SSEF Swiss Gemmological Institute

IDENTIFICATION OF COLOURLESS HPHT TREATED DIAMONDS (e.g. GE POL)

SSEF Swiss Gemmological Institute identifies GE POL treated diamonds as a routine laboratory service

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The SSEF Swiss Gemmological Institute announced at Basel 2000 Jewellery Fair in March that they have found key features for the identification of GE POL treated diamonds. Since that date the identification of HTHP treatment of IIa diamonds is performed as a routine laboratory task offering the **detection service** to the public and trade. The new service is part of the Diamond Grading routine, since all stones submitted for a quality grading have to be checked for possible **HPHT treatment**

After having developped a routine for the detection of organic fillers in treated emeralds, the SSEF Swiss Gemmological Institute is again successful in solving a major problem of the trade and current gemmology.

Abstract:

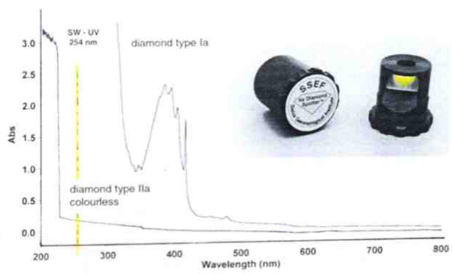
An identification method for high pressure/high temperature (HPHT) treated IIa diamonds is presented. **GE POL** diamonds are **identified in a two step process**:

First, as almost all GE POL diamonds were found to be type IIa near-colourless diamonds, stones of this type are separated from other diamonds of similar colour using the "**SSEF IIa Diamond Spotter**" in connection with a short wave UV light unit (254 nm). This result can be checked by FTIR-spectrometer (Chalain et al., 1999).

Second, a Raman spectrum of these IIa diamonds is obtained using the 514.5 nm laser emission with of a Raman spectrometer system and cryogenic sample cooling. The recording of the **photoluminescence spectrum at liquid nitrogen temperature** (LNT) cools the sample down to approx. minus 180 °C provides an excellent signal/noise ratio. If a luminescence pattern at 3737 cm^{-1} and 2043 cm^{-1} is observed, this proves the presence of a small number of **N-V centres** (a single nitrogen linked to a carbon vacancy) in the stones. These peaks are related to a 637 and 575 nm peak in the VIS spectrum. That is characteristic of the material used for the GE process, as all studied GE POL diamonds exhibit these emissions.

Most but not all natural, i.e. non-treated colourless IIa diamonds show an N-V$^-$ (637 nm) and the N-V^0 (575 nm) feature. The peak height **ratio 637/575** is considered indicative for treatment identification (Fisher & Spits, 2000). We found that diamonds with high ratios > 2.8 are HTHP treated, whereas diamonds with low ratios < 1.6 are natural. Further spectroscopic observations as well as possible gemmological features reinforce the **SSEF identification routine** which can provide identification criteria for GE POL diamonds not showing N-V features. (pers. comm. George Ringwood, 2000).

UV transparency of type IIa diamonds



Background

Since March 1999, the Diamond Trade was in a difficult situation with a relatively small amount of near-colourless to colourless diamonds, which have been treated through a high tech process. A high pressure/high temperature (HPHT) treatment transforms brownish diamonds of type IIa into colourless stones of a higher value. The product has initially been named "GE POL processed diamonds". According to **General Electric**, who performs the quality improvement and the former distributor of the stones, **Pegasus Overseas Limited**, the treatment is not detectable, will remain detectable (Rapaport Trade Alert, 19 March 1999) and is permanent. The stones are, however, quality graded by **GIA Gemological Institute of America**, who mentions the treatment on the certificate, and refers to an inscription "GE POL" branded on the girdle of each of the cut diamonds.

Since this **laser inscription** is very shallow it can be removed with apparently no loss of weight, the disclosure of treatment is **not safely linked to the stone**. It is interesting to note that the reported prices of GE POL treated diamonds were essentially the same as for untreated stones of comparable quality. The problem of identification of treated gemstones is not new, but the identification of GE POL stones is a serious challenge to gemmological laboratories. First publications regarding identification concentrated on **inclusions**, e.g. Johnson et al (1999), Moses et al. (1999). **Spectral features** (Yuan, 1999; Chalain et al., 1999 and 2000 a, b) were found to provide discrimination features for identification which do not require the presence of laser inscription or inclusions.

Chronology of our research developments:

In December 1999, **SSEF Swiss Gemmological Institute published the first results** of their research on GE POL treated diamonds. Although on a basis of only two stones, essential characteristics and a distinct methodology of research were shown in the Revue de Gemmologie No. 138/139. Meanwhile two more manuscripts with SSEF research results on GE POL treated diamonds has been published in the "Journal of Gemmology" and in the "Zeitschrift der Deutschen Gemmologischen Gesellschaft". The data in the papers that appeared so far have been taken from **room temperature spectra**. The GE POL research project as done at SSEF is in co-operation with Universities of Nantes and Basel. The results and analytical procedure have been discussed with De Beers DTC Research Centre, and their results have also been published recently by Fisher and Spits in the latest Gems & Gemology issue.

At **SSEF**, the latest advancements that enabled the detection breakthrough were based on the developments of a cryogenic sample stage and recording **spectra at liquid nitrogen conditions**. The careful comparison of different kinds of IIa diamonds led to the detection of the correlations between the observed spectroscopic features.

Conclusions

Despite claims that the GE POL treatment was not detectable, within one year of intense research a small group of people from SSEF and two European universities (**Nantes and Basel**) have independently found an identification method. Research scientists of De Beers DTC have at the same time presented their method for identification. Both groups are basing their identification on **N-V centres, a feature that has not yet been described in near colorless IIa diamonds** unless published by Chalain et al (1999). A careful evaluation of **luminescence spectra** as e.g. produced with a Raman laser system at low temperature allows a gemmological laboratory equipped accordingly **to identify HPHT treated IIa diamonds**, e.g. GE POL stones. Further spectral features and possible characteristic inclusions may confirm the conclusion.

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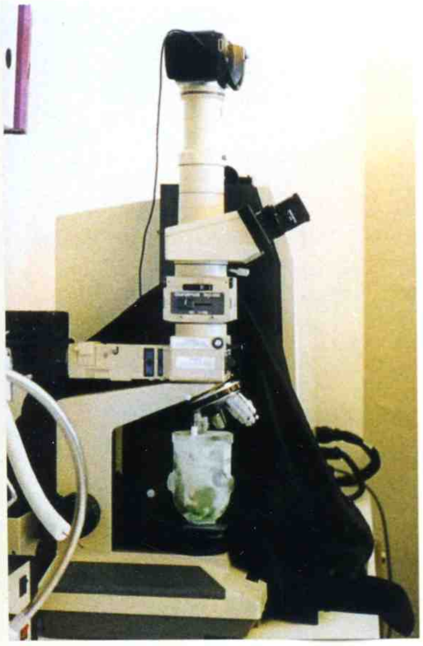

RENISHAW Raman Microscope System with cryogenic sample stage at SSEF

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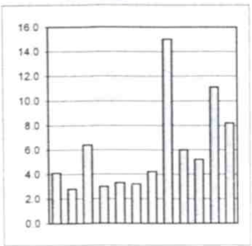
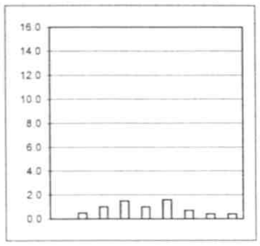
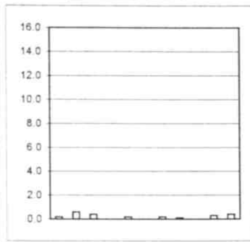
Ratio of 637/575 for GE POL



Ratio of 637/575 for Untreated colourless



Ratio of 637/575 for Untreated brown



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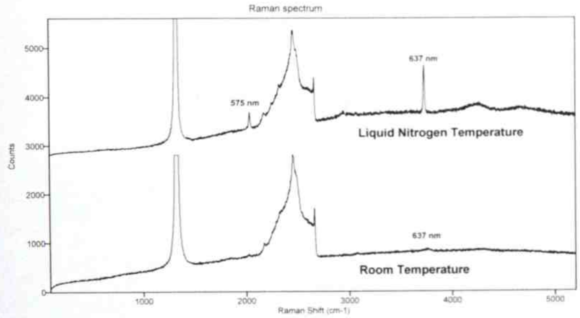
Raman spectrum



Sample: GE POL 1, Colour: E (yellow), round, brilliant, 0.75 ct

637 / 575 = 2.8

Comparison of room temperature and LNT (-180 °C) of same GE POL E colour

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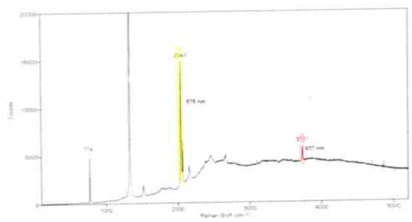
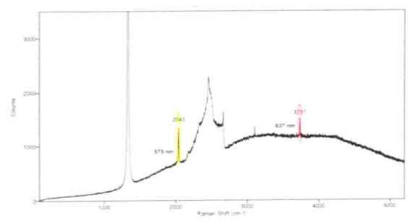
Before submission to a laboratory:	- Check for girdle inscription (GE POL). - Check if the diamond is a type IIa (using DiamondSure, SSEF Diamond Spotter or crossed polarizers: Tatami graining) : 1% of all diamonds. - Check inclusions: halo of expansion surrounding inclusions, haziness, etc. (see Gems& Gemology, Vol. 35, No. 3, pp. 14-22.
Laboratory Procedure:	Observations: - a yellow body colour is suspicious. So far type IIa untreated colourless or near-colourless diamonds have only a brown, pink or pinkish brown hue. - Inclusions, for more data. - Strength and quality of the graining, for more data. FTIR to confirm the type IIa Raman spectrum at Liquid Nitrogen Temperature: In general: - if 637 / 575 > 2.8, then HPHT treated diamond (e.g. GE POL) - if 637 / 575 < 1.6, then untreated diamond - so far no diamonds have shown a ratio of 637 / 575 between 1.6 and 2.8 - In a few extreme cases: - Either 637 or 575 are not measurable, then we will refer to further properties.



Sample: Untreated Brown, Colour: K, Marquise, 1.108 ct

637 / 575 = 0.1



Sample: Untreated Colour D, Internally Flawless, Marquise, 1.613 ct

637 / 575 = 0.5

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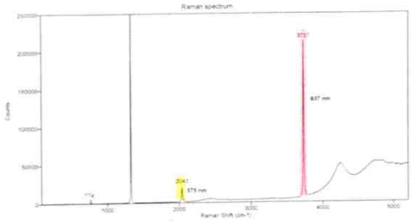
Raman spectrum



Sample: GE POL 12, Colour: L, pear-shaped, 1.120 ct

637 / 575 = 11.1

Luminescence spectra taken at -180 °C of natural and treated IIa diamonds.
up: untreated brown middle: untreated D colour down: GE POL L colour
Compare peak ration 3737 and 2043 cm^{-1} !

Formula to transform Raman shift in cm^{-1} into nanometer scale

$$\lambda_{[nm]} = \frac{10'000'000}{v_o - v_\Delta}$$

v_o = Laser excitation in wavenumbers (cm^{-1}) e.g. 19435.1 cm^{-1} (514.5 nm)

v_Δ = Raman shift in wavenumbers (cm^{-1}) e.g. 3737 cm^{-1} (N-V$^-$)

λ = wavelength in nm 637.1 nm (N-V$^-$)

References:

Chalain J-P., Fritsch E., Hänni H.A. (1999) Detection of GE POL diamonds: a first stage. Revue de Gemmologie A. F. G., No. 138/139, pp.30-33.

Chalain J-P., Fritsch E., Hänni H.A. (2000a) Identification of GE POL diamonds: a second step. Journal of Gemmology, 27, 2, pp. 73-78

Chalain J-P., Fritsch E., Hänni H.A. (2000b) Zur Bestimmung von GE POL Diamanten: Erste Erkenntnisse. Z.Dt.Gemmol.Ges., 49, 1, p. 19 - 30, april 2000

Collins A.T. (1992) Colour centres in diamonds, Journal of Gemmology, Vol. 18, No.1,pp. 37-75.

Collins A.T. (1999) Things we still don't know about optical centres in diamond. Diamond and Related Materials, Vol. 8, pp. 1455-1462.

Fisher, D. & Spits, R.A. (2000) Spectroscopic evidence of GE POL HPHT-treated natural IIa diamonds. Gems & Gemology, Spring 2000, pp 42-49.

Fritsch E. (1998) The nature of diamonds. G.E. Harlow Editor. Cambridge University Press & American Museum of Natural History, Cambridge, UK, pp. 38-40.

Johnson M.L., Koivula J.I., McClure S.F., DeGhionno D. (1999) A review of "GE-processed" diamonds. Gem News. Gems and Gemology, Vol. 35, No. 2, pp 144-145.

Moses T. M., Shigley J. E., McClure S. F., Koivula J. I., Van Daele M. (1999) Observations on GE-Processed Diamonds : A Photographic Record. Gems and Gemology, Vol. 35, No 3, pp. 14-22.

Rapaport Diamond Report (1999) http://www.diamonds.com Consulted from March 1999 to January 1999.

Ringwood, George, (2000) personal communication.

Robertson R., Fox J.J., Martin A.E. (1934) Philosophical Transactions, Vol. A232, London, pp. 463-535.

Schmetzer K. (1999) Behandlung natürlicher Diamanten zur Reduzierung der Gelb- oder Braunsättigung. Goldschmiede Zeitung, Vol. 97, No. 5, pp. 47-48.

Woods G. S., Collins A. T. (1983) Infrared absorption spectra of hydrogen complexes in type I diamonds. Journal of Physics and Chemistry of Solids, Solid State Communications, Vol. 45, pp. 471-475.

Yuan J.C.C. (1999) Diamond Researching. Solstar International Inc. Internal Report, NY (USA).