

Detection of GE POL diamonds : a first stage

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Abstract

This article presents the study of two diamonds having undergone a new process to make them more colourless.

These two GE POL colourless diamonds (respective colours : E and F) are of type IIa. Using polarised light they show crossed strain patterns that appear to be colourless using non-polarised light. Around their crystalline inclusions, one can note an atoll of expansion whose shape is that observed in corundum treated at high temperature.

In both GE POL diamonds, several fluorescence bands have been observed using Raman spectroscopy. One of these band (detected in both GE POL diamonds) indicates the presence of N-V centres (637 nm). This unexpected detection in diamonds of type IIa initiates the foundations of a more complete comparative study that will aim to find a spectroscopic method to identify diamond treated with this new process.

A simple device, the « SSEF IIa Diamond Spotter » is presented in this paper. In connection with a short wave UV light unit (254 nm), it enables a quick identification of type IIa diamonds.

I - Introduction

Since March 1999, a new process producing colourless to almost colourless diamonds shocks the diamond market. General Electric (GE) proposes this process in the United States. It would make it possible to improve the colour of certain diamonds, i.e. to make them more colourless. According to GE, this process would not be detectable. The stones are known as Pegasus diamonds and are labelled GE POL. They are marketed by Pegasus Overseas Limited (POL), a subsidiary of Lazare Kaplan International Company (LKI) a significant De Beers sight holder in New York (Rapaport Trade Alert, March 19, 1999; Johnson et al., 1999). Thanks to the generosity of two European dealers, Mr R. Biehler of Munich and Mr R. Totah of Geneva who both bought one GE POL diamond in June 1999, the SSEF-Swiss Gemmological Institute could study these stones.

This preliminary study is thus based on the examination of two stones only. It presents

results primarily related to a meticulous observation of their inclusions. It must be completed by a systematic and thorough study of a representative sampling of the production of GE POL diamonds, in particular for the spectroscopic part which is outlined here. Both GE POL diamonds are accompanied by certificates of the Gemmological Institute of America (GIA), n°: 10531016 for the marquise cut of 0.56 ct and n°10626480 for the round brilliant of 0.75 ct. The quality of the stones is described in *table 1*.

1 - QUALITY OF TWO TREATED GE POL DIAMONDS AS DESCRIBED ON GIA DIAMOND GRADING REPORTS

	GE POL1 Diamond	GE POL2 Diamond
GIA diamond grading report Nr.	10626480	10531016
Weight	0.75 ct	0.56 ct
Color grade	E	F
Clarity grade	SI2	VS1
Shape and cutting style	round brilliant	marquise brilliant
Polish	very good	very good
Comments :	« GE POL » is present on the girdle. Pegasus Overseas Limited (POL) states that this diamond has been processed to improve its appearance by General Electric Company GE	« GE POL » is present on the girdle. Pegasus Overseas Limited (POL) states that this diamond has been processed to improve its appearance by General Electric Company GE

II - History of the GE POL process.

In March 1999, LKI and General Electric (GE) jointly announced an agreement for a 10 years exclusive marketing of diamonds treated by GE, starting April 1, 1999.

This process is described in various press releases as improving in an irreversible way the colour and the brightness of 1% of diamonds on the market. It is also specified that the process consists neither of an irradiation, or a filling of cracks, nor in a coating of the surface of the stones.

LKI also declared that the process is not detectable and will remain so, GE promising financial compensation to LKI if not. To support this declaration, LKI states that a large number of treated diamonds had already been sent to the largest gemmological laboratories and that the process was never detected. To date the authors are still unaware of

which laboratories, except the GIA, received the stones.

LKI announces the marketing of these cut diamonds via a subsidiary company in Antwerp (Pegasus Overseas Limited - POL.) and a sales goal of 200 million US \$ over 3 years (Rapaport Trade Alert, March 19, 1999). Lastly, LKI justified its decision to sell these diamonds at the same price than their untreated counterparts based on the fact that the process is not detectable.

Following a strong mobilisation of both professionals and GIA, it was agreed that these treated diamonds will be all subjected to a GIA certification and that their girdle will carry a laser engraved inscription GE POL. In return for the GIA exclusivity on GEPOL diamond reports, to describe the process, the term "processed" will be used on GIA reports instead of the term "treated".

In May 1999, following its annual congress organised in Bern, the CIBJO declared that all GE POL diamonds must be declared as treated (Press release CIBJO, May 1999).

III - Gemmological testing

Traditional and systematic gemmological tests were carried out on both GE POL treated diamonds. The whole of the results is given in *table 2*. The round brilliant cut diamond weighing 0.75 ct is named GE POL1 and the marquise cut diamond weighing 0.56 ct is named GE POL2. Their refractive index was evaluated on a Presidium Duotester reflectometer, calibrated beforehand to a value of 100 using a reference diamond. Both stones have a reflecting power of 100, which indicates that, within the limits of the sensitivity of the method, refractive indices remain unchanged after processing. Specific gravity was measured on a Mettler (AE 500 C) balance. GE POL1 diamond has a specific gravity of 3.521

2 – GEMMOLOGICAL PROPERTIES OF TWO GE POL TREATED DIAMONDS

	GE POL1 Diamond	GE POL2 Diamond
Reflecting Power ⁽¹⁾	100	100
Specific Gravity	3.521 ± 0.001	3.51 ± 0.01
Electrical conductivity	none	none
Thermal conductivity	that of diamond	that of diamond
UV light fluorescence (366 nm)	none	none
UV light fluorescence (254 nm)	none	none
Visible absorption	none	none

(1): Before measurement, a non treated colourless diamond was used to calibrate the reflectivity meter to a normalised value of 100.

± 0.001. The specific gravity of GE POL2 diamond whose weight measured in water is lower than 0.5 ct is evaluated with a lesser precision.

Its specific gravity is 3.51 ± 0.01. Thus, both GE POL treated diamonds have a specific gravity consistent with the 3.52 theoretical value. Their electrical conductivity was tested in various crystal orientations on a Calrad GIA Instruments voltmeter. Both GE POL treated diamonds are electrically insulating. Their thermal conductivity was checked on a Presidium Duotester thermal conductimeter. For both stones, the instrument indicates the thermal conductivity of diamond.

Their fluorescence was observed under ultra-violet light (UV) with 366 nm and 254 nm. Both GE POL diamonds are inert under both long and short UV light. Lastly, their absorption spectra were observed using a System Eickhorst prism spectroscope. No band nor absorption line are visible.

IV – Observation with a binocular microscope

4.1 – Observation using nonpolarised light

With the binocular microscope and in reflected light, one notes that the girdle of the GE POL diamonds is faceted and that the inscription "GE POL" is engraved (*Figure 1*). The black engraving made with the laser is not very deep. A control with the x10 loupe ensures that the inscription is quite readable at that magnification. At the time of a graduation, the inscription will be taken into account like an external characteristic and will thus not affect the purity of the stone. The small cracks and other observable defects lying

around the girdle of yellow green faceted diamonds treated at high pressure and high temperature (Reinitz & Moses, 1997) are not present.

The observation of inclusions in dark field brings the first revealing elements of the process. No clear growth structure or coloured plastic deformation (i.e. graining) is observed.

These characteristics are frequently seen during the graduation of diamonds, but are not necessarily present in all diamonds.

On the other hand, in both GE POL diamonds (purity SI₂ and VS₁) the inclusions show an unusual appearance. All of them are encircled by an «atoll»-like pattern. When they are illuminated using a fiber optic, these atolls appear brilliant. They consist of myriads of small points laid out around the central inclusion (*Figure 2*). This last observation is of course easier in the stone of purity SI₂ than in the other.

4.2 – Observation using polarised light

In gemmological laboratories, the observation of diamonds between crossed polarisers is almost systematic since synthetic diamond is produced in dimensions that make it a stone usable in jewelry (Koivula & Fryer, 1984). The observation using polarised light reveals the internal stress as interference colours induced between crossed polarisers. This stress may be due to the presence of crystal inclusions, growth defects, plastic deformation, twins, etc. Interference colours are very often brown yellow or orange and blue to violet. The observation between crossed polarisers of both GE POL diamonds revealed the presence of crosshatched patterns parallel to the octahedral faces of the crystal (sometimes named tatami strain).

In GE POL1, the interference colours are very high (*Figure 3*), and only sometimes grey. In GE POL2, the grey colour is prevalent, although some irisations are also noted. The observation between crossed polarisers of inclusions surrounded by an atoll that are present in both GE POL diamonds, does not

reveal any interference colours (*Figure 3*). This last observation is also valid for certain inclusions with expansion fissures in diamonds that have not been submitted to heat treatment.

4.3 – Synthesis of observations

Using reflected light it appears that, due to the nature of the engraving and its low depth, a repolishing of the girdle would erase the inscription without a significant loss of weight. Moreover, while reading the inscription is easy when GE POL diamonds are in a paper, it will not appear as easily when they are set one beside the other in a piece of jewellery or in a closed setting.

When observed with dark field illumination, the particular shape of the atoll surrounding all the inclusions (made of myriads of brilliant points) indicates that both GE POL diamonds likely underwent annealing. These observations were described mainly in corundum (Nassau, 1981; Hänni, 1982; Kammerling et al., 1990). The observed atoll is the trace of both the differential expansion of the crystal inclusion inside the crystal host and its return to its initial dimension during cooling. Crystal inclusions seen in nonheated diamonds are often surrounded by stress patterns. The difference in pressure between the interior of an olivine inclusion and diamond host is sufficient to deform the cubic symmetry of diamond (Izraeli et al., 1999). This generates a halo of anomalous double refraction around the inclusion, which one can highlight between crossed polarisers.

At high temperature, crystalline inclusions dilate in the directions of lower mechanical resistance, this is traced by the halo of «birefringence». During the process, because of the particular conditions, the internal stress is healed, giving place to the formation of the atoll. Expansion fissures of some black inclusions present in non-treated diamond also show no internal stress.

The sales reports from the Antwerp market, indicates that in the last few years LKI bought large quantities of diamonds of a particular type and of a brown colour (Rapaport Trade Alert: March 19, 1999). Thus, the high temperature treatment is probably carried out on

brown rough diamonds of type IIa, because around the girdle of GE POL diamonds one does not observe the defects which appear around the girdle of green yellow faceted diamonds treated at high temperature and high pressure (Reinitz & Moses, 1997).

To enable a quick identification of type IIa diamond, the authors created a small device named "IIa Diamond Spotter". This instrument uses the fact that type IIa diamond is transparent to UV short wave (254 nm). The device is made of a screen strongly fluorescent when exposed to UV short wave. The diamond to be tested is placed between the UV source and the "IIa Diamond Spotter" (Figure 4). When the diamond is transparent to the UV source, the screen shows a strong green fluorescence, thus the diamond is a type IIa. If the screen does not fluoresce, it means the diamond has absorbed the UV short wave, thus is not a type IIa.

V – Spectroscopic study

5.1 – infrared Spectrometry

The absorption spectra of the two GE POL diamonds were recorded on a Philips PU9800 Fourier Transform Infrared spectrometer using a resolution of 2 cm⁻¹; 200 scans were averaged for the analysis of each stone. Both GE POL diamonds completely transmit the infrared light in the area known as the nitrogen area (between 1000 cm⁻¹ and 1400 cm⁻¹). This indicates that these diamonds do not contain any detectable quantity of nitrogen using this method. Therefore, both GE POL diamonds are type IIa diamonds (Figure 5).

In GE POL2, a very small quantity of hydrogen is detected by its absorption at 3107 cm⁻¹ (Figure 5). This is unusual, since the presence of hydrogen is described only in type I diamonds (Woods & Collins, 1983; Fritsch et al., 1991). This weak signal undoubtedly reveals - indirectly - a concentration of nitrogen, as low as about 1024 m⁻³ (Collins, 1999).

5.2 – Near infrared, visible and ultraviolet spectrometry

The absorption spectra of both GE POL diamonds were recorded in the near infrared, visible and ultraviolet range at low temperature. The range between 200 nm and 800 nm

was recorded on a UVIKON spectrophotometer using a resolution of 0,5 nm and a scan speed of 20 nm/mn. The stones were cooled down to -130°C. No particular absorption was detected.

The near infrared absorption spectra of both stones in the range 700 nm -1100 nm were recorded on a J & M spectrometer at the Department of Physics of the University of Basel. The stones were cooled down at -170°C and were placed between two optical fibres, one for the incident beam the other directed towards the detector. We detected no absorption around the H2 centre (986 nm) which is described in some coloured diamonds treated at high temperature (Reinitz & Moses, 1997; Buerki et al., 1999). The absence of absorption between 200 nm and 1100 nm is not surprising. On the one hand the stones are colourless, thus their absorption is inevitably weak. And on the other hand they are of type IIa (without nitrogen), nitrogen being almost always responsible for the yellow colour of diamond and related to the H2 center.

5.3 – Raman spectrometry

Using Raman spectrometry, in addition to the Raman peak of diamond located at 1332 cm⁻¹, several bands of low intensities are observable (Yuan, 1999). The spectra of 50 diamonds were recorded on a Raman Renishaw System 1000. It is equipped with a CCD detector cooled by Peltier effect, the source of 25 mW uses a ionised argon laser (green ray at 514 nm). The fifty analysed diamonds are :

- both colourless GE POL diamonds of type IIa,
- 47 untreated diamonds whose colours range between D and Z. These diamonds are type IaA and IaAB,
- a pink diamond of natural colour, graduated: «fancy light», of type IIa. This stone presents a strong colourless graining.

37 of the untreated colourless diamonds show a band system between 3000 and 6000 cm⁻¹ with maxima at about 4202 and 5198 cm⁻¹ ± 2 cm⁻¹. They are identified as signals of fluorescence, recognizable at their accompanying vibronic systems (Figure 6).

Ten untreated diamonds do not present any fluorescence bands in this spectral range. Both GE POL diamonds, an untreated dia-

mond (colour F) and the pink diamond of type IIa present a band at 3760 cm⁻¹. It corresponds to an emission at 15674 cm⁻¹ approximately, that is to say 637 nm (Figure 6). This system is well-known. It is the N-V centre, an association of a single nitrogen (N) atom linked to a carbon vacancy (V). It is characteristic of treated pink diamonds of type Ib, where it forms during annealing after irradiation.

This can appear to be surprising for the two GE POL diamonds and for the pink diamond which are of type IIa (Figure 7) and therefore do not contain nitrogen, but it is much less surprising for the untreated near colourless diamond (colour F) which is a type Ia (thus containing nitrogen). However, this absorption system has been described for type IIa natural pink diamonds (Harlow, 1998).

The number of studied GE POL samples is too weak to judge the value of this criterion for the separation of untreated from GE POL diamonds with certainty, but this result is encouraging.

VI – About the GE process

Although all GE POL diamonds are mostly of type IIa, one must consider the existence of a GE patent to discolour diamonds of type Ib and/or Ia, using high temperature and high pressure - the high pressure avoiding the graphitisation of diamond - (US Patent N° 4,124,690, date : 7.11.1978). This patent fell into the public domain four months before the LKI and GE declared a contract between them (Schmetzer, 1999).

This suggests that a small part of GE POL diamonds (type I diamonds) could have undergone the patented process. Indeed, even if the majority of GE POL diamonds are type IIa (as the two stones being the subject of this study), some are type Ia, even Ib (GIA Loupe Special Symposium Edition, 1999).

It was recently confirmed that it is indeed a high temperature and high pressure treatment (Rapaport, October 4, 1999). The starting material would consist of type IIa brown diamonds or another type, but then containing very little nitrogen otherwise at high temperature the N3 center would form and induce a yellow colour. The diamonds are probably

treated as rough (refer to 4.3 Synthesis of the observations). The whole colour of the stones is thus improved (understand, the stones are more colourless). Several side effects of this process seem to occur.

First of all, when the stones contain inclusions, they take an unusual aspect, this is seen with a binocular microscope using an optical fiber and also using polarised light. Then, some N-V centres could have been formed during the high temperature treatment although the majority of GE POL diamonds are of type I_{IIA}. However, the detected N-V centres could also be preexistent prior to treatment, and one could consider that they are precisely a particularity of the stones to be treated. Nevertheless, we showed that this extremely weak N-V centre is detectable by its laser fluorescence using Raman spectrometry and is present in both GE POL dia-

monds (Figure 6), as well as in the one described by Yuan (1999).

VII – Conclusion

It has been established that both GE POL diamonds were detectable thanks to :

- the observation of inclusions surrounded by an «atoll», well known in heated corundum but not yet observed in untreated diamonds. This observation was also made by GIA, which studied more than 800 GE POL diamonds [Conference of James Shigley at the International Gemmological Conference, Goa (India), September 30, 1999]. During this study, we have presented a simple device named «SSEF I_{IIA} Diamond Spotter» that enables to quickly identify type I_{IIA} diamonds. We have also proposed a potential criterion of spectroscopic nature

- the presence of N-V centers in both GE POL diamonds, those being detectable by means of their laser fluorescence.

LKI did not provide to any laboratory the stones before and after process. This would be an excellent test of the preliminary criteria, which we propose. It is important to analyse a large quantity of GEPOL diamonds, and at the same time type I_{IIA} untreated colourless to slightly tinted diamonds. This last task will be complicated by the scarcity of type I_{IIA} diamonds. It is also necessary to take into account the GIA study which showed that most of GE POL diamonds are of a purity equal or higher than VVS (Johnson et al., 1999). The development of an identification method nonrestricted to the observation of inclusions is thus necessary. The spectroscopic criterion suggested must thus be tested in priority.

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Notes : All mentioned press releases can be consulted on the Internet: <http://www.diamonds.com>

The T. Moses and al. paper « Observations on GE-processed diamonds : a photographic record » published later to the submission of the present article is quoted in the references but not in the text.

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