Surface coating of gemstones, especially topaz – a review of recent patent literature

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Abstract: *Different methods of surface coating of gem materials are reviewed with respect to various patent documents published recently. In addition to the longer known techniques of simple sputtering and dye-coating, two different types of coating processes are used: first, heat treatment of a faceted gem in contact with a transition metal-bearing powder, and secondly deposition of a coating on the facets of a sample and subsequent heat treatment of the coated stone. The reaction mechanisms, nomenclature and recognition of treated stones are discussed.*

Introduction

Various types of surface-treated topaz have been seen in the gem market and described by different authors (see, for example, Millington, 2005). One major treatment process, producing pink, orange and red coloration, was characterized as a simple coating of the faceted stone with an easily removable dye layer. In contrast, a cobalt-bearing layer on another type of treated green, blue-green and blue topaz was more resistant to a simple scratching test (see, for example, Johnson and Koivula, 1998; Underwood and Hughes, 1999). Due to the lack of technical information describing the exact production processes, there was speculation about a possible 'diffusion' mechanism of this coloured layer into the surface of faceted colourless topaz samples (McClure and Smith, 2000). Schmetzer (2001) cited the first technical information from patent documents about the production process of green, blue-green, and blue surface-treated topaz as published in the international patent application WO 98/48944 A1 and in the American patent US 5,888,918, both by R. Pollak (documents 3 and 4 in *Table I*). According to these descriptions, the faceted topaz samples are heat treated within a finely divided powder of cobalt metal or cobalt oxide.

Such or similar treated stones have even found their way not only onto the markets of gem consuming but also into the trade of gem producing countries such as Nigeria (see, for example, Krzemnicki, 2002; *Figure 1*) and, in the opinion of the present author, understanding the technical procedure of treatment mechanisms is essential for correct nomenclature of treated gems. In addition, detailed knowledge of treatment processes is one of the key features for the recognition of treated samples and for their distinction from untreated gem materials. Thus, the present review briefly summarises the contents of different patents related to surface treatment of gem materials, and especially of topaz.

*Table I: Patent documents describing surface treatment of gem materials, especially topaz**

Document/patent family**	No.	Issued	Inventor/applicant	First step of treatment	Coating/diffusion material	Colours (examples)	Remarks
WO 96/06961 A1 US 6,197,428 B1	1 2	7.3.1996 6.3.2001	Rogers/Deposition Sciences, CA, USA	Chemical vapour deposition or sputtering or others	Various oxides or plastics	Golden orange in transmission and blue in reflection or green in transmission and silvery pink in reflection	Alternating layers with high and low refractive indices creating an interference filter
WO 98/48944 A1 US 5,888,918 US 6,376,031 B1 US 2002/0174682 A1 EP 1 017 504 B1 DE 698 17 380 T2	3 4 5 6 7 8	5.11.1998 30.3.1999 23.4.2002 28.11.2002 20.8.2003 24.6.2004	Pollak/Pollak, Encinitas, CA, USA	Contact heat treatment with powder	Cobalt metal or cobalt oxide, optional: additional metals or metal oxides	Blue, blue-green, green-blue, green	Additional heat treatment after coating is possible
US 5,853,826	9	26.12.1998	Starcke *et al.*/Azotic Coating Technology, Rochester, Minn., USA	Sputtering or chemical vapour deposition or physical vapour deposition or others	Thin coating of the pavilion of a stone with one or several thin layers, especially Ti, TiO_2, Zr, ZrO_2, also other metals, metal oxides, nitrides, sulfides and carbon	Green to violet (at different angles)	Various reflection and interference phenomena are observed when viewed at different angles of observation
EP 0 888 730 A1 US 5,981,003 US 6,146,723	10 11 12	7.1.1999 9.11.1999 14.11.2000	Arends/Fitness Innovations & Technologies, Chester, N.J., USA	Adhering coloured ink to the surface, drying	Transparent ink including a dye	Red, blue, green, yellow	Removable coating
BR 2000-1034 A	13	27.11.2001	Soares Sabioni *et al.*/Soares Sabioni, Ouro Preto, Minas Gerais, Brazil	Contact heat treatment with powder	Mixtures of topaz powder and metal powder or metal oxide powder or metal salt powder	Blue (cobalt)	a. Preparation of mixture of powder b. heat treatment of mixture c. diffusion by contact heat treatment with powder; repeated treatment with different metals is possible

Document/patent family**	No.	Issued	Inventor/applicant	First step of treatment	Coating/diffusion material	Colours (examples)	Remarks
BR 2000-2321 A	14	30.4.2002	Soares Sabioni and Mendonça Ferreira/Soares Sabioni, Ouro Preto, Minas Gerais, Brazil	Vacuum sputtering	Transition metal	Yellow to reddish orange (iron)	a. deposition of transition metal coating to crown or pavilion b. heat treatment of coated stone
US 2002/0128145 A1 US 6,635,309 B2	15 16	12.9.2002 21.10.2003	Pollak/Pollak, Encinitas, CA, USA	Contact heat treatment with powder	Copper metal or copper oxide, optional: additional metals or metal oxides	Yellow to red	Iron can produce similar colours; additional heat treatment after coating is possible
US 2003/0008077 A1 EP 1 394 293 A1 US 6,872,422 B2	17 18 19	9.1.2003 3.3.2004 29.3.2005	Gupta and Goyal/Gupta and Goyal, Jaipur, Rajasthan, India	Chemical vapour deposition or physical vapour deposition or others	Metals, metal oxides, metallic compounds, alloys	Blue, green (cobalt); yellow, reddish yellow, orange, pinkish yellow (iron); green (chromium); blue (cobalt and chromium); blue to green (cobalt and nickel); imperial (iron and chromium and nickel)	a. deposition of coating to the faceted stone b. heat treatment of coated stone
DE 102 15 141 A1	20	16.10.2003	Anonymous/Meelis, Idar-Oberstein, Germany	Spraying	Iron oxide	Yellow-orange	a. deposition of coating to the faceted stone b. heat treatment of coated stone
RU 2 215 454 C1	21	10.11.2003	Balitsky *et al.*/Institute of Experimental Mineralogy RAS, Chernogolovka, Moscow district, Russia	Sputtering	Iron	Yellow to yellow-orange or orange	a. deposition of coating to the faceted stone b. heat treatment of coated stone
RU 2 215 455 C1	22	10.11.2003	Balitsky and Balitskaya/Institute of Experimental Mineralogy RAS, Chernogolovka, Moscow district, Russia	Contact heat treatment with powder	Cobalt oxides and zinc oxide	Dark blue	Cobalt of various valence states
US 2004/0083759 A1	23	6.5.2004	Starcke *et al.*, Rochester, Minn., USA	Sputtering or chemical vapour deposition or others	Any dielectric material, e.g. oxide, nitride, carbide, sulphide, with dopant	Yellow (titania and vanadium oxide); blue (silica and cobalt oxide)	Additional heat treatment after coating is possible or necessary

* patent documents are sorted in patent families (i.e., groups of patent documents with similar contents related to the same inventor or applicant, frequently based on the same priority application); patent families are presented chronologically according to the first member of a patent family published

** Abbreviations: BR Brazil; DE Germany; EP Europe; RU Russia; US United States of America; WO World Intellectual Property Organization

Figure 1: This surface-coated topaz is coloured by a thin iron-bearing layer on the pavilion of the stone; similar stones have been offered to gem dealers in Nigeria as natural topaz. The stone measures 10.1 × 8.0 mm, weight 2.95 ct. Photo by M. Krzemnicki, SSEF, Basel.

Review of the patent literature

A number of different patent documents have been published describing various techniques of surface enhancement of gem materials, which relate to the formation of surface coloration of natural and synthetic gemstones, especially topaz, quartz and sapphire. A general overview is given in *Table I*. The review covers documents published in the period 1996 to 2005.

Three patent documents describe simple coating technologies without specific heat treatment. In the US patent by Starcke *et al.* (document 9), a thin coating of a metal, metal oxide, nitride, sulphide or carbon is deposited on the pavilion of a faceted gem. Different colours are seen at different angles of observation, a feature which is caused by various reflection and interference phenomena. A more complex coating process is applied by Rogers (documents 1, 2). An optical interference coating is made of alternating layers of materials with relatively high refractive indices and relatively low refractive indices. The refractive indices and thickness of the alternating layers are chosen so that at least part of visible light incident on the gemstone is reflected. In this way, the coating creates an optical interference filter. Different colours are observed in transmission and reflection as well as at different angles of observation. Stones with the features described in these patents (*Figure 2*) have been seen on the market with various trade names such as 'aqua aura' for surface-coated topaz and quartz or 'tavalite' for surface-coated cubic zirconia (Kammerling and Koivula, 1992; Johnson and Koivula, 1996 a,b).

Figure 2: These two 'fire topazes' are surface-coated with thin metallic layers deposited on the pavilion or the crown facets. Such stones may appear under different trade names. Various optical reflection, transmission and interference phenomena cause different coloration (from green to violet) when the samples are viewed at different angles. The stones are 9.2 × 7.0 mm, weights 2.27 and 2.21 ct. Photo by M. Glas.

Figure 3: The colour of this surface-coated pink topaz is due to an easily removable dye. The stone is 18.0 ×13.0 mm and weighs 15.17 ct. Photo by M. Glas.

A coating of transparent ink including a red, blue, green or yellow dye and which is removable has been described by Arends (documents 10-12). The permanent ink is made from n-propanol, n-butanol and

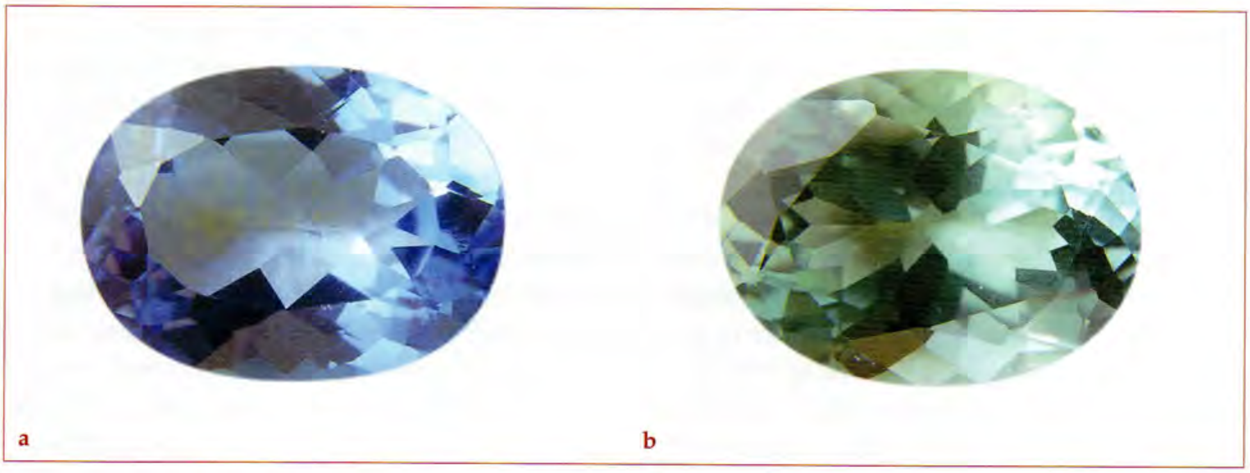

Figure 4 a, b: The colour of these surface-coated blue and green topazes is caused by cobalt-bearing layers with cobalt in different valence states. The stones are 16.2 × 12.0 mm (blue) and 20.2 × 15.2 mm, weights 10.57 and 21.84 ct. Photo by M. Glas.

diacetone alcohol and is adhered to the facets of the gemstone, for example cubic zirconia or white sapphire. The coating is easily removable in isopropyl alcohol. Nowadays, pink dye-coated topazes are not uncommon on the market (*Figure 3*).

Two major techniques are used for a more permanent surface coating of mostly colourless, natural and synthetic gem materials, especially for topaz, quartz and sapphire. The first technique is based on heat treatment of faceted gem materials in a transition metal-bearing powder (see documents 3-8, 13, 15, 16 and 22). The colour-causing transition metal may be present as metal or metal oxide. The transition metals used by Pollak are cobalt for blue, blue-green or green colours (*Figure 4 a, b*) and copper for yellow to red colours (documents 3-8, 15, 16). Using this technology, Pollak also mentioned that iron surface treatment produces colours comparable to copper (documents 15, 16). Furthermore, Pollak reported that various additional metals or metal oxides can be added to the cobalt- or copper-bearing powder used for treatment (documents 3-8, 15, 16). The colour of the material obtained by these processes can be changed by subsequent heat treatment of the coated gem material in different atmospheres without further contact with a metal- or metal oxide-bearing powder (documents 3-8, 15, 16). In this subsequent step of treatment, a shift of blue-green topaz colouration to a more pure blue or the development of a red hue in yellow surface-treated topaz is achievable.

A special mixture of cobalt oxides and zinc oxide has been used by Balitsky and Balitskaya (document 22). For this type of contact heat treatment with powder, the powdered material used to surround the faceted gem during heat treatment can also contain fine grained material of the same gem mineral. In a Brazilian patent by Soares Sabioni *et al.* (document 13), the inventors used a mixture of powdered topaz with a powder of a metal or a metal oxide or a metal salt, which was heat treated in a first step before placing faceted topaz in this pre-heated powder for a second step of heat treatment. Repeated heat treatment is possible in powders containing various metals, in this way creating a succession of differently doped layers on the surface of the treated samples.

The second major technique requires two steps of treatment, (a) the deposition of a coating on the faceted stone and (b) heat treatment of the coated gem (documents 14, 17-19, 20, 21, 23). The coating of the gem may be carried out by vacuum sputtering, chemical vapour deposition, physical vapour deposition, spraying, or other techniques.

The coat may consist of metals, metal oxides, metallic compounds or alloys. As described by Gupta and Goyal (documents 17-19), a wide variety of colours is obtainable after subsequent heat treatment of the coated material, such as blue to green (cobalt or cobalt and chromium or cobalt and nickel), green (chromium), yellow to orange (iron; see *Figure 1*). The appearance of 'Imperial' topaz is obtainable by a combination of iron, chromium and nickel. The colour of the sample can be controlled using different treatment conditions. For topaz with cobalt-bearing surface layers, heat treatment in air in a temperature range from 900 to 1000°C produces a green coloration, while under heat treatment in a temperature range of 950 to 1050°C a blue/green colour is obtained. Heat treatment in nitrogen or in a reducing environment, on the other hand, results in a blue coloration of the surface-coated topaz.

Another type of colour reaction within the surface layer is described by Starcke *et al.* (document 23). For topaz with a very light grey surface coating consisting of titania and vanadium oxide, a yellow body colour was obtained after heat treatment at 450°C. In another topaz with a colourless surface layer consisting of silica and cobalt oxide, a light blue colour was developed after heat treatment at 450°C.

Reaction mechanism

For both major techniques mentioned above, exact details of the chemical reactions are, in general, not disclosed. For both methods, 'diffusion into the outer surface' as well as 'chemical bonding to the surface' are claimed as reaction mechanisms (documents 3-8, 15, 16, 17-19). 'Diffusion into the outer surface' of a faceted gemstone indicates the production of a coloured zone or layer without a distinct interface, for example the diffusion of cobalt atoms into the crystal structure of topaz. 'Chemical bonding to the surface' of a faceted gemstone indicates the production of a coloured zone or layer with a distinct interface between the surface coating and the underlying gemstone.

According to the descriptions in the Brazilian patents of Soares Sabioni and co-authors (documents 13, 14), some transition metals such as cobalt are diffused into the surface of the treated topaz. Consequently, both techniques – i.e. contact heat treatment with a metal-bearing powder and heat treatment of a surface deposited metal-bearing layer – result in a diffusion reaction between a cobalt-bearing layer or powder with the topaz crystal and the formation of a cobalt-bearing zone on the outer surface of the topaz crystal. Consequently, the treated sample might consist of an outer layer of a cobalt-bearing material deposited on to the surface and an inner layer in which cobalt is diffused into the topaz crystal structure. The exact composition and the crystalline and/or amorphous phases present within the surface layer or surface layers may vary according to treatment conditions and are unknown at present (see Underwood and Hughes, 1999). A detailed examination of the outer layers of variably treated gem materials, for example by a combination of X-ray powder diffraction with an electron microscope or with the electron microprobe, is necessary to clarify this point.

It is mentioned that other compounds than cobalt such as iron oxide diffuse less easily into the topaz crystal structure. For such compounds, contact heat-treatment with a metal-bearing powder is less effective and, consequently, iron-bearing layers are first deposited on the surface of topaz for subsequent heat treatment if, for example, a yellow to orange or reddish-orange coloration is desired (see documents 14, 17-19, 20, 21). After heat treatment, the iron-bearing layer is not easily removable from the topaz surface. As described in some documents cited, the iron-bearing layer or atoms of this layer are 'bonded' to the topaz surface. This description reflects the more or less stable formation of a topaz-iron oxide composite surface layer.

A special mechanism is claimed by Starcke *et al.* (document 23). These authors describe heat treatment of the surface-coated gemstone without any diffusion from the surface coating into the gemstone. This is due to heat treatment "at an elevated temperature below that at which there occurs substantial diffusion of material from the coating into the gemstone". The temperatures applied, however, are up to 1150°C and, consequently, in a temperature range in which other authors describe diffusion.

Figure 5: These two pink topazes are dye-coated on the pavilion facets of the samples. Different colour intensities are observed when viewed through the colourless crown and through the dyed pavilion. The stones are 18.0 × 13.0 mm and 15.8 × 12.0 mm, weights 15.17 and 10.59 ct. Photo by M. Glas.

Figure 6: This dye-coated pink sapphire shows small colourless patches on pavilion facets. Magnification 30×. Photo by J.-P. Chalain, SSEF, Basel.

Detection of treatment

According to the various treatment techniques applied for surface coating of topaz and other gem materials, the criteria for the detection of treated material may vary (see also Millington, 2005). Thin metallic coatings causing interference and other optical effects (*Figure 2*) are not found on faceted examples of natural untreated stones. In coated stones different colours may be observed when the stones are viewed from different directions. For a number of samples such as some pink topazes examined recently (*Figure 3*), which are dye-coated on pavilion facets, the colour intensity observed through the colourless table will differ from that on the pavilion (*Figure 5*). Surface-coated samples of this type show colourless spots or small colourless patches on facets (*Figure 6*) or along facet junctions.

For a number of samples produced by contact heat treatment with powder or by heat treatment of a metal-bearing layer (*Figures 1, 4 a, b*), an irregular or somewhat spotty colour distribution on coated facets or facet junctions can also be observed. There are also frequent references in the literature to small colourless areas, also described as colourless chips within the coating (see, for example, Johnson and Koivula, 1998; Underwood and Hughes, 1999; McClure and Smith, 2000; Krzemnicki, 2002).

Nomenclature and conclusion

In summary, various mechanisms are described for different treatment techniques. The properties of the resulting type of coating are due to the actual process applied, but are also dependent on the main transition metal or group of transition metals, for example cobalt, iron or copper, used for coating. The different minerals such as quartz, topaz or corundum, subjected to a particular transition metal and treatment technique, may well show different reactions. Consequently, when naming a stone whose treatment history is not known, only a reference to the general technique applied should be made. All techniques described above are processes of surface-coating and, consequently, a description of a stone that has undergone any of these as 'surface-coated' reflects the applied treatment technique and distinguishes these gem materials from irradiated or simply heat-treated gemstones.

References

Johnson, M.L., and Koivula, J.I. (Eds), 1996a. Gem News. "Tavalite," cubic zirconia colored by an optical coating. *Gems & Gemology*, **32**(2), 139-40

Johnson, M.L., and Koivula, J.I. (Eds), 1996b. Gem News. Coated quartz in "natural" colors. *Gems & Gemology*, **32**(3), 220-1

Johnson, M.L., and Koivula, J.I. (Eds), 1998. Gem News. Surface-treated topaz. *Gems & Gemology*, **34**(2), 143-4

Kammerling, R.C., and Koivula, J.I., 1992. An examination of 'Aqua Aura' enhanced fashioned gems. *Australian Gemmologist*, **23**(2), 72-7

Krzemnicki, M.S., 2002. Orange topaz with synthetic hematite coating. *Gems & Gemology*, **38**(4), 364-6

McClure, S.F., and Smith, C.P., 2000. Gemstone enhancement and detection in the 1990s. *Gems & Gemology*, **36**(4), 336-59

Millington, G., 2005. The things that turn up. *Gems & Jewellery*, **14**(3), 58-9

Schmetzer, K., 2001. Some light on the 'topaz-type diffusion process' of natural corundum. *Journal of Gemmology*, **27**(6), 360-1

Underwood, T., and Hughes, R.W., 1999. Surface-enhanced topaz. *Gems & Gemology*, **35**(3), 154-5

Patent documents

1. Rogers, D.Z. (1996): *Novel gemstones and decorative objects comprising a substrate and an optical interference film.* WO 96/06961 A1
2. Rogers, D.Z. (2001): *Gemstones and decorative objects comprising a substrate and an optical interference film.* US 6,197,428 B1
3. Pollak, R. (1998): *Method for enhancing the color of minerals useful as gemstones.* WO 98/48944 A1
4. Pollak, R. (1999): *Method for enhancing the color of minerals useful as gemstones.* US 5,888,918
5. Pollak, R. (2002): *Method for enhancing the color of minerals useful as gemstones.* US 6,376,031 B1
6. Pollak, R. (2002): *Method for enhancing the color of minerals useful as gemstones.* US 2002/0174682 A1
7. Pollak, R. (2003): *Method for enhancing the color of minerals useful as gemstones.* EP 1 017 504 B1
8. Pollak, R. (2004): *Verfahren zur Verstär Kung der Farben von Mineralen, die als Edelsteine benutzt werden.* DE 698 17 380 T2
9. Starcke, S.F., Kearnes, R.H., Bennet, K.E., Edmonson, D.A. (1998): *Method of improving the color of transparent materials.* US 5,853,826
10. Arends, R.W. (1999): *An enhanced gem stone, a jewellery enhancement kit and a method of simulating the appearance of an expensive gemstone.* EP 0 888 730 A1
11. Arends, R.W. (1999): *Gem stone having an enhanced appearance and method of making same.* US 5,981,003
12. Arends, R.W. (2000): *Enhanced gem stone and a method of simulating the appearance of an expensive gem stone.* US 6,146,723
13. Soares Sabioni, A.C., Mendonça Ferreira, C., Magela da Costa, G. (2001): *Processo de coloração e/ou modificação de cores de gemas lapidadas por dopagem em etapas múltiplas.* BR 2000-1034 A
14. Soares Sabioni, A.C., Mendonça Ferreira, C. (2002) *Processo de coloração de gemas lapidadas por dopagem ou recobrimento químico de seu pavilhão ou coroa.* BR 2000-2321 A
15. Pollak, R. (2002): *Process for the color enhancement of gemstones.* US 2002/0128145 A1
16. Pollak, R. (2003): *Process for the color enhancement of gemstones.* US 6,635,309 B2
17. Gupta, S., Goyal, M. (2003): *Process for imparting and enhancement of colours in gemstone minerals and gemstone minerals obtained thereby.* US 2003/0008077 A1
18. Gupta, S., Goyal, M. (2004): *Process for imparting and enhancement of colours in gemstone minerals and gemstone minerals obtained thereby.* EP 1 394 293 A1
19. Gupta, S., Goyal, M. (2005): *Process for imparting and enhancement of colours in gemstone minerals and gemstone minerals obtained thereby.* US 6,872,422 B2
20. Anonymous (2003): *Verfahren zur Behandlung von Edelsteinen.* DE 102 15 141 A1
21. Balitsky, V.S., Balitskaya, L.V., Volkov, V.T. (2003): *Method for coloring of natural and artificial jewelry stones.* RU 2 215 454 C1 [in Russian]
22. Balitsky, V.S., Balitskaya, L.V. (2003): *Method for coloring of natural and artificial jewelry stones.* RU 2 215 455 C1 [in Russian]
23. Starcke, S.F., Kearnes, R.H., Bennet, K.E. (2004): *Coatings for gemstones and other decorative objects.* US 2004/0083759 A1