NOTES AND NEW TECHNIQUES

# FLUX-INDUCED FINGERPRINT PATTERNS IN SYNTHETIC RUBY: AN UPDATE

By K. Schmetzer and F.-J. Schupp

*Chatham, Knischka, and Lechleitner, as well as other manufacturers, are known to have treated Verneuil flame-fusion synthetic rubies by immersion in a flux melt to induce patterns like the "fingerprints" seen in some natural rubies. Some of these products are on the market and may require careful microscopic examination for identification. Also seen marketed as natural is a synthetic ruby of unknown manufacture with a distinctly different flux-induced pattern. This pattern—a continuous, three-dimensional, honeycomb-like cellular structure of flux-filled fractures—is easily recognizable with a gemological microscope.*

In the trade, we occasionally encounter synthetic rubies grown by the Verneuil flame-fusion method in which fingerprint-like patterns have been induced. Briefly, a "fingerprint" is a pattern of isolated dots and/or interconnected tubes that develops when a natural fluid or a synthetic flux is trapped by the healing of a fracture during growth. "Fingerprints" are induced in Verneuil synthetic corundum to imitate the fingerprint-like inclusions seen in natural rubies and to mask the curved growth striations that usually occur in flame-fusion synthetic rubies (Koivula, 1983).

In general, we do not know the names of the individuals and companies who commercially treat synthetic rubies by this process. Their products have appeared under trade names such as "Shinna," which we believe originated in Japan. However, we do know that three manufacturers familiar to gemologists—Chatham, Knischka, and Lechleitner—have treated Verneuil-grown synthetic rubies in this fashion. In personal communications since 1983, T. Chatham and P. O. Knischka have maintained that they have induced fingerprint-like inclusions in synthetic rubies primarily for growth studies rather than for commercial purposes. However, Lechleitner synthetic rubies with induced fingerprint patterns have been produced commercially and marketed in considerable quantities (Kane, 1985; Schmetzer, 1986a). In fact, samples from all three manufacturers have been encountered in the trade and could be submitted to a gemological laboratory for determination of origin. Other, unidentified products of similar or even identical growth and treatment methods undoubtedly exist.

We have a general idea of the methods by which these flame-fusion synthetic rubies are treated (Koivula, 1983; Kane, 1985; Schmetzer, 1986a and b, 1991), although experimental details such as the exact composition of the fluxes and the temperatures used are proprietary. The process

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*Figure 1. Induced fingerprint-like patterns of residual flux are seen here in a Verneuil-grown synthetic ruby treated by Chatham Created Gems. Photomicrograph by K. Schmetzer; immersion, magnified 40×.*

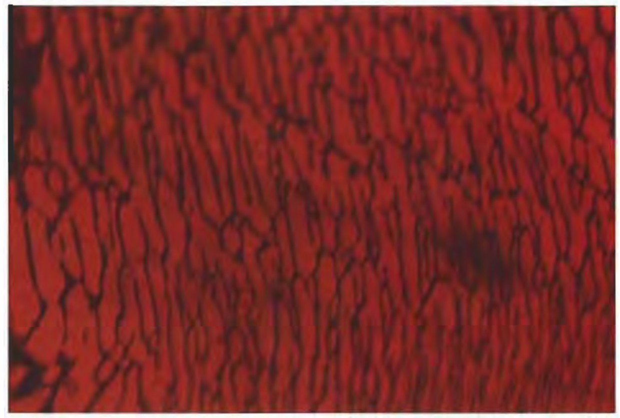


*Figure 2. Healing fractures are commonly seen in natural ruby, like this stone from Sri Lanka. Photomicrograph by K. Schmetzer; immersion, magnified 60×.*

usually begins with heat treatment, followed by rapid cooling by immersion in a liquid or melt (Koivula, 1983). This quenching process produces fractures and fissures within the synthetic ruby crystals, which are subsequently immersed for a time in a flux melt that typically contains dissolved aluminum oxide. The fractures become filled with flux and are partly healed by slow cooling of the flux during this last step, which causes the formation of "fingerprint" patterns of residual flux (figure 1). The result may somewhat resemble the healing fractures found in natural rubies (figure 2). Note that it has not been proved experimentally whether any of the commercially available Chatham, Knischka, or Lechleitner Verneuil-grown synthetic rubies with induced flux fingerprints were submitted to the initial heating and rapid cooling steps before immersion in flux. In at least some of these treated synthetic rubies, the "induced fingerprints" may actually be simple healing structures in fissure-bearing Verneuil material that was never submitted to quench crackling.

Since 1989, the authors have also encountered about 60 synthetic rubies, usually set in mountings, that revealed a flux-induced pattern distinctly different from the flux-induced "fingerprints" typically seen in the Verneuil-grown synthetic rubies described above (figure 3). Some were identified from the stocks of several dealers in Germany, and about 20 others were submitted to the authors for gemological testing. Many were either labeled or represented as natural rubies from Afghanistan. Two such stones (see, e.g., figure 4) were purchased by one of the authors for more detailed study, including spectroscopy and chemistry.

This article reviews what is known about those synthetic rubies with flux-induced fingerprint-like inclusions that are typically seen on the market, and presents the results of our examination of the distinctly new flux-treated synthetic rubies.

*Figure 3. In several flux-treated synthetic rubies seen in the trade over the last few years, the healing fractures have a distinctive continuous, three-dimensional, honeycomb-like cellular structure. Photomicrograph by K. Schmetzer; transmitted light, magnified 40×.*

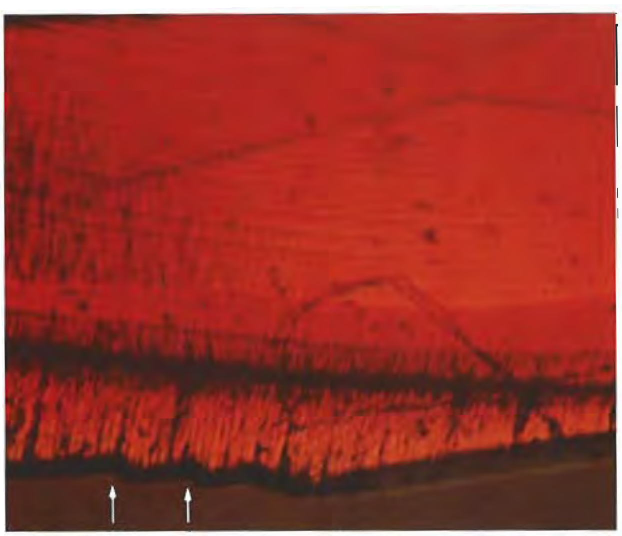
## TYPICAL SYNTHETIC RUBIES WITH FLUX-INDUCED FINGERPRINT PATTERNS

Whether or not heat treatment is the first step, the process of inducing "fingerprints" usually involves placing small, irregularly shaped or preformed samples—or even complete boules—of Verneuil synthetic ruby in an aluminum oxide-bearing flux melt for days or weeks. This results in the formation of a layer of flux-grown synthetic ruby on the Verneuil

*Figure 4. Flux-induced inclusions like those shown in figure 3 were seen throughout this 9.93-ct sample (approximately 10.3 × 14.8 mm) of a new type of treated synthetic ruby. Photo © GIA and Tino Hammid.*

"seed". This skin of flux-grown synthetic ruby often contains parallel growth lines. In some cases, there occur distinct crystal faces that are typical of the flux used for growth (figure 5). After faceting, synthetic rubies treated by this process may actually retain some of the flux-grown synthetic ruby skin over the Verneuil core; more commonly, cutting and polishing removes the flux overgrowth, so that only the Verneuil seed remains.

*Figure 5. A curved line marks the boundary between the Knischka Verneuil-grown synthetic ruby "seed" and the flux-grown synthetic ruby skin. Curved striae are visible in the core, and the skin reveals oscillating dipyramidal faces n(22$\bar{4}$3) due to a tungsten-bearing flux. Photomicrograph by K. Schmetzer; immersion, magnified 60×.*



In samples that retain the flux-grown synthetic ruby skin after cutting, a distinct boundary may still be seen between the Verneuil portion and the flux-grown skin, and may even extend to the surface of the polished stone (figure 6). The flux-grown layer may contain inclusions of relatively coarse residual flux material (figure 7). In some specimens, magnification reveals small, doubly refractive crystals confined to the boundary between the Verneuil and flux-grown components. The fact that the refractive indices of these included crystals approximate those of the host material indicates that they are synthetic corundum crystals

*Figure 6. On the surface of this faceted Lechleitner synthetic ruby, the boundaries between the Verneuil-grown "seed" (center) and the partially removed flux-grown skin are readily apparent. Photomicrograph by K. Schmetzer; immersion, magnified 50×.*

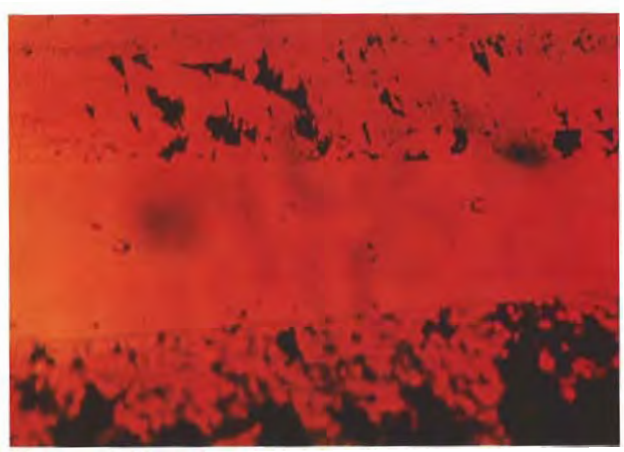


*Figure 7. Note the coarseness of the residual flux in this overgrowth on a Lechleitner synthetic ruby. Photomicrograph by K. Schmetzer; immersion, magnified 100×.*

that are oriented differently from the host material.

Whether or not the flux-grown layer of synthetic ruby remains after faceting, the Verneuil-grown seed material generally contains a variety of flux "fingerprint" inclusions that often resemble the patterns found in partly healed fractures in natural ruby (compare figures 1 and 2). When these occur, other diagnostic features may be needed to determine the natural or synthetic origin of a ruby. In most cases, Verneuil-grown synthetic ruby contains curved growth striations (figure 8), but these are sometimes difficult to resolve; occasionally, gas bubbles confined to curved growth layers provide conclusive evidence of synthesis (figure 9).

If magnification does not reveal any diagnostic features, trace-element analysis may provide conclusive results (Schmetzer, 1986a and b). Treated Chatham and Lechleitner synthetic rubies with Verneuil seeds contain traces of molybdenum and/or lead (from the flux) that can be detected by X-ray fluorescence spectroscopy. Similar material produced by Knischka is most often characterized by traces of tungsten and/or lead. Mo, Pb, and W are also found in treated flame-fusion synthetic rubies from unknown producers.

## A NEW TYPE OF TREATED SYNTHETIC RUBY

Over the course of the last five years, the authors have observed distinctly different flux-induced inclusions in approximately 60 synthetic rubies that had been represented as natural in the gem trade (again, see figure 4). When viewed with magnification in reflected light, each stone revealed a net-like pattern of whitish to colorless material that reached the surfaces of these faceted samples (figure 10). In transmitted light, it can be seen that the included material forms a thin, continuous, three-dimensional, honeycomb-like cellular structure (again, see figure 3).

To characterize these new treated synthetic rubies, we tested 20 samples by standard gemological methods using a binocular gemological microscope, a standard gemological refractometer, and hydrostatic weighing. We then submitted two of these samples (1.99 ct and the 9.93 ct—shown in figure 4—both the intense red common to synthetic rubies) to energy-dispersive spectroscopy on a scanning electron microscope (SEM-EDS) for chemical analysis of the inclusions, and to energy-dispersive X-ray fluorescence (EDXRF) for qualitative chemical analysis of the whole sample.

*Figure 8. In this Lechleitner flame-fusion synthetic ruby, both curved striae and the "fingerprint" patterns of residual flux are readily visible. Photomicrograph by K. Schmetzer; immersion, magnified 85×.*

*Figure 9. Gas bubbles follow the curved growth layers in this Chatham flux-treated flame-fusion synthetic ruby "seed," thus proving that it is a flame-fusion synthetic. Photomicrograph by K. Schmetzer; immersion, magnified 25×.*

**Gemological Properties.** Refractive indices, specific gravities, and reactions to long- and short-wave ultraviolet radiation for the study samples (as well as for the other samples of this material previously encountered) are within the overlapping ranges for natural and synthetic rubies. We recorded refractive indices of $n_o$=1.770–1.771, $n_e$=1.762–1.763, with a birefringence of 0.008. Specific gravity was found to range from 3.99 to 4.01, and the stones fluoresced an intense orange-red to both long- and short-wave ultraviolet radiation. We noted that the absorption spectra of the two samples are typical for low-iron rubies—that is, with chromium-related features and without iron-related absorption bands. This is normal for most synthetic rubies.

**Microscopy.** As noted above, a net-like pattern of whitish to colorless material was observed with reflected light (again, see figure 10); in transmitted light, the included material appeared to form a thin, continuous, three-dimensional, honeycomb-like structure (again, see figure 3).

In one small area of the 1.99-ct sample, we observed a discontinuous pattern of included material that visually resembled the fingerprint pattern of a healing fracture in natural ruby. This feature is probably due to residual melt that was trapped during the primary synthetic growth process.

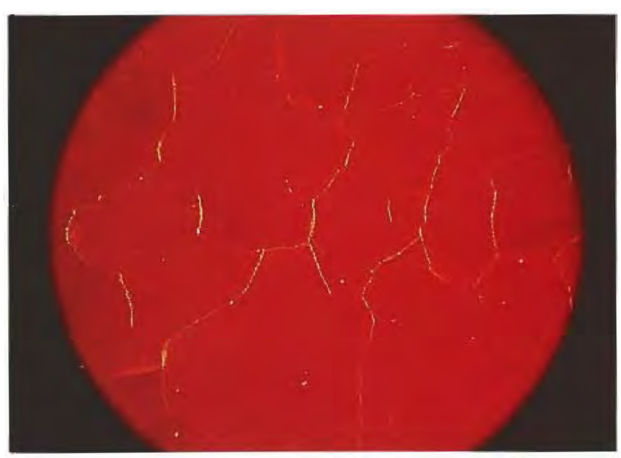
After intense examination with the microscope, we resolved extremely weak curved growth striae in a zone confined to the girdle area of the 9.93-ct sample. Because these striations are so weak, we cannot state conclusively that the original material submitted to flux treatment was Verneuil-grown synthetic ruby. It might be an example of the more expensive Czochralski-grown material that has been immersed in a flux melt.

**Chemistry.** SEM-EDS analysis of the colorless to white material that forms the cellular patterns in both samples revealed the presence of calcium and lead, and the absence of aluminum. One sample showed the presence of other impurity elements in some areas exposed to the surface, but these are probably residuals of the cutting and polishing process. EDXRF analysis of both samples revealed Ca and Pb from the included material as well as distinct amounts of chromium and small amounts of iron. The amounts of Ca and Pb can be related to the flux in which these synthetic rubies were treated. $PbF_2$ and/or PbO are the most commonly known components of fluxes (Schmetzer, 1986a and b), and $CaF_2$ has been used in the flux growth of ruby since the early work of Fremy and Verneuil in the late 19th century (Elwell and Scheel, 1975). Presumably, these synthetic rubies were treated by immersion in a flux composed of a mixture of $PbF_2$ and $CaF_2$ to induce the three-dimensional cellular pattern we observed.

## COMPARISON OF GROWTH CONDITIONS

All previously reported Verneuil synthetic rubies with flux-induced fingerprint patterns appeared to

*Figure 10. The flux-filled fissures in this new type of treated synthetic ruby form a distinctive cellular pattern. Photomicrograph by K. Schmetzer; reflected light, magnified 32×.*



have passed through a step in which they were immersed in a flux containing dissolved aluminum oxide (Koivula, 1983; Schmetzer, 1986a and b). It is less certain whether all were also subjected to heat and subsequent rapid cooling (quench crackling) prior to immersion in the flux. However, the observable differences in the residual flux that is trapped in the healing fractures can most probably be attributed to differences in flux-melt composition and/or differences in temperature, time, and/or temperature cycling of the treatment.

In contrast to the discontinuous patterns of Mo-, Pb-, and tungsten-containing inclusions that are typical of flux-treated Verneuil synthetic rubies, the fissures in the new treated synthetic rubies described here are continuously filled with a flux material containing lead and calcium. Apparently, the flux melt used in the processing did not contain aluminum oxide, which usually promotes the healing process. This missing component may be one reason why the typical flux-induced fingerprint-like healing patterns (which resemble the partly healed "feathers" in natural ruby) did not form. Another possibility is that the seeds were not immersed in the melt long enough to cause partial healing of fissures or cracks. It is also possible that this represents a new treatment process, unlike any described to date.

## CONCLUSION

Verneuil-grown synthetic rubies with flux-induced fingerprint-like inclusions continue to appear on the gem market, often misrepresented as natural rubies. In recent years, they have been joined by treated synthetic rubies with a distinctly different inclusion pattern—a continuous, three-dimensional, honeycomb-like cellular structure of fractures filled with flux material. Although the treatment process normally tends to obscure evidence of curved growth striae in the host synthetic, the distinctive inclusion pattern generally does not resemble inclusions in natural rubies or the fingerprint-like patterns previously induced in synthetic rubies. Therefore, this new type of treated synthetic ruby can be readily identified with a microscope or even a hand lens.

## REFERENCES


Elwell D., Scheel H.-J. (1975) *Crystal Growth from High-Temperature Solutions.* Academic Press, London—New York—San Francisco.

Kane R.E. (1985) A preliminary report on the new Lechleitner synthetic ruby and synthetic blue sapphire. *Gems & Gemology,* Vol. 21, No. 1, pp. 35–39.

Koivula J.I. (1983) Induced fingerprints. *Gems & Gemology,* Vol. 19, No. 4, pp. 220–227.

Schmetzer K. (1986a) *Natürliche und synthetische Rubine—Eigenschaften und Bestimmung.* Schweitzerbart, Stuttgart.

Schmetzer K. (1986b) Production techniques of commercially available gem rubies. *Australian Gemmologist,* Vol. 16, No. 3, pp. 95–100.

Schmetzer K. (1991) Lechleitner synthetic emeralds, rubies, and sapphires. *Australian Gemmologist,* Vol. 17, No. 12, pp. 516–523.