CHANGING THE COLOR OF DIAMONDS
THE HIGH PRESSURE HIGH TEMPERATURE PROCESS EXPLAINED

Introduction
For hundreds of years, cutting and polishing was the only way to make diamonds look better. Changing the body color of diamond was not possible until the early 1900’s when science discovered how to manipulate diamonds at an atomic level with radiation. That discovery made it possible to produce artificially colored diamonds for the first time.

In the 1950’s, High Pressure High Temperature experiments culminated in the successful production of the first synthetic diamonds. HPHT was first used to change the color of diamond in research laboratories in the 1970’s. These early experiments were successful in producing yellow and green colors, but there was no mention of processing gem quality diamond, nor was there reference to decolorizing diamond with the process at that time.

Over the last two years, US companies introduced High Pressure High Temperature processes to change the color of gem quality diamonds. First, General Electric startled the diamond industry by proving type IIa brown diamonds could be improved to a colorless state. Next, NovaDiamond caused and aftershock by transforming brown diamonds to yellow to green vivid colors. Now, a number of companies around the world use HPHT to modify diamond color and produce synthetic diamonds. Russian scientists have been using the “BARS” apparatus this way for about ten years.

Changing diamond color through High Pressure High Temperature is one of the most intriguing areas of gem technology today. At the same time, HPHT technology raises some concerns about the color origin of colored diamonds; even those certified years ago. This puts tremendous pressure on laboratories to develop reliable, efficient detection methods for HPHT colored and colorless diamonds.

To be successful, laboratories must strive to understand the process itself and how it affects diamonds. This makes it imperative for gemologists to collaborate with the scientific community and work with advanced testing equipment. This clearly illustrates that gemology is merging with modern science.

European Gemological Laboratory USA is heavily involved in HPHT research. Our gemologists conducted research at numerous facilities including the NovaDiamond gem-technology center in Provo Utah, and several in Russia. In fact, EGL made the first announcements, that HPHT colored diamonds were circulating in the trade, and to design a grading report especially for HPHT colored and colorless diamonds; using the term “enhancement” instead of “treatment”, due to their proven stability to high heat. Our research results have been presented at international scientific conferences and to many gemological groups around the world.

So how does the HPHT process work? How are brown diamonds changed to colored or colorless? The following pages explain the HPHT process in detail and show how gemological laboratories identify HPHT processed diamonds. This booklet is based on over one year of research by EGL including a poster presented at the European Diamond Conference in Portugal in 2000 by Branko Deljanin and Dr. Emanuel Fritsch.

Starting Material
Dark to light natural brown rough diamonds, sawable octahedrons and dodecahedrons, 2-10ct, VS-SI clarity (figure 1), with none to medium fluorescence, none or weak 415 and 503 nm lines in their visible spectra (figure 2), mostly type IaAB, some dark orangy brown crystals showing “amber” center absorption in infrared spectrum around 4165 cm⁻¹ (figure 3).
Containment Cube
Two diamond crystals are embedded in a mixture of powdered graphite and magnesium oxide and hand compressed to form a capsule which is inserted in a pyrophyllite tube with a surrounding coat of soap stone (figure 4). Metal thermocouples are placed on either end to conduct electricity. The capsule is positioned in the center of a specially designed "prismatic press" (figure 5).
"Prismatic press" is a multimillion-dollar computer controlled diamond press developed by the Hall family at NovaDiamond Corporation, USA (figure 6). An electrical current passes through the metal thermocouples on containment to produce temperature up to 2300 degrees C. At the same time hydraulic arms apply equal pressure from all sides to produce a pressure of up to 65 kilobars.

Similar temperatures and pressures are accomplished with multi anvil split-sphere device known as "BARS" at various institutes in Russia (figure 7). These presses are mainly used to growth synthetic diamonds but they are also used for treatment of natural and synthetic diamonds to obtain "neon" colors.
Color Activation Graph
The phase diagram of carbon shows the diamond/graphite equilibrium line. The shaded area represents the Region of Color Activation for NovaDiamonds (figure 8). Pressures of 55 to 60 kilobars and temperatures of 1900 to 2050 degrees C are required to produce yellow to greenish yellow colors, while pressures of 60 to 65 kilobars and temperatures of 2050 to 2200 degrees C are necessary to produce green-yellow to yellowish green colors. Based on our latest research, pressures of 50 to 60 kilobars and temperatures of up to 2300 degrees C are required to lighten the color of type IIa brown diamonds. The duration of the procedure using "prismatic press" is very short (up to 3 minutes).
Results of the HPHT process
As a result of processing, diamond crystals are covered with a thin layer of black graphite (figure 9). It is removed by heating in a kiln at 400 degrees C for 15 min. These diamonds have characteristic "neon" bright greenish yellow to yellow-green color due to strong green luminescence to visible light (figure 10). The later is often referred to gemologists as "green transmission" and is present along plastic deformation lamellae (graining lines) when strong focused light is applied directly on the stone (figure 11). This luminescence is the result of emission of the H3 system.
IDENTIFICATION OF ENHANCED COLORED DIAMONDS

Color and Fluorescence
Intense to vivid yellow to yellowish green diamond colors correspond to typical strong fluorescence colors to long-wave UV radiation (approx. 365nm).

The H3 center, a carbon vacancy trapped at an A aggregate, is responsible for the green fluorescence which contributes the bright greenish color to these diamonds. The related absorption line at 503nm (H3) is very weak to moderate in yellow and greenish yellow stones and fluorescence is likewise weak to moderate, but in green-yellow to yellowish green diamonds fluorescence is strong to very strong due in part to a strong absorption at 503 nm.

Observation Under Magnification
The clarity of HPHT diamonds is normally lowered by one to two grades (e.g., from SI1 to SI2). This happens because existing fractures enlarge under the high pressure. Temperatures and pressures are very close to those of the diamond graphite transition region and this results in graphitization of the walls of solid inclusions and discoidal stress cracks around them (figure 14). Some open cavities and fractures contain graphite for the same reason (figure 15). Facet junction and girdle often have a frosted appearance indicating that they had been "burned" by high temperatures.
Visible and near-infrared spectra of HPHT diamonds

Typical visible absorption spectra shows weak 415 nm (N3), weak 497 nm (H4), weak to strong 503 nm (H3), emission line at 513 nm, accompanied sometimes by a small 637 nm (N-V center). Characteristic lines in the near-infrared region are the 986 nm (H2 center, negative charge state of the H3 center) with an extra band at 871 nm (figure 16 and 17). Absorption at 986 nm and its associated vibronic structure gives the de saturated green component to the diamond, so the higher the temperature the stronger the H2 center and the greener the stone.
Mid-infrared spectra and Diamond type

Mid-infrared spectra of most HPHT processed diamonds show a moderate amount of nitrogen, with typically more nitrogen in B aggregate form than A aggregate form. They are therefore type Ia B>A. The type is not expected to have been modified by treatment. The amber center around 4165 nm is absent and platelet peak near 1360 cm⁻¹ is reduced in most of the diamonds after HPHT treatment. Decrease of platelet peak with increasing temperature might explain the production of B aggregates during the HPHT process (figure 18 and 19).
Lightening the color of brown natural diamonds

Using pressures of approximately 55 kilobars and temperatures from 1800 to 1900 degrees C, type Ia brown diamonds with low nitrogen (like those from Argyle mine), can become much lighter yellow, yellow-green or brownish pink. The reduction of brown color is attributed to the annealing of plastic deformation (brown graining).

In order to produce completely colorless diamonds it is necessary to process nitrogen-free type IIa brown natural diamonds. General Electric uses these rare diamonds to produce colorless, near colorless and pink diamonds by re-aligning the diamond lattice by an undisclosed HPHT process (figure 20 and 21).
Summary

Colored diamonds enhanced by the HPHT Process can be separated from similar looking natural color diamonds by the following tests:

UV Fluorescence: strong chalky fluorescence to long-wave UV light is first indicator of HPHT process. The fluorescent colors of the diamonds correspond closely to their body colors.

Magnification: careful examination under microscope could reveal signs such as stress fractures around crystalline inclusions, graphite in fractures and frosted girdle or naturals.
Spectroscopy: Analyses with UV-VIS-NIR and FTIR spectrometers are necessary to positively identify these diamonds as treated. An intense H2 absorption in greenish yellow to yellowish green diamonds is the strongest proof that a HPHT process has induced color.

Additional research: HTHP, colorless type IIa and light-colored type Ia HPHT diamonds are more difficult to identify, and different identification methods must be developed, such as laser-induced photoluminescence spectroscopy using Raman systems, and cathodoluminescence. There is no single test to identify such diamonds. EGL, and leading companies like SSEF, Gubelin, DeBeers, and others, are working diligently in this area.

References:


