CHAPTER 2

HISTORY OF GEMSTONE ENHANCEMENT

Mawe, J. (1813) reported that ruby is not changed by the most intense heat. Feuchtwangler, L. (1838) had also reported that ' If the red Sapphire (Ruby) is exposed to a great heat, it becomes green, but when cold, returns to its original colour'; he also reported that 'Many Sapphire may be deprived of their specks by a careful calcinations in a crucible [sic] filled with ashes or clay, and they assume then a more agreeable and purer colour and greater transparency.'

Tennent, E. J. (1859) discussed various methods of counterfeiting and adulterating precious stones. Most interesting is the following description of heat treatment: the tinge of blue which is frequently found in the stone (giving it the name of neelakantia) is easily removed by burning. The process is simple and is as follows: – The stone is enclosed in a thick coating of *chunam* [lime] (that which is used by the natives with their betel-leaves) and then exposed to a strong heat. The operation is repeated until the whole of the blue tinge is removed. But care should be taken to subject only such stones as are perfectly free from cracks to this, for one with cracks, if subjected to heat, is said to crumble down in pieces.

Kluge, K. E. (1860) mentioned that the heating of topaz to turn it pink, the loss of color of sapphire, zircon, amethyst, etc., when strongly heated and, usually, buried in iron filings or burned lime. Using a mixture of iron filings and sand, a careful but less intense heating can remove spots and defects even in ruby. A pearl which has lost its luster may be fed to a chicken which is slaughtered after one minute.

Doelter, C. (1909) reported that some of the irradiation-induced colors would fade on exposure to light. He found that colorless fluorite irradiated to become violet faded completely in light, that pink topaz irradiated to orange faded partly, but that irradiation-colored diamond did not fade. Hearing accelerated the fading: 100 ^{o}C was enough to bleach fluorite rapidly and 300^{o}.C did the same for the yellow color produced in the blue corundum , as well as for rose quartz, citrine, and smoky quartz.

Michel, H. (1926) had discussed on synthetics and irradiations and he gave a fairly detailed description of various kinds of doublets, an outline of color-changing heat treatments, including brown topaz to pink, zircon to colorless or blue, and amethyst to yellow. He also discussed the dyeing of agate, chalcedony, opal and the like , as well as the production of dendritic patterns by the use of a silver nitrate solution, the production of crackled quartz, and but a brief mention of foils.

Based on a report published by Michel, H. (1927), the significant changes known at that time were the development of yellow, green, or blue in diamond, brown in the quartzes, yellow in corundum, red or yellow in tourmaline, orange in topaz, and green in kunzite.

Caley, E. R. (1927) stated that in 19th Century, the people used the Grind alum and melt it carefully in vinegar. Put the stones therein, boil it up, and leave them there over night. Rinse them off, however, on the following day and color them as you wish by use of the recipes for coloring.

Ball, S. H. (1950) mentioned that Pliny and Cellini had written various books on the gemstones. Cellini written a book " Pirotechnia of Vannoccio Biringuccio 10" which was printed in 1840 in Venice language and Translated it into English in1898 . He reported that others used the blue dye indigo for tinting diamond, particularly yellow ones which converts they make green ,hence the yellow diamond with the blue tint made an admirable water; and, if it be well applied, It becomes one colour ,neither yellow as heretofore nor blue owing to the virtue of the tint, but a variation ,in truth, most gracious to the eye '.Here he uses the quality term ' water of the diamond ' in the sense of achieving the most desirable pale blue –green or smoky colours, not in the usually attributed colorless sense. Could this perhaps have been the origin of this designation ? Another technique was is very harder and much more lustrous and transparent then any other thing .I f the skin of its earthiness is cleaned with art and then it is given its polish, it becomes very brilliant when a lustrous black colour is placed underneath .' Cellini given different heat treatment in crucible along with gold ,heating one to thee timing to achieve appropriate clarity and colour [Nel quale sia dell ' oro che s 'abbia a struggere].

Next there is John Baptista Porta (1957) who had published various books and in his book in Natural Magic he covered a variety of topics, including the making of colored glass imitation and various treatments. He had written in his report on the topic of 'How Gems are coloured', is devoted to dyeing sapphire, amethyst, topaz, chrysolite, and emerald. In a detailed passage he teaches how:

According to Rackham, H. (1963), Vinegar is used to make dull stones shiny and 'smaragdi [emeralds in part].In spite of their varied colours ,seem to be green by nature, since they may be improved by being steeped in oil'. He also stated that Dyeing and staining were widely used. Even pigments made from ground-up malachite and azurite were thus improved: 'Armenian [azurite] is a mineral that is dyed like malachite.Amber can be tinted, as desired, with kid-suet and the root of alkanet [a natural dye]. Although, as I have mentioned, it can be dyed any colour'. He also gave various simple processes of that the sugar-acid process for dyeing agates and other porous stones black is apparently reported by Pliny, although the description has not always been accepted as such; this will be discussed in more detail in report under quartz. Finally there is this passage on the making of triplets. He also gave various descriptions regarding the gemstone enhancement in his report. there are descriptions as to how to give the color of *smaragdus* [emerald] to *crystallus* [rock crystal] and how to imitate other transparent gems: for example, how to make a *sardonychus* [sardonyx] from a *sarda* [carnelian, in part sard]: in a word to transform one stone into another. To tell the truth, there is no fraud or deceit in the world which yields greater gain and profit than that of counterfeiting gems.

Bauer, M. (1968) published and translated various books and articles in English on Precious Stones. In his books, he had mentioned that the loss (or change) of color with heat is described by Bauer for smoky quartz, amethyst (to yellow), zircon, and topaz (to pink); this plus burning, the heating of carnelian to become red and the dyeing of cracked rock-crystal are further discussed. Foils and other colored backings are covered, as well as pigments applied to the girdle of a stone. Doubles of varying types, including hollow ones, are discussed, as is the heating of some brown ones become grayish. Diamond-topped doublets and blue-tinted diamonds are described. He also stated that the

Sapphire may be lose its color with heat and may be backed with a blue-silver foil, while unevenly colored ruby may have the color evened by a heat treatment. Foils are used on aquamarine. Some yellow topaz may be burned to pink, while some yellow or pale blue stones may lose their color on exposure to sunlight. Zircon can be made lighter in color or completely colorless by heating, and some fade when exposed to light. Opal can be oiled and backed by foil, etc., or treated to become black by an unknown process. He also identified that the luster of colorless quartz can be slightly increased by heating; smoky quartz turns yellow and then colorless on heating. Amethyst may be burned to give citrine and rock crystal may be dyed to look like amethyst. The yellow color of tiger's-eye can be removed with acid. Chrysoprase may lose its green color on heating or on exposure to sunlight; this may be restored with water or with dyes, which latter can also be used on chalcedony, sard, agate, etc., to imitate Chrysoprase as well as to obtain other colors. Yellow , brown, gray, and other colors of sard, carnelian, etc., may be heated to obtain red or other colors. The color of fluorite is altered or lost on being heated and this material may also be resin impregnated.

Dick, W. B. (1974) published Encyclopedia of Practical Receipts and Processes, in which he had mentioned various recipes among the 6422 recipes given, there are instructions for dyeing or bleaching ivory, alabaster, marble, etc., a cement for amber, as well as a variety of shiny and colored foils with instructions for their use.

Nassau, K. (1983) worked on the physics and chemistry of colour of the gemstone in the Laboratory and he had buried some corundums for one month in a radium salt and obtained, in colorless corundum, a yellow color, while a blue corundum turned an emerald green, and so on.

The Gemstone treatments is that of an anonymous Egyptian whose writings have survived in the form of two papyri believed to date from the third or fourth centuries AD (Nassau, 1984). The second, known as the Stockholm Papyrus or *Papyrus Graecus Holmiensis,* details methods of counterfeiting and treating gems. Below is but a small sample: Grind alum and melt it carefully in vinegar. Put the stones therein, boil it up, and leave them there over night. Rinse them off, however, on the following day and color them as you wish by use of the recipes for coloring.

Heat altered gem material is changes or improves the color. Some heat treatment is permanent and can lighten, darken, or completely change the color of the gem. Some heat treatment is unstable and can revert to the original pretreated color with time. Zircon can be unstable and after heat treatment the stones can be exposed to sunlight for several days and then stored in the dark up to a year to remove the unstable stones (Hurlbut and Kammerling, 1991).

Heating will remove *yellow* color of beryl and turn the stone to a more desirable blue; this same treatment is done with morganite, turning the stone from peach to a pink beryl. "In both these cases it is believed that the heating converts yellow-color-producing Fe^{3+} to Fe^{2+}, the latter having no effect on body color when it occurs in the structural sites in which the Fe^{3+} produces the yellow coloration" (Hurlbut and Kammerling, 1991).

"The heat treatment of corundum is one of the most widespread and commercially significant of gemstone enhancements. It is generally believed that the vast majority, if not all, of the blue sapphires and rubies seen in the jewelry trade today have been subjected to one or more high-temperature heatings" (Hurlbut and Kammerling, 1991).

Diffusion treatment is a process which alters the color by exposing the surface to certain chemicals and heating. It has only been successful with corundum, especially with blue sapphire. Faceted stones that did not respond to heat treatment alone, are coated with a slurry of aluminum oxide plus iron and/or titanium (if want blue), chromium oxide (if want red or pink), nickel compound (if want yellow). The stones are heated to temperatures that approach melting and the color-causing agents diffuse into the stones, creating a thin layer of color (Hurlbut and Kammerling, 1991).

Artificial irradiation is the most controversial process used to alter a gems appearance and many times the colors are not stable in light or low heat. Health risk is a concern, as there are still questions about the acceptable levels of radioactivity a gem can carry. The Nuclear Regulatory Agency is currently working on establishing standards. "Commercially three types of facilities are used to treat gemstones: gamma ray facilities

(often using cobalt-60), linear accelerators (producing high-energy electrons), and nuclear reactors (producing high-energy neutrons) (Hurlbut and Kammerling, 1991).

"The first documented artificially irradiated gemstone was diamond, in which a green color was induced by burying the stone in radium salts" (Hurlbut and Kammerling, 1991).

Blue topaz is the most commercially produced irradiated gemstone in today's market. Natural blue topaz is pale but radiated material creates a deep blue, referred to as *Electra Blue*, *Swiss Blue*, and *Max Blue*, among other names. Irradiating topaz may produce a secondary yellow to brown color that is converted to blue with heat treatments. "Linear accelerator (linac) treatment is a preferred enhancement method for topaz today (Hurlbut and Kammerling, 1991).

Fracture filling, or clarity enhanced diamond, effects the clarity grading of diamonds and is a concern in the trade. The process was begun in the 1980s by Zvi Yahuda of Ramat Gan, is Israel and is a method of filling cracks with a glass-like lead-bismuth oxychloride like glass substance to improve the overall appearance.. The fillings might up the clarity grade but have been slightly yellow, lowering the color rating. Some of the time laser drill holes were made to reach an internal fracture in order to fill it, or introducing a *fracture* that was not originally there! Detection of fracture fillings in diamond include: an orange flash or blue or green flash interference effect with dark-field illumination; a melted or flow structure in filled breaks; flattened trapped gas bubbles in the filling material (fingerprint pattern); crackled texture in the filling resembling cracks on a dry riverbed (Hurlbut and Kammerling, 1991).

The purpose of coatings is to protect dye treatments, to improve the polish by masking small scratches, grainy textures, or surface irregularities, and to stabilize porous gemstones (Hurlbut and Kammerling, 1991).

Dyeing is a treatment that alters the body color of a gem and has been done for thousands of years. For the dye to penetrate, fractures must exist. If the gem is not porous or fractured naturally, the opening for the dye to enter the stone is produced by "quench

crackling," a heat-induced thermal shock, that creates a network of fractures. Bleaching is used to lighten or remove color and is done with chlorine compounds or concentrated hydrogen peroxide. This enhancement is done to pearls, black coral, and chatoyant tiger's eye (in an effort to imitate cat's eye chrysoberyl) (Hurlbut and Kammerling, 1991).

According to Sersen, W. J. (1991), Heat treatment of corundums has been mentioned in a number of early works. He stated that inn Sri-Lanka and its environs, ruby is treated by fire. People take pebbles from the earth and crush and compress them into a mass with the aid of water. This mixture is daubed completely around a dry stone. Then, the whole thing is placed on a rock with other rocks set down around it. Dry firewood is thrown on top, lit and blown upon [with bellows]. The blowing is applied, along with more wood, till any black overtones on the ruby have disappeared. The amount of fire and the application of wood depends on the extent of the blackness present. People know this by experience. They heat-treat stones for at least one hour and, at most, twenty days and nights. Then, they carefully extract the ruby, its blackness having disappeared. The ruby is not heat treated a second time. After one treatment, its color can neither improve nor diminish.

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Heat treatment is some time change colour and clarity of gemstone This treatment may permanent and can be fade or darken after some time some treatment is unstable and can be revert to original treated colour with time .Zircon can be unstable and after heat treatment the stone can be exposed to the sunlight for several days and then store in a dark up to one year to remove the unstable colour in gematone (HurlbutKammerling,1991)

Field, J. E. (1992) had developed the new method for producing yellow and orange sapphires is a natural outgrowth of the traditional heating methods. Rough sapphire especially from Tanzania, Sri Lanka, and Madagascar is usually found

associated with spinel, zircon, tourmaline, chrysoberyl and other gemstones. The mine run material is always very difficult and time consuming to separate before cooking Thai burners notices that some of these other gemstones could actually influence the burn, More specifically, it was discovered that the introduction of small quantities of natural chrysoberyl in the crucible would increase the preponderance of yellow and orange colors in the sapphires being burned. He discovered that beryllium from the chrysoberyl (beryllium) was being diffused in extremely small quantities and barely measurable quantities and that this was a critical aspect of the chemical reaction which affected the coloration in many of the sapphires. Whether beryllium is acting as a catalyst or not is still the subject of debate. The treatment can produce complete and total color penetration and is undetectable by conventional non-destructive gemological testing methods. Although new laser ablation technologies can detect and measure beryllium and other trace elements, these determinations are too expensive to be used for general gemological purposes. The brief studies shows that beryllium has important medical effects. Beryllium is a silvery white metal and possesses some of the best mechanical properties of the light elements. It is also found in several other forms. In its oxide form, beryllium can cause illness, this effect is true whether inhaled or through skin contact.

High-Temperature (2000^0 C) High Pressure (70,000 atmospheres) treatment or HTHP was developed by General Electric in 1999, to lighten or totally remove a brownish hue in some Type IIa diamonds, Type I diamonds have nitrogen impurities that absorbing some of the blue light spectrum, thereby making the diamond appear yellow, while Type II diamonds have structural defects crated during crystal growth, that can cause a brownish color. High Temperature treatment replaces deformations, whitening the diamond's look. Type I diamonds which have nitrogen impurities can also have their color altered using High-Temperature High-Pressure treatment. Using HTHP methods we creates fancy colors in vivid hues of yellow and green, bypassing the need for irradiation. The correct disclosure of Be-diffusion treated sapphires, as testing based on traditional non-destructive methods (e.g. X-ray fluorescence XRF) is no longer providing all data necessary for a complete characterization of such treated material. In some cases, the Be-

diffusion treated sapphires show a yellowish orange rim when observed in immersion liquid (Peretti and Gunther, 2002; Hanni and Pettke, 2002; Emmett et al., 2003).

Krzemnicki, M. S. and Hanni, H. A. (2004) have been first time applied Laser Induced Breakdown Spectroscopy (LIBS) in gemology. They stated that the safe detection of Be-diffused was based on LIBS instrument. They mentioned that the beryllium even at very low concentration (2 ppm) can be detect with LIBS. They stated that the LIBS is a powerful tool for gemological laboratories to detect Be-diffusion treated sapphires.