

SOME ASPECTS OF PRECIOUS OPAL SYNTHESIS

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Abstract

In this paper the authors describe the developmental research and basic steps involved in their synthesis of all-silica opal at the Center for Applied Research in Dubna, Russia. The structure and essential features of this attractive, relatively non-porous synthetic opal are illustrated, and cut and polished examples of this synthetic opal are illustrated.

INTRODUCTION

Precious opal has been known from ancient times. It is a valuable raw material for use in jewellery¹. On the world market, the price of the precious opal continuously increases with time. The old European opal mines are now depleted, and the main supplier of the precious opal to world markets is Australia. To meet the rising demand for precious opal, in many countries attempts have been made to synthesize opal. However, the synthesis of opal is very complicated.

Precious opal was synthesized for the first time in early 1970's by Pierre Gilson of France². Since 1993 the authors of this paper have been working to create synthetic opal of jewellery quality. Now some interesting results have been achieved in this field, and these advances are reported below.

THE SYNTHESIS OF OPAL

As researched and developed by the authors, the synthesis of opal is a multi-step process that can be divided into several individual stages.

Stage 1

In the first stage, using our modification of the Steber method³, the synthesis of monodisperse particles of silica in alcoholic sols is carried out. The particles are formed by the hydrolysis of tetraethyl ester of orthosilicic acid, Si(OC₂H₅)₄, or TEOS, in ethanol. The catalyst for this reaction is ammonia. In this solution the hydrolysis of TEOS occurs by the following reaction:



Simultaneously, the polymerisation of orthosilicic acid occurs by the reaction:



In this process, small nuclei (with a diameter about 10 nm) are formed first from the liquid phase. Then the growth of the silica particles takes place. By adding further amounts of TEOS, the particles of silica grow up to the diameter desired—that is to about 300 nm size (see figure 1).

Stage 2

In the second stage, 'raw' precursor of opal is precipitated either by spontaneous sedimentation, or by centrifuging.

In precious opal, the particles of silica are arranged in very dense structures, or 'blocks', that form 'photon crystals'. Diffraction of light at these 'blocks' produces the vivid display of spectral colours of the opal. The bigger the blocks, the brighter and more variable will be the opal's *play-of-colour*, and consequently, the higher is its price.

It has been observed that the 'blocks' of smallest dimension occur in precursor opal precipitated by centrifuging. It is for this reason, that at this time spontaneous

sedimentation is used in our technique of synthesis. Nevertheless, this method (sedimentation) only provides satisfactory results for highly diluted sols, because in very concentrated sols the silica particles cannot be arranged immediately into an organized structure (see figure 2); cannot find their proper site; and, from above, further sedimenting particles are crowded⁴. As the existence of this zone of the dense precipitation is an obstacle for the formation of big monocrystalline 'blocks', the only way to prevent this phenomenon is to decrease the concentration of the particles in the sol. However, this produces both an increase of the sedimentation time, and an increase in the dimensions (height) of the sedimentation vessels that are required to be used in the process. So it is necessary to find a reasonable compromise between the time and quality of the sedimentation process that results. At this stage of our work, our chosen sedimentation time is about seven months.



Fig. 1. Electron-microscope photograph of synthesized spherical particles monodisperse silica.

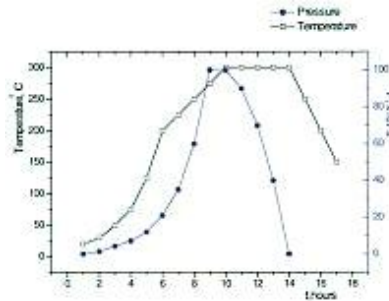


Fig. 4. Regime of the supercritical drying used in the synthesis of our opal.



Fig. 2. Electron-microscope photograph of the ordered structure in precious opal, showing its light diffracting 'photon crystals'.



Fig. 5. Opal substance after superficial drying.



Fig. 3. Precursor opal in its sedimentation vessel.

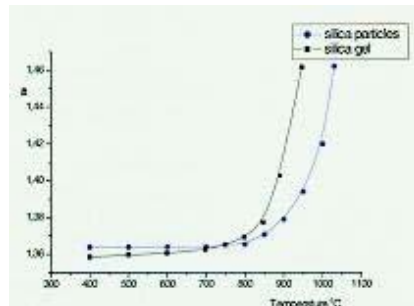


Fig. 6. Dependence of the refractive indices of the monodisperse silica particles and the silica gel on applied sintering temperature.

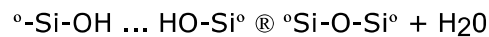
Stage 3

In the third stage of the synthesis, the precursor opal (see figure 3) has to be dried in order to remove liquid from its pores. At this stage the precursor opal is viscous, does not have a very compact structure, and it is impossible to dry under normal conditions without damaging it. Even if the process of drying is carried out very slowly (over more than three months), the capillary forces and the forces of surface tension in pores

between particles leads to the formation of internal stresses-which sooner or later generate a network of 'breaks' (crazing) over the total volume of the opal. Consequently, it is impossible to prepare samples of opal with dimension greater than 1 cm using this method.

In order to solve this problem, the authors employ a method of supercritical drying in an autoclave to obtain defect-free samples of practically any dimension within a time span of 10-12 hours⁵. In this process, precursor opal, produced by sedimentation, is placed in an autoclave containing ethanol. The autoclave is then heated and, when the critical temperature for ethanol ($T_k=516$ K, $P_k=6.4$ MPa) is reached, all of the liquid within the autoclave - and in the pores of the raw opal - transforms into vapour without boiling. The vapour is then exhausted from the autoclave at a constant temperature that is higher than the critical temperature of ethanol. The regime of the supercritical drying that is used in our synthesis is shown in figure 4.

By using this method of drying, internal weaknesses do not occur in the synthetic opal. Also, during supercritical drying, samples become significantly stronger-since at higher temperatures of about 300⁰C, additional siloxane bonds are formed between the neighbouring silica particles, by the reaction:



A defect-free sample of the dried precursor opal, obtained by this method of supercritical drying, is shown in figure 5. It has a diameter of 12.5 cm and a width of 5.5 mm.

Subsequently, this substance (dried precursor opal) must be strengthened by thermal treatment in a furnace. After this treatment, the opal substance becomes a fragile, non-transparent material that has an open porosity about 35 per cent.

Stage 4

For the production of synthetic opal, it is then necessary to fill pores in the opal substance with a silica gel. In this stage proper consideration must be given to the difference in the indices of refraction that occur between the gel and the monodisperse particles in the forming opal (see figure 6). In response to this challenge, the authors have experimentally proved that in opal this difference can be substantially higher than 0.02⁶, without causing some decrease in the *play-of-colour* of the opal. Further experiments were carried out, with the aim of obtaining the best diffraction colours from the opal, and, simultaneously, attaining the necessary hardness of natural opal - which is 5½ - 6½ on Mohs scale.

After the supercritical drying of stage 3, the samples of precursor opal were then sintered in a furnace at temperatures of 600, 800 and 1000⁰ C. After saturation of these samples with silica sols, polymerisation of sol into gel and subsequent drying of the gels, these samples were sintered at 400 and 800⁰ C. In figure 7, the dependence of hardness of the opal on the number of saturations with the silica gel is shown. It was discovered that the synthetic opal, produced at these sintering temperatures, had a really good *play-of-colour* despite the big difference in refractive index between the precursor opal and silica gel filling its pores. At the present time, both the opal and its filling silica gels are sintered at the temperature 825⁰ C.

Another very important task, solved by the authors, was the development of a 'soaking' technology based on high-pressure (600-700 atmospheres) saturation of precursor opal with the gels. As a result synthetic opals with 'closed' (very little) porosity are now produced.

GEMMOLOGICAL PROPERTIES

The characteristic gemmological properties of this Russian all-silica synthetic opal are given in Table 1.

CONCLUSIONS

All of the properties of the opals synthesized by the authors - that is their absence of characteristic micro and macrodefects (see figures 8 and 9), their 'closed' porosity, their chemical composition (silica and water up to 8 per cent), and their hardness (about 6 on Mohs scale) - are identical to those of natural precious opals. The total time of the synthesis is nowadays 10 months, compared to that of Gilson (12 months or more), and Chatham on www.chatham.com (~18 months). In addition, our rough synthetic opal can be easily cut and polished for use in jewellery (see figure 10).

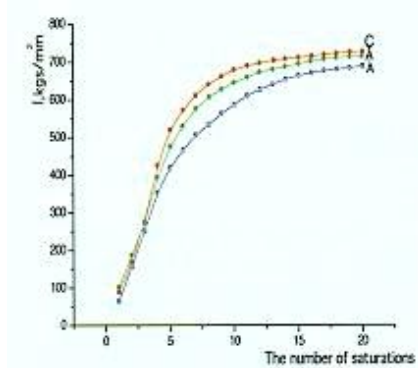


Fig. 7. Dependence of the microhardness of the opal substance on the number of saturations with the silica gels (temperatures of the sintering of the opal substance and the gel: A - 600⁰C, 400⁰C; B - 800⁰C, 800⁰C; C - 1000⁰C, 400⁰C).



Fig. 9. Rough white synthetic opal of 52 gm weight.

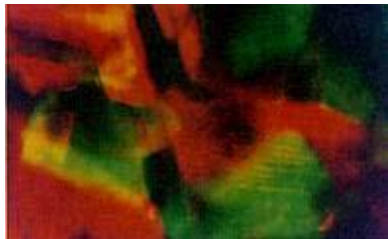


Fig. 8. Photograph of the *play-of-colour* of Russian black synthetic opal (x100)

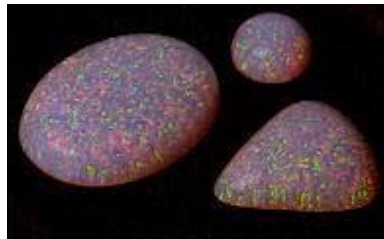


Fig. 10. Russian synthetic opal cabochons produced by the German opal cutting firms of Weiss, and Litzenberger. The cabochons weigh 10.2 ct, 1.6 ct and 4.8 ct.

PROPERTY	Light (White) synthetic opal	Black synthetic opal
Chemical composition	Silica and water (up to 8%)	Silica, water (up to 8%), and carbon (less 1%)
Hardness	5.9-6.0	5.9-6.0
Fracture	Conchoidal	Conchoidal
Cleavage	None	None
Specific Gravity	1.96-2.03 (depends on water content)	1.96-2.03 (depends on water content)
Refractive Index	1.41-1.43	1.41-1.43
Diaphaneity	Transparent to semi-transparent	Translucent to opaque
Lustre	Vitreous (glassy)	Vitreous (glassy)

Fluorescence	- LWUV - SWUV	None None	None None
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Table 1. Identifying properties of Russian 'all-silica' synthetic opal.

Acknowledgement

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