A HISTORY OF DIAMOND TREATMENTS

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Although various forms of paints and coatings intended to alter the color of diamond have likely been in use for almost as long as diamonds have been valued as gems, the modern era of diamond treatment—featuring more permanent alterations to color through irradiation and high-pressure, high-temperature (HPHT) annealing, and improvements in apparent clarity with lead-based glass fillings—did not begin until the 20th century. Modern gemologists and diamantaires are faced with a broad spectrum of color and clarity treatments ranging from the simple to the highly sophisticated, and from the easily detected to the highly elusive. The history, characteristics, and identification of known diamond treatments are reviewed.

For as long as humans have valued certain materials as gems, those who sell them have sought ways to make them appear brighter, shinier, and more attractive—to, in other words, make them more salable and profitable. From the earliest, most basic paints and coatings to the most sophisticated high-pressure, high-temperature (HPHT) annealing processes, the history of diamond treatments parallels that of human advancement, as one technological development after another was called upon to serve the "King of Gems" (figure 1). And, much as the pace of human technological advances accelerated in the past hundred-plus years, gemologists of the 20th century witnessed the introduction of gem treatments that the earliest diamond merchants could scarcely have imagined—and that literally reshaped the world of contemporary diamantaires.

Because of their potential to deceive, gem treatments, including those applied to diamond, have long had an aspect of fraud about them, whether a treatment was intended to mask or remove color (e.g., figure 2); to add, enhance, or alter color (e.g., figure 3); or to change other characteristics such as apparent clarity. That being said, there have also been long periods, both ancient and modern, when diamond treatments were conducted in the relative open, and their practitioners were regarded by some as experts and even artists. Gem treatments, it must be recognized, are neither good nor bad in themselves—fraud comes about only when their presence is concealed, whether by intent or by negligence. This fact places a specific responsibility for full treatment disclosure on all those handling gem materials, and most especially on those selling diamonds, given their long and enduring value. That responsibility is one of knowing and understanding what happens as a result of treatment, having the expertise to recognize treated stones when they are encountered, and knowing when suspect stones should be examined by properly equipped gem-testing laboratories.

This article is not intended to be a complete review of the history of diamond treatments, as such

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See end of article for About the Authors and Acknowledgments.
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Figure 1. Once rarely-seen collectors' items, colored diamonds are now widely available as a result of a variety of treatments that can change off-color stones to attractive hues. Shown here is a collection of jewelry set with treated-color diamonds. The "cognac" diamond in the ring is 1.07 ct; the blue diamond in the brooch is 0.85 ct and is set with 0.60 ct of purple diamonds; the stud earrings contain 1.74 ct of green diamonds and 0.30 ct of yellow diamonds; the hoop earrings contain 0.95 ct of colored diamonds. All the colored diamonds were treated by irradiation. Composite of photos by azadphoto.com; courtesy of Etienne Perret.

an endeavor could easily fill a book (see, e.g., Nassau, 1994; Shigley, 2008). Rather, it is intended to provide a broad overview of the subject and a resource for those wishing to delve further into the literature. Information presented is derived from the published literature and the authors' (primarily JES) experience with diamond testing. The subject will be addressed in roughly chronological order, with the discussions divided by color and clarity treatments.

COLOR TREATMENTS

Paints and Coatings. *Early History*. The coating, dyeing, and painting of gems to alter their appearance is an ancient practice, and one that likely started soon after human beings began valuing minerals for personal adornment. The first use of diamond as a gemstone was almost certainly in India (e.g., figure 4), probably well before any contact with Western cultures around the Mediterranean, as Indian lapidary arts in the Indus Valley were already fairly advanced by the second millennium BC (Krishnan and Kumar, 2001). Whether treatment of diamonds there was as common as with other gems is another matter, however. Diamonds were objects of great religious and cultural significance in ancient India (see, e.g., Brijbhusan, 1979), and there were strong taboos against altering them in any way (Tillander, 1995). Further, as with many other things in India, diamonds were classified by color according to a rigid caste system (Brijbhusan, 1979; Tillander, 1995), and consequently there must have been strong social pressure against altering a stone's color. This hardly means it did not occur, of course. Since colorless stones occupied the highest caste, there would have been strong *economic* incentives to find ways to reduce the apparent color of off-color

Figure 2. A blue coating on a yellowish diamond can neutralize its bodycolor and make it appear more colorless. Variations on this treatment have been used for centuries. Photomicrograph by John I. Koivula; magnified 5×.

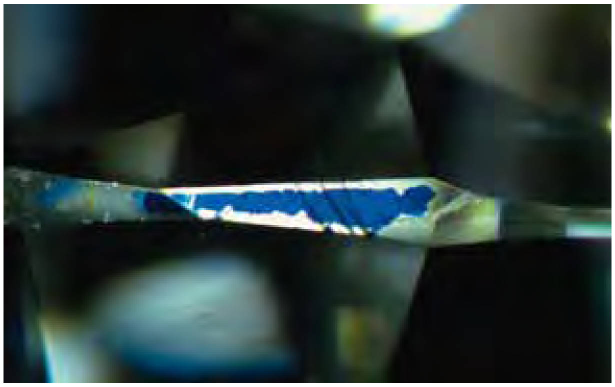

Figure 3. This attractive green diamond (3.06 ct) owes its color to irradiation. Photo by Robert Weldon.

stones—though the party responsible no doubt risked much in doing so. Gill (1978), for example, reported the historic use of ultramarine in India to improve the color of yellowish stones, as well as of other pigments to produce apparent colors.

Diamonds were largely unknown to the early Greeks. Ball (1950) placed the arrival of diamonds in Greece no earlier than about the fifth century BC (and then only as "the rarest of curiosities," p. 242), and in Rome at about 65 BC. Although Pliny mentioned the dyeing and foiling of a variety of gems, diamond is not among them. Instead, his discussion of diamond is largely confined to its resistance to fire and blows—though not goat's blood, which was reputed to soften it* (Ball, 1950). Nevertheless, diamond crystals were used on occasion in jewelry during this period, so it is likely that some enterprising jewelers were painting and coating them as well, since dyeing is known to have been a common practice with other gems during this period (Ball, 1950).

Although cleaving of octahedral diamond crystals to create various simple shapes (usually point cuts) may have taken place as much as 2,000 years ago (Tillander, 1995), true cutting and polishing to create new shapes and facet arrangements is thought to have evolved slowly beginning some time in the 14th century (Balfour, 2000). As cutting techniques developed, and early diamond manufacturers learned which methods best improved brilliance and color, it is likely that different types of coatings followed closely behind. It is interesting to note that one of the oldest surviving accounts of early diamond cutting, by Italian master jeweler Benvenuto Cellini (Cellini, 1568), also contains detailed instructions on how to improve a diamond's appearance by applying various substances to the pavilion surface.

Cellini told the story of a large diamond that had been given by Holy Roman Emperor Charles V to Pope Paul III, which Cellini was commissioned to mount. Interestingly, not only was the coating of diamonds legal at this time, it was also such an accepted practice that Cellini conducted the coating in the presence of several of his colleagues in order to impress them with his artistry. He applied a mixture of pure gum mastic, linseed oil, almond oil, turpentine, and lampblack to the base of the stone, and so "seemed to remove from it any internal imperfections and make of it a stone of perfect quality" (p. 39). The results were dramatic enough that his audience declared that he had increased the value of the diamond from 12,000 to 20,000 scudi (the forerunner of the modern Italian lira).

Cellini also described how the appearance of yellow diamonds could be improved by replacing the lampblack with indigo (a blue dye): "[I]f it be well applied, it becomes one colour, neither yellow as heretofore nor blue owning to the virtue of the tint, but a variation, in truth, most gracious to the eye" (p. 36).

The mastic/lampblack recipe is one that appears to have been employed for several centuries, as it is described by Thomas Nichols in his 1652 work, *A Lapidary, or, The History of Pretious* [sic] *Stones*. Yet, a review of the literature does not seem to indicate that matters progressed much beyond this until the mid-20th century. There is a passing mention of coating diamonds in John Hill's annotated translation of Theophrastus' *History of Stones* (1774), among several other works (see Nassau, 1994), but little else. Although the recipes changed as the science of chemistry evolved (potassium permanganate [$KMnO_4$] was commonly used in the late 1800s [see Gill, 1978], and aniline blue [a histological stain] was popular in the early 1900s ["Gemmology. . .," 1940]), the same basic approach was still being used well into the 20th century (see, e.g., "Gemological glossary," 1934; Briggs, 1935; Crowningshield, 1959).

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*Nassau (1994) traced this curious myth, which persisted for over 1,500 years, to a recipe in an Egyptian papyrus dating to about 400 AD (though copied from a much older version). Dipping in goat's blood was actually the last step in a quench-crackling process in preparation for dyeing crystalline quartz. Over the ensuing centuries, this use with quartz was apparently confused with other colorless gems, including diamond.

Figure 4. These untreated Mogul-cut diamonds (9.27 and 9.54 ct) may be from India's Golconda region, possibly fashioned several centuries ago. Photo by Nicholas Del Re.

Contemporary Treatments. It was not until the 1950s that modern technology began replacing these centuries-old methods. Following up on a report in *The Gemmologist* the previous year ("Improved gem brilliancy. . . ," 1949), Gübelin (1950) described experiments with sputter-coated fluoride thin films (CaF_2, BaF_2, MgF_2) in combination with a titanium oxide substrate and a protective silica top coating in order to increase light transmission, brilliance, and color appearance in gems, including diamond (e.g., figure 5). These optical coatings had been developed for military purposes during World War II in order to obtain improved performance from binoculars, bombsights, periscopes, and similar optical devices (MacLeod, 1999), and they were the subject of numerous patents in the post-war years (e.g., Moulton and Tillyer, 1949, which mentions possible use on gem materials). The process is carried out in a vacuum chamber containing a cathode of the coating material and a substrate that serves as the anode. Positively charged ions of the coating material flow across the chamber in gaseous form and adhere to the substrate (Quorum Technologies, 2002).

Among other effects produced by these coatings, Gübelin (1950) stated, "slightly yellowish tinted diamonds may appear blue-white" (p. 246). It is interesting to note that he reports the best results were obtained when the coatings were applied to the top of the stone. However, this also resulted in anomalous refractometer readings (i.e., the RI of the coating rather than that of the diamond, which is over the limit of a standard refractometer), and the appearance of an obvious iridescent film on the crown and table. Diamond treaters apparently recognized these problems as well, and coated diamonds seen in the trade over the ensuing years had such coatings applied only to their pavilions or girdles (Miles, 1962).

Schlossmacher (1959) reported seeing such coated diamonds in the German gem center of Idar-Oberstein, and Miles (1962, 1964) reviewed GIA's experiences while grading diamonds at the Gem Trade Laboratory in New York City. Miles also described several practical visual means by which these coated "near-colorless" diamonds could be recognized by gemologists. Most stones were treated with a bluish coating in order to mask (or compensate for) light yellow bodycolors and thereby create a more colorless appearance. Several treaters were performing coatings with varying degrees of skill, and Miles reported that at least one company was actively offering its services to the New York diamond trade. As the technology advanced and treaters became more experienced, detection of these coated stones became a serious challenge (Miles, 1962). Although U.S. Federal Trade Commission (FTC) guidelines issued in 1957 required jewelers to disclose coated diamonds ("Jewelry industry . . . ," 1957), the rules were widely ignored. The problem became so serious that in 1962 the New York State Legislature was forced to pass a law making the sale of coated diamonds without disclosure a criminal offense (see Overton, 2004, and references therein for a more detailed discussion of the legal elements of treatment disclosure). This law had the effect of forcing the practice outside of mainstream markets, though diamonds with such coatings are still periodically seen in the GIA Laboratory. Sheby (2003), for

Figure 5. A sputtered coating—visible here as indistinct dark spots on the bezel and upper girdle facets—has been applied to this 5.69 ct pear-shaped diamond. Such colored spots are a classic feature of sputter coatings intended to create a more colorless appearance in off-color stones. Photomicrograph by Vincent Cracco; magnified 23×.

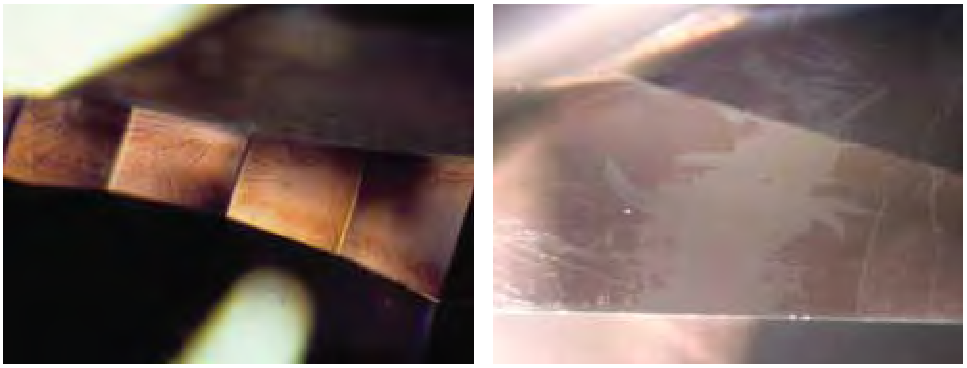


Figure 6. The diamond on the left proved to be a cape stone with a pink coating on the girdle. Note the iridescence and irregular surface features. At right, scratches in the pink coating on this stone are also indicative of this treatment. Photomicrographs by Andrew Quinlan, left (magnified 63×), and Wuyi Wang, right (100×).

example, described a yellowish diamond coated with a blue material to improve its apparent color, similar to those reported 40 years earlier by Miles.

Although it was known that these thin film coatings could also mimic fancy colors (see Schiffman, 1969; Crowningshield, 1975), such color-coated diamonds were not seen in meaningful numbers until fairly recently. In fact, even natural fancy-color diamonds were virtually unknown to most consumers until the 1980s and ’90s (Shor, 2005). Pink diamonds were among the first natural fancy colors to gain widespread attention, so it is not surprising that pink-coated diamonds began to appear in the late 1990s (figure 6). Crowningshield and Moses (1998), Evans et al. (2005), and Wang et al. (2006) all described recent examples of polished diamonds colored pink by sputter-coated thin films. Epelboym et al. (2006) reported seeing both pink- and orange-coated diamonds that were possibly colored by a silica film doped with gold rather than the fluoride coatings previously in use. Shen et al. (2007) described a method by which a wide variety of colors could be produced using multiple microthin coatings of varying chemistries. In this same article, Shen et al. reported that the GIA Laboratory was also seeing an increase in diamonds colored pink by coating with calcium fluoride (CaF_2).

Despite all these advances, however, traditional methods of painting and coating have not disappeared, and examples have appeared on occasion in the trade. Crowningshield (1965) reported on assistance GIA gave to law enforcement authorities who were prosecuting a jeweler for selling painted diamonds. Fryer (1983) related an interesting (and no doubt distressing for the parties involved) story of a large natural-color pink diamond being switched for a yellowish stone that had been painted with pink nail polish. Other methods, such as coloring girdle facets with permanent markers and solutions made from colored art pencils, have also been seen (S. McClure, pers. comm., 2008).

Identification. Most coated diamonds can be identified by an experienced gemologist, provided the opportunity exists to examine the entire stone with a gemological microscope. Typically, coatings betray themselves through the presence of spots, scratches, uneven color concentrations, and similar surface irregularities, in addition to iridescent reflections and interference-related colors (again, see figures 5 and 6); these latter features are best seen with reflected light. In addition, diamonds that are coated to appear more colorless often display an unnatural grayish or bluish cast, which can make color grading difficult to impossible (Sheby, 2003). Paler colors present a greater challenge, but immersion in methylene iodide can help reveal color concentrations in surface areas. “Near-colorless” coatings are necessarily more difficult to detect than those intended to impart a bodycolor to the diamond, especially if they are applied to very small areas of the stone, as is often the case. Visual detection of surface coatings on melee-sized diamonds can also present greater difficulties.

When available, Nomarski differential interference contrast microscopy (Sato and Sasaki, 1981; Robinson and Bradbury, 1992) can enhance the visibility of irregularities such as scratches or uneven coatings on facet surfaces (e.g., figure 7). If destructive testing is permitted, applying a polishing powder with a lower hardness than diamond (such as corundum powder) to the facets will produce scratches and thus reveal the presence of a surface coating.

Advanced methods, such as scanning electron microscopy (which can examine the coated areas at much higher magnification) and chemical analysis (which can reveal the presence of elements that do not occur naturally in diamond), will provide definitive confirmation when any doubt remains.

The durability of diamond coatings varies considerably depending on the substances used and how they are applied. Simple paints can be wiped off or removed with solvents such as alcohol and

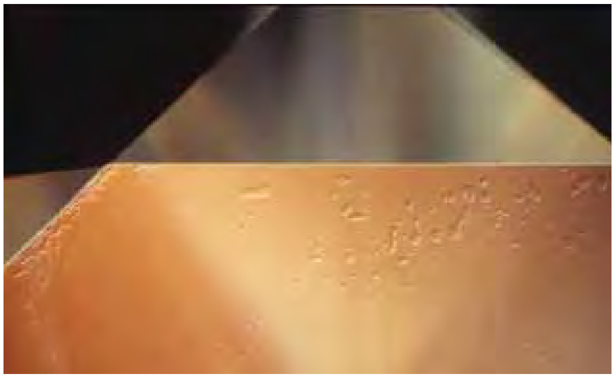


Figure 7. It is clear from this Nomarski image that a coating has been applied to the table of this diamond. Photomicrograph by John I. Koivula; magnified 30×.

acetone. Optical coatings are more durable, but they can still be scratched or removed with acids; they are also unstable to some jewelry repair processes (Shen et al., 2007), as are paints.

Synthetic Diamond Thin Films. Finally, a word must be said about the potential use of synthetic diamond thin films on natural diamond. Koivula and Kammerling (1991) reported an experiment in which boron-doped synthetic diamond was deposited as a thin coating by chemical vapor deposition (CVD) on several colorless faceted diamonds, which became dark bluish gray as a result (see also Fritsch and Phelps, 1993). Although there is no indication that this process has ever seen commercial use, recent advances in—and commercialization of—CVD diamond synthesis (see, e.g., Wang et al., 2003, 2005b, 2007; Martineau et al., 2004) mean that it remains a possibility. Such a diamond coating might be far more durable than anything previously seen on the market. As an illustration, CVD diamond coatings applied to machine tools can typically extend the useful life of such tools by 10–50 times (CVD Diamond Corp., 2007). In light of this, and the fact that such a coating would be chemically homogeneous with the coated stone, identification methods such as the polish test and chemical analysis might not be reliable means of detection.

Irradiation. The era of artisanal diamond treatments came to an end shortly after the turn of the 20th century. In 1896, French scientist Henri Becquerel accidentally discovered radioactivity while performing experiments with phosphorescence (Becquerel, 1896). Seeking to measure the phosphorescent reaction of a sample of the mineral zippeite [potassium uranyl sulfate; $K_2UO_2(SO_4)_2$] on a set of photographic plates, Becquerel found that the uranium in the sample had exposed the plates before the experiment even began. Further research by Marie and Pierre Curie led to the discovery of the element radium in 1898. Radium's intense radioactivity made it a useful source of radiation for experimentation by subsequent researchers, one of whom was an English scientist named Sir William Crookes (box A).

In 1904, Crookes presented a paper to the Royal Society of London detailing his experiments exposing diamonds to radium, both to its radioactive emissions and to direct contact (Crookes, 1904). While the former had no lasting effect, packing the stones in radium bromide gave them a bluish green to green color after several months. As might be expected, this discovery created an immediate stir in the nascent gemological community.

Over the ensuing decades, a series of researchers repeated Crookes's experiments (as did Crookes himself; see, e.g., Crookes, 1914; Lind and Bardwell, 1923a,b; Dollar, 1933). Their work established that the color change was due to alpha radiation, that the color was confined to a very shallow surface layer of the diamond, and that the green or blue-green color could be changed to various shades of yellow to brown by sufficient heating.

However, Crookes and other researchers also discovered that radium treatment of diamonds created long-lasting residual radioactivity that could present a health risk (Crookes, 1914), which effectively limited any legitimate commercial use of this method. Although these treated diamonds (some of which were colored by exposure to other radioactive isotopes such as ^{241}Am or ^{210}Pb) were occasionally seen in the trade anyway, they remained for the most part no more than scientific curiosities and are encountered today only very infrequently (see, e.g., Hardy, 1949; Crowningshield, 1961; Webster, 1965; Henn and Bank, 1992; Ashbaugh and Moses, 1993; Reinitz and Ashbaugh, 1993). It is worth noting, though, that they can remain radioactive for periods of up to several hundred years.

Radium and similar materials were not the only sources of radiation that might be used to treat diamonds, however. In the early 1930s, Professor Ernest Lawrence at the University of California at Berkeley developed a device that became known as the cyclotron, which could accelerate charged atomic particles to high velocities using a magnetic field (e.g., Lawrence, 1934). Through the 1940s and into the 1950s, various researchers experimented with

BOX A: SIR WILLIAM CROOKES

Sir William Crookes (1832–1919) was one of the great Victorian men of science (figure A-1). His life was characterized by wide-ranging, enthusiastic research across multiple fields, from hard sciences such as physics and chemistry to more philosophical work in spiritualism and metaphysics (see D'Albe, 1923; this brief biography is adapted from that book). Although he is known in gemology for his discovery of the effects of radiation on diamond near the end of his life, Crookes had already had a long and distinguished career as a chemist and physicist prior to this work.

Crookes was educated at the Royal College of Chemistry in London. His initial studies in inorganic chemistry received a great boost after Gustav Kirchhoff and Robert Bunsen published their pioneering work on spectroscopy in 1860 (Kirchoff and Bunsen, 1860). Using their methods, Crookes was able to identify a new element, thallium, in 1861 during an analysis of pyrite ore used for making sulfuric acid. This discovery cemented his reputation and led to his election to the Royal Society in 1863. In the 1870s, Crookes turned his attention to cathode rays, cathode-ray tubes, and cathodoluminescence, and his work in this area remains the foundation of the field, though some of his theories about these discoveries were later shown to be in error. (Crookes believed cathode rays were a new, fourth state of matter rather than electrons.)

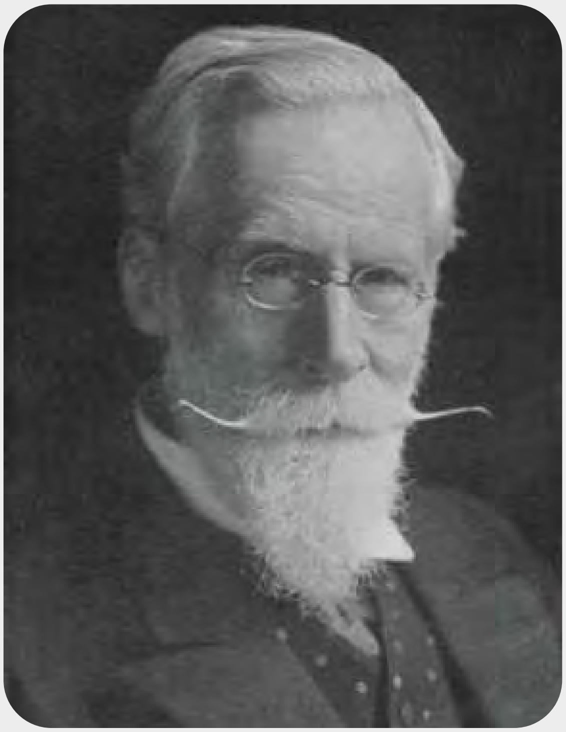
In chemistry, he contributed greatly to the evolution of spectroscopy, and published a wide range of papers and treatises on the subject. Much of his chemical research was directed toward practical questions of the day, and he was a recognized authority on water quality and public sanitation (a notable pamphlet, which he published in 1876, was *The Profitable Disposal of Sewage*).

Crookes also had an interest in diamonds, and in 1896 he toured the Kimberley mines in South Africa as a guest of De Beers (Crookes, 1909). His research into the luminescence of minerals naturally led him to experiment with radioactivity after Becquerel's discovery that same year. He continued studies in this field almost up to the time of his death. In addition to his work with diamonds, he also achieved the first separation of protactinium (Pa) from uranium, and invented a simple device for detection of radioactivity, the spinthariscope.

Crookes's dabblings in Victorian mysticism (e.g., Crookes, 1874), which led him to conduct a series of séances and form relationships with noted mediums, were viewed with some consternation by his colleagues and nearly led to his expulsion from the Royal Society. History has been kinder, however, and these works have come to be seen as merely another sign of his indefatigable energy and insatiable curiosity.

Crookes was knighted in 1897 and appointed to the Order of Merit in 1910. He died in London on April 4, 1919, and is buried in Brompton Cemetery.

Figure A-1. Sir William Crookes is best known in gemology for his discovery of the effects of radiation on diamonds. Photo by Ernest H. Mills, approx. 1911.



exposing diamonds to cyclotron radiation, usually alpha particles, deuterons (^{2}H nuclei), and protons (e.g., Cork, 1942; Ehrman, 1950; Pough and Schulke, 1951; Pough, 1954, 1957). The diamonds turned various shades of blue-green, green, yellow, and brown, though the yellow-to-brown colors were eventually determined to be the result of heating caused by the bombardment. The stones did become radioactive, but only for a short period afterward. The colors were confined to near-surface layers—though visibly

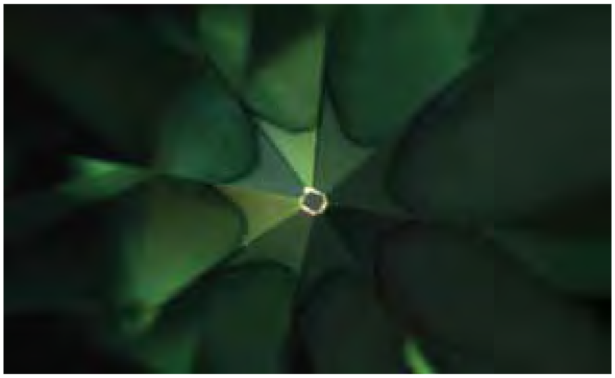


Figure 8. The distinctive feature around the culet of this irradiated diamond, commonly referred to as the umbrella effect, *is a tell-tale sign of treatment in a cyclotron. The umbrella effect is not a result of the cyclotron beam striking the culet, but rather the girdle area; its appearance at the culet is caused by internal reflections. Photomicrograph by John I. Koivula; magnified 10×.*

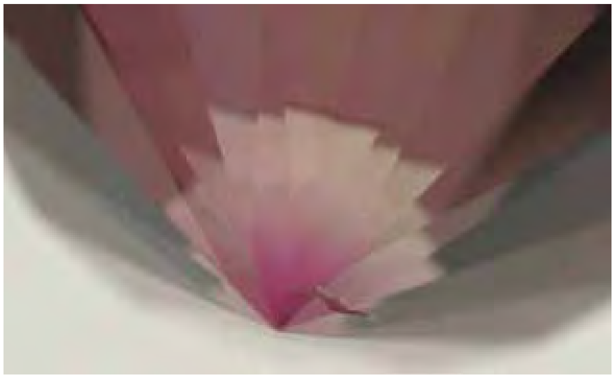


Figure 9. Lower-energy electron irradiation in a linear accelerator can create a thin layer of color beneath the pavilion facets which, because of internal reflections within the diamond, also appears as a concentration of color at the culet of the stone. In this instance, the color concentration is rather intense, which would not be the case if the thin layer of induced color was less saturated. Photomicrograph by Wuyi Wang; magnified 5×.

deeper than those seen with radium-treated stones—and were also induced in strongly defined color concentration patterns related to the facet arrangement (e.g., figure 8), since color was created only where the beam of radiation struck the diamond. The commercial applications of these treated colors were obvious, and cyclotron-treated diamonds soon appeared in significant numbers in the market, with sometimes embarrassing results (box B).

Early linear accelerators (linacs) were also used to bombard diamonds with electrons (Clark et al., 1956a,b; Pough, 1957). However, as the energies were relatively low (on the order of 0.5–3.0 MeV; Dyer 1957; Schulke, 1961), the beam did not completely penetrate the stone, and the color was also confined to thin layers beneath facet surfaces that were exposed to the radiation (e.g., figure 9; Collins, 1982; Fritch and Shigley, 1989).

As nuclear reactors became more commonplace in the 1950s, these too were used to irradiate diamonds (Dugdale, 1953). However, because neutrons—which make up the most significant portion of radiation from nuclear fission—can completely penetrate even a large stone, the resulting green color was created more uniformly throughout the diamond (i.e., a “bodycolor”) rather than being confined to thin zones near the surface (Dyer, 1957; Pough, 1957). Likewise, when more powerful linacs came into common usage in the 1960s and 1970s, the higher-energy electrons (10–15 MeV; Ashbaugh, 1988) that were generated with these devices were also able to create uniform color (Parsons, 1996). Without the tell-tale facet-related color concentration patterns of early electron irradiation, these treated diamonds would prove to be a significant identification challenge, requiring the use of advanced spectroscopic techniques.

Diamonds can also be colored by exposure to gamma ray emissions from a radionuclide such as ^{60}Co, similar to that used to sterilize food products and medical equipment (Dyer, 1957; Pough, 1957; Ashbaugh, 1988). Although the process has been known from the early days of diamond irradiation, it is rarely used because it is much slower than other methods, typically taking several months (Collins, 1982). It is worth noting here that the gamma rays do not themselves color the diamond; rather, they generate secondary electrons as they pass through the stone, and these electrons induce color in the same fashion as those from a linac (Collins, 1982).

Nowadays, the most common methods are neutron irradiation in a reactor and high-energy electron irradiation in a linac (e.g., Nassau, 1994). The process selected will depend on the exposure time, costs, potential damage to the diamond, and the treated colors desired.

Radiation-induced color in diamond is the result of damage caused as the radiation (whether neutrons or charged particles) passes through the stone. Collisions between these particles and the carbon atoms create vacant positions in the atomic lattice by knocking the carbon atoms out of their normal positions (Collins, 1982). These vacancies give rise to a broad region of absorption in the visible and near-infrared regions of the spectrum (and a sharp peak at 741 nm, known as the GR1 band), thus creating a

BOX B: THE IRRADIATED DEEPDENE

Out of all the uncounted carats of diamonds subjected to one treatment or another, perhaps none is more famous than a large yellow stone named after the country estate of the Bok family outside Philadelphia. The Deepdene (figure B-1), as it is known, is believed to have been mined in South Africa in the 1890s (*The Deepdene Diamond*, 1997; Balfour, 2000; most information here is taken from these two references). Consistent with this source, its original color is thought to have been a dark cape (Pough, 1988). The Boks purchased the stone from Los Angeles diamond dealer Martin Ehrmann, who would, interestingly enough, later conduct a series of early experiments in diamond irradiation (Ehrmann, 1950; there is no evidence Mr. Ehrmann was involved in treating the Deepdene). The Boks sold the stone to Harry Winston in 1954.

Sometime in 1955, Dr. Frederick Pough was hired to cyclotron irradiate and anneal the diamond and thereby intensify its yellow color (Pough, 1980, 1988). Dr. Pough was then a recognized authority on the subject and had, perhaps not coincidentally, just published an article on diamond irradiation in *Jewelers' Circular-Keystone* (Pough, 1954). Afterwards, the stone was repolished slightly to remove obvious signs of treatment, specifically the umbrella effect (again, see figure 8).

The diamond was next seen when it came up for auction in 1971. Before the sale, Christie's had engaged two gemological laboratories to determine an origin of color, and both reported that it was untreated. After the sale, this conclusion was disputed by famed gemologist Dr. Edward Gübelin, and it was then sent to the Gem Testing Laboratory in London, where Basil Anderson concurred with Dr. Gübelin's opinion, and to New York, where Robert Crowningshield (who had seen the diamond before it was treated) confirmed Dr. Gübelin's original doubts. The sale thus had to be rescinded and the diamond returned to its owners. Controversy over this incident would simmer for another decade. Not until the 1980s did Dr. Pough come forward to publicly confirm that he had irradiated the stone (e.g., Pough, 1988).

There is some uncertainty in the literature as to when, exactly, Dr. Pough learned of the controversy, and how long he waited to come forward. Both Balfour (2000) and a later auction catalog (*The Deepdene Diamond*) suggest that he was not aware of the debate for some time afterward, perhaps not until the early 1980s. Pough himself did not clear up this ambiguity in a *Lapidary Journal* article a few years later (Pough, 1988) and further insisted that the controversy was "foolish and hardly seems to matter" (p. 29).

In fact, Dr. Pough was aware of the controversy all along. In an interview with GIA Library director Dona Dirlam in 2004 (Pough, 2004), he described how he was contacted shortly after Dr. Gübelin's examination of the diamond in 1971, and how he confirmed to Dr. Gübelin that he had irradiated the stone. Only a confidentiality agreement with the party who had commissioned the treatment prevented him from going public at the time.

The Deepdene came up for sale again in 1997—this time with full disclosure—and was sold to diamond dealer Lawrence Graff for $715,320.

Figure B-1. The Deepdene diamond (currently 104.53 ct), which was irradiated and heated in 1955 to intensify its yellow hue, is perhaps the most famous treated-color diamond in the world. Photo courtesy of Christie's.

blue-to-green coloration (Walker, 1979; Collins, 1982; Clark et al., 1992). The strength of the overall broad GR1 absorption, and thus the saturation of the induced color, is directly related to the amount of radiation received (Clark et al., 1956a). Under conditions of extreme exposure, the induced color can become so dark that it appears black, though the blue or green hue can usually still be seen by holding the treated diamond over a strong light source such as a fiber-optic cable (e.g., Moses et al., 2000; Boillat et al., 2001).

Heating of most irradiated diamonds above about 500°C in an inert atmosphere will change the blue-to-green colors to brownish or orangy yellow to yellow or, rarely, pink to red (e.g., figure 10). This is the result of radiation-induced vacancies migrating through the lattice and pairing with nitrogen to create new color centers, such as H3 (503.2 nm) and H4 (496 nm) for yellow to orange, and N-V^0 (637 nm) for pink to red (Collins, 1982). These color alterations are accompanied by specific features in the visible and luminescence spectra of treated diamonds that aid in the identification of the treatments (see, e.g., Collins, 1978, 1982, 2001, 2003; Clark et al., 1992).

Identification. Recognition of laboratory-irradiated (and sometimes heated) faceted colored diamonds has been a major focus of gemological research since the early 1950s (Scarratt, 1982). For example, Crowningshield (1957) reported on the detection of treated yellow diamonds by means of an absorption band at 5920 Å (592 nm) seen in the desk-model spectroscope. The availability of more sensitive spectrometers has since refined the location of this band to 595 nm and established a number of other identifying clues (Scarratt, 1982; Woods and Collins, 1986; Fritsch et al., 1988; Clark et al., 1992; Collins, 2001).

Although initially believed to be diagnostic of laboratory treatment, a weak 595 nm band was subsequently found in the spectra of some natural-color diamonds. This discovery, along with the increasing abundance and variety of treated-color diamonds in the market, led gemological researchers to realize that identifying treated diamonds would require more comprehensive study of both known natural-color and known treated-color stones, and the collection of a database of their gemological properties (color, UV fluorescence, absorption spectrum, and other visual features) and more sophisticated spectral information (visible, infrared, and luminescence). Correct identification, when possible, requires an evaluation of all of these factors. Thus, even today, many artificially irradiated diamonds cannot be identified by a gemologist with standard gem-testing equipment, and they must be submitted to a laboratory for an “origin of color” determination.

Diamonds with a blue-to-green bodycolor present a special identification problem, since their color may be due to natural radiation exposure. Some rough diamond crystals display a very thin (several microns) green surface coloration due to exposure to natural alpha-particle radiation in the earth. If green naturals are left on the finished stone, these can contribute to a green face-up color, but this layer is often mostly or completely removed during the faceting process. Natural diamonds with a saturated blue-to-green bodycolor are very rare, but they do exist; perhaps the best example is the famous 41-ct Dresden Green diamond (Kane et al., 1990; see also King and Shigley, 2003). Despite work over the past five decades, identifying origin of color in these cases remains very challenging for gemological researchers, and still it is not always possible for gem-testing laboratories to conclusively establish whether a green diamond is or is not

Figure 10. A broad array of colors are currently achievable by exposure to radiation. All of these diamonds (0.12–1.38 ct) were color treated by irradiation and—except for the black, blue, and green stones—subsequent heat treatment. Photo by Robert Weldon.

laboratory irradiated unless it can be examined from the rough through the faceting process.

HPHT Annealing. The most important recent treatment of diamonds involves annealing them at high pressure and high temperature to either lighten off-color stones or create certain fancy colors. Although the commercial uses of this process in the jewelry trade were not realized until the late 1990s, scientists had recognized more than 30 years earlier that treatment under such conditions could change diamond color.

In the late 1960s, Soviet researchers reported experiments in which HPHT treatment both removed color from light yellow diamonds and turned yellow and yellow-green diamonds predominantly green (Nikitin et al., 1969). A few years later, Evans and Rainey (1975) successfully induced yellow color in colorless type Ia diamonds. Research by Chrenko et al. (1977) at General Electric (GE) and by Brozel et al. (1978) at the University of Reading, England, demonstrated that HPHT treatment could change the aggregation state of nitrogen impurities in diamond. Changes from single substitutional nitrogen (Ib) to nitrogen aggregates (Ia), and from Ia to Ib, were both possible under the right conditions of temperature and pressure and the appropriate starting diamond. By altering these nitrogen-containing optical defects, and thereby changing how they caused the diamond to absorb portions of the spectrum of incident light, the process altered the color of the stone. Figure 11 illustrates the relative experimental conditions of this early work, as well as that of later researchers.

In the late 1970s, researchers at GE obtained two U.S. patents on processes for removing yellow and yellow-brown color from type I diamonds, again by converting type Ib nitrogen to type Ia (Strong et al., 1978, 1979; see also Schmetzer, 1999a,b). Type Ib nitrogen creates a broad absorption below about 560 nm toward the ultraviolet, leading to an observed strong yellow color (Collins, 1980, 1982). Type IaA and IaB nitrogen aggregates, however, absorb only in the infrared, so converting Ib nitrogen to aggregated form would remove most of the yellow hue (provided, of course, that other nitrogen-based color centers, such as H3 and N3, were not created in the process). Parallel work by De Beers Industrial Diamond Division led to a similar patent a few years later (Evans and Allen, 1983). Commenting on these discoveries, Nassau (1984, p. 129) said, "The possible commercial significance of these experiments regarding the decolorizing of natural or synthetic yellow diamonds is not yet clear."

In the early 1990s, GE researchers apparently also discovered that HPHT treatment could be used to strengthen (i.e., improve strength and hardness by reducing lattice defects) colorless CVD synthetic diamond, which is type IIa (i.e., without detectable nitrogen and boron) and incidentally also reduce the color in stones with a brown component (Anthony et al., 1995a,b, 1997). Similar work was ongoing with other groups. In their report on synthetic dia-

Figure 11. This carbon phase diagram illustrates the diamond-graphite stability field (defined by the dashed red equilibrium line) and the plastic yield limit of diamond (solid blue line). Diamond is the stable form of carbon above the diamond-graphite equilibrium line, whereas graphite is stable below this line. The high pressures of the HPHT process are required to prevent diamond from converting to CO_2 *gas or graphitizing while heated to the high temperatures needed to change the color. Diamond is rigid to the left of the yield-strength line, whereas it can plastically deform under conditions corresponding to those to the right of this line. Pressure-temperature ranges of early HPHT experiments and selected patents are also shown. Note that the upper pressure limit of Evans and Allen (1983) was undefined. Modified from DeVries (1975) and Schmetzer (1999b).*

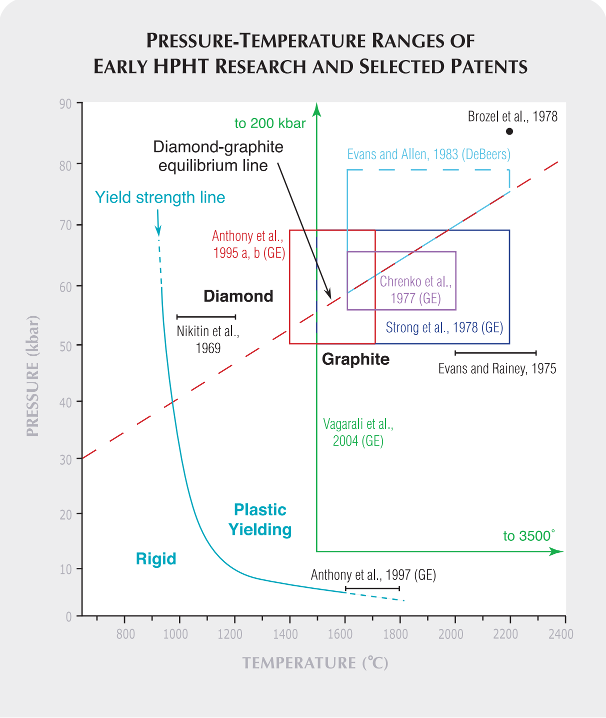


Figure 12. These examples illustrate some of the fancy colors that can be produced by HPHT treatment of type Ia (left), type IIa (center), and type IIb (right) diamonds. Photos by Robison McMurtry, left; C. D. Mengason, center; Jessica Arditi, right.

monds from Russia, Shigley et al. (1993) examined three greenish yellow to yellow samples that had been HPHT treated to alter their color. In 1997, Reinitz and Moses reported on several yellow-green diamonds submitted to the GIA laboratory that displayed features later considered indicative of HPHT treatment (Reinitz et al., 2000). Again, the commercial possibilities of the HPHT process were not clear to those in the trade, though there was some limited speculation (K. Scarratt, as reported in Even-Zohar, 1994). This latter report followed up on claims by Russian scientists that yellowish Ib diamonds could be made whiter by conversion to type IaAB, as discussed above, but there is no evidence that this process has ever seen commercial use. Treated-color yellow-to-green diamonds continued to appear on the market in the late 1990s (Van Bockstael, 1998; Henn and Millisenda, 1999).

Despite more than three decades of research, along with technical publications and patents, the trade was taken by surprise in March 1999 when GE and Lazare Kaplan International (LKI) announced the commercial use of the HPHT process to remove color from type IIa diamonds (Rapaport, 1999). This development caused substantial controversy and criticism, especially since the initial press release asserted that the stones would be “indistinguishable” from natural diamonds (Moses et al., 1999; Schuster, 2003). Some of this criticism was blunted after GE and LKI agreed to laser inscribe their diamonds and work with GIA and other industry groups to establish reliable means of identification, though GE initially refused to release specific details about the process itself. The need for proper detection criteria became even more critical after a few treated diamonds with their identifying laser inscriptions removed began appearing later that year (Moses et al., 1999).

Fortunately, gemological researchers were not as ill-prepared as the trade for this development, and reports by Schmetzer (1999a), Collins et al. (2000), Fisher and Spits (2000), and Smith et al. (2000), among others, did much to clear the confusion about what GE was doing. What mystery remained around the GE process began to dissipate in October 2001, as related patent applications began to be published (Vagarali et al., 2001, 2004). Although GE’s initial work involved removing color from type IIa brown diamonds (Smith et al., 2000), subsequent developments by GE and others have led to the production of a wide range of colors in both type II (pink or blue; Hall and Moses, 2000, 2001) and type I (orangy yellow, yellow, to yellow-green; e.g., Henn and Millisenda, 1999; Reinitz et al., 2000; Deljanin et al., 2003; Hainschwang et al., 2003) diamonds (e.g., figure 12).

The exact mechanism of the color change in brown diamonds is still a subject of debate. Although brown color in natural diamonds was once believed to be associated with plastic deformation of the carbon lattice (see, e.g., Wilks and Wilks, 1991; Fritsch, 1998), it is now thought that this is not entirely correct, as the lattice deformation is not affected by the HPHT process even though the brown color is removed. Recent research has suggested a link between brown color and vacancies and vacancy-related extended defects (e.g., Bangert et al., 2006; Fisher et al., 2006). Such extended defects can give rise to an absorption spectrum similar to that of brown type IIa diamonds.

It is believed (Collins, 2001) that the absorptions responsible for blue and pink colors are not a result of the HPHT process, but rather are preexisting, and the blue or pink color is revealed only when the predominant brown component is removed, as the resulting stones show certain properties similar to natural-color blue and pink stones (Hall and Moses, 2000, 2001). Yellow-green to green colors in HPHT-treated stones are the result of vacancies pairing with nitrogen to form H2 and H3 centers, while pure yellows can be created from type Ia diamonds through disaggregation to type Ib nitrogen (Collins, 2001; Hainschwang et al., 2003). Processes to remove color from type IaB brown diamonds have also shown some promise (Van Royen et al, 2006).

Other U.S. companies as well as treatment facilities in Russia, Sweden, and Korea have since entered the market with their own products (e.g., Henn and Millisenda, 1999; Smith et al., 2000; Reinitz et al., 2000; Deljanin et al., 2003; Wang and Moses, 2004; Wang et al., 2005a). When combined with irradiation (e.g., Wang et al., 2005a), colors across nearly the entire visible spectrum can be achieved for type I and type II diamonds, and such treated-color diamonds have now become nearly ubiquitous in the market (e.g., Perret, 2006; again, see figure 10). Further, unlike paints and coatings, the colors of HPHT-treated diamonds are permanent to standard jewelry manufacturing, wear, and repair situations.

Identification. The identification of HPHT-treated diamonds, especially through standard gemological testing, remains a challenge (Collins, 2006). Although these stones may occasionally display distinctive visual features that can be seen with magnification (such as graphitized inclusions or internal cleavages, or damaged surfaces [figure 13]; see Moses et al., 1999; Gelb and Hall, 2002), in general these indicators either are not always present or are not adequate to fully establish a stone's correct identity. Type IIa diamonds—which comprise the vast majority of colorless HPHT-treated diamonds—are relatively easy to identify by their short-wave UV transparency with simple equipment like the SSEF Diamond Spotter (Chalain et al., 2000; Hänni, 2001), but further testing is still necessary to determine if a stone is natural or treated color. The De Beers DiamondSure instrument (Welbourn et al., 1996) will also "refer" type IIa stones, but it cannot make a definitive identification of treatment (and the cost is out of the reach of most gemologists).

When the proper laboratory equipment is available, a variety of spectroscopic clues can identify HPHT treatment (Newton, 2006). Some of the earliest work in this area actually began in the 1980s at the De Beers DTC Research Centre (Fisher and Spits, 2000). This and subsequent research (see, e.g., Chalain et al., 1999, 2000, 2001; Collins et al., 2000; De Weerdt and Van Royen, 2000; Smith et al., 2000; Vins, 2002; Collins, 2003; Novikov et al., 2003), helped establish various features seen with infrared and, particularly, low-temperature photoluminescence (PL) spectroscopy as reliable indicators of treatment. The relative strength of the N-V luminescence at 575 and 637 nm when excited by a 514.5 nm laser has been found to be useful for type IIa diamonds (Collins, 2001). It is very important to note, though, that it is the *combination* and relative strength of various defects that is key to identification, rather than the mere presence or absence of a single type of defect (Newton, 2006). For this reason, definitive identification requires testing in a properly equipped gemological laboratory. In general, the precise methods and criteria of identification are considered proprietary by most labs.

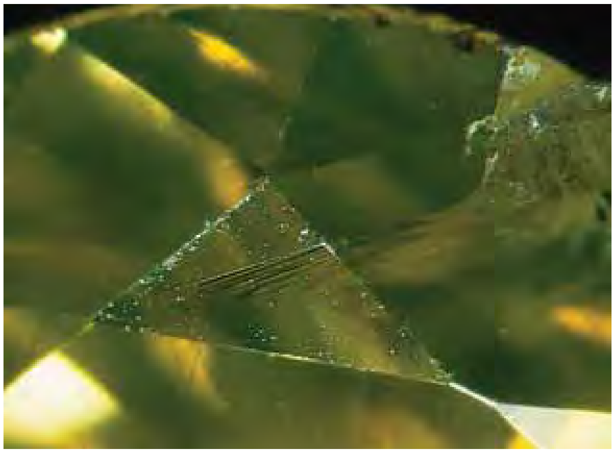


Figure 13. This 0.52 ct green-yellow diamond shows abraded facet edges and frosted facets, indicative of HPHT treatment. Typically, such features will be polished off before a stone is offered for sale. Photomicrograph by Shane Elen; magnified 15×.

Low-Pressure, High-Temperature Annealing. Heat treatment under low pressures can be used to create black diamonds by inducing large-scale graphitization within surface-reaching fractures (Hall and Moses, 2001; Notari, 2002). First seen in the early 2000s, these diamonds are now common enough to greatly outnumber natural black stones on the market (Cheung and Liu, 2007). In general, these treated-color black diamonds are not difficult to identify. Strong illumination will reveal graphite inclusions confined to fractures, in contrast to the random "salt and pepper" appearance of natural black stones (Hall and Moses, 2001; Notari, 2002). They also generally lack the pitted and knotted surface features common in natural black diamonds, and they can display a characteristic surface iridescence. As with other treatments, though, melee-sized stones can be difficult to fully characterize.

As a review of this section, figure 14 shows a graphic representation of the range of treated colors now available in the market, through coating, irradiation, HPHT treatment, and low-temperature annealing.

CLARITY TREATMENTS

Laser Drilling of Inclusions. One effect of the dramatic increase in the supply of diamonds in the late 19th and early 20th centuries (largely due to discoveries in South Africa) was a desire to rank them by perceived quality factors, and one obvious criterion was clarity. Diamonds with visible dark inclusions were not as highly valued as those that were eye-clean. This trend led to the development of various methods to rate a diamond's clarity—the most commonly used today being the GIA grading scale (e.g., Liddicoat, 1955)—and the presence of eye-visible inclusions became a matter of economics as well as aesthetics.

Until the invention of the diamond saw, there was no way to remove a dark inclusion deep in a stone short of polishing or cleaving away large amounts of material—obviously an unattractive and uneconomic solution. The diamond saw allowed manufacturers to cut through a stone and essentially "slice out" dark inclusions, but even this was not always economic, as it might require dividing an otherwise profitable piece of rough into two much less valuable stones, or the inclusion might be so large that slicing it out would result in too much loss of material.

Figure 14. Shown here are examples of the wide range of treated-color diamonds now available on the market. Colors across the entire visible spectrum are now achievable with the proper starting material and combination of treatments. Colors shown are based on what has been seen to date, and other colors may appear in the future. Figure by Christopher M. Breeding.

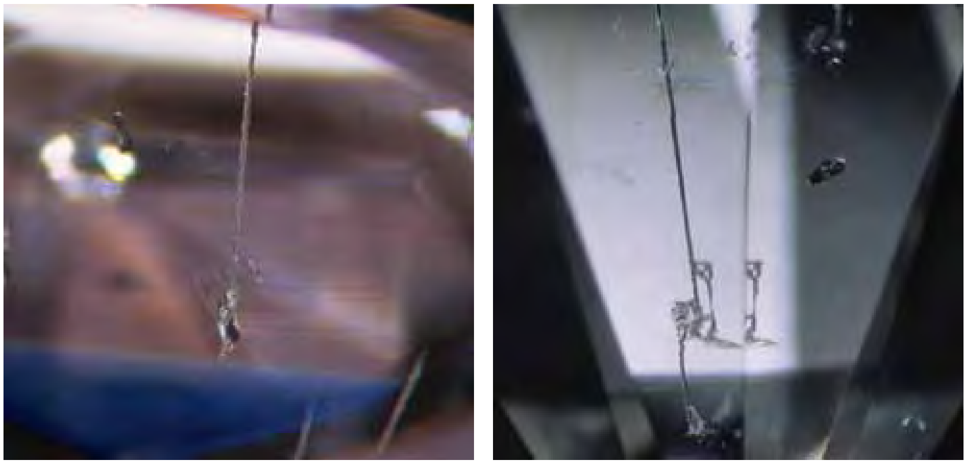


Figure 15. The laser drill holes in these diamonds serve as a conduit from the diamond's surface to mineral inclusions, which have been lightened or removed by acid boiling. Photomicrographs by Shane McClure (left) and John I. Koivula (right); both magnified 10×.

Dark inclusions in diamond are generally composed of graphite or sulfide minerals, or other, iron-containing mineral phases (Kammerling et al., 1990; Titkov et al., 2003), most of which can be dissolved by strong acids. Diamonds have long been boiled in acid for cleaning purposes after faceting (to remove lap metal and other debris, particularly from bruted girdles), and diamond manufacturers surely noticed that this process also often removed surface-reaching dark inclusions. In the early 1960s, a more thorough process, referred to as *deep-boiling*, was conducted under pressure in order to force the acid deeper into surface-reaching cleavages (Rapaport, 1987). When such a cleavage was connected to a dark inclusion, the acid would be able to bleach it to a lighter color or remove it entirely. However, this process did not affect dark inclusions sealed inside the stone. The industry had to wait a few more years before technology provided a solution.

For most of history, diamonds could only be manufactured using mechanical means: cleaving, sawing, grinding, and polishing. This began to change in the 1970s, following the development of lasers of relatively low cost and sufficiently high power to vaporize diamond (see Caspi, 1997). Although laser sawing, kerfing, and bruting would not become established in the trade until the 1980s, as early as 1970 Crowningshield reported that lasers were being used as part of a process to bleach or dissolve dark inclusions. Further, he mentions having heard rumors about this process for several years before seeing an actual laser-drilled diamond. This timing is significant because it was less than 10 years after the invention of the laser in 1960 (Cooper, 1991). Laser drilling proved to be the first widespread treatment ever used to alter the clarity of polished "colorless" diamonds.

One of the earliest trade reports of the process gives credit for its invention to Louis Perlman of Perlman Brothers in New York, who—allegedly—first tested his idea in collaboration with technicians at Raytheon Co. in Massachusetts in 1963 (Ward, 1972). This would have been shortly after a report appeared in the trade press about GE researchers using a laser to drill 0.02-inch-diameter holes into an industrial diamond ("A beam of light . . .," 1962). It is unknown whether this report gave Perlman the idea, but it seems likely that some in the trade made the connection.

The basic laser-drilling process is relatively simple. A 1064 nm solid-state neodymium-doped YAG laser is used to vaporize a tiny channel from the surface down to a dark inclusion using a pulsed, focused beam. Because the absorption of diamond at 1064 nm is negligible (i.e., the beam will normally pass through the diamond without effect), the process must be started by marking the target spot with dark ink. The ink will absorb enough heat to convert the underlying diamond to graphite, which is then converted to carbon dioxide gas. Once the graphite conversion begins, the process is self-sustaining (Cooper, 1991). With this open conduit to the inclusion, the diamond can be deep-boiled in acid to bleach or remove the internal feature (figure 15).

Although Perlman's first efforts were not successful, by 1969 he had refined the process sufficiently for commercial use (Ward, 1972). By the early 1970s, it was widely enough available to members of the trade that refinements and alternatives were already being discussed (see, e.g., Crowningshield, 1971; Lenzen, 1973, 1974), and the ethics of the process and its disclosure were already creating controversy (Leadbeater, 1972; Alexander, 1973; Egyes, 1973; Pagel-Theisen, 1976).

The FTC rules in place at the time did not require disclosure of laser drilling (as it was a permanent treatment; see Overton, 2004), but many in the trade still felt that it should be disclosed to consumers anyway ("Lasering. . .," 1980). The controversy would persist until the early 2000s, when the FTC finally updated its disclosure rules to require it (Overton, 2004).

Refinements in laser technology allowed more precise drilling and smaller, less-visible channels, but the basic process went unchanged until the end of the 20th century. In the early 2000s, examples of several new methods began to appear. The first, referred to as *KM treatment* (KM stands for *kiduah meyuhad*, or "special drill" in Hebrew), opened channels from dark inclusions to the surface not by burning through the diamond but rather by using the focused heat of the laser to expand (or even create) feathers around the inclusion (McClure et al., 2000; Horikawa et al., 2001). The process was sufficiently controllable that a series of tiny step-like cleavages could be created in order to take the shortest route to the surface. In some stones, the treatment created irregular worm-like channels with some resemblance to natural etch channels (McClure et al., 2000) or sugary disk-like features with irregular boundaries (Cracco and Kaban, 2002).

Variations in the appearance of drill holes and the internal features they reach continue to be seen (e.g., Astuto and Gelb, 2005), and as laser drilling is a versatile tool, it is likely that new permutations will arise in the future. Diamonds that display evidence of what seems to be accidental laser damage—that is, laser-created holes that do not connect to any inclusions—have also been noted (S. McClure, pers. comm., 2008).

Laser drilling is a permanent treatment, since there is obviously no way to replace the diamond burned out of the drill hole. (However, the drill hole can be glass filled to make it less apparent.) Some in the trade do not consider laser drilling a treatment at all but rather an additional step in the manufacturing process, though the consensus of diamond trade organizations is otherwise, and—as mentioned above—current FTC guidelines require that laser drilling be disclosed as a treatment. The presence of laser-drilled channels is also recorded as a clarity feature on typical diamond grading reports.

Identification. From a gemological standpoint, the detection of conventional laser drilling is straightforward, since the drill hole is easily visible with a gemological microscope provided the entire stone can be examined. When a drill hole is absent (e.g., with the KM treatment), recognition of laser action on inclusions can be more difficult, but it is not terribly challenging if one is familiar with the characteristic features (McClure et al., 2000). Note, however, that even melee-sized diamonds can be laser drilled, and it may not be practical to examine every stone in a large parcel.

Glass Filling of Surface-Reaching Cleavages. Like coating and painting, the use of oils and waxes to hide surface-reaching cracks and improve luster is an ancient practice, at least with colored stones. Wax treatment of jade, for example, has been detected in Chinese artifacts more than 2,500 years old (Qiu et al., 2006), and the oiling of emeralds has been recorded at least as far back as the 14th century (Nassau, 1994).

Diamonds, however, seem to have escaped such filling treatments until recently. Because of diamond's very high refractive index, filling with a low-RI material—such as the oils used in emerald filling—would not significantly reduce the visibility of a crack. Diamond filling likely had to wait until modern chemistry could supply fillers with sufficiently high RIs. Although lead-oxide glasses have been known since antiquity, their maximum RIs are around 1.7 (Newton and Davidson, 1989), well below that of diamond. Modern lead-bismuthate glass, however, can have an RI well into the 2-plus range (Dumbaugh, 1986). When such a glass is forced into surface-reaching cracks, the improvement in apparent clarity can be dramatic (figure 16; see Kammerling et al., 1994, for a discussion of the optics of glass filling).

It is not generally known exactly when the commercial filling of diamonds with high-RI glass began, but it appears to have been invented in Israel by diamond dealer Zvi Yehuda in the mid-1980s. The first published reports of the treatment appeared in 1987 (e.g., Koivula, 1987), but several sources (e.g., Rapaport, 1987; Everhart, 1987a,b) stated that Mr. Yehuda had been treating stones with this process since 1981. This would mean that such filled diamonds might have been in circulation for more than five years without having been detected by either dealers or gemological laboratories—possible, but unlikely given that diamonds are carefully examined during the quality grading process and the treatment was detected almost simultaneously by a variety of parties during 1987 (as discussed in Koivula, 1987; Koivula et al., 1989).

Although the exact details of the filling process and the formulas of the fillers are proprietary (and

Figure 16. Introduction of a glass filler into this 0.30 ct diamond's cleavage cracks produced a dramatic change in apparent clarity (before filling, left; after filling, right). Photomicrogaphs by John I. Koivula.

closely guarded), there is general agreement that the diamonds are filled in a vacuum or near-vacuum so as to evacuate the air from surface-reaching cracks (see Nelson, 1993; Nassau, 1994; Kammerling et al., 1994). Because of the low melting point of the glass, ordinary laboratory equipment can be used to melt the filler materials and mix in the diamonds (Nassau, 1994).

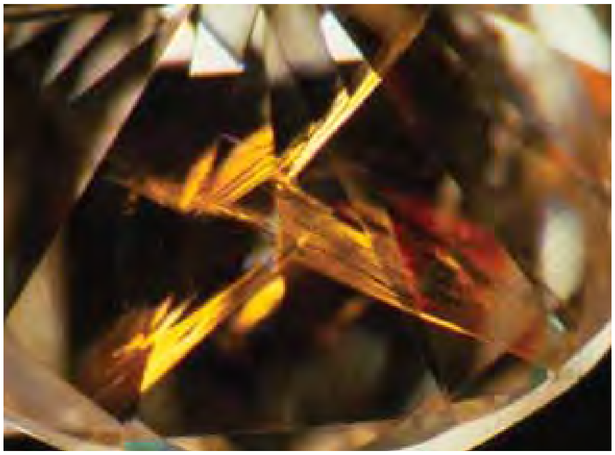
Initial controversy over this treatment was intense, with a few diamond bourses going so far as to ban filled stones altogether, and many others threatening expulsion for any member who sold filled stones without disclosing the treatment (Everhart, 1989; Shor, 1989). The situation was further complicated by the fact that within five years there were a number of firms marketing filled diamonds and filling services. Competing claims in the trade press regarding the detectability, durability, and effectiveness of various methods made it very difficult for diamond dealers to know what to believe.

Gemologists quickly determined reliable methods to detect fillings in diamonds based on straightforward examination with a microscope: flow structures, gas bubbles, a "crackled" texture, and, most prominently, different "flashes" of color seen with brightfield and darkfield illumination (e.g., Koivula et al., 1989; Hänni, 1992; Scarratt, 1992; Schlüssel, 1992; Kammerling et al., 1994; Sechos, 1994; McClure and Kammerling, 1995; figure 17). Although some manufacturers would subsequently claim that their filling process did not show one or another of these features, particularly the flash effect, further research determined that, in fact, all filled stones on the market at the time could be identified by this approach.

The precise mechanism behind the flash effect has itself been the subject of some discussion. Although early reports referred to it as an interference-related phenomenon, Nelson (1993) showed that it was actually the result of differences in dispersion between the diamond and the filling material (see also Kammerling et al., 1994). Nelson (1995) later speculated that the flash effect could be eliminated by using a filling material with an RI curve that closely matched—but did not intersect with—that of diamond in the visible range. However, there has been no evidence that this approach was ever adopted by those performing the treatment.

One drawback of the glass-filling process is that it may result in a lower color grade for the diamond, something that was noted almost immediately after treated stones began showing up in the market (e.g., Koivula et al., 1989). This side effect is believed to result from the color of the filler, as lead-bismuthate

Figure 17. The intersecting cleavage cracks in this diamond have been filled with a high-RI glass, but the bright flash-effect colors betray the presence of the filler. Photomicrograph by Shane F. McClure; magnified 5×.



glasses are frequently yellow when seen in large pieces. In some rare filled diamonds, fairly thick areas of filler have shown a yellow color (Kammerling et al., 1994). Although this effect is undesirable with colorless to near-colorless diamonds, it does raise the possibility that colored fillers could be used to add or enhance color in off-color stones. However, only a few such stones have been reported. Yeung and Gelb (2003, 2004) described two diamonds that had been colored pink by a filling substance (see, e.g., figure 18), though the results were generally poor and the treatment was easily detected with magnification. There are some reports of natural fancy-color diamonds having been glass filled (see, e.g., Sechos, 1995), but these appear to be less common since there is more acceptance of lower clarity grades in colored diamonds.

Glass filling is not a permanent treatment, but it is stable under normal conditions of wear and use of jewelry (Kammerling et al., 1994). However, because of the relatively low melting point of the glass, it can be damaged during jewelry repair if the diamond is subjected to substantial direct heat, as from a jeweler's torch or during repolishing (Crowningshield, 1992; Kammerling et al., 1994; Shigley et al., 2000).

Identification. The detection of glass filling is normally a matter of examination with a gemological microscope to identify the features discussed above: flow structures, trapped gas bubbles, crackled textures, and—most importantly—flash-effect colors. Detection of flash effects is best conducted with fiber-optic illumination, which provides an intense, focused beam of light (Kammerling et al., 1994; McClure and Kammerling, 1995).

Figure 18. This 1.02 ct diamond is colored by a pink residue in the large fractures that reach the surface through the crown. The actual bodycolor of the diamond is near-colorless. Photo by Elizabeth Schrader.

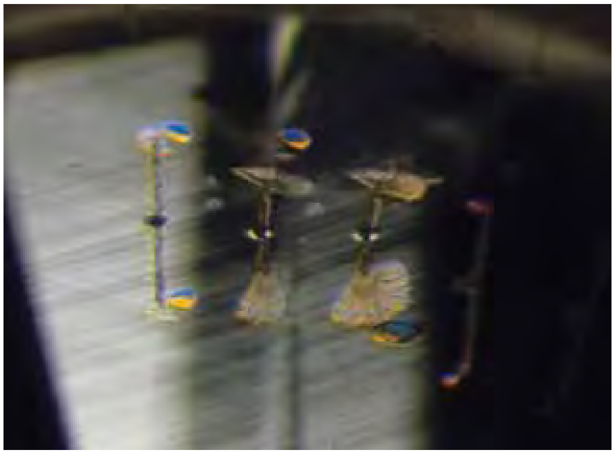


Figure 19. The drill holes in this laser-drilled diamond have been filled with high-RI glass to reduce their visibility. Note the flash-effect colors around the filling. Photomicrograph by John I. Koivula; magnified 25×.

COMBINED TREATMENTS

It is important for the gemologist to remember that, in most cases, there is little to prevent a treater or manufacturer from employing more than one process to achieve a desired result. In recent years, quite a few examples of combined treatments have been reported. Laser drilling and glass filling are perhaps the most commonly combined processes (figure 19), common enough to scarcely merit mention in the literature. These may be used in concert simply to disguise the drill holes or because a particular stone has both dark inclusions and clarity features that can be made less visible, but examples have been seen in which the combination of treatments made possible results that would not have been achievable using either process in isolation. Crowningshield (1993) reported on a diamond in which a large feather under the table had been glass filled after a laser was used to open a channel to the surface. Absent the laser drilling, the filling would not have been possible.

As noted above, the use of irradiation followed by moderate-temperature heating began in the 1950s. More recently, irradiation and HPHT annealing have been used in combination. In addition to the pink-to-red stones described by Wang et al. (2005a), Wang et al. (2005c) reported on two orange diamonds that were likely treated by a similar combination of HPHT annealing, then irradiation, followed by low-temperature annealing.

Other combinations are certainly possible. One of the pink filled stones that Yeung and Gelb (2004) described had been filled both to improve apparent clarity and to induce a pink color. Irradiated glass-filled diamonds have also been seen: Gelb (2005) reported a bluish green diamond that displayed both an obvious color zone around the culet (figure 20) and flash-effect colors from the filler. Gelb and Hall (2005) reported a large yellow diamond that proved to be irradiated, but that also displayed very unusual textures and structures within surface-reaching cracks. They speculated that the diamond might have been glass filled by one party, and then irradiated by another party unaware of the filling, which was damaged by the post-irradiation annealing necessary to create the yellow color.

SYNTHETIC DIAMONDS

Though not directly addressed in this article, which focuses on natural diamonds, it is important to note that gem-quality synthetic diamonds are potential candidates for all of these color and clarity enhancement processes. Irradiation and heating treatments have already been used to produce red, pink, and green colors in synthetic diamonds (Moses et al., 1993; Shigley et al., 2004; Schmetzer, 2004), just as they are used with their natural counterparts. Shigley et al. (1993) described several synthetic diamonds whose colors had been modified by HPHT annealing. Wang et al. (2005a) discussed the use of HPHT treatment to improve the color of CVD synthetic diamonds. Application of these color treatments does not necessarily make the diamonds more difficult to recognize as being synthetic, however.

Figure 20. This 1.22 ct round brilliant diamond shows both an obvious color zone at the culet and flow structures from glass filling. It was apparently subjected to artificial irradiation followed by glass filling treatment. Photomicrograph by Thomas Gelb; magnified 30×.

Figure 21. Recent developments in diamond treatment have made previously rare diamond colors much more available to jewelry designers. This platinum engagement ring contains a 1.57 ct HPHT-treated orange diamond. Photo by Ralph Gabriner; courtesy of Etienne Perret.

Although synthetic diamonds exhibiting evidence of laser drilling or glass filling have not been reported, there is no reason why these processes could not be used, especially since the metallic flux inclusions often present in (and characteristic of) HPHT synthetics could conceivably be removed by acid boiling after laser drilling to open a channel to the surface.

THE FUTURE OF DIAMOND TREATMENT

The wide variety of treatments now available on the market presents both opportunities for designers (e.g., figure 1 and figure 21) and an ongoing challenge to all those who handle diamonds. While "low-tech" treatments such as glass filling and laser drilling can be identified with sufficient training, the days when a diamond's color could be presumed natural after rinsing in alcohol to remove possible paints are gone forever.

There are several treatments that are not discussed in this article because there is no evidence that they are used widely, if at all, in the trade at this time. These include, for example, ion implantation to produce a thin surface layer of color (e.g., Moses et al., 2000) and foil backing, which—though common centuries ago—has largely died out for use with diamonds, and is more properly considered a lapidary technique (e.g., Cellini, 1568).

The most likely areas of future development lie in further combination of treatments and advanced coating materials. New combinations of irradiation and heating may expand the possible starting material that can be converted to gem-quality diamond. In addition, some laboratories have seen evidence of laser drilling to reportedly mask signs of HPHT treatment (Bates, 2004). Future generations of surface coatings will likely be more durable, and the observation of film damage, the most reliable method used now for detection, may become less useful. Newer coatings may be applied to laser-drilled and/or glass-filled diamonds, since such treatments are typically used on lower-quality diamonds that are more difficult to sell in their untreated state. Such coatings could interfere with detection of laser drill holes or flash-effect colors, making these stones more difficult to fully identify, especially in smaller sizes. CVD synthetic diamond thin films may also see commercial use as a coating on natural diamond, as CVD methods evolve and become more economic.

For all treatment types, identification using standard gemological techniques will likely grow even more difficult. Working in the modern diamond market will continue to require constant vigilance and the assistance of a professional gemological laboratory.

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