

High pressure high temperature treatment of diamonds — a review of the patent literature from five decades (1960–2009)

Dr Karl Schmetzer

Abstract: The relevant patent literature describing high pressure high temperature treatment processes of natural and synthetic diamonds is reviewed. A general overview about high pressure high temperature treatment for various technical applications is presented and colour changes for jewellery-quality diamonds are described in detail. Three major groups of patent documents exist that deal with the treatment of intense yellow type Ib synthetic diamonds, the colour alteration of brown natural diamonds and colour improvement of chemical vapour deposition grown synthetic diamonds, respectively. The reaction mechanisms involved in various processes of colour alteration are briefly discussed. In an extended version on the worldwide web, the different types of patent documents are explained, and the most relevant technical descriptions of a range of equipment used to perform HPHT treatment of diamonds are summarized in appendices.

Keywords: cause of colour, CVD, colour alteration, colour centres, defects, HPHT, natural diamond, synthetic diamond, treated diamond



Introduction

Within the last two decades, the major challenge for gemmological laboratories has moved from problems of distinguishing natural gemstones from their synthetic counterparts more towards the recognition and proper disclosure of various treatment processes. Detailed knowledge of possible treatment processes is essential for the recognition of treated gemstones in the laboratory. Since the late 1990s, in addition to the diffusion treatment of rubies and sapphires, a 'new' treatment process

for diamonds, mainly a decoloration of natural brown stones, caused major irritation in the trade when the first faceted stones that had undergone this enhancement for colour alteration in the laboratories or production plants of General Electric were brought to the market in 1999 (Moses *et al.*, 1999).

According to a comparison with patents issued by General Electric and De Beers in the late 1970s to early 1980s, which dealt with colour alteration of type Ib natural and synthetic intense yellow diamonds, first speculations

pointed towards a possible application of a high pressure high temperature (HPHT) treatment for the 'new' process (Schmetzer, 1999a), which was later confirmed by General Electric (Anthony and Casey, 1999). Patent documents by General Electric, which had been filed and issued in the 1990s, were discussed

Above: This type Ia diamond of 0.07 ct was originally brown and treated in a three-step process by a) HPHT, b) electron irradiation and c) annealing. Photograph by courtesy of T. Hainschwang, Gemlab, Gemological Laboratory, Balzers, Liechtenstein.



Figure 1: This type IIa diamond of 1.20 ct was originally brown and treated in a HPHT process. Figures 2 and 3: These type Ia diamonds of 1.00 ct and 1.60 ct respectively, were originally brown and treated in a HPHT process. Photographs courtesy of E. Erel, Carat Gem Lab, Gemological Laboratory, Montigny-les-Metz, France.

by Schmetzer (1999b, 2000). These documents are considered to describe a precursor of the new treatment, mainly the enhancement of synthetic diamonds grown by chemical vapour deposition (CVD). The reduction of defects and strain and the improvement of optical properties are caused in CVD-grown synthetic diamonds by the HPHT treatment process.

The application of HPHT treatment to natural type IIa brown diamonds also causes the reduction of defects and strain and results, at least partly, in a decoloration (Smith *et al.*, 2000) or in a transformation into light yellow, pink (Figure 1) or blue diamonds. In contrast, the application of HPHT treatment to type Ia brown diamonds causes a colour alteration to yellowish green, greenish yellow or yellow (Figures 2 and 3; Reinitz *et al.*, 2000; Hainschwang *et al.*, 2005).

Although the patent documents from the late 1970s to the mid 1990s mentioned in the papers by Schmetzer (1999 a,b, 2000) were briefly reviewed recently by Overton and Shigley (2008), only some of the documents (which describe treatments of mostly brown or brownish natural stones), published mainly within the last decade, were mentioned in this article. Other, older, processes dating back to the 1960s as well as some additional technical developments and applications of HPHT treatment processes described since then for natural and synthetic diamonds are largely unknown to gemmologists. Thus, the author presents an overview of five decades of HPHT treatment of diamonds as disclosed in issued patent documents and patent application publications.

More details about patent documents can be found in an expanded version of this paper on the worldwide web where

a short summary about patents and types of patent documents is given in Appendix A. Because technical details of the processes applied are largely unknown to gemmologists and only briefly discussed in gemmological papers, Appendix B is dedicated to the technical aspects of HPHT treatment processes.

General overview and chronology of HPHT treatment processes

The patent documents dealing with HPHT treatment of diamonds are listed in Table I; numbers in the right-hand column relate to superscript numbers in this text, and n, s and c relate to natural, synthetic (HPHT) and CVD-grown diamonds. The oldest documents known to the author date to the 1960s and describe diffusion treatment with aluminium and boron and the formation of diamond with semiconductor properties for electrical devices. In these two patents by General Electric¹ first hints towards a possible colour change are also given.

In later decades, numerous patents were filed by the two global players in diamond crystal growth on the world market, General Electric and De Beers (including their subsidiaries), by other companies involved in diamond synthesis (Sumitomo in Japan and Iljin in Korea), by research institutes (e.g. Carnegie Institution of Washington) and by companies involved in the application of diamond for electronic devices (e.g. Nippon Telegraph and Telephone Corporation or Akhan Technologies).

A group of patent documents from the late 1970s/early 1980s^{2,3} described the treatment of natural and synthetic

diamonds to alter and improve colour. In 1975, a first patent was filed by General Electric which described the improvement of mechanical properties of diamonds by annealing the samples in the field of plastic deformation.⁴ A similar process was described by The Australian National University in 1990.⁵ From 1988 to 1990, patent applications by Sumitomo again described the formation and alteration of specific defects (colour centres) and the improvement of colour in synthetic diamonds.^{6,7,8,9} Since 1995, patent applications have been filed by General Electric which described the improvement of toughness and strength in diamonds. Parts of these applications dealt with synthetic diamonds grown by the HPHT technique,^{10,11} but other documents described the treatment of synthetic diamonds grown by the CVD method.^{12,13} In general, how defects in the diamond lattice are relieved and voids and stresses are removed by HPHT treatment were described. As mentioned above, the documents of this series are considered as precursors of the processes developed for decoloration and colour change of natural brown diamonds, the results of which were released to the market in Spring 1999.

A first document by Umeda¹⁴ described the improvement of brightness and colour tone of jewellery-quality diamond. Shortly thereafter, the treatment of brown natural diamonds was described in a series of worldwide applications by General Electric^{15,16,17,18} and De Beers.^{19,20,21} The treatment of different types of diamond was described for decoloration of brown diamonds, and for changing this colour into yellow, orange, greenish yellow and yellowish green (Figure 4) and into pink and blue in such stones. All



Figure 4: These type Ia diamonds of 1.20 ct (left) and 1.10 ct were originally brown and treated in a HPHT process. Photograph courtesy of E. Erel, Carat Gem Lab, Gemological Laboratory, Montigny-les-Metz, France.

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Table 1: Chronology of HPHT patent applications and granted patents for the HPHT treatment of diamonds.

Author(s), applicant priority publication/ date and/ or WO publication/ date	Related patents (patent family)/ date	Temperature (°C)	Pressure (kilobars)	Time	Results	No. *
Cannon, General Electric US 3,134,739 (1964) Wentorf, General Electric US 3,141,855 (1964)	DE 1168396B (1964) FR 1341561A1 (1963) GB 1014226A (1965)	700–1500 1300–2000	10–60 8.5 or 63	20 min 12 or 15 min	Diffusion of aluminium to modify electrical characteristics and colour Diffusion of boron to modify electrical characteristics and colour	1 n, s n, s
Strong <i>et al.</i> , General Electric US 4,124,690 (1978) Strong <i>et al.</i> , General Electric US 4,174,380 (1979)	DE 2732793A1 (1978) GB 1578987A (1980) FR 2359071A1 (1978)	1500–2200 1500–2200	48–80 48–80	1 min–50 hr 1 min–50 hr	Partial or total conversion of Ib to Ia nitrogen, lighter yellow colour Partial or total conversion of Ib to Ia nitrogen, lighter yellow colour	2 n s
Evans and Allen, De Beers EP 0014528A1 (1980)	EP 0014528B1 (1983) US 4,399,364 (1983)	1600–2200	80	20 min–6 hr	Reduction of yellow colour in irradiated type Ib synthetic diamond	3 s, (n)
De Vries <i>et al.</i> , General Electric US 4,181,505 (1980)	DE 2519116A1 (1975) GB 1500817A (1978) FR 2275405A1 (1976)	Below 1500	Below 55	1–30 min	Improving mechanical properties of crystals by annealing in the field of plastic deformation	4 n, s
Ringwood, The Australian National University WO 86/01433A1 (1986)	US 4,874,398 (1989) US 4,948,388 (1990) US 4,985,051 (1991) EP 0191067B1 (1992)	1100–1600	10–40	3–60 min	Improving mechanical properties (hardness, strength) by annealing in the field of plastic deformation	5
Tsuji and Sato, Sumitomo Electric JP 63–291896A (vvvvv, JP 01–183409A, JP 63–291896 (1988)		1500–2200	10–30		Conversion of Ib to Ia nitrogen in irradiated type Ib synthetic diamond	6 s
Tsuji and Sato, Sumitomo Electric JP 01–020689A (1989) JP 02–000385A (1989)	EP 0275063A2 (1988) US 4,880,613 (1989)	1700–2500	> 30	> 20 hr	Conversion of Ib nitrogen in irradiated type Ib diamond, irradiation and heat treatment after HPHT treatment	7 s
Satoh and Tsuji, Sumitomo Electric JP 01–183409A (1989)	EP 0324179A1 (1989) EP 0324179B1 (1992) US 4,959,201 (1990)	> 1600	> 30	5–30 hr	Treatment of an irradiated Ib diamond to produce a green colour	8 s
Nakajima <i>et al.</i> , Sumitomo Electric JP 02–018980A (1990)		> 2000	> 30	> 5 hr	Formation of N3 centres in a type Ib synthetic diamond for use as diamond laser element	9 s
Jackson and Park, General Electric US 5,523,071 (1996)	JP 07–165494A (1995) EP0638670A1 (1995) EP 0638670B1 (2001)	800–1600	Up to 45	5 min–10 hr	Annealing in reducing atmosphere to improve the toughness and strength of diamond grains	10 s
Banholzer <i>et al.</i> , General Electric	EP 0668377A1 (1995) JP 08–002997A (1996)	900–2000	10–70	5 min–10 hr	Annealing in non-oxidizing atmosphere to improve the toughness and strength of diamond grains	11 s

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Anthony <i>et al.</i> , General Electric JP 09-164329A (1997)	EP 0671482A1 (1995) JP 07-331441A (1995)	1000–2000	10–200	minutes– several days	Remove voids and stress to improve toughness in colourless CVD synthetic diamond	12 c, (n,s)
Anthony <i>et al.</i> , General Electric US 5,672,395 (1997)		1100–2300	above 3	2–60 min	Annealing in a non-oxidizing medium to improve the toughness of CVD synthetic diamond thin films by removing stress and voids	13 c, (n,s)
Umeda & Miyamoto, Umeda JP 09-164329A (1997)					Improve the quality and colour tone of jewellery-quality diamond	14
Anthony & Vagarali, General Electric WO 01/14050A1 (2001)	EP1210171B1 (2006) EP 1645328A1 (2006) CA 2382785A1 (2001) DE 60027441T2 (2006)	1500–3500	10–100	30 sec–96 hr	Production of yellowish-green, greenish–yellow and neon greenish-yellow stones from discoloured natural diamonds	15 n
Vagarali <i>et al.</i> , General Electric US 2001/0031237A1 (2001)	US 2002/0081260A1 (2002) US 2003/0143150A1 (2003) US 2004/0146451A1 (2004) US 2005/0249655A1(2005) US 6,692,714B2 (2004) US 7,323,156B2 (2008)	1500–3500	10–100	30 sec–96 hr	Production of colourless stones from discoloured natural diamonds	16 n
Vagarali <i>et al.</i> , General Electric, US 2002/0172638A1 (2002)		1500–2700	50–200	30 sec–500 hr	Production of colourless, yellow, greenish yellow, pink, red, and blue stones from discoloured (mostly brown) natural diamonds	17 n
Anthony <i>et al.</i> , General Electric WO 02/13958A2 (2002)	EP 1315558B1 (2006) EP 1637218A2 (2006) US 2005/0260935A1 (2005) US 7,241,434B2 (2007)	1500–3500	10–100	30sec–96 hr	Production of colourless and fancy coloured stones from discoloured natural diamonds	18 n
Burns and Fisher, De Beers WO 01/72404A1 (2001)	EP 1272264B1 (2006) CA 2405362 (2001) DE 60123591T2 (2007)	1900–2300	69–85	10 min–10 hr	Production of pink stones from discoloured natural brown diamonds	19 n
Burns <i>et al.</i> , De Beers WO 01/72405A1 (2001)	EP 1272266B1 (2006) CA 2405409A1 (2001) DE 60123593T2	1800–2600	67–90	10 min–20 hr	Production of blue stones from discoloured natural brownish grey or grey diamonds	20
Burns <i>et al.</i> , De Beers WO 01/72406A1 (2001)	EP 1272265B1 (2006) CA 2405420A1 (2001) DE 60123592T2 (2007)	2200–2600	76–90	90 min –5 hr	Production of colourless stones from brown diamonds	21 n
Frushour and Li, Diamond Innovations US 2003/0230232A1 (2003)	US 6811610B2 (2004)	1500–2900	at least 40	1–30 min	Improving optical, electrical, thermal and mechanical properties of synthetic CVD diamonds	22 c
Frushour and Li, Diamond Innovations WO 2005/031033A1 (2005)		1500–2900	at least 40	1–30 min	Improving optical, electrical, thermal and mechanical properties of synthetic CVD diamonds	23 c

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Table 1: Chronology of HPHT patent applications and granted patents for the HPHT treatment of diamonds (continued)

Author(s), applicant priority publication/date and/or WO publication/date	Related patents (patent family)/date	Temperature (°C)	Pressure (kilobars)	Time	Results	No. *
Vins, Vins RU 2237113C1 (2004) WO 2004/113597A1 (2004)	EP 1645664A1 (2006) US 2007/0053823A1 (2007)	> 2150	60–70	10 min	Production of fancy red diamonds, irradiation and heat treatment after HPHT treatment	24 n
Baek <i>et al.</i> , Iljin Diamond KR 20040042576 (2004)					Colour change of diamond from brown to yellow, greenish yellow, yellowish green or colourless	25 n
D'Evelyn <i>et al.</i> , General Electric US 2004/0000266A1 (2004)	US 2006/0096521A1 (2006) US 7,175,704B2 (2007) EP 1378591A1 (2004) EPI715086A1 (2006) JP 2004–161604A (2004) JP 2007–015918A (2007)	1000–2000	55	30 min	Reduction of defect concentrations and strain in various non-diamond crystals, e.g. SiC, GaN, GaAs	26
Gill <i>et al.</i> , Element Six WO 2004/07457A1	US 2007/0054124A1 (2007)				Annealing CVD synthetic diamonds to enhance the wear rate	27 c
Godfried <i>et al.</i> , Element Six WO 2004/046427A1 (2004)	US 2004/0229464A1 (2004) GB 2432592A (2007) GB 2433737A (2007) GB 2433738A (2007)				Annealing CVD synthetic diamonds to enhance optical properties and to reduce strain	28 c
Twitchen <i>et al.</i> , Element Six WO 2004/022821A1 (2004)	CA 2495840A1 (2004) US 2004/0175499A1 (2004) US 2007/0079752A1 (2007) US 2009/0291287A1 (2009) US 7,172,655B2 (2007) GB 2430194A (2007)	1200–2500	65–80	3 sec–835 hr	Production of a desired colour in CVD–grown synthetic diamond, e.g. colourless or pink or green	29 c
Hemley <i>et al.</i> , Carnegie Institution of Washington US 2005/0025886A1 (2005) US 2006/0144322A9 (2006)	WO 2005/007936A2 (2005) WO 2005/007937A2 (2005) US 2006/0185583A1 (2006) US 2007/0290408A1 (2007) US 2008/0241049A1 (2008) US 7115241B2 (2006) US 7309477B2 (2007)	1800–2900	50–70	1–60 min	Enhancement of diamonds grown by microwave plasma chemical vapour deposition, lightening brown or yellow coloration, improvement of mechanical properties, e.g. hardness	30 c
Hemley <i>et al.</i> , Carnegie Institution of Washington US 2006/0065187A1 (2006)	WO 2007/018555A2 (2007) US 7594968B2 (2009)	2000–2700	50–70	10 min	Enhancement of diamonds grown by microwave plasma chemical vapour deposition, removal of brown coloration, increase of hardness	31 c

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Namba <i>et al.</i> , Sumitomo Electric Industries WO 2005/041279A1 (2005)	EP 1713116A1 (2006) US 2006/017792A1 (2006)	800–1800	30–80	10 hr	Producing n-type semiconductor diamond by annealing Li- and N-bearing ion-implanted crystals	32 s
Tkachenko and Timofeev RU 2281350 C2 (2006)		1700–2300	60–90	8–30 min per step, 1–3 hr in total	Decoloration of diamond in several annealing steps at different temperatures	33 n
Summerton <i>et al.</i> , Element Six WO 2006/061707A2 (2006)	US 2009/0258229A1 (2009)	2100–2500	60–80	0.1–48 hr	Improving the quality of type IIa HPHT-grown synthetic diamond	34 s
Williams <i>et al.</i> , Element Six WO 2006/136929A2 (2006)	GB 2428690A (2007) US 2010/0015438A1 (2010)	1200–3000			Improvement of CVD-grown synthetic diamond	35 c
Kasu <i>et al.</i> , Nippon Telegraph and Telephone Corporation WO 2006/137401A1 (2006)	EP 1895579A1 (2008) US 2008/0134959A1 (2008) US 2008/0134960A1 (2008) US2008/0217626A1 (2008) US 2009/0261347A1 (2009)	1200	60		Improving the properties of ion-implanted diamond semiconductor elements	36 c
Twitchen <i>et al.</i> , Element Six WO 2007/066215A2 (2007)	US 2009/0127506A1 (2009)	1600–2500	60–80	0.1–48 hr	Improving the quality of HPHT-grown synthetic diamond which is used as seed for CVD growth	37 s
Khan, Akhan Technologies WO 2008/019404A2 (2008)	US 2008/0073646A1 (2008) DE 112007001892T5 (2009)	1200	60	1 hr	Improvement of properties of boron-doped diamond field effect transistor	38 c

* n: natural diamonds;

s: synthetic HPHT-grown diamonds;

c: synthetic diamonds grown by chemical vapor deposition (CVD)

■ HPHT treatment predominantly for colour improvement

■ HPHT treatment in combination with diffusion of aluminium or boron into the diamond

■ HPHT treatment in combination with irradiation

■ HPHT treatment predominantly for the improvement of mechanical properties

■ HPHT treatment predominantly for the improvement of parts for electrical devices

Notes:

1. Patents related to the design of the equipment to create the temperature and pressure conditions for diamond synthesis are not included in this table.
2. Related patents (patent family members) are patents with the same title and/or by the same inventors and/or by the same applicant; only a selection of patent family members are given, others in different languages, e.g. Japanese, Chinese, Russian, may also have been published.
3. The patent country codes are as follows: CA – Canada, DE – Germany, EP – Europe, FR – France, GB – Great Britain, JP – Japan, KR – Korea, RU – Russia, US – United States, WO –World Intellectual Property Organization.

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Table II: Colour change of diamonds by HPHT treatment

Starting material*	Original colour	Treatment	Colour after treatment	Mechanism	No.
n,s		HPHT + diffusion of boron	Patches of dark blue colour or dark blue surface regions	Diffusion of boron into the diamond structure	1
n,s		HPHT + diffusion of aluminium	Clearer and more colourless	Diffusion of aluminium along fractures	1
s Ib	Greenish yellow or intense golden yellow or yellow	HPHT	Towards yellow, paler yellow or almost colourless	Aggregation of single nitrogen atoms	1,2,30
n Ib or Ib–Ia		HPHT			2
s Ib		1) Irradiation 2) HPHT	Reduction of colour	1) Displacement of atoms 2) aggregation of single nitrogen atoms	3,6
s Ib	Bright yellow	1) Irradiation + 2) HPHT	Green	Formation of N-V-N centres	7
n Ia, IIa	Brown	HPHT	Colourless or almost colourless	Removal of brown colour centres	16,17,18,21,25
n IIa	Brown	HPHT	Pink		16,17,18,19
n IIIb	Brown, brownish grey or grey	HPHT	Blue		16,17,18,20
n IaB and Ia A/B	Brown	HPHT	Yellowish green to greenish yellow or intense to light yellow	Removal of brown colour centres combined with the mobilization of vacancies, dissociation and association of A and/or B nitrogen defects, formation of N-V-N and other nitrogen-vacancy defects (colour centres)	15,16,17,18,25
n Ia	Near colourless to brown	1) HPHT + 2) irradiation + 3) annealing	Intense pink to red	1) Dissociation of A centres, 2) formation of vacancies 3) mobilization of vacancies and formation of N-V colour centres	24 (compare Ref. 7 for similar treatment of type Ib synthetic diamonds)
n	Brown, yellow and yellowish green	HPHT with annealing in different subsequent steps at various temperatures	Decoloration		33
c with variable nitrogen contents	Brown or orange brown or pinkish brown	HPHT	Near-colourless, pale brown or green or pink brown	Removal of an absorption band at 350 nm, at higher temperatures additional removal of a 510 nm band and a NIR absorption	29
c	Brown or yellow	HPHT	Colourless or near-colourless, reduces or eliminates yellow or brown colours	Removal of defects	30,31

* n: natural diamonds; s: synthetic HPHT-grown diamonds. c: synthetic diamonds grown by CVD.

HPHT treatment predominantly for colour improvement

HPHT treatment in combination with diffusion of Al or B into the diamond

HPHT treatment in combination with irradiation

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Figure 5: This type Ia diamond of 1.51 ct was originally brown and treated in a three-step process by a) HPHT, b) electron irradiation and c) annealing. Photograph by courtesy of V. Vins, Institute of Single Crystals, Novosibirsk, Russia.

these documents contain the most detailed descriptions of colour alteration in natural brown diamonds. A similar application was also filed by Iljin in Korea.²⁵ A special process for the production of red and pink diamonds was described by Vins using a combination of HPHT treatment, with subsequent electron irradiation and annealing (Figure 5).²⁴ An application by Tkachenka and Timofeev also described the decoloration of natural diamond.³³ With the exception of the Umeda¹⁴ and the first General Electric¹⁷ patents, the various applications mentioned in this paragraph for colour improvement of natural, mostly brown or pale brown diamonds, have been published within the last decade.

After the year 2000, although there were some applications dealing with the improvement of mechanical properties of synthetic diamonds grown by the HPHT technique,³⁴ most were for diamonds grown by CVD^{22,23,27,28,35} and for related superhard materials.²⁶ One document contains a description of how to improve the properties of HPHT-grown synthetic diamond crystals which are used as seeds for the growth of larger CVD synthetic diamonds.³⁷ The interest for possible improvement of CVD-grown synthetic diamonds is based on technical progress in CVD-related processes resulting in the growth of synthetic diamond layers or crystals with larger thickness; such products could be cut as faceted stones for jewellery purposes. Consequently, HPHT treatment is also applied to change

or improve the colour of CVD-grown synthetic diamonds,^{29,30,31} mainly to alter yellow and pale brown tones. The improvement of properties of specifically doped CVD synthetic diamonds for semiconductor application has also been described recently.^{32,36,38}

Colour alteration of diamonds by HPHT treatment

In natural or synthetic diamonds destined for jewellery, the alteration and improvement of colour is the main purpose for application of HPHT treatment processes, although colourless type IIa synthetic diamonds have also been processed to improve quality and optical features.³⁴ The patents dealing with colour alteration clearly reflect the natural and synthetic material available and the desired colour changes to attain marketable material.

Diffusion treatment with boron and aluminium

Diffusion treatment with boron or aluminium is the oldest patent¹ dealing with the HPHT process applied for colour alteration of natural or synthetic diamonds which is known to the author. This described HPHT annealing in the presence of boron-bearing compounds which resulted in a blue coloration, at least of parts of the surfaces of the samples. Diffusion treatment with aluminium, on the other hand, was described to whiten the treated diamonds. It is not known to the author whether either process has been carried out commercially and samples released to the market, or whether any practical tests are available to detect this type of diffusion treatment and distinguish them from natural pale-blue to fancy-blue diamonds.

On request, the author received the following information from Victor Vins, Novosibirsk, Russia, which is helpful in assessing the potential of these two processes:

“In the mid 1980s we conducted experiments of thermal diffusion of boron and aluminium from the surface of natural

diamonds. The experiments were carried out at high P and T conditions, boron and aluminium were in the graphite mixture. We did observe the colour change and we at first thought that we had managed to introduce these elements into the diamond lattice. Then we examined these samples more closely and found out that the colour change was due to thin layers on the surface of natural diamonds. We gradually etched the diamond surface and soon the conductivity decreased from metallic to zero conductivity.”

Boron diffusion into type I and type II natural diamond up to a depth of about 2 μm at low pressure and high temperature has been described by Popovici *et al.* (1995 a,b), Sung *et al.* (1996) and Krutko *et al.* (2000).

Thus, two explanations are possible to explain the results mentioned above:

- (a) Thin layers of synthetic HPHT-grown boron-containing diamond were formed on the surface of the natural diamond crystals. These layers were removed by subsequent etching.
- (b) Boron was diffused into an extremely thin surface layer of the diamond, a layer that could be removed by subsequent etching.

In summary, a possible diffusion treatment of boron would produce a blue coloration only in thin surface layers, but would definitely influence the colour of faceted diamond. However, it is questionable if the thin blue layer produced by this technique would survive any re-cutting and re-polishing.

Transformation of colour centres

The patent applications available as public documents which are relevant to colour alteration of diamond are numbered in Table II and can be considered in three groups dealing with

- Colour improvement and alteration of intense yellow type Ib natural and synthetic diamond;
- Colour improvement and alteration of brown type I and natural brown type II diamond;
- Colour improvement and alteration of yellow to brown synthetic diamond grown by CVD.

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Some applications also mention the lightening or decoloration of type Ia natural pale yellow diamonds.

In some patent documents, the 'prior art' (patent documents or scientific papers known to the applicant at the time of writing the text of the application or documents identified as relevant by an officer researching a patent application), including the mechanism of colour change and colour improvement is discussed, but in other documents only the desired process of colour alteration is stated, with no mention of the exact mechanism of colour change. From scientific research and review papers published within the last decade (e.g. Collins *et al.*, 2000; De Weerd and Van Royen, 2000; Vins, 2001; Collins, 2001 a,b; De Weerd and Collins, 2003; Avalos and Dannefaer, 2003; Katrusha *et al.*, 2003; Vins and Yelissev, 2008; Erel, 2009; Fisher, 2009; Fisher *et al.*, 2009) and patent documents the following general reaction mechanisms can be summarized as follows.

According to the type of nitrogen defects present in the diamond crystal and as a function of the annealing temperature(s) and the stabilizing pressure(s), nitrogen-related centres may associate and dissociate. In synthetic and natural type Ib diamonds containing isolated nitrogen atoms on carbon lattice sites (C centres), for example, nitrogen can migrate within the diamond structure and can form A centres (consisting of adjacent substitutional pairs of nitrogen). In natural type Ia diamond, A centres can transform into B centres (consisting of a vacancy trapped by four surrounding nitrogen atoms). A centres, on the other hand, can dissociate into isolated nitrogen atoms.

If vacancies (V) are produced, e.g. by electron or neutron irradiation, these vacancies can combine with existing nitrogen defects to form the following centres:

- C centre + V \rightarrow N-V centre (a substitutional nitrogen atom adjacent to a vacancy);
- A centre + V \rightarrow H3 centre (N-V-N centre, a vacancy trapped by a pair of substitutional nitrogen atoms); if an

electron is trapped at the H3 centre (with C centres as electron donors), the H2 centre is formed;

- B centre + V \rightarrow H4 centre (4N-2V centre, consisting of two vacancies and four nitrogen atoms).

H4 centres, on the other hand can become unstable upon HPHT treatment and dissociate into two H3 centres.

Furthermore, in brown diamonds, brown colour centres can be removed by HPHT treatment. In this process, vacancies are also formed or released, which combine with existing nitrogen defects according to the possible reaction processes given above. Some of the new colour centres may become unstable and dissociate.

In the following paragraphs, only short explanations will be given about the various processes; it is beyond the scope of the present paper to discuss all possible processes at different temperatures and the interpretation of spectroscopic measurements in detail. For these discussions, the reader is referred to the numerous scientific papers available. Furthermore, the mechanisms described in various patent documents are not always consistent with each other, but it would be extremely confusing to discuss these differences and discrepancies. Consequently, for these details the interested reader should refer to the original documents (*Table I* and Appendix C).

Colour improvement and alteration of intense yellow type Ib natural and synthetic diamond

Several patents deal with colour improvement and colour alteration of type Ib diamonds containing predominantly isolated nitrogen atoms (C centres). Most synthetic diamonds grown by the HPHT process are of this type and reveal a greenish yellow or intense golden yellow to yellow or even orange coloration. This coloration, which is sometimes too brown or dark for jewellery purposes, can be changed to a brighter yellow (*Figure 6*) or towards a somewhat paler yellow or even approaching colourless, if desired.^{1,2,30} The A centres formed by this treatment do



Figure 6: This type Ib synthetic diamond of 0.33ct was originally intense yellow and treated in a HPHT process. Photograph by courtesy of T. Hainschwang, Gemlab, Gemological Laboratory, Balzers, Liechtenstein.

not absorb light in the visible range and this explains the lightening of the yellow coloration. Although the same process is also described for natural diamonds,² type Ib natural 'fancy yellow' diamonds are very rare and sought after, and therefore the practical application of this treatment to such stones is assumed to be limited.

The same process can be carried out in a shorter overall time by first irradiating the diamond in a separate step before the HPHT treatment is performed.^{3,6} Another patent application by Sumitomo Electric described electron irradiation to type Ib synthetic diamonds before HPHT treatment.⁸ In this process, vacancies are formed which associate with two nitrogen atoms and form N-V-N centres (H3 and H2 centres). The colour of the processed diamond is green. This type of treatment was performed by Sumitomo for samples marketed by Chatham (for a gemmological description see Shigley *et al.*, 2004).

Colour improvement and alteration of type I and type II natural brown diamond

Details of the causes of colour in natural brown diamonds are still in debate (Hainschwang, 2003; Hainschwang *et al.*, 2005). Until recently, it was generally assumed that the coloration of most natural brown diamonds was associated with plastic deformation, which the diamonds had undergone between their formation and subsequent transport to the Earth's surface. Now, however, results of experimental research and theoretical considerations point towards a model in

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Table III: Colour alteration in diamond by HPHT treatment*

Diamond type	Colour before annealing	Medium	Pressure (in kbar)	Temperature (in °C)	Time (in min)	Colour after annealing
Ila	Steely grey brown	Graphite	80	2300	18	Colourless
Ia	Light brown	Graphite	80	2300	20	Pale green
Ia	Light brown	Graphite	80	2300	18	Yellow
Ia	Light brown	Graphite	77	1900	18	Light brown
Ia	Light brown	NaCl	80	2400	12	Yellow
Ia	Medium brown	NaCl	77	1900	18	Medium brown
Ia	Medium brown	NaCl	79	2050	18	Light yellow
Ia	Light yellow	NaCl + KNO ₃	79	2200	18	Greenish golden yellow
Ia	Dark brown	Graphite	80	2300	17	Yellow
Ia	Light brown	NaCl	80	2200	18	Light greenish yellow
Ia	Dark brown	NaCl + KNO ₃	80	2200	18	Greenish golden yellow
Ia	Light brown	NaCl	80	2300	18	Light yellow
Ia	Light brown	NaCl	80	2300	18	Light yellow
Ia	Light yellow	NaCl	80	2400	18	Brownish yellow
Ia	Very light brown	NaCl	80	2200	18	Light yellow
Ia	Light yellow	NaCl	80	2400	18	Orange
Ia	Light brown	NaCl	80	2400	18	Orange
Ila	Light brown	NaCl	80	2300	18	Colourless
IaA/B	Light brown	Graphite	79	2300	18	Deep yellow
IaA/B	Dark brown	Graphite	79	2300	18	Very light yellow
IaA/B	Dark brown	Graphite	79	2300	18	Colourless
IaA/B	Light brown	Graphite	79	2000	18	Colourless
IaB	Brown	Graphite	79	2000	18	Brown
IaB	Brown	Graphite	79	2000	18	Brown
Ilb	Light steely brown	Graphite	79	2300	18	Light blue
Ila	Medium brown	Graphite	80	2300	18	Light pink

* From US 2002/0172638 A1,¹⁷

Inventors: S.S. Vagarali, S.W. Webb, W.E. Jackson, W.F. Banholzer, T.R. Anthony; applicant: General Electric Company, Schenectady, NY, USA

which vacancy clusters are assumed to be responsible for the brown coloration of natural diamonds. A recent review by Fisher (2009) summarizes these aspects. Because these vacancy clusters are altered and become partly unstable by HPHT treatment, this process is applied to large quantities of natural brown diamonds to transform their colour into one that is more desirable for jewellery purposes.

This more recent interpretation that

the brown is due to vacancy clusters, however, is not referred to in the various patent documents which are reviewed and summarized in the present paper. If the cause of colour change is discussed in a patent, the older interpretation based on the removal of colour centres associated with plastic deformation is normally quoted.

Table III shows examples of HPHT treatment of pale to dark brown

diamonds, based on a patent application by General Electric which had been filed in October 1997 but only published in 2002.¹⁷ It shows how different the colours can be after treatment and the major types of change are shown in a diagrammatic overview in Figure 7.

In nitrogen-free type II and almost nitrogen-free type I natural diamonds, the removal of brown colour centres results in colourless (Figure 8) or almost

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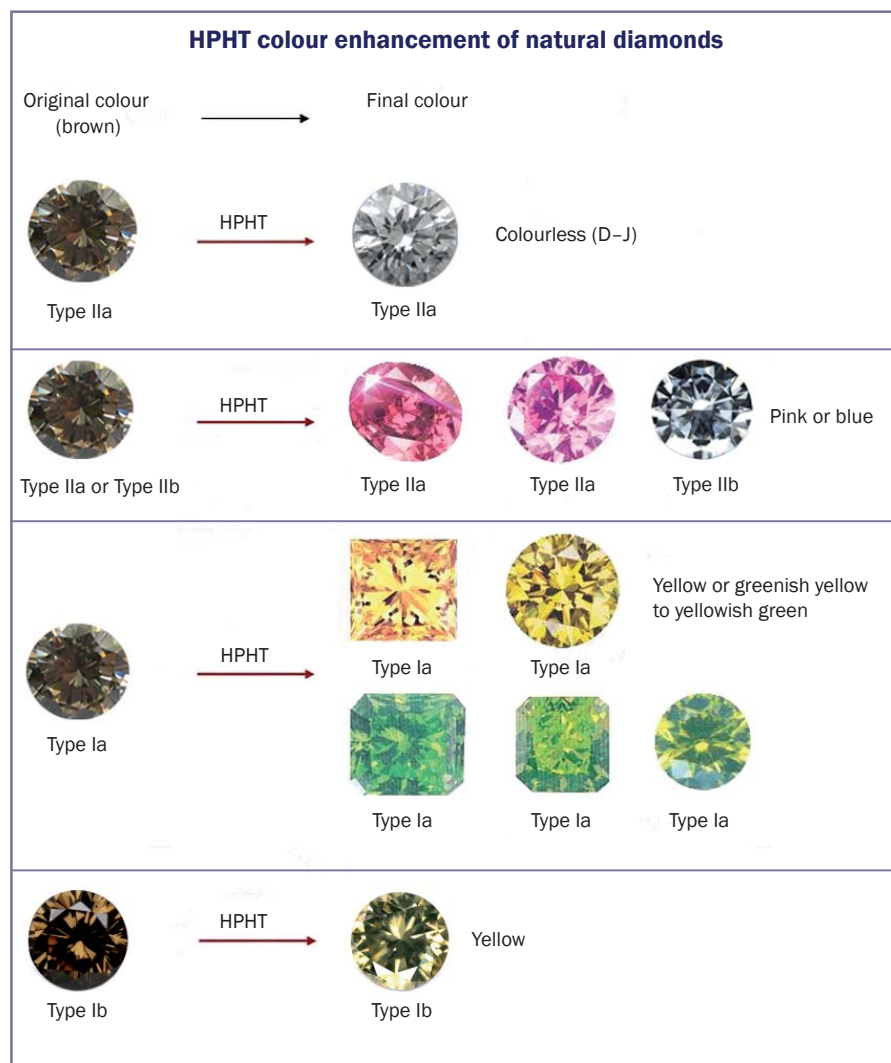


Figure 7: Systematic overview of possible colour alteration by HPHT treatment of natural brown type I and II diamonds. This diagram is based on a somewhat smaller schema by V. Vins, Institute of Single Crystals, Novosibirsk, Russia, which has been extended by the present author.

colourless diamonds.^{16,17,18,21,25} If pink colour centres or their precursors, whose exact nature is still in debate, are present in the untreated material but hidden by the brown coloration, after HPHT treatment and removal of the brown colour centres and possible alteration of precursor centres, the diamonds become pink (Figure 9), a colour which is highly sought after.^{16,17,18,19} A similar mechanism applies to brown, brownish grey, grey or olive green samples with boron contents (type IIb diamonds, Figure 10). The HPHT treatment causes removal of brown colour centres and a possible change of blue precursor centres and can result in stones with the highly appreciated and extremely rare blue to pale blue coloration of natural

diamonds.^{16,17,18,20} Details of the reaction mechanism involved in the formation and/or alteration of the blue and pink coloration of natural diamonds by HPHT treatment were recently summarized by Fisher *et al.* (2009).

Brown nitrogen-bearing natural diamonds can contain a range of brown colour centres, nitrogen related A and B centres and, rarely, C centres (type Ib natural brown diamond); they may also contain nitrogen trapped as N3 centres (3N-V centre, consisting of one vacancy and three nitrogen atoms) as well as N2 centres (another nitrogen-related defect). If only N3 and N2 colour centres were present, a more or less pale to intense yellow coloration would result from



Figure 8: This type IIa diamond of 0.70 ct was originally brown and treated in a HPHT process. Photograph by courtesy of J.-P. Chalain, SSEF Swiss Gemmological Institute, Basel, Switzerland.



Figure 9: This type IIa diamond of 0.50 ct was originally brown and treated in a HPHT process. Photograph by courtesy of E. Erel, Carat Gem Lab, Gemological Laboratory, Montigny-les-Metz, France.

treatment (Figure 11). The colours of these types of natural brown diamonds resulting from treatment (Figure 11) show some variability between yellowish green, greenish yellow, a more or less intense yellow, orange and greenish orange.^{15,16,17,18,25} The different colours (Figures 12, 13 and 14) are a function of the different ratios of N3 and N2 centres versus H4, H3 and H2 centres present in the treated samples. The intensity of the yellow component is related to the relative concentration of N3, N2, H3 and H4 centres and the intensity of the greenish yellow to green component is related to the concentration of H2 centres. Many HPHT-treated brown nitrogen-bearing natural diamonds also exhibit green H3 luminescence which increases the amount of green perceived.

The complex reaction mechanism is summarized as follows: brown colour centres are removed or modified, a process which is associated with the mobilization of vacancies. The vacancies are trapped at various nitrogen defects

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present, e.g. at A and B centres forming N-V-N (H3) and other colour centres. The H4 centres formed in this process may become partly unstable and dissociate into H3 centres. The concentration of N3 centres may also be changed within these complex processes, especially when the samples are treated in a sequence of several steps at various temperatures.

Formation of intense pink to red diamonds by a three-step treatment process

The process discussed in this section is applied to natural type Ia colourless to brown diamonds.²⁴ HPHT treatment is performed for dissociation of A centres into N atoms that are isolated in the diamond structure (C centres). Subsequent electron irradiation forms a high concentration of vacancies, which combine with the isolated nitrogen atoms in a subsequent annealing step and form the desired N-V colour centres, which are responsible for the intense pink to red coloration of the diamonds (Figure 15). Due to the formation of other nitrogen-vacancy defects, the colour of a diamond after this three-step treatment process can vary between violet, purple red, red, orange red and orange (for a gemmological description and spectroscopic characterization of such kinds of stones see Wang *et al.*, 2005). A similar process but in four steps is applied to synthetic type Ib diamonds:⁷

1. irradiation,
2. HPHT treatment,
3. second irradiation, and
4. annealing.

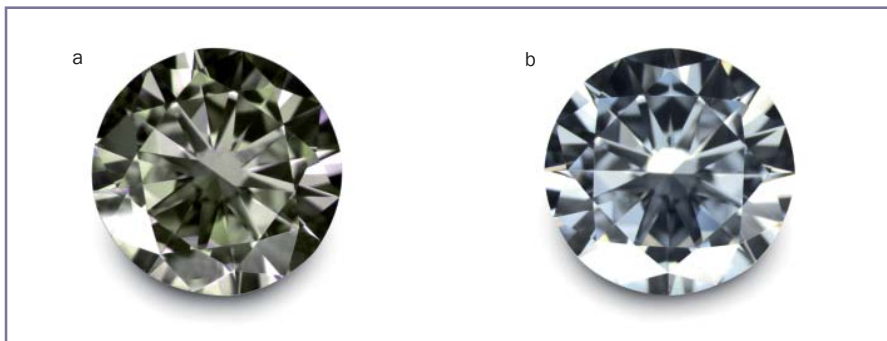


Figure 10 a,b: This type IIa diamond of 0.50ct (a) was originally olive green and treated in a HPHT process and became pale blue (b). Photograph by courtesy of T. Hainschwang, Gemlab, Gemmological Laboratory, Balzers, Liechtenstein.



Figure 11: Suite of originally brown to yellowish brown diamonds before (above) and after HPHT treatment; weights range from 0.75 to 0.95 ct. Photograph by courtesy of J.-P. Chalain, SSEF Swiss Gemmological Institute, Basel, Switzerland.

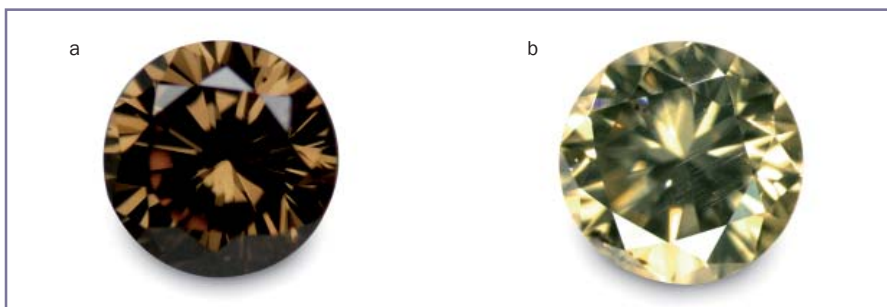


Figure 12 a,b: This originally brown type Ib diamond of 0.13 ct (a) was treated in a HPHT process and became pale yellow (b). Photograph by courtesy of T. Hainschwang, Gemlab, Gemmological Laboratory, Balzers, Liechtenstein.



Figure 13: This type Ia diamond of 1.30 ct was originally brown and treated in a HPHT process. Photograph by courtesy of E. Erel, Carat Gem Lab, Gemmological Laboratory, Montigny-les-Metz, France.



Figure 14 a,b: This type Ia diamond of 2.10 ct (a) was originally brown and treated in a HPHT process and became yellowish green (b). Photograph by courtesy of T. Hainschwang, Gemlab, Gemmological Laboratory, Balzers, Liechtenstein.

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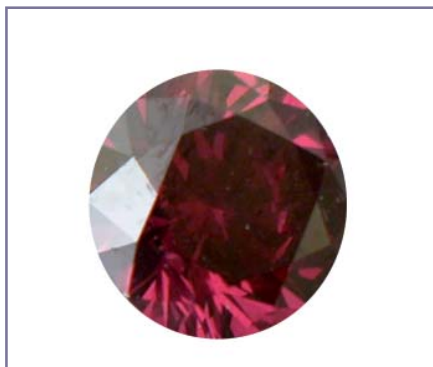


Figure 15: This type Ia diamond of 1.25 ct was originally brown and treated in a three-step process by a) HPHT, b) electron irradiation and c) annealing. Photograph by courtesy of V. Vins, Institute of Single Crystals, Novosibirsk, Russia.

In steps 1 and 2, some of the isolated nitrogen atoms (C centres) are transformed into aggregated nitrogen (A centres). In step 3, vacancies are formed which combine with C and A centres in step 4 to form N-V and H3 centres. Although the patent application primarily describes the production of synthetic diamond for laser applications, it is obvious that with the actual parameters within this four-step process, e.g. nitrogen contents of the sample and variable treatment conditions (irradiation doses, annealing temperatures) a great variety of colours may be produced.

Colour improvement and alteration of yellow to brown synthetic diamond grown by CVD

The progress in crystal growth within the last decade in application of the CVD

technique leads to synthetic diamonds grown on diamond seeds or other diamond layers with sufficient thickness and quality to be cut as gems. The as-grown material may be brown, orange brown, pinkish brown or yellow. HPHT treatment is applied to remove defects in CVD-grown synthetic diamonds, which — at least partly — are different from the major defects found in natural and synthetic HPHT-grown diamonds. The resulting colour of the samples is closely related to the treatment temperature and the concentration of different defects in the as-grown diamond crystals or diamond layers.^{29,30,31} It is reported that the resulting coloration after HPHT treatment is colourless or near colourless (Figure 16), but pale brown, green or pinkish brown colours may also result.

Conclusion

HPHT treatment of natural brown diamonds has become an important technical process of colour alteration in order to transform such diamonds into marketable qualities. With the progress of diamond synthesis by CVD, the importance of treatment of yellow to brown jewellery-quality CVD-grown synthetic diamonds is also increasing. The application of HPHT treatment in combination with electron irradiation is performed to acquire some specific rare colours, e.g. to transform the colour of natural diamonds into red or pink or to alter the colour of yellow synthetic diamonds to green or other colours.

Acknowledgements

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Figure 16: This pale brown CVD-grown synthetic diamond of about 0.25 ct (left) was treated in a HPHT process and became almost colourless (right). Photograph by courtesy of J.-P. Chalain, SSEF Swiss Gemmological Institute, Basel, Switzerland.

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More bibliographic data on patent documents cited in this review are given in Appendix C in the expanded version of the paper at www.gem-a.com/publications/journal-of-gemmology/the-journal-online.aspx.

The Author

Dr Karl Schmetzer
D-85238 Petershausen, Germany
email: SchmetzerKarl@hotmail.com

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Appendix A. Patents and patent documents

Patents are granted for new products, methods or processes. Patent documents disclose the invention for which protection is sought (in the case of a patent application) or the claimed invention, setting forth its scope of protection (in the case of an issued patent). The benefits of patents are:

- Protection of the claimed invention and its exclusive use during the patent term;
- Provision of new knowledge and information to the public;
- Definition of the extent of the protection conferred by the patent on the inventor;
- Information about the ability to make, use or sell the invention after expiration of the patent term.

Patent documents are published by national patent offices in many countries, regional patent offices (such as the European Patent Office in Munich, Germany), and the World Intellectual Property Organization (WIPO) in Geneva, Switzerland. Two main types of patent documents are published worldwide by these offices: patent application publications (patent applications) and patent specifications (issued patents, granted patents). The former consists of a description, technical drawings and claims which were submitted originally by the applicant to the patent office, and therefore, patent application publications are unexamined patents. The latter consist of a description, technical drawings and claims setting forth the scope of protection of the granted patent after examination by the patent office.

Eighteen months after filing, unexamined patent applications are published. These documents are identified by a publication number. The date of publication of an issued patent (granted patent) depends on the length of patent prosecution; patent specifications are identified by a patent number. Occasionally, a patent application is not published if the patent prosecution results in the issue of a patent prior to the end of the 18-month period. In this case,

Table A1: Examples of publication numbers and patent numbers of patent documents*

Country or publishing organization	Publication numbers of unexamined patent application publications	Year of issue	Patent numbers of examined patent specifications (issued patents, granted patents)	Year of issue
European Patent Office	EP 0 014 528 A1 ^a EP 1 120 164 A2 ^b EP 1 120 164 A3 ^c	1980 2001 2002	EP 0 014 528 B1 EP 1 120 164 B1	1983 2007
France	FR 2 275 405 A1	1976	FR 2 275 405 B1	1979
Germany	DE 25 19 116 A1 DE 10 2004 039 763 A1	1975 2006	DE 25 19 116 C2 DE 103 25 110 B3 DE 10 2004 039 763 B4 DE 600 27 441 T2 ^d	1984 2005 2007 2006
Great Britain	GB 2 378 945 A	2003	GB 2 378 945 B	2004
Japan	JP 55-126 521 A JP 01-183 409 A JP 2007-015 918 A	1980 1989 2007	JP 62-043 960 B JP 2 571 808 B2	1987 1997
Russia	RU 2002 129 106 A	2004	RU 2 293 602 C2 RU 2 237 113 C1	2007 2004
World Intellectual Property Organization	WO 01/14050 A1 ^a WO 02/13958 A2 ^b WO 02/13958 A3 ^c WO 2004/113597 A1 ^a	2001 2002 2002 2004		
USA	US 2004/0 175 499 A1	2004	US 4,181,505 US 6,294,684 B1 US 7,172,655 B2	1980 2001 2007

* corresponding documents of the same invention (patent applications and patent specifications) are placed in the same line

^a published with search report

^b published without search report

^c search report

^d translation of a granted European patent specification

the granted patent is the first national publication and no patent application is published. If a patent is not granted, only a document representing the unexamined application is published. Prior to 2001, the United States patent office published only granted patents, but since then this office has also published both types of document — patent application publications and issued patents (patent specifications, granted patents). The WIPO publishes patent applications only.

Publication numbers and patent numbers consist of a two-letter country code followed by a document identification number and a status code

(see *Table A1*). In some countries but not all, the document ID number contains the publication year. Again, in some but not all countries, the document ID numbers of the patent application publication and the related granted patent are identical. The different levels of publication are distinguished by the status code which, in general, contains an 'A' for patent application publications, and a 'B' or 'C' for issued patents (patent specifications, granted patents). The status code can also indicate if the document is published with or without a search report. The search report contains a listing of documents found by the patent examiner to be

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relevant as ‘prior art’ and will identify the claims in the application to which they are pertinent (see below). A ‘T’ in the status code indicates a translation of a patent document (e.g. the translation of a European-granted patent into a national language). Frequently, the document ID numbers and especially the status codes used in different patent offices have changed several times within the last decades (examples of some publication numbers and patent numbers are given in *Table A1*).

In the course of a patent examination process, the examiner conducts a search to find the ‘prior art’ most pertinent to the claimed invention, i.e. in other patent documents or scientific references published before the patent application date (priority date) of the application. The closest ‘prior art’ is published in various ways: as international search report in WO A1 and A3 documents, as European search report in EP A1 and A3 documents, in unexamined patent application publications of different countries (e.g., France, Germany, Great Britain) or in issued patents (e.g., United States of America). The WIPO publishes only patent application publications and/or search reports, it neither carries out complete examinations nor grants patents. An ‘International Worldwide Patent’ which one may have seen referred to in an advertisement, does not exist.

When, upon examination, no ‘prior art’ pertinent to the claimed invention in the application which would be sufficient to reject the application has been found, a patent is granted. Otherwise, the examiner rejects the application if it has not already been abandoned by the applicant. The scope of protection of the patent is set forth in the phrasing of the main claim and further independent claims (if present). Independent claims frequently belong to different patent categories, for example a product such as a diamond with specific properties or a piece of equipment such as a facility to perform the HPHT process, or secondly a process such as a particular kind HPHT treatment of diamond.

The decision about whether or not to grant a patent may differ from country

to country because of different national patent laws, but most criteria are based on novelty and non-obviousness. As an example, non-obviousness may be denied (i.e. obviousness may be assumed) if the properties of an apparatus according to an independent claim are known from two published documents (patent documents or scientific references) within the same technical field (e.g. a facility for HPHT treatment of diamond with properties known from two published documents about the HPHT treatment or synthesis of diamonds).

Most commonly, a patent application is filed at a national patent office first. The date of this first submission becomes the application date, and this can be used as the priority date for further international applications. After an application is filed, it is possible for the applicant to publish the contents of the application, to sell a product or an apparatus described in the patent application, or to use a process according to the application without loss of rights. Within 12 months of filing an application at a national patent office, the same application can be filed at another patent office and the priority of the filing date of the first application can be claimed. The second or subsequent patent office can be WIPO, a regional patent office (e.g. the European Patent Office), or another national patent office.

An applicant can also file a first application at the WIPO or at the European Patent Office. Eighteen months after the priority date, a patent application is published by all patent offices at which an application was filed.

To give an example: the first application for a patent was filed in Great Britain and submitted within the priority year to the European Patent Office, to the Japanese Patent Office and to the patent office of the United States. After the period of 18 months from the priority date, the patent application was published by all offices concerned with the filing, i.e. in this case, in Great Britain, Japan and the USA as well as the European Patent Office (here, together with a European search report). After the application has been examined according to national or

European law, patents may be granted by the different organizations involved.

In another example: the first application for a patent was filed in Russia and submitted within the priority year to the WIPO. Eighteen months after the first filing, the patent application was published by the Russian patent office and by the WIPO together with an international search report (in Russian). Subsequent to this publication, the applicant may designate countries within a period of 30 months from the priority date for the application to enter the national phase for patent prosecution. In our example, the applicant might decide that the application should be submitted to the European Patent Office and to the patent office of the United States for further examination. Consequently, the application will be published again by the European Patent Office (in French, German, or English) and by the United States Patent Office (in English). The subsequent examination for granting a patent in these offices would follow European or US law respectively.

According to different statutes and rules in national patent laws, an application may be divided into different parts which are examined independently. Different parts of an application may lead to separate publications of patent applications and issued patents in different countries. All patent documents derived from a first national, regional or international priority application belong to a patent family. Patent families may contain numerous members, frequently exceeding 20 in a range of languages.

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Appendix B. Information concerning HPHT equipment and procedures from patent sources

A series of extracts from patent documents (indicated by superscript numbers relating to numbers in *Table I* and Appendix C) are given below which summarize the most important stages in development of modern techniques. The passages in quotation marks are extracts from the original wording in the patents except for the occasional typographical error. The figure numbers in square brackets indicate changes from the original figure numbers in the patents to clarify understanding in this paper.

A brief summary of the HPHT processes for diamond treatments is given in WO 01/72404 A1 by Burns, Fisher and Spits, De Beers Industrial Diamonds Limited (2001):¹⁹

“Conventional high temperature/high pressure apparatus may be used. Various reaction vessel configurations which provide for indirect or direct heating of the reaction mass are disclosed in the patent literature and are useful in carrying out the HPHT annealing process. These reaction vessels usually consist of a plurality of interfitting cylindrical members and end plugs or discs for containing the reaction mass in the centremost cylinder. In the indirectly heated type of reaction vessel one of the cylindrical members is made of graphite which is heated by the passage of electric current there through and which thereby heats the reaction mass. In the directly heated type of reaction vessel, the reaction mass is electrically conductive, thereby eliminating the need for an electrically conductive graphite cylinder, and electric current is passed directly through the reaction mass to heat it.

“The method may be used to treat a single diamond or a plurality of discrete diamonds. If a plurality of discrete diamonds is treated simultaneously, each diamond should be separated from its neighbours by the pressure transmitting medium. The

maximum volume of diamond which may be treated is limited only by the capacity of the high pressure/high temperature apparatus used.

“In the method, a reaction mass is created by providing diamond in a pressure transmitting medium which completely encloses a diamond.

The pressure transmitting medium is preferably a homogeneous pressure transmitting medium which evenly spreads the pressure which is applied over the entire surface of the diamond which is being treated. Examples of suitable mediums are those which have a low shear strength such as

Belt-type HPHT apparatus

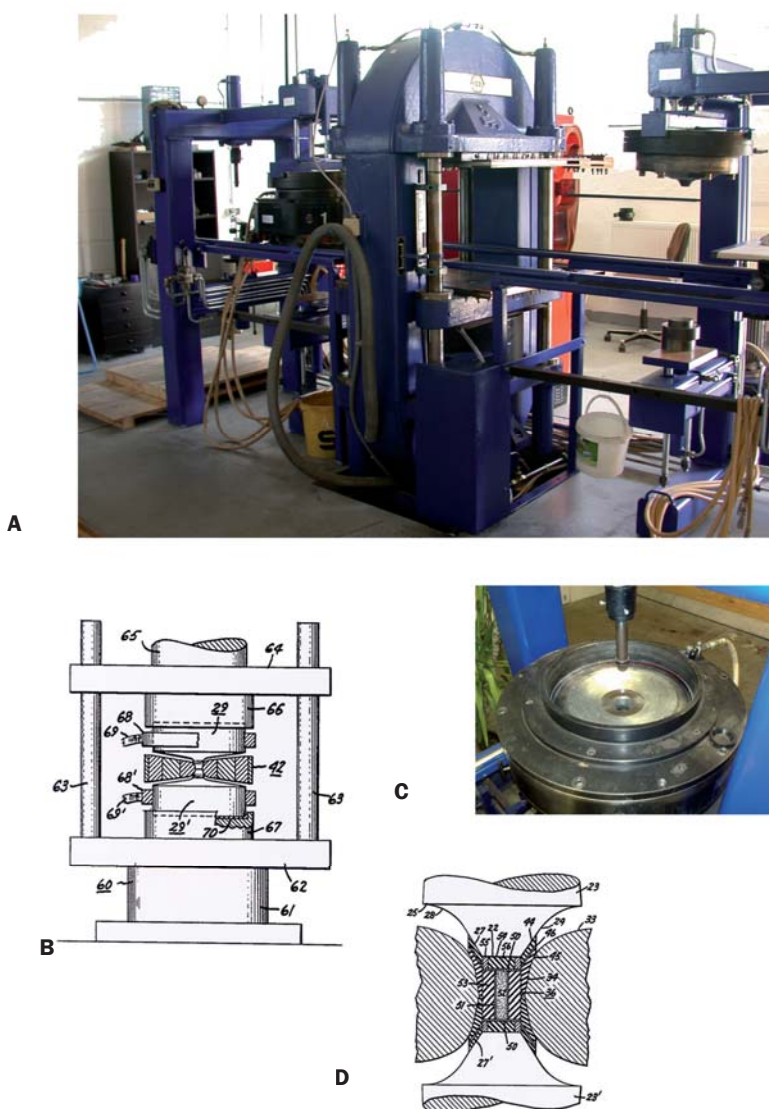


Figure B1: Belt-type HPHT apparatus for diamond synthesis and diamond treatment; A) the belt apparatus is located on a hydraulic press, the lower part of the apparatus is seen to the left, the upper part of the apparatus is raised and seen to the right; B) schematic drawing of a belt apparatus on a hydraulic press between the two anvils; C) lower half of an opened belt apparatus; D) schematic drawing of a HPHT sample cell between the two anvils of the belt apparatus. A and C, photographs by courtesy of H. Vollstädt, Sedkristall, Seddiner See, Germany; B and D from US Patent 2,941,248,39 inventor: H.T. Hall, applicant: General Electric.

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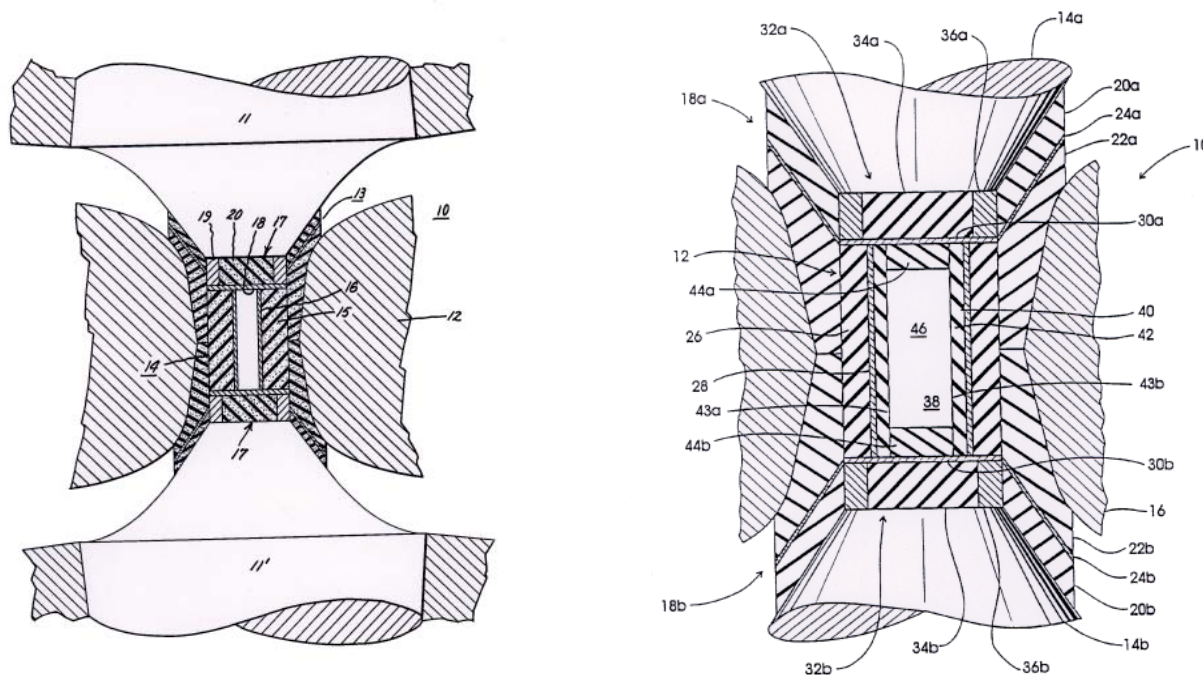


Figure B2 (left): HPHT cell for diamond diffusion treatment between the two anvils of the belt apparatus; for details see text. From US Patent 3,141,855,1 inventor: R.H. Wentorf Jr., applicant: General Electric.

Figure B3 (right): HPHT cell for diamond treatment between the two anvils of the belt apparatus; for details see text. From International Patent Application Publication WO 01/14050 A1,15 inventors: T.R. Anthony and S.S. Vagarali, applicant: General Electric.

metal halide salts. Examples of suitable metal halide salts are potassium bromide, sodium chloride, potassium chloride, caesium chloride, caesium bromide, copper chloride and copper bromide. Such mediums have been found to provide the desirable even spread of pressure which ensures that any graphitisation which may occur on the diamond surface is kept to a minimum. A particular advantage of using a metal halide salt as the pressure transmitting medium is that the diamonds can be easily recovered after treatment by dissolving the medium in hot water.”

Comparing the reaction vessels described over five decades for diamond treatment in a conventional belt type apparatus [Figure B1], we realize that the principal design of the cell has not changed.

For example, in the patent US 3,141,855 by Wentorf, General Electric Company (1964), for diffusion treatment of diamond¹, the cell is described as follows:

“Referring now to the drawing [Figure B2], there is illustrated one preferred embodiment of a high pressure high temperature apparatus 10. Apparatus 10 includes, generally, a pair of punch assemblies 11 and 11’ which together with a belt member 12 define a reaction zone. Suitable stone gasketing 13 is positioned between the punches 11 and 11’ and belt 12’ to seal the reaction zone and to undergo compression to permit punches 11 and 11’ to move towards each other to compress a reaction vessel 14. Reaction vessel 14 comprises a hollow electrically nonconducting cylinder 15 adapted to contain an electrically conducting tube 16 which is the sample material depository. On each end of cylinder 15 there is an end cap assembly 17 which includes an electrically conductive disc member 18 and an electrically conductive ring 19 encircling a plug of electrically insulating material 20. By connecting the punches to a suitable source of electrical power, current is caused

to flow through one of the punch assemblies, for example 11, through ring 19, disc 18, tube 16 and/or through the material itself to provide electrical resistance heating of the sample material, and in reverse order to punch 11’.”

This cell is almost identical with a cell described in WO 01/14050 A1 by Anthony and Vagarali, General Electric Company (2001), for colour improvement of diamond:¹⁵

“Looking to Figure B3, an illustrative HP/HT apparatus useful in the practice is shown generally at 10 to comprise a generally cylindrical reaction cell assembly 12 interposed between a pair of punches, 14a and 14b, and surrounded by a generally annular belt or die member 16. Preferably, both punches 14 and belt member 16 are formed of a relatively hard material, such as cemented tungsten carbide. Between punches 14 and belt member 16 are a pair of insulating assemblies, 18a and 18b, each of which is formed of a pair of thermally- and electrically-

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Modified Bridgman-type HPHT apparatus



Figure B4: Modified Bridgman-type HPHT apparatus for diamond synthesis and diamond treatment; left) the lower half of the apparatus is placed on a hydraulic press, the open space in the centre receives the reaction container with gasket; right) the upper half of the apparatus is raised, the two tubes are for water cooling. Photographs by courtesy of H. Vollstädt, Sedkristall, Seddiner See, Germany.

insulating members, 20a-b and 22a-b, each preferably formed of pyrophyllite or the like, and having an intermediate metallic gasket, 24a and 24b, disposed there between.

“As shown, reaction cell assembly 12 includes a hollow cylinder 26, which may be formed of a material, such as salt or the like, which is converted during HP/HT by phase transformation or compaction to a stronger, stiffer state or, alternatively, of a talc material or the like which is not so converted. In either case, the material of cylinder 12 is selected as being substantially free of volume discontinuities or the like, under HP/HT as may occur, for example, with pyrophyllite or alumina materials.

“Positioned concentrically within salt cylinder 26 is an adjacent cylinder 28, which is provided as a graphite electrical resistance heater tube. Electrical connection with heater tube 28 is achieved via an adjacent pair of conductive-metal end discs, 30a and 30b, which are axially-disposed with respect to heater tube 28. Adjacent each disc 30 is provided an end cap assembly, shown generally at 32a and 32b, each of which

comprises an insulating plug, 34a and 34b, surrounded by an electrically conductive ring, 36a and 36b.

“It will be appreciated that the interior of heater 28, along with end discs 30, salt cylinder 26, and end cap assemblies 32, defines a generally-cylindrical inner chamber, shown at 38, having defined axial and radial extents and containing a pressure transmitting medium 40. Pressure transmitting medium 40 is selected as having a relatively low coefficient of internal friction to make it semi-fluid at HP/HT conditions, and may be provided as a cylindrical salt liner 42, which defines radial pressure transmitting medium layers 43a and 43b, and is fitted with an axial pair of salt plugs, 44a and 44b, each of which defines an axial pressure transmitting medium layer. Preferably, salt liner 42 and plugs 44 are formed of a graphite material or of sodium chloride, but also may be formed of any chloride, iodide, or bromide of sodium, potassium, or calcium or a mixture thereof. Alternatively, pressure transmitting medium 40 may be provided in powdered or particulate form. In either case, medium 40

defines a cavity space, as is shown at 46, which is configured to receive the discoloured diamond to be annealed. Such is the configuration of a representative HP/HT apparatus for practicing the method.”

A typical HPHT cell used together with a belt-type press measures 40 mm in diameter and is 40 mm high. The internal space for the sample and the pressure transmitting medium measures about 20 mm in diameter and 20 mm in height. For a typical run at pressures in the range of 60–65 kbar and temperatures up to 2200°C, the samples cell is loaded with about 10 ct of diamond, the run takes between two and three hours (H. Vollstädt, pers. com. 2010). There are, however, also larger cells up to 100 mm in diameter and 130 mm in height used for larger belt-type apparatus, especially for the production of synthetic diamond powder.

HPHT treatment of diamonds is not restricted to the so-called belt press and the cell related to this design (see above). In principle, all different types of presses and cells which were developed for diamond synthesis can be applied. Compared to the belt apparatus, a somewhat simpler design of the HPHT apparatus is based on a reaction cell (container) of, e.g., limestone, pyrophyllite or talc, which is subjected to the desired high pressure between two profiled dies [Figure B4]. Different variants of this HPHT facility were developed, e.g. in Russia (see, e.g., Katrusha *et al.*, 2003). These types of apparatus can be described as modifications and improvements of the basic design of Bridgman in the first half of the twentieth century. In all these variants, the pressure is applied between the surfaces of two dies. The main improvements are related to the form of the profiled sample cell and especially to the gasket of the sample cell. Three examples are given below [Figure B5].

The first example is based on US 3,746,484 by Vereschagin *et al.* (1973):⁴⁰ “The apparatus for developing high pressures and temperatures includes a pair of substantially identical cooperating dies 1 [Figure B5 A],

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each die 1 having a central cavity in an end face thereof, the cavity being shaped similar to a segment of a sphere, each die including a tapering peripheral surface surrounding the cavity. Each die 1 is firmly embraced by a ring 2 made of high-strength steel, the ring 2 engaging the side wall of the respective die 1. Disposed between the end faces of the two dies 1 is a container 3 made either from lithographic stone, or from talc, or else from pyrophyllite.

“Shown in the *Figure B5 B* is an enlarged part view of the high-pressure chamber defined by the cavities of the two cooperating dies 1, and the gap 5 formed between the respective tapering surfaces of the face ends of the dies 1, when the two dies are forcibly brought together. The numeral 4 in Figs. B5 A,B indicates a sample subjected to the high pressure developed by the dies, the sample being assembled with a heater element, e.g. graphite heater, of any commonly known type.

“Development of extremely high pressures, in excess of 40 kilobars, in the herein disclosed apparatus is possible. When a pressure as high as 50 to 90 kilobars is to be developed with the dies made of tungsten-cobalt hard alloy, known under the trade name of ‘carballoy’.

“The herein disclosed apparatus operates, as follows. The reaction composition together with the electrical heater, indicated in the appended drawings as the sample 4, is positioned in the container 3. The container 3 in this assembled state is placed in the high pressure chamber formed between the opposing end faces of the spaced dies 1. Then the two dies 1 are driven toward each other under the action of an associated press, whereby the peripheral area of the container 3 becomes gradually deformed and fills the gap 5. The plastic flow of the material of the container 3 being limited when, the compression stroke of the associated press progresses the desired pressure

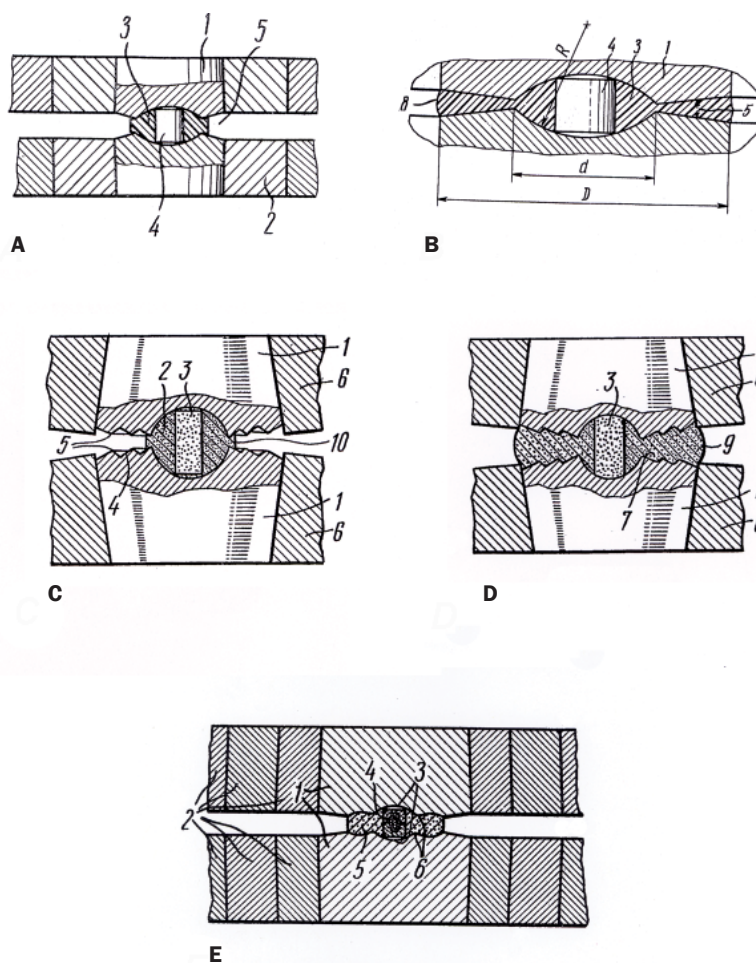


Figure B5: Three examples of sample cells placed between two profiled anvils representing a modified Bridgman-type HPHT apparatus for diamond synthesis and diamond treatment; for details see text. A and B) from US Patent 3,746,484,40 inventors and applicants: L.F. Vereschagin et al.; C and D) from US Patent 3,790,322,41 inventors and applicants: N.N. Sirota et al.; E) from US Patent 4,196,181,42 inventors and applicants: L.F. Vereschagin et al.

is developed within the high pressure chamber.

“Electric power, i.e., voltage for heating the sample 4 can be supplied to the heater of the sample through the dies 1, in which case at least one of the two dies should be electrically insulated from the rest of the press structure.”

Another example was described in US 3,790,322 by Sirota *et al.* (1974):⁴¹

“The device comprises two identically shaped and dimensioned dies 1 [Figure B5 C] with centre recesses forming together a chamber and a container 2 made of a thermal and electric insulating material, such as lithographic stone, ductile under omnidirectional compression and

filled with reactive compound 3.

The reactive compound can be also enclosed in a tubular graphite-made heater of a conventional type. The oppositely adjacent faces of the dies carry ridges 4 which impart to said surfaces a serrated profile in the diametrical cross section. Apexes 5 of the ridges 4 are disposed on a common tapered surface with the apex of the latter surface lying on a line through the centers of curvature of the recesses in the dies 1. The dies 1 are fitted with fixing rings 6.

“When the dies 1 [Figure B5 D] are drawn together, concentric circular compartments 7, 8 and 9 are formed between the faces of dies. The compartments are filled with the

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material of a container 2 in the course of the dies being drawn together. The container 2 [Figure B5 C] is provided with a fan-shaped shoulder 10 which in the initial position (prior to compression) fills, partially or fully, the space of a compartment 7 being the closest to the recesses.

“The device functions as follows. When the dies 1 under the action of a press are drawn together, compression of the container is initiated and the pressure inside the chamber is increased. The material of the container 2, as the process goes on, is partially displaced from the chamber and fills at first the innermost concentric circular compartment 7. As the dies 1 continue being drawn closer together and simultaneously with compressing lithographic stone in the chamber and in the first inner compartment, filling is initiated in an adjacent compartment 8 with the further displaced material of the container and so on until all the compartments are fully filled.

“In the device constructed according to the present invention a pressure is reached of at least 70-80 kilobars. Electric power for heating the reactive compound or a tubular heater is supplied through the dies and at least one of them should be electrically insulated from a press.”

This type of container was further improved by Vereschagin *et al.* (1980) as described in US 4,196,181:⁴²

“The chamber illustrated in Figure B5 E consists of two halves and is formed by two centrally-mounted punches 1 opposing each other, pressed into a structure of concentric binding rings 2 ensuring a sufficient axial support for the punches 1. The best material for the punches 1 was found to be a hard alloy based on tungsten carbide (94% WC, 6% Co). An alloy of steel has proven to be a satisfactory material for the binding rings which support the punches 1.

“The high pressure chamber shown in Figure B5 E is sealed with dense limestone referred to as a lithographic

stone which is simultaneously used as the medium for conveying the pressure to a reaction cell 4. The lithographic stone is used for making a pellet 5 whose face surfaces repeat the configuration of the mould made from the surface of the hollows 3 of the punches 1. A channel located in the centre of the pellet 5, and perpendicular to its surface, accommodates the reaction cell 4. The height of the pellet 5 has been selected experimentally. When the punches 1 are brought together and compressed, the material of the pellet 5 forms a shaped seal between them which makes it possible to reliably lock the high pressure chamber Figure B5 E at all changes in the pressure and temperature and, in particular, during the pulse heating of the precompressed reaction cell 4. “The reaction cell 4 is placed into the pellet 5 between the faces of the punches 1. In the capacity of the compressible element the reaction cell 4 comprises a heater. The heater consists of two parts which, taken together, form a round hollow cylinder closed at the ends, the height of which is equal to, or larger than, the height of the pellet 5 while its diameter ensures tight fitting of the heater into the pellet 5.

“The chamber ensures the building-up of the pressure required for transforming the non-diamond carbon-bearing material into a microcrystalline monolithic material of carbon with a diamond structure. The chamber is placed between the anvil plates of a suitable press (not shown in the drawing) then the halves of the chamber are brought together in the direction perpendicular to the chamber plane and, as a result, the pellet 5 and the reaction cell 4 are compressed to a point in which a high pressure is reached inside the reaction cell. The rise of the temperature in the high pressure chamber inside the reaction cell 4 is achieved by passing an electric current through the conducting section of the reaction cell 4.”

The space for the sample and the pressure transmitting medium typically measures 15 mm in diameter with a height of about 10 mm. This indicates that typically 5-6 ct of diamond can be treated in one single run (H. Vollstädt, pers. com., 2010).

Numerous designs exist and were developed for HPHT apparatus which contain more than two punches or dies, also called multianvil presses - tetrahedral with 4 anvils, cubic with 6 anvils, octahedral with 8 anvils or prismatic with (3 + 2) or (5 + 2) or (6 + 2) anvils [Figure B6].⁴³⁻⁴⁹ The cubic design particularly is widely used for diamond synthesis and treatment [Figure B7]; see also Barnard, 2000; Sundance Diamonds, 2006).

A further development of a multianvil press works with several groups of anvil polyhedra and is known as the BARS type of apparatus. Many Russian research institutes and commercial companies work with this type of press for HPHT crystal growth and treatment. The apparatus

Figure B6: In the late 1950s to early 1960s, numerous designs for multianvil presses were developed. The so-called prismatic presses (A and B) consist of several prismatic anvils plus a pair of upper and lower anvils. In the schematic drawing (A), examples of 3+2, 5+2 and 6+2 anvils are shown, a more detailed construction of an example with 3+2 anvils is shown in (B). Tetrahedral presses (C and D) consist of four anvils which are oriented towards the centre of a regular tetrahedron; the four hydraulic rams are interconnected by bolts parallel to the edges of the tetrahedron and support the stability of the construction. In drawing (C) three anvils can be seen in a perspective view and the fourth is behind the vertical anvil; drawing (D) shows a view to the centre of the high pressure cell with three anvils only (the fourth anvil is pointing towards the observer). Cubic high pressure machines E and F consist of six anvils pointing towards the faces of a regular cube; different constructions for guiding the anvils and pressure generating units are shown. A and B) from US Patent 3,159,876,43 inventor: H.T. Hall, applicant: Research Corporation; C) from US Patent 2,918,699,44 inventor H.T. Hall, applicant: Research Corporation; D) from US Patent 3,182,353,45 inventor H.T. Hall, applicant: Research Corporation; E) from US Patent 3,440,687,46 inventor and applicant: H.T. Hall; F) from US Patent 6,336,802B1,47 inventor and applicant: D.R. Hall. →

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Modified Bridgman-type HPHT apparatus

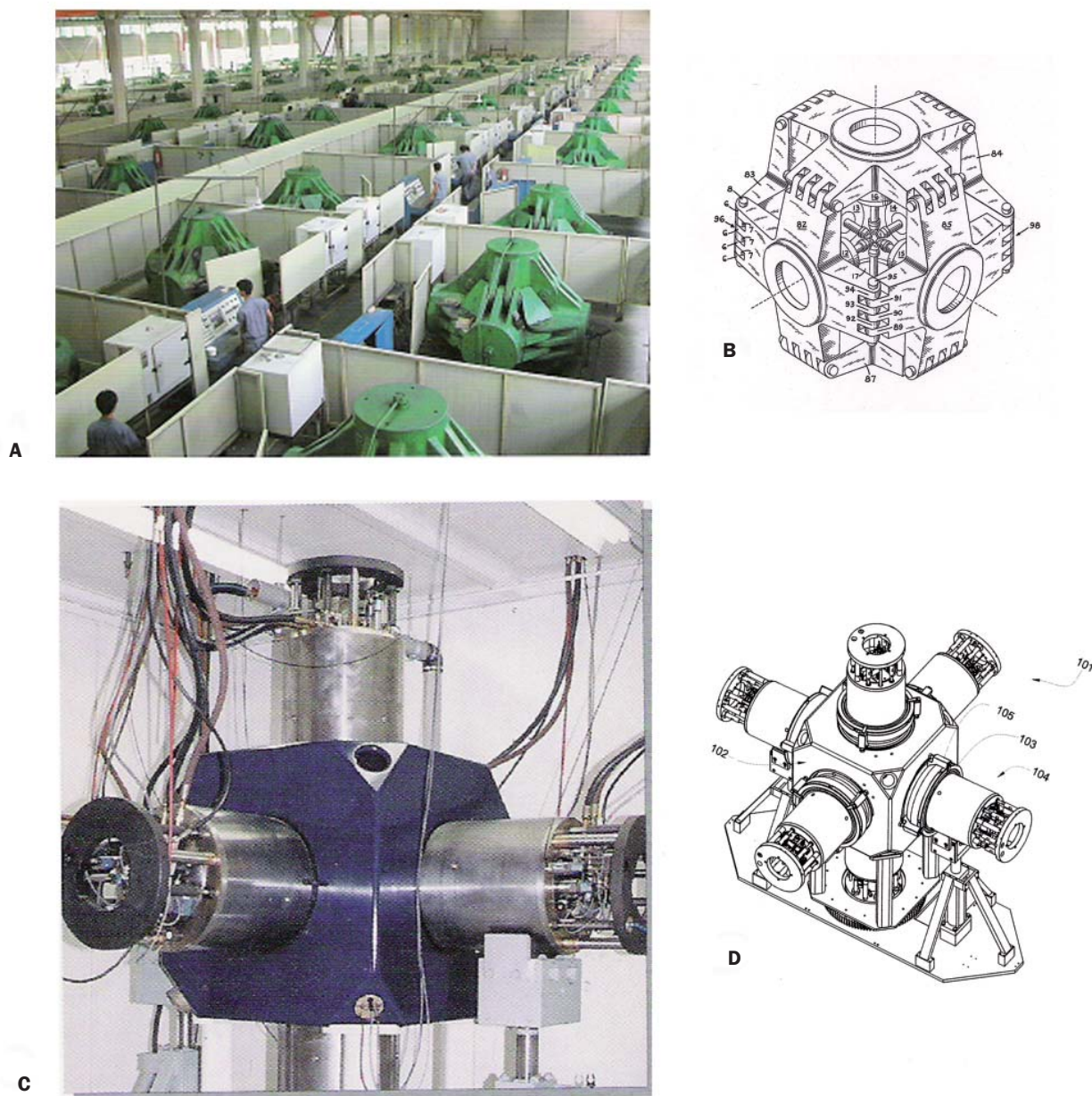


Figure B7: Cubic presses for synthesis or treatment of diamond. A) view into the production hall of Henan Huanghe Whirlwind Company, Zhengzhou, Henan, China; a schematic drawing of these cubic presses with six hydraulic pressure generating units for the six anvils pointing towards the faces of a cube is shown in B); a specially designed frame supports the stability of the unit. C) Cubic press applied at Novatek Company, Provo, Utah, USA; a schematic drawing of this cubic press with six hydraulic pressure generating units is shown in D. A and C photographs by courtesy of H. Vollstädt, Sedkristall, Seddiner See, Germany; B from US Patent 2,968,837,48 inventors: A. Zeitlin, H. Herman, J. Brayman, applicant: Engineering Superdivision Company; and D from US Patent 7,467,937 B1,49 inventors and applicants: D.R. Hall et al.

was developed by Malinovski and Ran in the 1970s at the Institute of Geology and Geophysics of the Siberian Branch of the USSR Academy of Sciences, Novosibirsk. Two or three outer and inner anvil groups form a sphere, ellipsoid or cylinder which is sealed with a soft elastic shell

of compressible material such as rubber and subjected to pressure by means of a hydraulic liquid which acts on the outer surface of the anvil assembly.

According to the multistage combination of regular polyhedral anvil groups, the inner anvil is compressed by

the multiaxial compressive stress caused by compression of the outer anvil group or groups and this effect is intensified at each stage. A system with three anvil groups is disclosed in US 3,517,413 by Takahashi and Asami, Mitsubishi Power Industries (1970).⁵⁰

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“Figure B8 illustrates the cross section of an apparatus of a 8-6-8 faceted polyhedron combination as each three stage of anvils form the regular polyhedron in an inner space respectively. First stage or outermost anvils 1 are composed of eight identical pieces (four pieces of the first stage anvils are shown), and form a regular octahedron in its inner space made by the cutting of a part of the anvil. The regular octahedron corresponding to the space is divided to six identical pieces 2 and form the group of second stage anvils.

“The group of second stage anvils 2, which has the outside shape of a regular octahedron, is conformed with the inner regular octahedron of the first stage anvils and form a regular hexahedron (cubic) in its inner space made by cutting an edge of the anvil. The regular hexahedron is divided into eight identical pieces 3, forming the group of third stage anvils. The group of third stage anvils 3 which has the outside shape of a regular hexahedron, are conformed with the inner regular hexahedron of second stage anvils, and form a regular octahedron 0 in its inner space made by cutting a part of an edge of the anvil.

“Plastic pressure medium 0 containing a specimen is set in the innermost regular octahedron. In this way, important characteristics of the apparatus are characterized by the complex multistage combination of a regular polyhedron such as the combination of a regular octahedron and a regular hexahedron. Figure B8 also illustrates the case of a 6-8-6 polyhedron combination. Transmission of the compressed force is performed through the close contact of each stage of the anvil assembly. The generating pressure is inversely proportionate to the ratio of inner surface area and outer surface area in principle, and reaches its maximum value at the inner surface of the last stage anvil. Quasi-hydrostatic pressure acts on the plastic pressure medium occupied by the centre core 0’.

“The pressure transmitter 4 and 4’

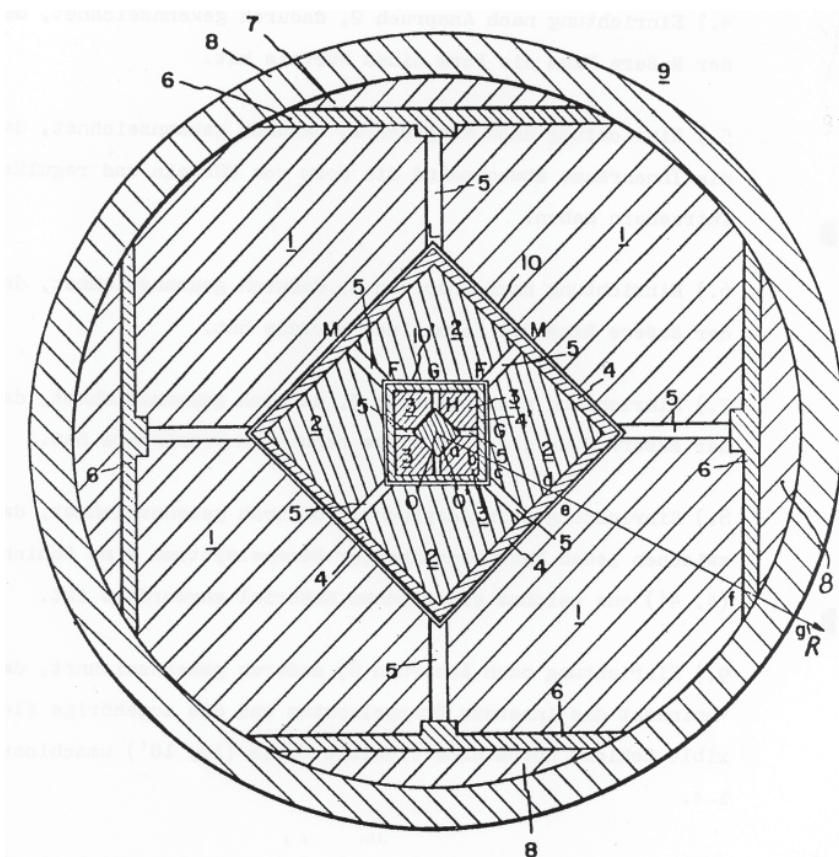


Figure B8: High pressure apparatus consisting of three groups of 8, 6 and 8 anvil polyhedra. This system is similar to the Russian BARS system, which normally uses a set of two groups of anvils; for details see text. From US Patent 3,517,413,50 inventors: S. Takahashi, N. Asami, applicant: Mitsubishi Atomic Power Industries.

organized by the inorganic plastic materials or organic plastic material is disposed between the first, second and third stage anvils to lubricate the mutual movement for compressing toward the centre, to insulate electrically each other, and to eliminate the component of shearing stresses in the anvil materials. The anvil guides 8 of the first stage anvil and the insulating plate 6 are established to avoid the pressing out of the soft elastic shell 7 into the anvil gaps, and it is useful to guide the anvils at the setting and compressing and to insulate electrically the anvils from each other.

“These above assemblies are sealed with the soft elastic shell 7, and compressed by the hydraulic liquid 9. The structure of the embodiment is enumerated from centre 0 to outside as follows: Plastic pressure medium

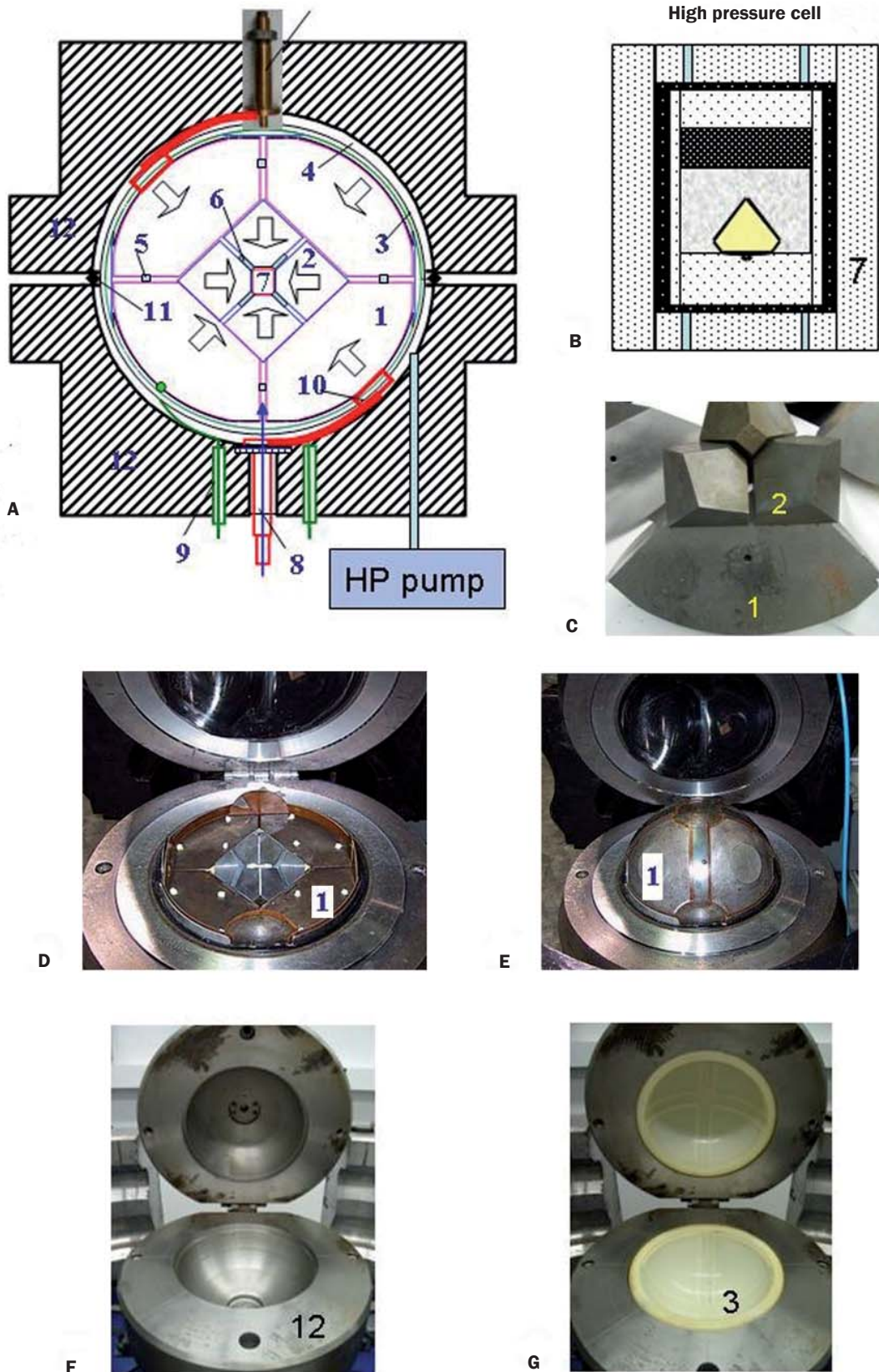
0’ containing the specimen, third stage anvils 3, pressure transmitter 4’, second stage anvils 2, pressure transmitter 4, first stage anvils,



Figure B9: View into a production hall with BARS type presses in Novosibirsk, Russia; the equipment is used for diamond synthesis and diamond treatments. Photograph by courtesy V. Vins, Institute of Single Crystals, Novosibirsk, Russia.

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Split-sphere BARS apparatus



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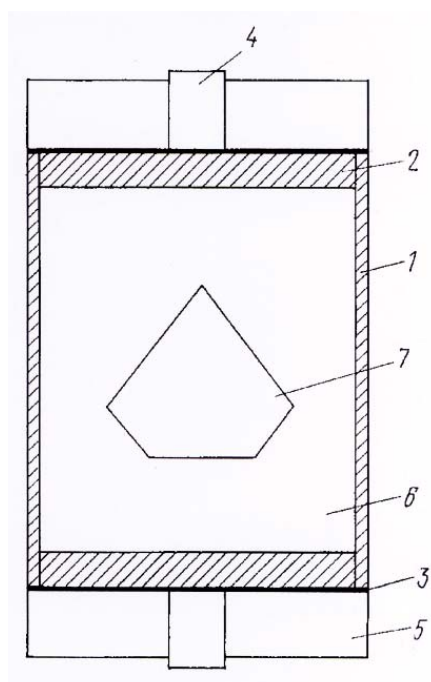


Figure B11: HPHT reaction cell used for treatments of diamonds to improve colour in the Russian split-sphere BARS apparatus; for details see text. From the Russian Patent 2201797 C1,51 inventors: A.A. Chepurov, A.V. Bulatov, applicants: M.A. Turetskij, E.N. Gajnullin.

insulating plate 6 anvil guides 8, soft elastic shell 7 and hydraulic liquid 9. This hydraulic liquid is able to an ultrahigh pressure at the centre space 0. It is possible to make the other combinations of 6-8-6, 8-6-8-6 or 6-8-6-8 or the like.”

A BARS apparatus which is commonly used in Russia for diamond synthesis and diamond treatment [Figure B9] works with two groups of anvils, an outer group consisting of 8 polyhedra, and an inner group consisting of 6 polyhedra [Figure B10]. A high pressure cell which is used in different Russian laboratories in combination with the BARS apparatus for HPHT treatment is described in RU 2 201 797 C1 by Chepurov and Bulatov (2003):⁵¹

“The method [Figure B11] includes press-fitting a diamond crystal 7 in disk-shaped backing 6 made of a composition whose proportion of ingredients is as follows, mas. %: MgO, 80-85; ZrO₂, 12-15; CsCl, 3-5; disk diameter does not exceed its height and exceeds size of press-

fitted diamond by at least two times. Backing 6 is placed in reaction cell incorporating coaxially mounted heating element 1 with current lead-in lids 2 and current lead-in rods 4, as well as closing pellets 5. After that cell is placed into multiple-punch apparatus and held therein at high pressures and temperatures for time sufficient to change colour of crystal.”

←

Figure B10: The Russian split-sphere BARS type HPHT apparatus is based on two groups of anvils which form an inner high pressure cell; the outer group of anvils form a sphere which is placed into a rubber shell. The rubber shell is surrounded by a liquid pressure medium, e.g. oil, and surrounded by two halves of a metallic sphere. The inner group of anvils form an octahedron (towards the outer group of anvils) and a regular cube (towards the inner high pressure reaction cell). A) schematic drawing, B) inner high pressure cell used for crystal growth, C) inner and outer groups of anvils, D) split sphere with some of the inner and outer anvils, E) split sphere with all the anvils; the diameter of the group of outer anvils is 300 mm, F) metallic components (12) of the split sphere apparatus, G) metal hemispheres lined with inner rubber shell (3). The sample cell for diamond synthesis or treatment measures 20 x 20 x 20 mm, the pressure and temperature limits are 70 kbars and 2300 °C, respectively.

(1) outer group of eight steel anvils, (2) inner group of six tungsten carbide alloy anvils, (3) rubber shell, (4) oil, (5) spacers, (6) gaskets, (7) inner high pressure cell, (8) current and water lead, (9) electrical feed-through for measurements; (10) copper electrode, (11) sealing ring, (12) top and bottom metallic hemispheres, (13) support clamps. Schematic drawings, photographs and information by courtesy of V. Vins, Institute of Single Crystals, Novosibirsk, Russia.

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Appendix C. Detailed reference list of patent documents

Only the basic application(s) of a patent family is (are) given in the following list; additional members of the patent families, which might contain more detailed technical information, are quoted in *Table I*. Further members of the different patent families in other languages may also exist.

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