recorded using various advanced spectroscopic techniques did not support this assessment. However, they were not wholly consistent with natural-color pink diamonds either. Rather, in the experience of the authors, the spectroscopic features recorded were more consistent with those seen in natural-color near-colorless to pale yellow diamonds. It was therefore determined that additional testing was needed to resolve the cause of the pink coloration in this diamond.

Further Investigation. When viewed with a microscope, the diamond revealed a somewhat uneven color distribution. This is not necessarily unusual in natural-color pink diamonds, but in such stones the pink coloration tends to be concentrated along so-called slip planes where plastic deformation has taken place. Closer examination showed that the uneven color distribution in this sample was actually related to “patches” where the pink color was absent (figure 4, left), revealing pale yellow regions with transmitted light. This raised the possibility that the diamond had been coated in some way to produce the pink color. Examination of the pavilion facets showed clear evidence of a coating that had

worn away at facet junctions and in the centers of some facets. The coating was most easily viewed using the Nomarski differential interference contrast technique (Robinson and Bradbury, 1992), as illustrated in figure 4 (right). No coating was observed on the table and crown facets. Once we had established the location of the coating, we were able to find it with the microscope using reflected light; the coating appeared as slightly yellower regions with the set-up used. This yellow color is likely due to interference associated with the thin film coating, as such effects are relatively strong in reflected light. No fluorescence associated with the coating was detected, but careful imaging with the Diamond Trading Company DiamondView instrument showed that the luminescence intensity was slightly lower from the coated regions. We concluded that the coating was fairly durable, as it had not been removed by the several cycles of cooling to liquid nitrogen temperatures and re-warming to room temperature the diamond experienced during the spectroscopic testing.

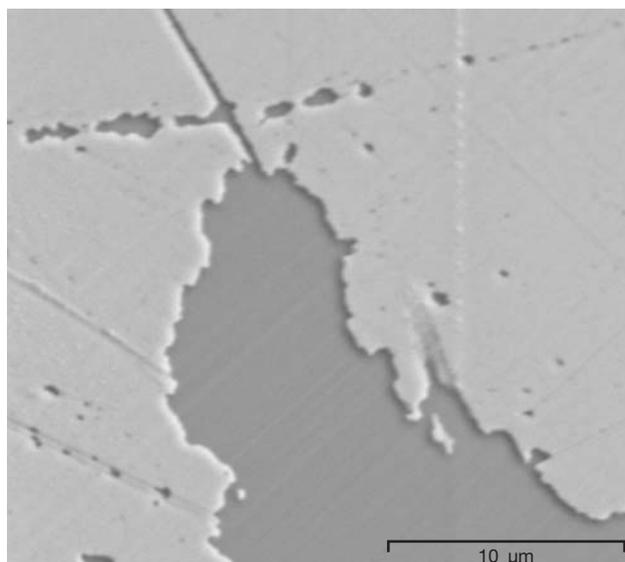
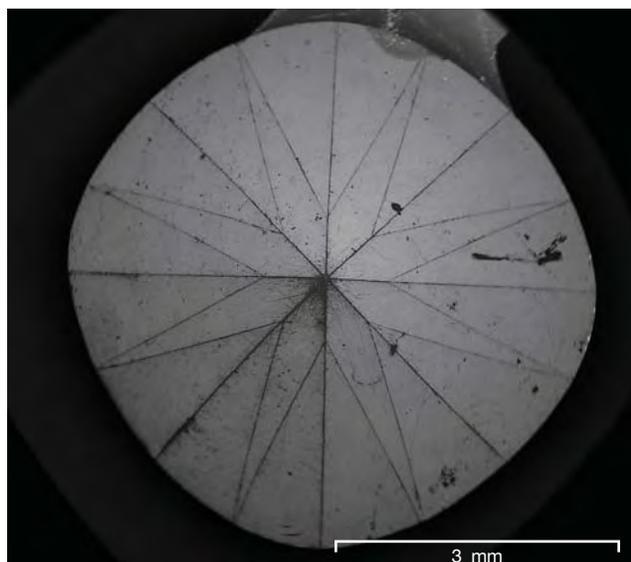
Following these observations, we conducted a detailed analysis to determine the composition of the coating. First, we examined the pavilion region with a Philips Quanta 200 low-vacuum scanning electron microscope (SEM). The microscope scans a beam of high-voltage electrons across the surface of the sample in a variable pressure chamber. As the

electrons impinge on the surface of the sample, they are scattered and X-rays of energies characteristic of the elements comprising the material are produced. The scattered electrons can be imaged to provide topographic information, and specific X-ray energies can be selected and mapped on the same scale to produce a distribution map of a particular element. The low-vacuum technique has benefit over a more conventional SEM analysis in that the sputtered metallic (usually gold) or carbon coating typically required for SEM work on nonconducting diamond was not necessary.

SEM imaging of the areas being analyzed clearly confirmed the presence of minor wear and removal of the coating (figure 5). Further analysis using energy-dispersive X-ray (EDX) mapping (figure 6) revealed that the coating was comprised of gold, calcium, and fluorine exclusively. Peaks associated with carbon from the underlying diamond and oxygen contaminant present equally in both the coating and the diamond also were observed. As the sample had not been conventionally prepared for SEM, the gold content was found to be a genuine component of the coating and not a specimen preparation artifact.

Discussion. Although the diamond had been presented as HPHT treated, spectral analyses and microscopic examination contradicted this conclusion and

Figure 5. These low-vacuum SEM backscattered electron images reveal damage and wear to the coating on the pavilion of the stone (left) and, at higher magnification, bright areas where the coating was intact and dark areas where it had worn away (right).



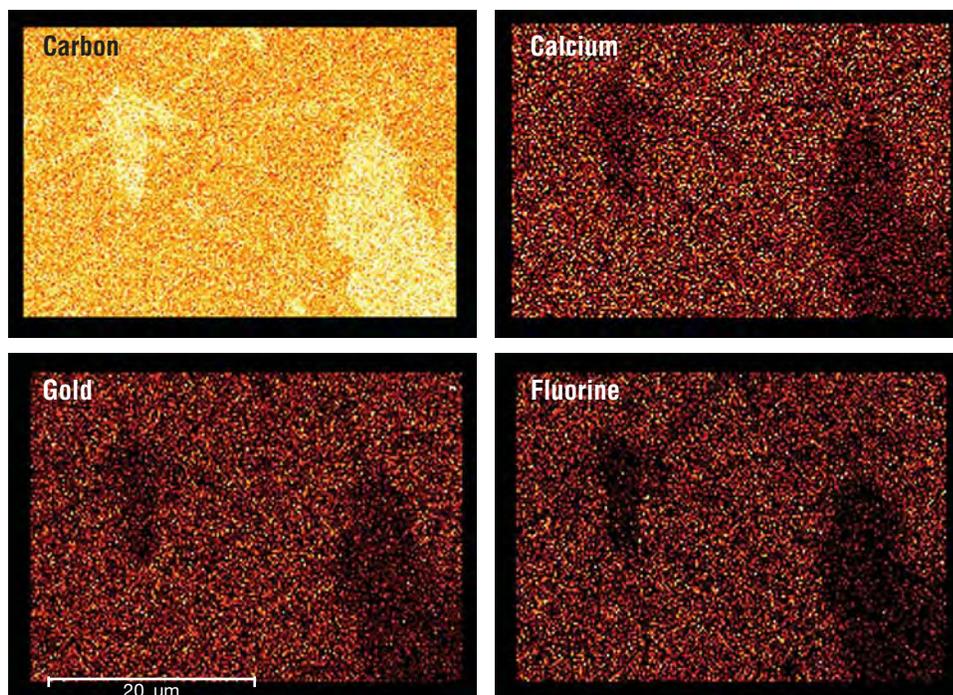


Figure 6. These energy-dispersive X-ray maps show the distributions of the main elements detected in the analysis: carbon, calcium, gold, and fluorine. Bright spots correspond to regions of high concentrations of the specific element. The feature to the lower right in each is the area where the coating was worn away in figure 5 (right). The carbon X-ray map shows a high signal where the coating has been removed (due to the underlying diamond). The calcium, gold, and fluorine signals are significantly stronger in the regions where the coating is intact.

established that the purple-pink color was the result of a topical coating.

The use of fluoride coatings on diamond has been reported previously as being “considered unsatisfactory by coaters, since they are easily detected by their purplish-blue iridescence” (Miles, 1962, p. 356). However, the present sample did not reveal such an iridescence effect. Calcium fluoride (CaF_2) is a material commonly used in optical components. Naturally occurring calcium fluoride (as the mineral fluorite) exists in a range of colors variously attributed to impurities or lattice defects due to irradiation (Deer et al., 1966), with the lattice defects having been associated with purple in some instances. There has been work on the implantation of calcium fluoride with gold to generate nanoparticles that can produce a broad absorption band at about 520 nm, similar to the broad absorption peak observed in this diamond (Henderson et al., 1997). While the gold may be responsible for the color in this case, it is also possible that it was used to promote the nucleation or adhesion of the coating. The exact form of the coating on this diamond is not known, but clearly it involves the deposition of calcium fluoride either as the color-producing layer or as a protective or host layer for gold particles, which themselves are responsible for the absorption feature resulting in the pink color.

CONCLUDING COMMENTS

Gemologists and gemological laboratories must contend with an ever-increasing number of sophisticated diamond treatments that can only be identified with advanced analytical techniques. Therefore, it is not surprising that the more traditional forms of color treatment may be overlooked when they are assessing whether a particular diamond’s color is natural or has been artificially induced. A recent *Gems & Gemology* lab note on coated diamonds (Sheby, 2003) emphasized the importance of keeping these earlier treatments in mind during a gemological examination.

For the diamond described in this report, the spectroscopic data conflicted with the stated HPHT origin of the pink color, whereas careful examination with the microscope revealed evidence of a coating. This coating produced a broad absorption band at around 550 nm, which imparted a pink color to an originally pale yellow stone. Analysis of the coating suggests that it is calcium fluoride with gold, but the data acquired do not allow for the determination of whether the gold or some other impurity doping the calcium fluoride is responsible for the color-causing absorption. This study serves to re-emphasize the importance of sound gemological observation when examining stones for the possibility of color treatments.

ABOUT THE AUTHORS

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The main criteria that determine the uniqueness of gemstones are: (1) aesthetic appeal, (2) purity (i.e., the number and nature of associated minerals) and perfection, (3) rarity, (4) historical importance, and (5) scientific significance. Based on these criteria, several categories of unique stones were recognized, their parameters tabulated, and valuations applied. Particularly unique samples are extremely difficult to value but, as a generalization, their price depends on size, purity, abundance and location of physical defects, availability of details on their geologic occurrence, and publications (scientific or popular) related to the particular specimen. BMS

Managing the commons: An economic approach to pearl industry regulation. B. Poirine, *Aquaculture Economics & Management*, Vol. 7, No. 3-4, 2003, pp. 179-193.

Unregulated use of tropical lagoons for pearl culture has created problems associated with overexploitation, which has led to declining profits (or losses) for pearl farmers. Various factors cause cultured pearl production to decline and oyster mortality to increase when a critical density is reached. Particular emphasis is placed on the problems facing the Tahitian black cultured pearl industry.

In lagoons owned privately by a single producer, overcrowding is not a problem because profits are maximized far below the critical density. However, in public lagoons, the author proposes that the government should regulate, by auction, the use by a single producer for a specific period of time, with rules to ensure equitable policies toward all producers. Arguments are also made for a global cultured pearl production quota to keep prices from falling due to excess supplies; both Australia and Japan have enacted successful oyster quota policies that have prevented overexploitation and the economic havoc that results from such practices. RS

Not forever: Botswana, conflict diamonds and the Bushmen. I. Taylor and G. Mokhawa, *African Affairs*, Vol. 102, No. 407, 2003, pp. 261-283.

Although Botswana, a peaceful democracy in southern Africa, has not been implicated in the campaigns against conflict diamonds, the policies of its government regarding tribes of Bushmen living in the Central Kalahari Game Reserve have come under fire.

Botswana is the world's largest diamond producer by value, and diamonds are responsible for 87% of its foreign exchange. The country, one of the poorest at independence in 1966, is now in the upper-middle income category (with a per capita Gross Domestic Product of more than \$6,000), though the distribution of wealth remains very unequal. Because the country is so depen-

dent on diamond revenues, its government launched a "Diamonds for Development" campaign to ensure differentiation from other African nations beset by wars that spawned the conflict diamond campaigns. However, a number of nongovernmental organizations (Survival International, in particular) have sought to link the government's policy of removing Bushmen tribes, known as the San, from the Reserve to diamond exploration efforts in that area.

The government cut off services, including water, to the area in January 2002 as part of a policy to resettle the San, claiming the action and the resettlements were to protect wildlife and foster tourism in the area. Survival International drew De Beers—a 50/50 partner in Botswana's diamond mining operations—into the controversy, as De Beers holds an exploration license near the affected area. De Beers has distanced itself from the government's resettlement policy and noted that its exploration area comprises only 20 km² of the Reserve's 55,000 km². Survival International continues to organize protests against De Beers and the Botswana government. RS

Strategies for sustainable development of the small-scale gold and diamond mining industry of Ghana. R. K.

Amankwah and C. Anim-Sackey, *Resources Policy*, Vol. 29, No. 3-4, 2003, pp. 131-138.

Small-scale mining of gold and diamonds has helped create employment and government revenue in Ghana. Since the government instituted reforms in 1989 that legalized such activities, more than 1.5 million ounces of gold and 8 million carats of diamonds have been produced. The Small-Scale Mining Law includes a technical assistance program that has helped with prospecting and development, legalized the purchase of mercury for gold recovery, and established a marketing authority to buy and export gold and diamonds. By the end of 2001, 420 small-scale mining concessions (nine for diamonds) had been licensed. These companies have generated employment for more than 100,000 people.

However, there are still thousands of illegal miners, called *galamsey* in local parlance, who have created problems for the government. First, conflicts have arisen over their encroachment on concessions held by larger mining companies. Some large firms have accommodated the illegal miners by ceding less-economic areas of their concession to them—in exchange for their registering with the government. Second, these illegal miners—and some legal mining enterprises—also cause a great deal of environmental damage. Mercury poisoning is a particular problem in some mining villages.

The government has launched an education program to promote cleaner, safer extraction methods. It also has encouraged the formation of small-scale mining associations to better regulate safe and productive mining practices. RS