
HEAT TREATING RUBY AND SAPPHIRE: TECHNICAL ASPECTS

By Kurt Nassau

Ruby and sapphire of natural or synthetic origin can be heat treated to improve asterism; to remove asterism or silk; to improve, add, or remove color; and even to alter imperfections. At least nine distinct processes can be identified, although several may occur simultaneously. Some of these treatment methods correspond to natural processes and may not leave any evidence of their use; others do not correspond to natural processes and are readily identifiable.

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In recent months, a variety of heat-treated sapphires and rubies with gemological characteristics different from any previously seen have appeared on the market. Contradictory rumors abound regarding the different manners and methods of treatment.

Examples of heat treatment methods that have been used to improve the appearance of gemstones include the conversion of green aquamarine to blue; the "pinking" of brown chromium-containing topaz; the "crackling" of quartz; the reddening of yellow agate, carnelian, and tiger's-eye; the development of the blue color of tanzanite; and the conversion of amethyst to citrine or to "greened amethyst." Such processes may be termed heating, burning, annealing, firing, high-temperature soaking, and so on. The use of these types of heat treatment is usually not specified.

The reaction of synthetic corundum (Nassau, 1980a) to various types of heat treatment has been studied widely, and the results are equally applicable to the natural material. Although most of the treatment methods described here have been known for some time, their use to improve rubies and sapphires has become widespread only recently.

The important parameters in any type of heat treatment are:

1. The temperature-time relationship
2. The oxidation-reduction conditions
3. The presence of chemical substances that can interact with the gemstone

Heat treatment of corundum can affect the presence of milkiness and asterism, the color, and even the internal structure (inclusions as well) of the material. A number of separate processes have been distinguished, although several may be performed simultaneously. The exact temperature, duration of treatment, and chemicals used

for each process will depend on the specific material being heated; considerable variation must be expected with corundum from different localities.

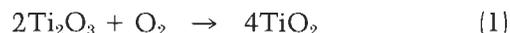
Nine possible treatment modes are summarized in table 1 and examined in turn below. Identifying characteristics of such treatment methods have been discussed in detail by Crowningshield and Nassau (1981); therefore, they will be touched on here only briefly.

It should be noted that no consensus has yet been reached as to whether any of these types of treatment need to be disclosed to the buyer. The parallel is sometimes drawn that since heat treatment is not customarily disclosed with other gemstones, such as heated blue aquamarine, why should such disclosure be necessary with sapphires and ruby? There may be validity in viewing some types of treatment in this way, especially those that mimic natural processes (as is the case with aquamarine). However, other treatment methods—diffusion in particular—do not have any parallel in nature. The results of diffusion treatment, for example, are readily recognized, and remind one more of Lechleitner synthetic emerald overgrowth on a natural beryl than of heated aquamarine.

PROCESS 1: DEVELOPMENT OF POTENTIAL ASTERISM

Some natural sapphire and ruby, as well as some synthetic material intended for star use, contains a significant amount of titanium oxide. If such corundum cools fairly rapidly from its growth conditions, the material remains clear; the titanium oxide is in "solid solution" in the form of Ti_2O_3 (titanium sesquioxide) replacing some of the Al_2O_3 (aluminum oxide).

If such material, which typically contains only a few tenths of a percent titanium oxide, is held at between 1100°C and 1500°C for some time (say, 1300°C for 24 hours), particularly under mildly oxidizing conditions, the Ti_2O_3 converts to TiO_2 (titanium dioxide) as follows:



In most cases, the TiO_2 will then form needles of rutile within the corundum and thus produce asterism. This process, which was patented for Linde Air Products Company by Burdick and Glenn (1949), is used to create all synthetic stars in corundum (Nassau, 1980a), and the analogous process also occurs in nature. In fact, if a piece of

TABLE 1. Heat treatment processes used on sapphires and rubies.

Treatment group	Specific process ^a	Result
Heating only	1. Moderate temperature (1300°C)	Develops potential asterism
	2. High temperature (1600°C), rapid cooling	Removes silk and asterism
	3. Reductive heating (1600°C)	Develops potential blue color
	4. Oxidative heating (1600°C)	Diminishes blue color
	5. Extended heating (1800°C)	Diminishes Verneuil banding and strain
Heating under unknown conditions	6. ?	Introduces fingerprint inclusions ^b
Diffusion of impurities into the material (extended heating at 1800°C)	7. Add TiO_2	Produces asterism ^b
	8. Add TiO_2 and/or Fe_2O_3	Produces blue color ^b
	9. Add Cr_2O_3 , NiO , etc.	Produces other colors ^b

^aTreatments 1 through 4 correspond to processes that also occur in nature; treatments 5 and 6 are used on synthetic material; treatments 7 through 9 do not correspond to natural processes. The temperatures given are representative only and will depend on the nature of the material and the length of time they are used.

^bEffect is limited to a region near the surface.



Figure 1. Left, milky white "geuda" corundum from Sri Lanka; photograph by Tino Hammid. Right, intense blue color induced in Sri Lanka "geuda" by the heating method described in process 3; photograph by Michael Havstad.

natural corundum contains sufficient titanium oxide but was not heated sufficiently in nature to develop a good star, perhaps showing only fine "silk," asterism can be developed by means of such heat treatment. Thus far, however, this process appears to have been used on natural corundum on an experimental basis only.

If rutile needles in natural corundum are too coarse to provide a good star, *process 2* can be used to return the titanium oxide to solid solution by the reverse of equation (1), and *process 1* can be used subsequently to form star-causing needles as described above. The heating conditions of *process 1* are relatively mild and often leave no evidence by which this treatment may be recognized with certainty.

It should be noted that the $\text{Al}_2\text{O}_3\text{-TiO}_2$ phase diagrams of Lang et al. (1952) and Lejus et al. (1966) show an intermediate compound Al_2TiO_5 , and that this and other compounds have been suggested as representing the needles (e.g., Phillips et al., 1976). However, detailed examinations always have pointed to the rutile form of titanium oxide as the principal component of the needles (e.g., Nassau, 1968; Phillips et al., 1980). Neither of the phase diagrams cited considers the solid solubility of TiO_2 or Ti_2O_3 in Al_2O_3 , which must, on theoretical grounds, be present (see also, for example, Bratton, 1971).

PROCESS 2: REMOVAL OF SILK OR ASTERISM

If corundum containing silk or asterism caused by rutile needles is heated to a sufficiently high temperature, typically between 1500°C and 1700°C ,

the rutile will dissolve in the corundum by the reverse of *process 1*:



When all the silk has disappeared, the corundum is cooled fairly rapidly, perhaps 30° per minute (Falkenberg, 1978), so that rutile needles do not re-form as in *process 1*. Asterism may be removed in a similar manner.

The suggestion by Sasaki (1980) that this form of heat treatment might be conducted successfully at 1000°F (538°C) implies a temperature that is as unreasonably low as the 4000°C reported by Tombs (1980) is unreasonably high (it is above the melting point!). Tombs also proposes that the silk may originate from substances other than titanium oxide, for example, from α -corundum present in β -corundum. But ordinary corundum is α -corundum. Such unsupported suggestions must be discounted unless and until concrete evidence becomes available. Nevertheless, it is possible that heat treatment may cause other inclusions or defects to disappear by a process of solid solution similar to that involving titanium oxide. Oughton (1971) quotes another unusual suggestion, namely that liquid may be used to fill the hollow tubes that cause silk, with the effect wearing off after about 12 months. This might work if only there were hollow tubes!

Process 2 appears to be used widely on silky Australian sapphire and on milky white to pale blue "geuda" corundum from Sri Lanka, which is turned blue by the simultaneous use of *process 3* (see figure 1). Gunaratne (1981) refers to this pro-

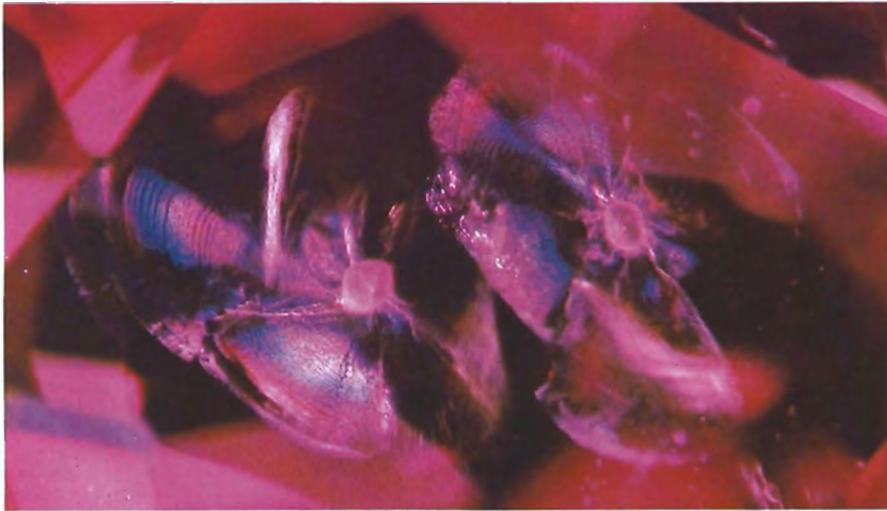


Figure 2. The stress fractures surrounding inclusions in this ruby were produced by a heat treatment method similar to the one discussed in process 2. Magnified 27 \times . Photomicrograph by Robert E. Kane.

cess, but most of his discussion of the genetic history of geuda material and of the treatment used must be taken as purely speculative, since it is in great part inconsistent with known data. Cloudy Burma rubies, too, are said to be improved in this way, with the color also benefiting from the removal of the silk.

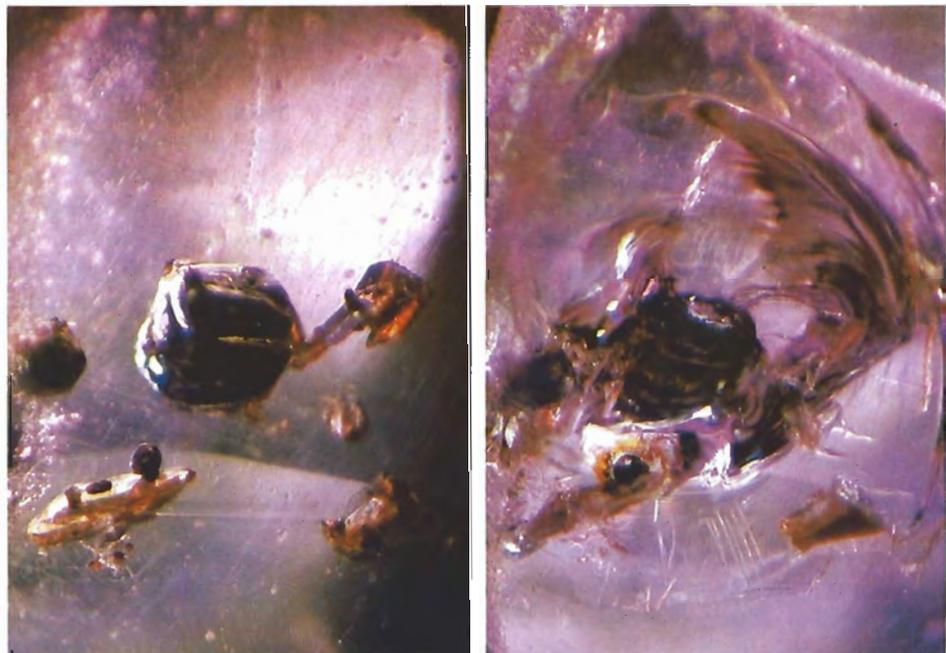
In many cases, this form of heat treatment may be identified by a dull, chalky green fluorescence and the absence of an iron line at 4500 Å in blue sapphire, and by internal stress fractures (figures 2 and 3). Pockmarked facets and abnormal girdles (figure 4) may also be seen if the stone has

not been properly repolished (Crowningshield and Nassau, 1981). However, none of these characteristics may be present in a given treated stone, or some may be present in stones that have not been treated.

**PROCESS 3:
DEVELOPMENT OF COLOR IN A
STONE WITH A POTENTIAL FOR BLUE**

The color in blue sapphire is explained by a "charge transfer" process (Nassau, 1980a, 1980b). This is widely accepted to originate from the iron-titanium combination (Townsend, 1968; Leh-

Figure 3. Left, phlogopite mica in a pink sapphire from Sri Lanka. Right, the same stone after heating to approximately 1000°C produced stress fractures surrounding the inclusions. Magnified 55 \times . Heat treatment and photomicrographs by John I. Koivula.



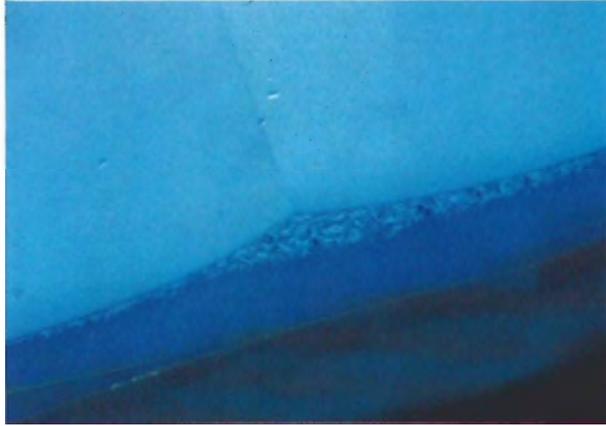
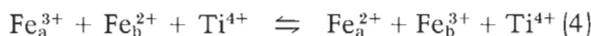


Figure 4. "Double girdle," where part of the original girdle was missed during repolishing. This indicates how the surface of a stone may become pockmarked during a high-temperature treatment. Magnified 25 \times . Photomicrograph by Robert E. Kane.

mann and Harder, 1970; Ferguson and Fielding, 1972; Eigenmann et al., 1972; Schmetzer and Bank, 1980). Recently, iron-iron charge transfer has been suggested as an alternative (Nikolskaya et al., 1978), though it is highly improbable; titanium is still essential, since the blue color never develops without it. Therefore, the process involved in these charge transfers is either



or



where *a* and *b* refer to different sites in the crystal. In each instance, a single electron is transferred from one atom to another atom and back again.

It is important to note that both processes require that some of the iron be in the divalent ferrous, Fe^{2+} , state. Also, sufficient quantities of iron and titanium must be present in the original stone to produce a deep blue.

A sapphire that contains adequate amounts of iron and titanium oxides but is too highly oxidized, so that not enough ferrous iron is present, may be pale blue, green, yellow, or colorless in its original state. Such material may be heated in a strongly reducing environment to convert some Fe^{3+} to Fe^{2+} , as follows:



This change can be achieved by an extended heating of the stone in a hydrogen atmosphere for equation (5) or by packing the material in charcoal, graphite, or another substance that produces carbon (such as mineral oil, sugar, and the like), so that combustion with only a small amount of air produces carbon monoxide



which then participates in equation (6).

The maximum color possible given the iron and titanium content of the stone can be achieved via equation (5) or (6). With sufficiently extended heating (hours to days?) at a high enough temperature (perhaps 1500°C to 1700°C), the reduction will penetrate throughout the stone and produce a uniform color (aside from any inherent banding due to uneven distribution of impurities). The reductive heatings of Schmetzer and Bank (1980) did not show this type of reaction, undoubtedly because the temperatures employed were too low (they heated in the hydrogen atmosphere at 1000°C and in the carbon monoxide environment at 1200°C). Eigenmann and Gunthard (1972) were successful with hydrogen at 1600°C.

As in the case of *process 2*, this treatment method appears to be used commonly on silky Australian sapphire and on milky white to pale blue corundum from Sri Lanka. Possible identifying characteristics include chalky green fluorescence, no iron line at 4500 Å, internal stress fractures (figure 5), pockmarked facets and/or abnormal girdles, and blotchy color banding or zoning within the stone. This treatment can be reversed by means of *process 4*.

PROCESS 4: LIGHTENING OF BLUE SAPPHIRE

If blue sapphire is heated for an extended period (hours to a day or so) in an oxidizing atmosphere (air or pure oxygen), all of the iron may be converted gradually to Fe^{3+} :



The result is the slow removal of one of the essential coloring ingredients, Fe^{2+} , on the left side of equations 3 and 4, thus lightening the blue color. If the process is continued long enough, a virtually colorless stone may result. This treatment has been described by Jobbins (1971), Eigen-

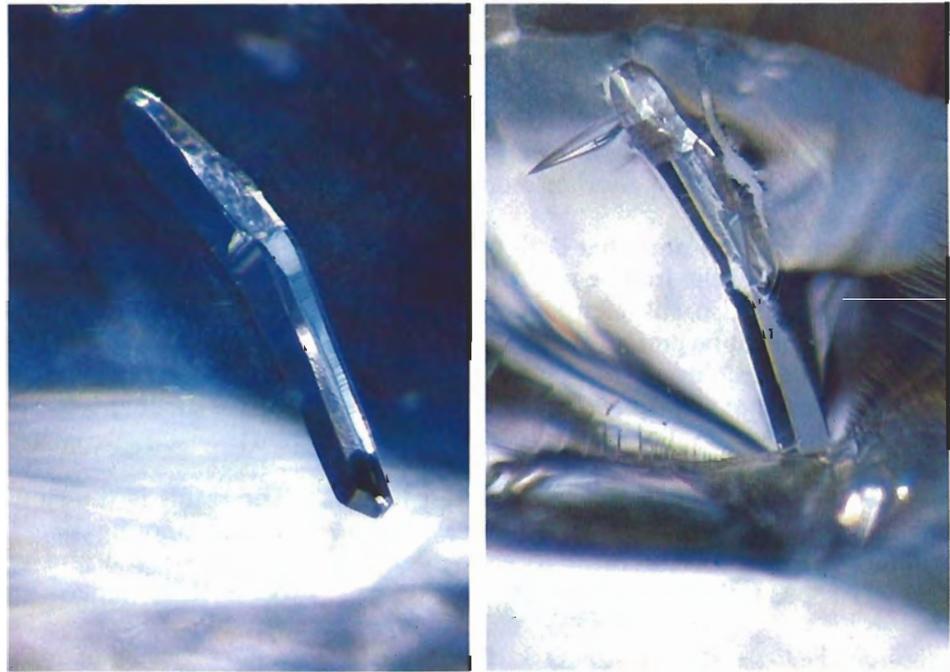


Figure 5. The stress fractures in this sapphire from Sri Lanka resulted from a heat treatment method like the one described in process 3. Photomicrograph by Robert E. Kane.

mann and Gunthard (1972), Harder (1980), and Schmetzer and Bank (1980). If an underlying yellow is also present, the final color may be green or yellow; a purple sapphire that also contains some chromium could lose the blue color entirely and end up as ruby (the oxidation has no effect on the red chromium coloration); and so on. Temperatures in the 1000°C to 1700°C range may be used, and this treatment can be reversed by using process 3; identifying characteristics are similar to those for process 3 (figure 6).

Process 4 is used to lighten dark blue, "inky" Australian sapphires (Gunaratne, 1981), sometimes producing a pronounced green dichroic direction in the stone. Undoubtedly, it has also been applied extensively to purplish and brownish Thai rubies, which were so common at one time but now are seldom seen (Crowningshield and Nassau, 1981). This process as used in Sri Lanka has been described by Gunaratne (1981); the reported difficulties in obtaining consistent results probably derive from the use of charcoal,

Figure 6. Left, fluid inclusion, probably carbon dioxide (CO₂), in a sapphire from Sri Lanka. Right, the same stone after heating to approximately 1000°C in air resulted in the almost total dissipation of color and the appearance of a large stress fracture around the inclusion. Magnified 45×. Heat treatment and photomicrographs by John I. Koivula.



which can lead to reduction rather than the desired oxidation if not performed carefully.

**PROCESS 5:
DIMINISHING VERNEUIL
BANDING AND STRAIN**

Extended heatings (for many days) at sufficiently high temperatures (1600°C and up), such as those associated with many of the processes discussed here, will result in a reduction of strain and will permit some smoothing of color irregularities. The curved striations typical of Verneuil-grown synthetic corundum originate from irregularities in the growth process; their main feature is a variation in the concentration of the impurities (Nassau, 1980a). Heating for an extended period permits a very slow diffusion to even out some of this variation, with the degree of improvement depending on the duration of the heating process.

This lengthy, high-temperature process is said to be performed in Bangkok on synthetic Verneuil blue sapphire. When used in conjunction with *process 6* (below), it results in improved color and less prominent curved growth lines. It is also more difficult to observe a positive Plato test in stones treated in this manner (Crowningshield and Nassau, 1981). A similar procedure should be possible in ruby and other colored corundum. The small gas bubbles associated with the Verneuil technique probably cannot be removed in this manner.

**PROCESS 6:
INTRODUCING FINGERPRINT
INCLUSIONS**

As reported by Crowningshield and Nassau (1981), some samples of "heat-treated natural blue sapphire" obtained from Bangkok turned out to be Verneuil synthetic sapphire with induced fingerprint inclusions. Both Verneuil synthetic ruby and pink sapphire showing fingerprints were also reported by Crowningshield (1980). Judging from the characteristics of these stones, it is clear that an extended heat treatment similar to that of *process 5* was involved.

At present, nothing definite is known about the treatment used with synthetic stones to mimic the fingerprint inclusions of their natural counterparts. The simultaneous occurrence of fingerprints, curved but weakened Verneuil banding, and occasional gas bubbles is clear evidence of such a treatment. According to some unsubstan-

tiated reports, a flux-type chemical such as sodium carbonate or borax may assist in this process. It should be noted that the formation of inclusions seems to be limited to a region close to the surface of the stone.

THE DIFFUSION MECHANISM

Diffusion in solids is a mechanism by which atoms may be moved from one region to another. The amount of movement increases with both the temperature and the length of the heating. Atoms of oxygen or hydrogen can move very rapidly in corundum, which explains why the effects of *processes 3* and *4* will penetrate fully throughout a stone in as little as a few hours in some cases (and no more than a day or so in others). The formation or removal of the rutile needles of silk and asterism in titanium-containing corundum is also diffusion controlled. Although titanium diffuses very slowly, the distances involved are so small, only a few micrometers, that *processes 1* and *2* as well require only a day or so to be effective. The banding in Verneuil-grown corundum is much coarser; this explains why extremely long heating would be required for the near-total removal of the banding by *process 5*, which involves the movement of the slowly diffusing color-causing transition metals such as chromium, iron, titanium, and nickel. It is not known if a total removal of the banding is possible, since other factors (the dislocation structure, for example) may prevent this from occurring.

The movement of color- and star-forming atoms into and within corundum is a very slow process; as a result, the effects of *processes 7*, *8*, and *9*, discussed below, are limited to a relatively thin skin on and just below the surface, typically to a depth of a few tenths of a millimeter. Very high temperatures must be used to obtain significant penetration in a reasonable time, since the fuel costs for these forms of heat treatment are considerable. As a consequence of the high temperatures required and the thin film that results, these treatment methods cannot be performed on rough material but must be applied to a preform or a cut stone; even so, only the lightest of polishing (or repolishing, since the surface is roughened by the treatment) can be used or the affected skin will be completely removed.

It is the localization of the effect of these treatment methods just below the surface of the stone,

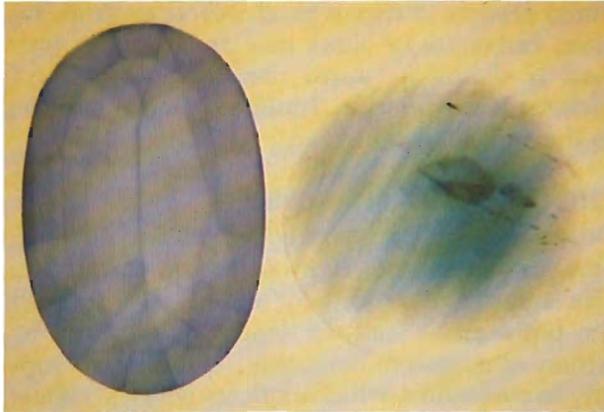


Figure 7. A diffusion-treated sapphire (left) lies next to a sapphire treated by a method like the one described in process 3 (right), both immersed in methylene iodide. Immersion reveals that the diffusion-treated stone has much greater relief, as exemplified by a blue outlining of facet junctions. The stone on the right has low relief and does not show any facet junctions except near the girdle where some areas are slightly abraded. Magnified 10×. Photomicrograph by Robert E. Kane.

the restrictions on polishing, and the high temperatures required that provide the clues to identifying that these processes have been used. Viewing such stones while they are immersed in methylene iodide reveals both the localized effect and a blotchiness from the combination of uneven diffusion and light repolishing (figures 7 and 8). Other signs are stress fractures, pockmarked faces, and abnormal girdles as discussed under processes 2, 3, and 4, and shown in figures 2

Figure 9. "Bleeding" of color around cavities and fractures in a diffusion-treated sapphire. Magnified 15×. Photomicrograph by Robert E. Kane.

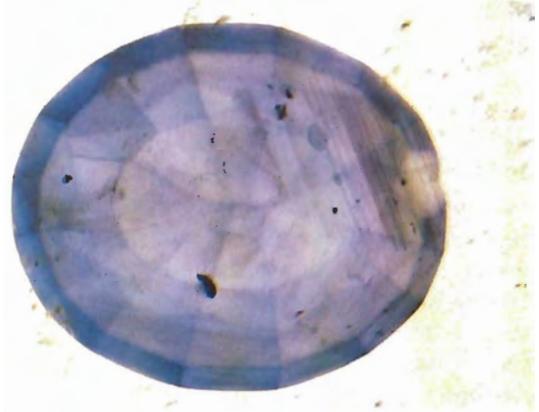
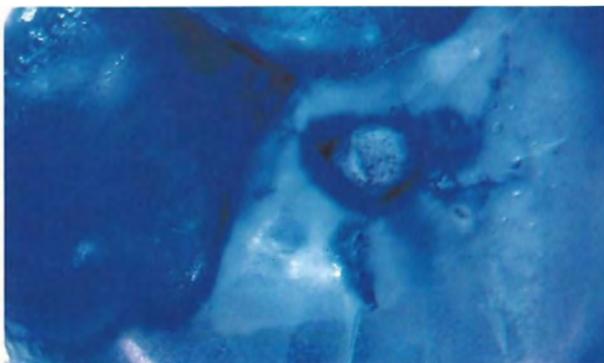


Figure 8. Diffusion-treated sapphire immersed in methylene iodide. Note the chip on the center right of the stone, which reveals the color of the untreated portion (both the blue color and the color in the chip area are much lighter than they would appear without immersion and under normal lighting conditions). Magnified 10×. Photomicrograph by John I. Koivula.

through 6 above, as well as a "bleeding" of color around pits and fractures (figure 9), as described by Crowningshield and Nassau (1981).

PROCESS 7: ADDING ASTERISM BY DIFFUSION

If the corundum does not contain any titanium oxide, or at least not enough to form good asterism, it is possible to diffuse some *into* the gemstone in the form of a thin layer at and just below the surface. This process was first described in a U.S. patent by Eversole and Burdick (1954), intended for the manufacture or improvement of synthetic Verneuil stars; a similar description appeared later in a patent by Carr and Nisevich (1975). Both patents were assigned to the Union Carbide (and Carbon) Corporation (Linde). Typically, to produce the desired effect, a slurry of aluminum titanate in water is painted onto the stone and then fired at about 1750°C for several days. The stone is cooled and a subsequent heat treatment, as in process 1, develops the asterism. The depth of penetration may be only one tenth of one millimeter.

Natural sapphires with added asterism, as well as those with added color from process 8, have been described by Crowningshield and Nassau (1981). The process appears to be applied primarily to fractured material that is unsuitable for fac-

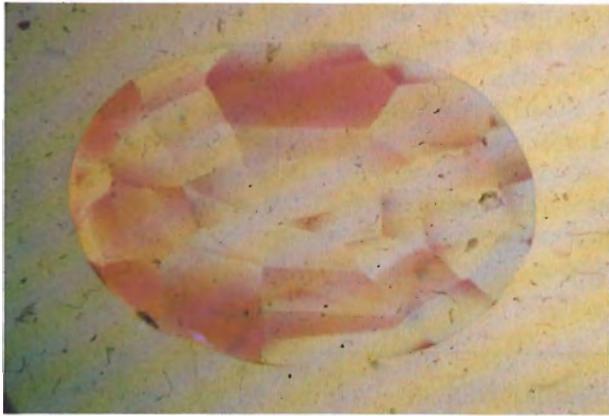


Figure 10. Immersion in methylene iodide reveals the localization and blotchiness of diffusion caused by the combination of uneven diffusion and heavy repolishing (which uncovered the color of the untreated portion) of an orange-red diffused sapphire. Magnified 8 \times . Photomicrograph by John I. Koivula.

eting; it can be recognized in stones by the unnaturally sharp stars caused by very fine rutile needles, by uneven color, by "bleeding" of the color at pits and fractures, and by other evidence of high-temperature treatment such as stress fractures and pockmarked surfaces.

PROCESS 8: ADDING BLUE BY DIFFUSION

If insufficient iron oxide or titanium oxide is present in a colorless, yellow, green, or pale blue sapphire, it is possible to add either or both of the missing ingredients by diffusion. A reducing atmosphere as in *process 3* is required, or a separate reductive heating step must follow oxidative diffusion. This type of diffusion is extremely slow, so that even with extended heating the penetration will be shallow. The result is a relatively thin skin of dark blue. This process was described in detail by Carr and Nisevich (Linde patent) in 1975 for the combination with *process 7*, and subsequently as a separate process (Carr and Nisevich, 1976, 1977). It appears to be in wide use (Crowningshield, 1980; Fryer, 1981), both on faceted stones and on cabochons. Identification includes immersion in methylene iodide as well as the other clues described above for *process 7*.

When Linde stopped producing synthetic gems about 1975, these U.S. patents were assigned to the Astrid Corporation Ltd. of Hong Kong, a firm set up to take over Linde's star corundum stock.

Accordingly, it would appear that any corundum diffusion treatment in this country (or the importation of such stones from abroad) could be performed legally only by Astrid or with their express permission.

PROCESS 9: ADDING COLORS OTHER THAN BLUE BY DIFFUSION

Just as diffusion of iron and titanium oxide can produce a blue skin, so can other color-causing impurities also be diffused, again as described by Carr and Nisevich (1975, 1976, 1977). Thus, the diffusion of chromium produces a red skin, nickel gives yellow, chromium plus nickel creates the pinkish orange "padparadscha," and so on; the colors that will be produced by the diffusion of different substances are well known from sapphire synthesis (Nassau, 1980a). Orange-red diffused stones (figure 10) were examined in detail by Crowningshield in 1979. There may be problems associated with oxidation/reduction conditions if variable valence ions such as iron are involved; the identifying characteristics are the same as those given for *processes 7* and *8*.

The colors produced by these diffusion processes are just as stable as the natural and synthetic colors produced by the same impurities. This contrasts with the yellow to orange color produced by irradiating sapphire, which is unstable and will fade on exposure to light.

COMBINATION TREATMENTS

As suggested above, several of these processes can be combined. Removal of silk and intensification of color can be achieved in a pale sapphire by heating the stone in a reducing atmosphere and then cooling it rapidly, in a combination of *processes 2* and *3*. The removal of silk will produce an improvement in color even in the absence of any other changes, since scattered white light no longer dilutes the color. Among the chemicals employed in this process as used on milky white to pale blue "geuda" Sri Lanka sapphires are a red liquid reported by Crowningshield (1980) and since shown to be mineral oil (its role is described under *process 3*), the soda (sodium [bi-]carbonate?) reported by Harder (1980) which is said to prevent cracking of the stone and possibly to remove some iron preferentially (?), and the "thick coating of local paste" used in oil, gas, or electric furnaces as mentioned by Gunaratne (1981).

Diffusion of iron and titanium oxides and a simultaneous reduction (as in *process 3*) can be performed, according to Carr and Nisevich (1975, 1976, 1977), by embedding pale or nonuniform star sapphire in a mixture of 0.25 weight percent ferric oxide and 13 weight percent titanium oxide, with the balance being aluminum oxide, and heating the material in a reducing atmosphere at 1750°C for 30 hours to produce a uniform-appearing dark blue sapphire; this is a combination of *processes 2, 3, and 8*. The dominant effect is, however, limited to a thin skin at the surface of the stone.

DISCUSSION AND SUMMARY

Silk, asterism, various colors, and even imperfections in ruby and sapphire can be intensified or diminished by appropriate heat and diffusion treatments, as summarized in table 1. One must sympathize with the gemologist in his attempt to establish whether any of these many treatment methods have been used on a given ruby or sapphire.

Processes 1 through 4 can intensify or remove silk, asterism, or the blue color of sapphire. These processes involve heating in oxidizing or reducing environments only and mimic processes that occur in nature. The development of potential asterism by heat treatment, for example, is successful only if this step was omitted in nature. It is this parallel behavior that renders ineffective most tests commonly used to establish whether a stone has been heat treated by man. Oughton (1971) cites one such test (of which he himself states that "the wisdom . . . is doubtful") in which the least valuable stone from a parcel is heated to observe the behavior. Unfortunately, even this rather risky procedure gives no definite answer in view of the many different types of heat treatment that could have been used previously, the analogous variety of ways in which the test could be performed, as well as the possibility of variation within the parcel. In the absence of reliable tests to identify such treated material, the report and disclosure situation is not clear-cut.

Processes 5 and 6 are used on synthetic material only, so the question of identification is most important but that of disclosure of treatment becomes irrelevant.

The diffusion *processes 7, 8 and 9* do not have a parallel in nature and their use can be identified.

Accordingly, it would seem that disclosure of color or stars synthetically enhanced by diffusion is essential.

Finally, it must again be emphasized that the reaction of a material to a given treatment method may produce a variety of results, depending on the exact composition of the stone as well as on its previous treatment history, both in nature and by man.

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