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A New Type of Composite Turquoise

Turquoise, known for its splendid blue colour is used to describe the colour of many materials has been used for adornment since antiquity. Chemically a hydrous copper aluminium phosphate, it has a cryptocrystalline structure composed of fine randomly oriented groups of triclinic crystals. This cryptocrystalline structure gives rise to the porosity making it susceptible to body oils, or any other daily use solvent or even dirt, which can result in the change in body colour. However for decades, such porous material is known to be impregnated with wax or plastics or polymers, known as 'stabilization' which not only enhances the durability but also the appearance i.e. the colour and the surface lustre. In addition, dyeing of light or pale coloured turquoise to turn rich blue is also known for many years. In recent times, few other proprietary treatments have been evolved on turquoise; the most talked about was 'Zachery treatment' which is used to improve the lustre and colour. Another method of treatment is marketed as 'Eljen Treated Turquoise', which are basically polymer-impregnated.

Recently, we had an opportunity to study few fancy colours of turquoise viz. purple, yellow green and blue (figure 1). We encountered these fancy coloured (especially purple and yellow green) turquoises for the first time at the Jaipur Jewellery Show 2008, but were not available in quantities at that time. However, since the beginning of 2010, these fancy coloured turquoises are more frequently seen in the stones received for identification at the Gem Testing Laboratory. Standard gemological testing identified these fancy coloured turquoises not only dyed but composites using coloured polymer matrix. Upon enquiry, the depositor revealed that pieces of natural turquoise are dyed and bonded together, although he did not know much about the process used; he also informed that this material is being manufactured in the USA. Later, M/s Dolphin Gems of Jaipur, India kindly donated us few rough and cut samples for study. This article reports the properties of these fancy coloured said to be dyed and composite turquoises.

Figure 1

Visual Characteristics. As mentioned earlier, the studied samples of dyed and composite turquoise ranged in colour from purple to purple pink to yellow green and blue (see, figure 1). The purple to purple pink colour is not associated with turquoise and indicates artificial colouration; the metallic veins when present, appeared bright golden yellow in colour as compared to the dull golden seen in natural turquoise. Except yellow green unveined varieties, all the specimens displayed an uneven body colour. Purple to purple pink (veined and unveined) and veined yellow green specimens displayed some distinct blue patches of the original turquoise used. Blue veined samples did not exhibit any obvious signs of dyeing and were appeared more as natural specimens; however, presence of thick veins gave rise to suspicion about the origin.

Purple to purple pink rough specimens (figure 2, left) displayed obvious reddish colour on the surface and hence can easily be identified as artificially coloured; the surface displayed a waxy to oily lustre associated with polymers / resins. The yellow green rough was less patchy with only one specimen displaying obvious colour coating of yellow-brown colour (figure 2, right).

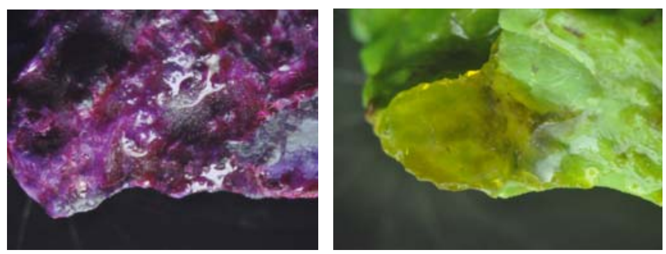

Figure 2

Gemmological Properties. The gemmological properties of the studied turquoise are described below:

Refractive Index. Except for two yellow-green specimens, all samples (whether veined or unveined) yielded a spot RI of approximately 1.61 with a moderate birefringence blink. This value is consistent with those reported for natural turquoise. Two anomalous yellow-green samples—one veined and one unveined—displayed spot RIs of ~1.54, and no birefringence was visible. This lower RI value could have been due to a thicker layer of polymer on the surface or to a larger percentage of polymer in the structure of the turquoise.

Specific Gravity. The samples displayed a wide range of SG values, from 2.03 to 2.60. Webster (1994) and O'Donoghue (2006) reported SGs of 2.60–2.91 for untreated turquoise, depending on its porosity. Although porosity can cause fluctuations in SG readings, we did not observe such

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fluctuations in our samples, as expected for polymer-treated material. Only one of the 15 cut samples had an SG of 2.60, while the rest were below that. These lower values are consistent with the presence of a polymer. No consistent variations in SG were seen across colours or between veined and unveined samples.

UV Fluorescence. The purple to purple pink varieties exhibited a distinct and striking patchy orange red; (figure 3, left, top and bottom). Blue varieties displayed a patchy blue fluorescence (figure 3, centre) while yellow green samples were mainly inert with only the blue areas giving some blue fluorescent reactions (figure 3, right, top and bottom). In all the samples, the veined areas were inert.

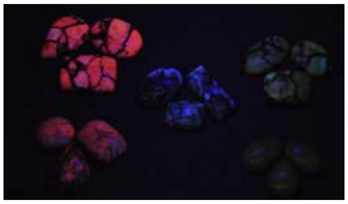


Figure 3

Spectroscope Spectrum. Purple to purple pink specimens displayed a series of three bands in the green and yellow regions between 500 and 600nm at around 510, 540 and 580 nm; the intensity of bands at 540 and 580 nm was stronger than that at 510 nm. In yellow green samples, a broad diffused absorption was seen in the blue region at 450 – 490 nm. No absorption features were seen in blue varieties.

Magnification. Microscopic examination revealed the following features.

Lustre Difference: Polymer filled areas and cavities displayed a distinctly dull to waxy lustre as compared to the turquoise areas (figure 4).

Figure 4

Colour Concentration: Most of the samples displayed distinct colour concentrations depending on the body colour. The yellow green samples displayed some yellow colour concentrations forming a flow pattern (figure 5.a). The yellow colour appeared to be superimposed on the blue base of natural turquoise pieces; this gave an overall green colouration to the specimen. Further, few cavities were filled with the same yellow coloured material. Similarly, purple to purple pink samples also displayed colour concentrations of red colour (figure 5.b), which were present as patches and in veins / cavities. The presence of deep cavities also indicated that these turquoises are not only dyed but also composites where individual pieces of turquoise are held together in a coloured polymer matrix. The blue samples did not display any colour concentrations, which indicated that they were not dyed; the polymer seen on the surface and in the ridges of those samples was colourless.

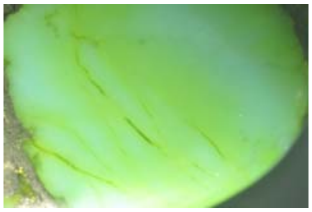


Figure 5.a

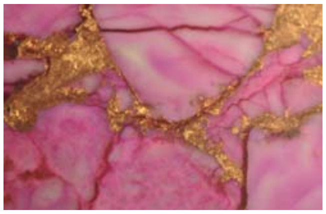


Figure 5.b

Veins: As also discussed in previous sections, the samples are available in veined and unveined varieties, as natural turquoise is. Natural turquoise usually consists of brown to black veins of limonite. Grains of pyrite / marcasite are also present in turquoise; often, these are present along the veins or matrix. However, in this case the veins primarily consist of bright golden coloured metallic flakes. In addition, brassy coloured crystals of pyrite/ marcasite were also embedded along the veins (figure 6).

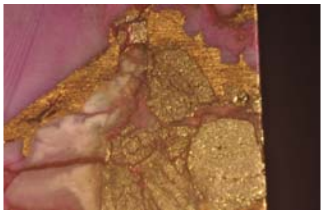


Figure 6

Reaction to a Metal Probe: When probed with a needle to check for the presence of a polymer, both rough and cut samples readily indented. The needle made indentations in the "golden" yellow veins or "matrix" as well, revealing the softness expected for a polymer; the duller brassy fragments were not affected by the metal probe.

Reaction to Solvents. A cotton swab dipped in acetone and rubbed on the surface of one unveined yellow-green sample did not result in any loss of colour. The same piece when soaked in acetone for 48 hours displayed an apparent loss of colour and became patchy (figure 7, right sample), while the acetone became pale yellow-green. The soaked sample also had significantly duller lustre and showed a pimply surface and numerous cracks.

Figure 7

One veined yellow-green sample soaked in methylene chloride showed significant changes after ~3 hours. The metallic-appearing substance that formed the veins started to leave the specimen and showed a flaky appearance (figure 8.a). After ~18 hours, individual pieces of the specimen were distinctly visible in the liquid, and the liquid turned slightly greenish yellow. After ~48 hours, the specimen had completely disintegrated into small grains and fragments (figure 8.b). The surface of the beaker in which the specimen was immersed also showed distinct colour concentrations released from the sample after the methylene chloride evaporated. In contrast, a piece of natural untreated turquoise remained unaffected.

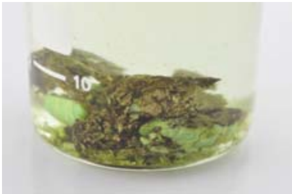
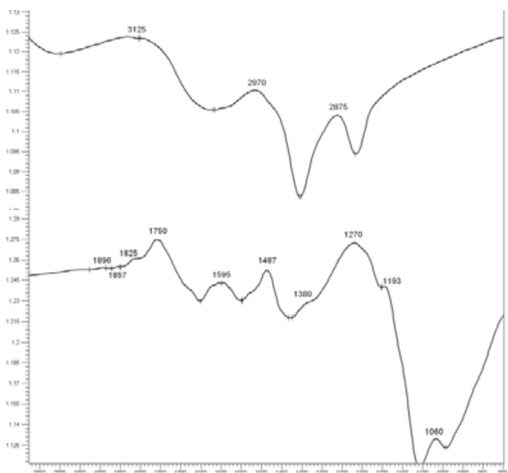


Figure 8.a

Figure 8.b

The reaction in the methylene chloride bath and the similar structural features (e.g., the presence of deep ridges) seen in all samples confirmed they are composites and not merely dyed and/or impregnated. At this stage, we do not know what impact common household cleaning products and other solvents might have on the polymer(s) used in these composites.

FTIR Analysis. FTIR spectroscopy has long been the most powerful tool in the nondestructive identification of polymer-treated stones. In this study, FTIR analysis of all cabochons (veined as well as unveined) displayed fairly consistent absorption features in the 3200–2800 cm^{-1} and 2000–1000 cm^{-1} ranges.



In the 3200–2800 cm^{-1} region, distinct absorption bands were visible at ~3125 (consisting of twin humps), 2970, and 2875 cm^{-1} (figure 9, top); the latter two are associated with polymers.

The 2000–1000 cm^{-1} region (figure 9, bottom) displayed major absorption bands at ~1750, 1595 (both related to polymers), 1487, 1270, and 1060 cm^{-1}, in addition to some fine absorption features at ~1896, 1857, 1825, 1380, and 1193 cm^{-1}. Peaks in the region 1045 to 1075 cm^{-1}, and at around 1015 cm^{-1} (not shown) are present in natural turquoise (not synthetic).

EDXRF Analysis. Qualitative EDXRF analysis of all cabochons (veined and unveined) revealed the presence of Al, P, Fe, and Cu, consistent with the chemical composition of turquoise. Veined samples displayed an additional Zn peak. EDXRF analysis of the "golden" metallic-looking material that flaked off after soaking a veined sample in methylene chloride (discussed above) confirmed the presence of Zn as well as Cu.

Conclusion

These composite turquoises, typically marketed as "stabilized" turquoise, consist of small fragments of turquoise bonded together with a coloured polymer (in the case of the purple to purple-pink and yellow-green samples) or a colourless polymer (blue samples). Furthermore, veined samples contain interstitial areas formed of a gold-coloured polymer containing fragments that resemble pyrite/marcasite.

These materials provide a wider range of turquoise colours for the consumer. Identifying them should not pose any problem. Careful microscopic examination along with UV fluorescence, spectroscope spectrum, and FTIR analysis should easily establish their dyed/composite nature.

Gem Testing Laboratory offered Free Gem Testing Services during the Jaipur Jewellery Show 2010

The Gem Testing Laboratory (GTL), Jaipur offered gem testing services 'free of cost' to the exhibitors as well as visitors during all the four days at the recently concluded Jaipur Jewellery Show (JJS) 2010, from 24th to 27th December 2010. GTL have been participating regularly in this largest jewellery show of North India and only second after IIJS, Mumbai since its inception and has offered this service free of cost. This time we took a step ahead and issued Gem Identification Reports on site and have seen a tremendous response to the service. Exhibitors were issued our routine 'formal reports' along with photograph of the stone tested, while visitors were issued a 'spot identification report'. In order to provide this service 'on-site', a full fledged laboratory including all classical gemmological instruments was set up at the booth, in addition to a high quality colour printer and a computer system.

Gagan Choudhary at GTL booth during JJS 2010

Most of the visitors and exhibitors appreciated the efforts, as this 'on-site' testing service helped the exhibitors to furnish the proof of authenticity with the stones they offered for sale. Hundreds of loose and studded stones were tested. In order to promote the awareness on treatments of sapphires, GTL also issued a special edition newsletter for the JJS covering mainly the beryllium treatment which is of major concern in the trade.

Yellow Sapphires – Challenge or Threat?

In the previous issues, we have been highlighting the beryllium treatment done on blue as well as yellow sapphires. This treatment has become a challenge in the trade and is quite difficult to detect with routine gem testing. However, in addition to the beryllium treatment, yellow sapphires are commonly irradiated with gamma rays or neutrons. The availability of irradiated yellow sapphires has increased tremendously in the recent past and is another major problem in the trade. The key concern with these irradiated sapphires is that the colour fades on exposure to strong light such as a 60W lamp or the sun. Therefore, a consumer always complains the seller regarding the fading of the colour and the associated fraud with it, but the seller is helpless and he does not have any explanation for the fading of the colour.

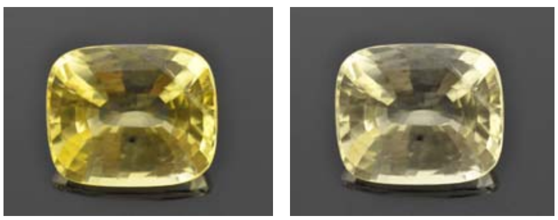


Figure 10: Colour representation of bleaching of irradiated yellow sapphire (left) on exposure to strong light (right)

So where the problem lies….

The major problem in this case is the identification of these irradiated sapphires. Till date, there is no gemmological test which can identify whether irradiation has been done or not on a said piece of yellow sapphire. However, there is one method, which indicates that whether the suspected sapphire is irradiated or not. *The 'Fade Test'*. The test which is destructive in itself, when done will bleach the body colour of the sapphire completely or partially. This test simply uses a strong bulb, e.g. a 60W or 100W. The suspected stone is kept directly beneath the lamp at a distance of around 4 – 6 inches. The colour will start to bleach in 5 minutes exposure time; more the exposure time more will be the loss of colour.

Now, since this test is a destructive method of testing, it does not fall into the regular method of gemmological testing and hence not performed in gemmological labs. As a result, no lab issues a certificate which discloses whether irradiation has been performed on the said yellow sapphire. However, laboratories do disclose whether the sapphire under test is heated or not. So, if a report states, that a sapphire is unheated, there is a possibility that the stone has undergone irradiation.

Another problem with yellow sapphires is that, some of the natural unheated and untreated stones may also fade on exposure to strong light, especially those originating from Sri Lanka. Therefore, even fade test is not 100% proof of irradiation. K. Nassau has described seven types of yellow sapphires, which may be encountered.

Type 1: Yellow colour derived from a yellow stable colour centre; colour may be lost by heating; restored by irradiation; usually from Sri Lanka

Type 2: Yellow developed by irradiation of colourless material; yellow fading colour centre; may have been found yellow but fades on exposure to light

Type 3: Yellow colour derived from iron, not heated

Type 4: Yellow type 3 colour, derived from iron, intensified by heating; may have been colourless when found

Type 5: Colourless or pale material with surface diffused yellow added, using Ni or other element

Type 6: Synthetic sapphire with Ni or other element present as yellow colourant

Type 7: Synthetic colourless sapphire irradiated to produce yellow

With the developing methods of treatments, two more types may be added to the list. One is the beryllium treated sapphires from Sri Lanka where the colour originates from the colour centre created by beryllium. Another one is yellow sapphire from Thailand, Australia or African sources where coloured is produced from iron containing brown / green sapphires.

Considering the above seven types of yellow sapphires, the first two types are of major concern. In the first type, if the colour is lost on exposure to light, it may be restored by irradiation. So, if fade test is performed and the sapphire looses its colour, it can again be turned yellow. This is what many of the traders and even few labs are doing. In type 2 sapphires, the mined stones are natural in colour but on exposure to light, may fade.

Therefore, such cases become a tough challenge when one wishes to differentiate a natural untreated sapphire and irradiated sapphire. However, in general one can anticipate that if the colour of a sapphire fades on exposure to light, it is most probably irradiated. A laboratory however, cannot perform fade test on routine and hence strongly recommends the traders to perform this (even if they have testing reports with stones), to ascertain whether the suspected sapphire is irradiated or not.

Written and Edited by: Gagan Choudhary, *Deputy Director (Tech. & Training)*

Contact for further details:

Meenu Brijesh Vyas, *Asst. Director (Tech. & Training)*

Radhamani Amma, *Asst. (Coordination & Info.)*

Kailash Chand Daurata, *Jr. Executive*

GEM TESTING LABORATORY
Rajasthan Chamber Bhawan
M.I. Road, Jaipur, India
Phone : 91-141-2568221, 2573565
Fax : 91-141-2567921
Email : gtl@gjepcindia.com
Website : www.gtljaipur.info