

The colour of Igemerald: I.G. Farbenindustrie flux-grown synthetic emerald

Dr Karl Schmetzer¹ and Dr Lore Kiefert²

1. Marbacher Strasse 22b, D-85238 Petershausen, Germany

2. SSEF Swiss Gemmological Institute, CH-4001 Basel, Switzerland

ABSTRACT: Seven samples of I.G. Farbenindustrie flux-grown synthetic emerald were examined. The synthetic emeralds were grown between 1929 and 1942 at Bitterfeld, Germany, in a lithium molybdate solvent. Gemmological, chemical and spectroscopic properties are given. The colour of the samples is caused by minor amounts of chromium and nickel and, thus, the secret ingredient mentioned by Espig (1960) is identified as a nickel-bearing compound.

Introduction

Historical background

The first emerald synthesis which produced facetable crystals above one centimetre in size was performed by I.G. Farbenindustrie (literally I.G. Dye Trust) at Bitterfeld, Germany. Facetable material had been grown since 1929 (Schiebold, 1935; Espig, 1960), but samples were released to the public only after the first announcement to the press in February 1935 (Anonymous, 1935). Gemmological descriptions of this synthetic emerald were published in the same year (Eppler, 1935; Jaeger and Espig, 1935; Anderson, 1935) and mineralogical investigations of the synthetic emerald crystals, e.g. by X-ray powder diffraction, were also performed (Schiebold, 1935; Espig, 1935; Anderson, 1935). Gemmological properties of these synthetic emeralds were examined later by various authors and their results were summarized and compared with the features of the first synthetic emeralds produced in the United States by Chatham in different articles in the '50s (e.g.

Webster, 1952, 1955, 1958; Wiegand, 1952; Gübelin 1953; Eppler, 1958a,b). Regarding the growth technology used, there was only speculation until three more or less detailed papers of one of the inventors of the I.G. Farbenindustrie process were published (Espig, 1960, 1961, 1962). Before this information was available, the synthetic emeralds were considered as hydrothermally grown (Webster, 1955, 1958; Wilke 1956).

Growth technology

Espig reported that the first attempts to grow synthetic emeralds at Bitterfeld started in 1911 and that he was involved in these experiments from 1924. Crystal growth in the final stage of the technical development was performed in platinum crucibles with lithium molybdate as the solvent. A schematic drawing of the growth conditions (Figure 1) which followed closely the descriptions of Espig was published by Recker (1973). A nutrient of BeO and Al₂O₃ with lithium chromate as colour-causing dopant was placed at the bottom of a

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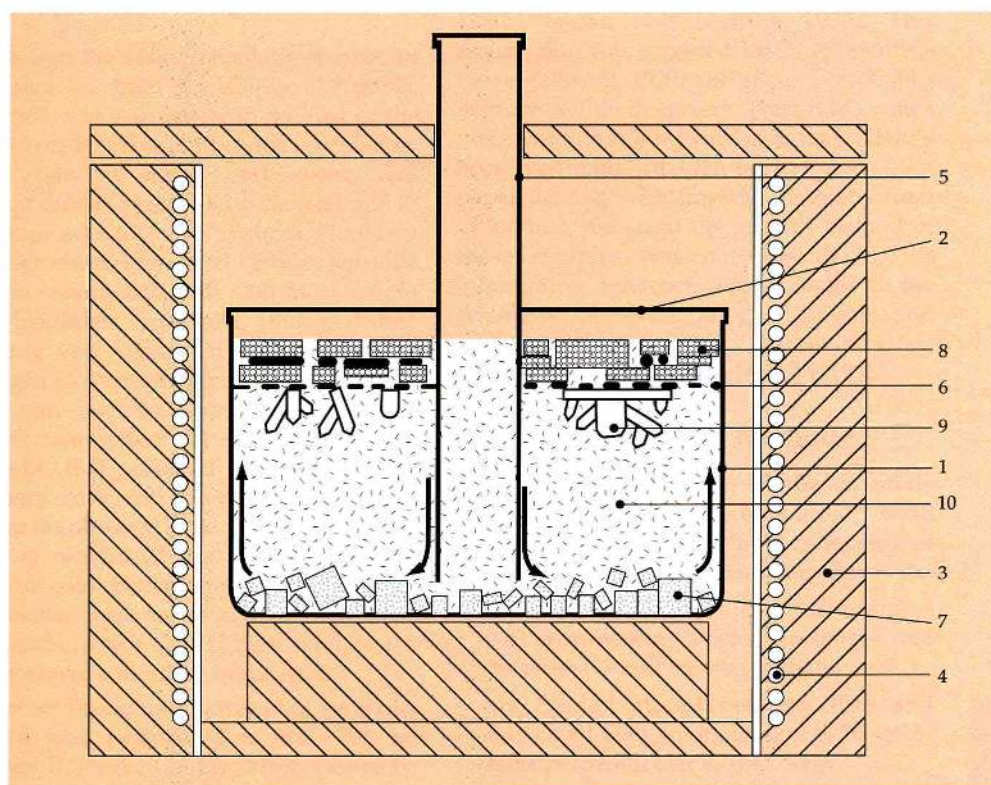


Figure 1: Schematic diagram of the process applied to flux growth of synthetic emerald by I.G. Farbenindustrie at Bitterfeld, Germany, from 1929 to 1942; Key: 1 = platinum crucible, 2 = platinum lid, 3 = insulation, 4 = heating system, 5 = central platinum tube for the addition of material to the nutrient, 6 = baffle, 7 = nutrient, 8 = quartz plates, 9 = growing crystals, 10 = lithium molybdate solvent (adapted from Recker, 1973).

platinum crucible. Subsequently, the crucible was filled with lithium molybdate and emerald seeds were positioned below a platinum baffle. Above this baffle, quartz plates of 8 to 10 mm in thickness were arranged. These quartz plates floated on top of the melt after heating the furnace to a constant temperature of about 800°C. This temperature was kept at a constant level over a growth period of 20 days, but new nutrient was added every second day by means of a central platinum tube to the material at the bottom of the crucible. After each growth period, the synthetic emerald crystals were examined and extremely impure layers of synthetic emerald material were removed. The largest crystals of prismatic habit which were obtained in about 18 growth periods during one year measured

2 or 3 cm in length (Espig, 1960, 1961, 1962). Faceted stones up to 1 ct in weight measuring 5 to 6 mm were cut from the rough.

Emeralds were produced at Bitterfeld from 1929 until 1942 in 12 furnaces (Espig, 1960), but due to the market situation for natural emeralds and the relatively high cost of crystal growth, there was no large-scale industrial production of synthetic emeralds at the I.G. Farbenindustrie (Anonymous, 1952; Wiegand, 1952). As a result, the synthetic emeralds were never sold commercially on the free market. The material was named Igmerald, standing for I.G. emerald, and was used for public relations purposes of the I.G. Farbenindustrie. In 1945, the complete platinum growth facilities were lost and production was not resumed after the war.

Colour of Igmerald

Although the basic technology of emerald production has been available to the public since 1960, a few sentences in the first of the three papers by Espig led to some speculation: 'Zwar steht in allen Lehrbüchern, daß Smaragd durch Chromoxyd gefärbt ist und in der Hauptsache trifft dies auch zu. Nachdem wir aber zum erstenmal große Kristalle erhielten, zeigte sich, daß Chrom allein ein kaltes bläuliches Grün gibt, und es waren Hunderte von Versuchen erforderlich, um diejenigen Stoffe ausfindig zu machen, die die Farbe zum warmen Grün einer Wiese im Frühling nuancierten.' [It is mentioned in all textbooks that emerald is coloured by chromium oxide, and this is generally correct. But after we obtained large crystals for the first time, we recognized that chromium alone causes a cold bluish green. Hundreds of experiments were necessary to find those compounds, which shifted the colour to the warm green of a meadow in spring.]

Another flux growth process of synthetic emerald was performed in the '20s by Professor R. Nacken in Frankfurt, Germany, using a molybdenum- and vanadium-bearing flux. Crystals up to 5 mm in size were described by Nassau (1978) and the growth technique was elucidated using Nacken synthetic emeralds from private and public collections, because no publication is available from Nacken himself describing the growth process (see also Webster, 1955, 1958). Nacken synthetic emeralds were also regarded as hydrothermally-grown synthetic emeralds until the chemical composition of a trapped molybdenum- and vanadium-bearing residual flux was established and the absence of water was confirmed experimentally (Nassau, 1978).

Knowing of vanadium as a colour-causing trace element in natural emeralds from certain sources such as Colombia, Nassau mentioned a possible co-operation of I.G. Farbenindustrie with Nacken and a possible use of vanadium as a colour-causing dopant in the I.G. Farbenindustrie growth process of Igmerald. He suggested that the secret ingredient of Jaeger and Espig may have been vanadium (Nassau, 1976, 1978,

1980; Nassau and Nassau, 1980). This assumption was accepted by other scientists (see e.g. Elwell, 1979) and seems reasonable, because synthetic green 'emeralds' which were coloured by vanadium had already been mentioned in 1926 by Bernauer (in a paper dealing with trapiche emeralds from Colombia), although the growth method of these samples was not described. This information, however, was available to the scientists involved in the growth and examination of I.G. Farbenindustrie synthetic emeralds (see Schiebold, 1935).

Materials and methods

Seven Igmeralds (I.G. Farbenindustrie flux-grown synthetic emeralds) were available from the research collection of E. Gübelin, Lucerne, Switzerland (Figure 2):

- one prismatic, slightly distorted crystal of 3.81 ct measuring 9.5 mm in length and between 6.0 and 6.8 mm in diameter;
- six faceted stones between 0.48 and 0.12 ct, all with an orientation of the table facet perpendicular to the c-axis.

All seven samples were tested by standard gemmological methods for optical properties, fluorescence, specific gravity and microscopic features. Inclusions were studied microscopically and identified by Raman spectroscopy with a Renishaw Raman Microscope. For a chemical characterization of the synthetic

Figure 2: Rough and faceted I.G. Farbenindustrie synthetic emeralds (left) compared to two Chatham synthetic emeralds (right). The rough crystal is 9.5 mm long (photo by H.A. Hänni).



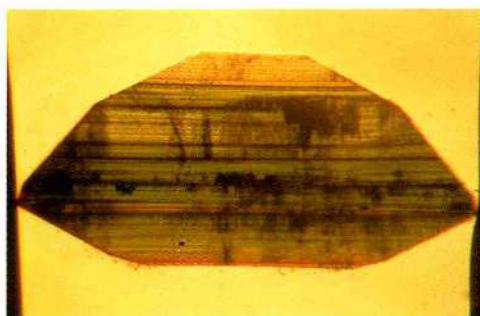


Figure 3: Growth and colour zoning parallel to the basal pinacoid in I.G. Farbenindustrie synthetic emerald. View perpendicular to the *c*-axis, immersion, 35x

emeralds, the rough crystal and the two larger faceted samples of 0.48 and 0.26 ct were submitted to energy-dispersive X-ray fluorescence analysis (EDXRF) using a Spectrace 5000 Tracor X-ray fluorescence spectrometer with a Tracor Northern Spectrace TX-6100 software system. Spectroscopic data in the visible and ultraviolet range for all seven samples were recorded with a Leitz-Unicam SP 800 spectrophotometer.

Results

Gemmological properties

Gemmological properties, e.g. refractive indices, specific gravity, and fluorescence data (Table I), are comparable to the properties

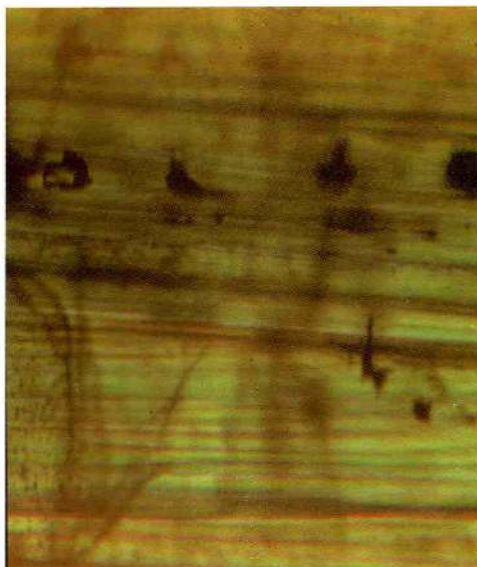


Figure 4: Growth and colour zoning approximately parallel to the basal pinacoid in I.G. Farbenindustrie synthetic emerald; some of the growth planes are not exactly parallel to each other. View perpendicular to the *c*-axis, immersion, 80x

of flux-grown synthetic emeralds of different producers, especially with those of synthetic emeralds which were grown in a solvent of lithium molybdate (see Flanigen *et al.*, 1967).

All samples revealed a characteristic growth zoning consisting of alternating

Table I: Properties of chromium- and nickel-bearing synthetic emeralds

	Chatham	Igmerald	Gilson*
Colour	bluish-green	grass-green	yellowish-green
Pleochroism parallel <i>c</i>	blue-green	bluish-green	intense green
perpendicular <i>c</i>	yellowish-green	yellow-green	yellow-green
Refractive indices n_o	1.564	1.563–1.566	1.563
n_e	1.560	1.559–1.561	1.559
Birefringence	0.004	0.004–0.005	0.004
Specific gravity	2.65	2.65–2.66	2.65
UV fluorescence long-wave	moderate red	moderate red	light yellowish
short-wave	light red	light red	light yellowish
Significant minor elements	Cr	Cr>Ni>>Fe	Cr≈Ni>(V,Fe,Cu)
Significant absorption bands	Cr	Cr>Ni	Cr≈Ni

* Schmetzer, 1989



Figure 5: Inclusions of prismatic beryl crystals with orientations different from that of the host synthetic emerald; inclusions of opaque residues of the solvent have been trapped in the prismatic beryl. Immersion, (a) in plane-polarized light, 100x, and (b) in cross-polarized light, 100x.

green, yellowish-green and sometimes even greenish-yellow layers more or less parallel to the basal pinacoid (Figure 3). Some of these growth boundaries were slightly inclined to each other, i.e. not all growth lines were exactly parallel, thus representing slightly uneven undulating planes within the beryl crystals (Figure 4). The rough crystal showed also small areas with growth zoning parallel to the hexagonal prism faces (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0), but these thin outer layers were completely removed by cutting in all six faceted samples.

Two types of birefringent crystals were present as inclusions: the first type consisted of prismatic, elongated crystals which contained numerous small opaque inclusions, most probably of residual flux. The refractive index of these prismatic crystals was close or identical to that of

the host beryl and, thus, the single prisms were sometimes difficult to observe. Under crossed polarizers, however, these prisms always became visible due to their interference colours (Figure 5). Consequently, these inclusions were identified as beryl with an orientation different from that of the host.

The second type of birefringent inclusions consisted of colourless crystals, mostly with somewhat rounded edges with refractive indices distinctly above that of the host. These inclusions were identified by micro Raman spectroscopy as phenakite, which is a common inclusion in flux-grown synthetic emeralds from different producers (Delé-Dubois *et al.*, 1986a, b).

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Figure 6: Cellular pattern of residual flux in I.G. Farbenindustrie synthetic emerald. View parallel to the c-axis, immersion, 60x.

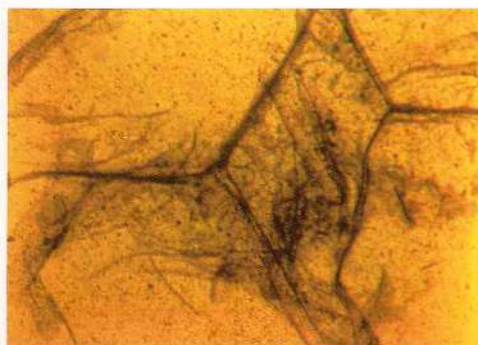
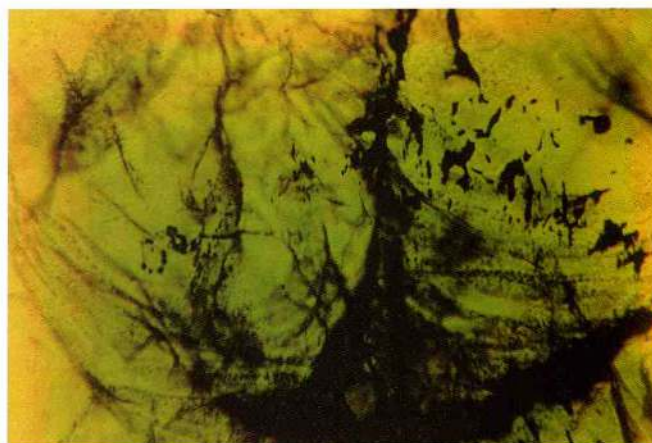


Figure 7: Residual flux trapped in I.G. Farbenindustrie synthetic emerald. Immersion, 60x.



Residual flux was present in various forms in all seven I.G. Farbenindustrie synthetic emeralds examined. In views parallel to the *c*-axis, a cellular pattern of flux particles was sometimes visible (Figure 6). In other directions of view, the wispy veils typical for flux-grown synthetic emeralds were commonly observed (Figure 7).

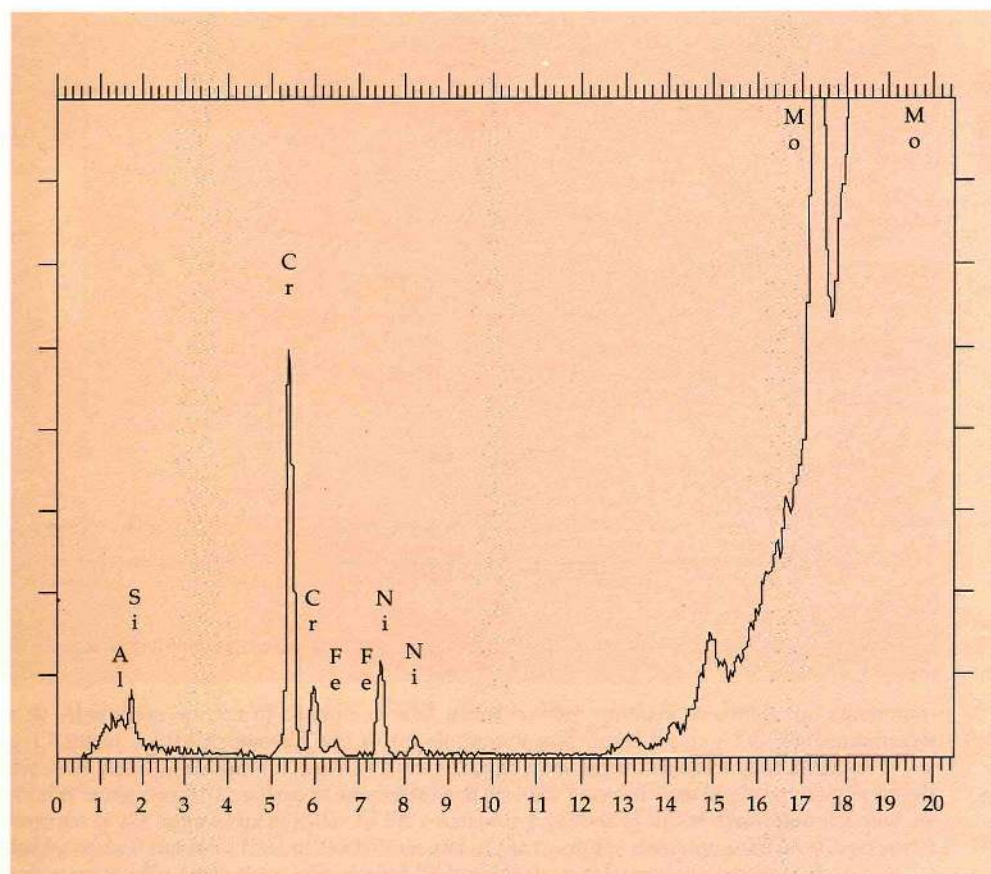
Occasionally, residual flux was also found in channels parallel to the *c*-axis. Raman spectroscopy of the compounds trapped in channels parallel to *c* indicates that at least three solid phases are present. The spectra are consistent with the Raman spectra of different polymolybdate molecules in solutions (Johansson *et al.*, 1979; Murata and Ikeda, 1983) and with the spectrum of residual polymolybdate fluxes in different

flux-grown emeralds (Delé-Dubois *et al.*, 1986a, b). In addition, the strongest Raman lines of orthorhombic molybdenum trioxide (Krasser, 1969; Py *et al.*, 1977; Delé-Dubois *et al.*, 1986a, b) were also observed.

Chemical and spectroscopic properties

The rough crystal and the two faceted samples which were examined by energy dispersive X-ray fluorescence revealed characteristic EDXRF spectra indicating the presence of molybdenum (from residual flux material), distinct amounts of chromium and nickel, and traces of iron (Figure 8). In all samples tested the relative abundances were $\text{Cr} > \text{Ni} \gg \text{Fe}$, but the characteristic emission lines of vanadium were not found.

Figure 8: EDXRF spectrum of a faceted I.G. Farbenindustrie synthetic emerald showing distinct amounts of Cr and Ni (chromophores) and Mo (from the flux).



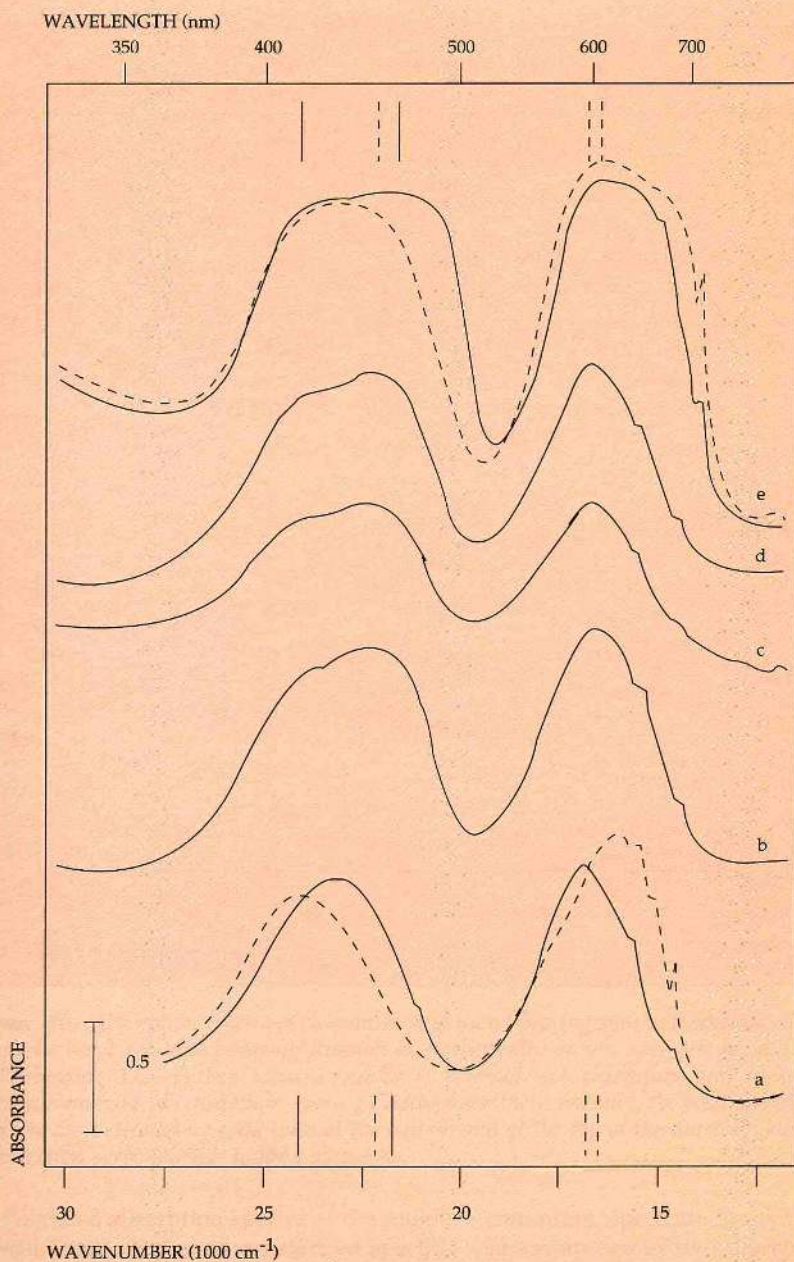


Figure 9: Absorption spectra of chromium- and nickel-bearing synthetic emeralds: (a) chromium-bearing Chatham synthetic emerald, (b) to (e) chromium and nickel-bearing I.G. Farbenindustrie synthetic emeralds; spectra (b), (c), and (d) were recorded from faceted samples with direction of the beam parallel to the c-axis, the polarized spectra (a) and (e) were recorded from faceted or rough crystals with direction of the beam perpendicular to the c-axis; the positions of nickel absorption maxima are indicated by dashed and solid lines at the bottom and at the top of the drawing; solid lines represent a polarization perpendicular to the c-axis, dashed lines represent a polarization parallel to the c-axis.

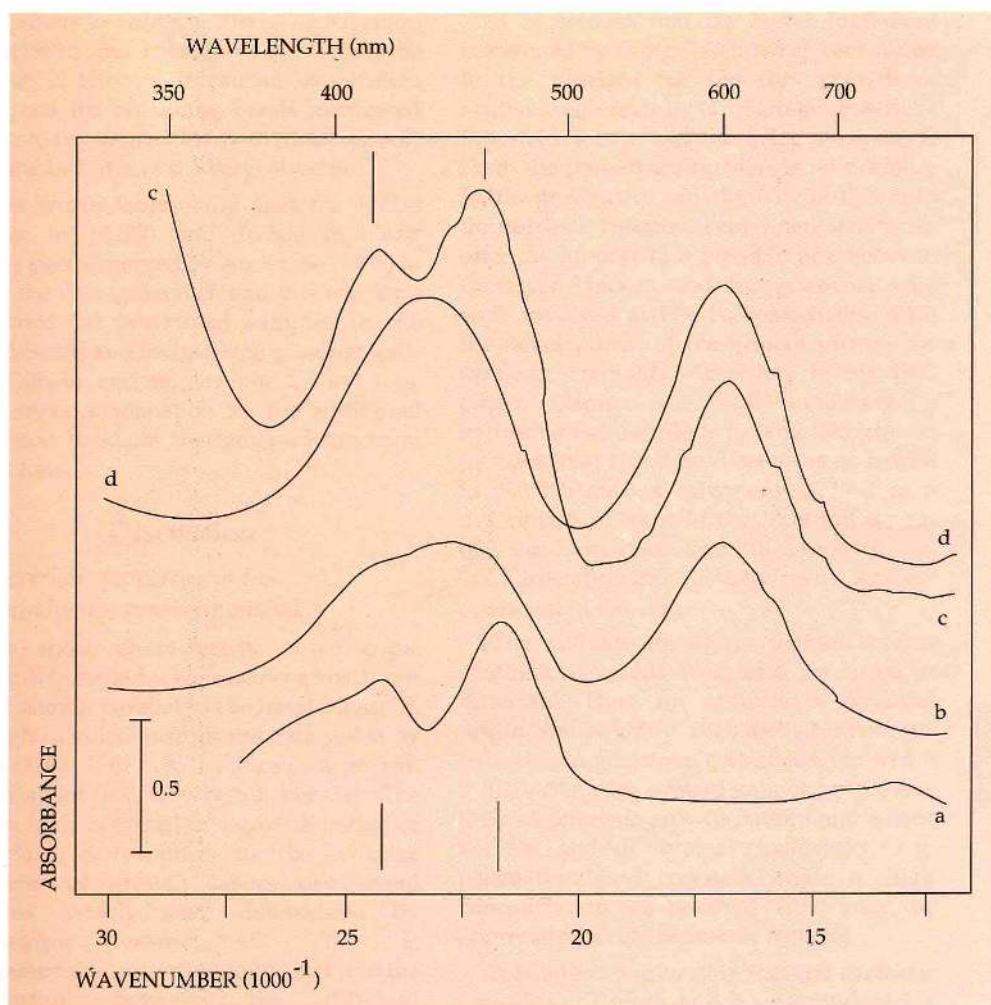


Figure 10: Absorption spectra of chromium- and nickel-bearing synthetic emeralds and nickel-bearing synthetic beryl: (a) nickel-bearing Russian hydrothermally-grown synthetic beryl, (b) chromium and nickel-bearing I.G. Farbenindustrie synthetic emerald, (c) chromium and nickel-bearing Gilson synthetic emerald, (d) chromium-bearing Chatham synthetic emerald; the positions of nickel absorption maxima are indicated by solid lines at the bottom and at the top of the drawing; all spectra represent polarization perpendicular to the *c*-axis.

Polarized absorption spectra of the rough crystal (Figure 9e) and non-polarized spectra of all six faceted samples (Figure 9b to d) where the incident beam was parallel to the *c*-axis, i.e. representing a spectrum with polarization perpendicular to *c*, consisted of the well-known absorption spectrum of chromium in beryl (see Figure 9a), superimposed by a series of nickel absorption bands. In particular, the

chromium spectrum perpendicular to *c* is superimposed by two absorption bands with maxima at 21 700 and 24 200 cm^{-1} (Figure 10) and the chromium spectrum parallel to *c* is superimposed by a doublet at 16 500 and 16 800 cm^{-1} and by an absorption band at 22 100 cm^{-1} . According to the examination of nickel-bearing hydrothermally-grown synthetic beryl and the assignments of the observed absorption bands to Ni^{2+} and Ni^{3+}

in the papers by Solntsev (1981a, b); Klyakhin *et al.*, (1981); and Lebedev *et al.*, (1986), the band at $22\,100\text{ cm}^{-1}$ is caused by bivalent nickel and the remaining bands mentioned are due to trivalent nickel, both replacing Al^{3+} in octahedral sites of the beryl structure.

It is worth mentioning that the nickel doublet at $16\,500$ and $16\,800\text{ cm}^{-1}$ had already been observed by Anderson (1935) in one of the first Igmeralds, and this was later confirmed for additional samples in the United States and Switzerland (Anonymous, 1937; Gübelin and Shipley, 1941). There was, however, no explanation for the additional absorption bands in the Igmerald spectrum at that time.

Discussion

Characteristic properties of I.G.

Farbenindustrie synthetic emeralds

The most characteristic microscopic feature of Igmerald is the distinct growth and colour zoning parallel to the basal pinacoid. A rough calculation from the data given by Espig (1960, 1961, 1962) indicates a growth rate of about 0.06 to 0.09 mm per day. The growth layer obtained in a growth period of two days corresponds to the average thickness of growth layers in faceted samples, which were determined by microscopic examination. This is understandable according to the fact that the equilibrium between the different components of beryl in the solvent was abruptly changed every second day by the addition of new material to the nutrient at the bottom of the crucible. Obviously, there were different periods of growth and even dissolution (see Espig, 1962) within these growth cycles, and these caused somewhat uneven undulating surfaces on different parts of the growth layers.

The inclusions of small prismatic beryl crystals with a high concentration of trapped opaque flux material is also characteristic for Igmerald, but this feature was only observed in some of the samples. Inclusions of phenakite and various forms of trapped flux are common in flux-grown synthetic emeralds from various producers.

It is evident that the secret ingredient mentioned by Espig (1960) which was added to the nutrient for the flux growth of synthetic emeralds by I.G. Farbenindustrie at Bitterfeld was a nickel-bearing compound. From the present study, there is no evidence for the presence of vanadium in the flux or in the nutrient. Thus, our experimental data can offer no support to a possible link between Professor Nacken and the scientists who were involved at I.G. Farbenindustrie with the development of the growth process for synthetic emeralds. According to his 1962 paper, Espig was still assuming a hydrothermal technique for emerald growth by Nacken at that time. There was no reason to publish such a statement in 1962 in a description of most of the technical details of the emerald growth process by I.G. Farbenindustrie, if there really was co-operation in the '20s.

The authors are aware that nickel-free synthetic emeralds were also produced at Bitterfeld. Thus, for samples of doubtful origin or possibly mislabelled synthetic emeralds in gemstone collections, for which a distinct nickel content cannot be proven, the characteristic growth pattern and colour zoning and/or typical inclusions, e.g. prismatic beryl crystals with a high concentration of residual flux, may be appreciated as characteristic features.

It is interesting to note that the synthetic emeralds of Zerfass, which were produced at Idar-Oberstein from 1963 (Eppler, 1964) by one of Espig's former co-workers with knowledge of the I.G. Farbenindustrie process (Nassau, 1976, 1980), were coloured only by chromium and did not contain nickel. Based on investigations of several samples of Zerfass synthetic emeralds by the present authors using absorption spectroscopy and X-ray fluorescence analysis, the emeralds examined display a normal chromium absorption spectrum and contain among the minor elements only molybdenum (from the flux) and chromium.

Colour of nickel-bearing synthetic emeralds

In general, distinct amounts of nickel are present in addition to chromium, iron and

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Colour of nickel-bearing synthetic emeralds

In general, distinct amounts of nickel are present in addition to chromium, iron and



Figure 11: Chromium- and nickel-bearing I.G. Farbenindustrie synthetic emerald (left) and chromium-bearing Chatham synthetic emerald (right). The right-hand sample measures 9 x 7.3 mm (photo by H.A. Hänni)

copper in both types of Russian hydrothermally-grown synthetic emeralds which are produced commercially (Schmetzer, 1988, 1996; Koivula *et al.*, 1996). These crystals are grown in autoclaves without precious metal liners, a technique which was also proven for samples of Lechleitner hydrothermal fully synthetic emeralds (Schmetzer, 1990). These samples also contained distinct amounts of chromium, iron, nickel and copper as colour-causing trace elements. The colour of all these hydrothermally-grown synthetic emeralds is a complex function of the relative concentrations of all four transition metals.

Traces of 0.04 wt.% NiO were analyzed by Schrader (1983) in one sample of Inamori flux-grown synthetic emerald, but according to the high chromium content of this stone, an influence of nickel on the colour of this sample is unlikely.

Another nickel-to-chromium ratio was found in an extraordinary yellowish-green Gilson flux-grown synthetic emerald, which contained similar amounts of chromium and nickel (Schmetzer, 1989). Comparing the absorption spectrum of this sample with the spectra of the seven Igmeralds examined in this study, it becomes evident that the relative intensity of nickel absorption bands compared to the chromium spectrum is stronger in the Gilson sample than in the Igmerald spectra (Figure 10). In terms of the colour and pleochroism of synthetic

emeralds, increasing nickel content relative to chromium causes the pleochroic colour parallel to *c* to shift from blue-green to bluish green and green, i.e. the bluish component is reduced. The pleochroic colour perpendicular to *c* shifts slightly from yellowish-green to yellow-green, i.e. the yellow component of the green is slightly increased. In general, the overall colour shifts with increasing nickel content from bluish-green to grass-green and yellowish-green (Figure 11, Table I).

These results are consistent with the data presented by Bukin *et al.* (1981), who found a complex relation between colour and the relative amounts of Ni^{2+} , Ni^{3+} and Cr^{3+} in individual samples. According to Bukin, a nickel content above 0.1 wt.% is able to change the colour of an emerald sample. With increasing amounts of nickel, a shift of colour is mainly observed parallel to *c*, and only a minor change is found perpendicular to *c*.

Obviously, the grass-green colour of chromium- and nickel-bearing synthetic emerald was more acceptable as a 'good' emerald colour in the '30s in Germany by the producers of Igmeralds than the more bluish-green of chromium-bearing, nickel-free emerald. As a consequence of the great efforts necessary to find the appropriate mixture of compounds in the nutrient which produced this 'good' emerald colour, this recipe was not disclosed in the papers of Espig (1960, 1961, 1962) and has been kept secret until now.

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