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COMPARISON OF DIFFERENT WAYS OF AGATE COLORING

Babintseva E.V.
Supervisor: candidate of geological and mineralogical sciences
Perfilova O.U.
Language adviser: Schepeleva V.I.
Siberian Federal University

Agate and onyx are banded aggregates of various colors with transparent and opaque layers of chalcedony (white, gray, yellow, brown, orange, red). Chalcedony is a fine-crystalline cryptocrystalline variety of quartz, consisting of fine fibers of silica. Agates differ incredible in color and stripe patterns. Since ancient times, they are used as an ornamental stone for seals, cameos, rings, brooches, pendants, for mosaic work and carving. Very often the pattern of agate looks like an eye. According to one of the ancient legends, this is the eye of white eagle, which fell down the earth and became a stone after the battle with a black magician. Its eye continued to stare at people and separate the good and evil deeds. Therefore, agate is sometimes called the "The Eye of the Creator". In onyx, unlike agate, the stripes of different color are always parallel. Some varieties of onyx have definite names. Since ancient times, onyx has been the favorite material for making cameos.

In nature agate and onyx have plain color with alternating light gray and white stripes. Therefore, for many thousands of years people have tried to add different color artificially. There are different ways of coloring. They are based on the property of chalcedony layers absorb a dye much easier because subtle channels are located parallel to fine silica fibers. The denser layers of quartz (usually white) are not colored entirely. More often, agate and onyx are artificially colored in distinguishing shades of red to simulate carnelian, carneol and bonito, in green, dark brown and black shades.

Most technologies of stones coloring date back to ancient times. The advances in modern chemistry have brought some improvements. Nowadays technology of coloring semi-precious stones (including agate) with aniline is widely used. Although some people like such unnaturally colored stones, the color is too bright and it is not resistant to light exposure. Much more stable and natural are colors after using inorganic dyes. For example, in natural agate and chalcedony the orange and red "dye" is fine hematite (Fe_2O_3). For artificial red coloring, agate is first boiled in the solution of iron nitrate, and then it is calcinated. In this way, it is possible to obtain different shades of red color. Natural yellow layers become red after calcinating. For yellow coloring, agate first impregnated with hydrochloric acid and then placed in a saturated solution of ferric chloride and warmed slightly. The result is a lemon- yellow color. Coloring in brown and black is achieved by treating agate with solution of sugar (or honey) and extreme heat. Recently, sulfuric acid has been used instead of heating. Similar results can be achieved with the help of cobalt nitrate.

Green coloring (chrysoprase imitation) of agate is achieved by impregnation with a solution of chromium salt or nickel nitrate and then calcinating.

Blue coloring is achieved by treating with ferrous iron. Agate is first dipped in a saturated solution of ferrocyanide (potassium ferrocyanide), and then boiled in vitriol (ferrous sulfate), which gives agate the blue color, because the Prussian blue setting is formed in the result of this reaction:

$$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6] + 3KCl$$

Both hot and cold ways of agate blue coloring is possible. In our research we compared the effectiveness of different ways of coloring and carried out several experiments with naturally colored toneless agate (agate from the river Kacha and fields of the Kemerovo region). For the experiment, we used small plates of agate 2-5 mm thick. All the samples were carefully degreased in detergent solution and then wiped with alcohol.

Some samples were placed into container with saturated solutions of red blood and ferric salts in equal proportions. Almost immediately, the final color of the solution changed to dark blue as a result of the reaction with the formation of fine setting of Prussian blue. The samples were kept in this solution for one week at room temperature. The other samples were divided into two parts; the first part was placed in the saturated solution of ferric chloride, the other into the saturated solution of red blood salt. The exposure time was 72 hours. After soaking in the solution of ferric chloride, the samples were placed into the blood red solution of salt and from the solution of potassium ferrocyanide into the ferric chloride solution for another 72 hours. After 144 hours, all agate samples were carefully rinsed in running water and dried.

The agates which were kept in the cold solution with Prussian blue were colored very slightly or not colored at all. The samples, which were placed in the solution of ferric chloride and then in the solution of red blood salt, were slightly colored in light blue (mostly along cavities). The samples that were first placed in the solution of red blood salt and then in the solution of ferric chloride, had more saturated blue color.

For the second series of experiments, we heat treated the samples by triple calcination in a pan at about 250 °C for 5 minutes and subsequent quenching in ice water. After heat treatment, tiny fractures appeared on the samples. Then the samples were washed with a detergent to degrease the surface for better absorption. Then some of the samples were subjected to heat treatment, we boiled them in a saturated red blood salt solution for 15 minutes. After that the agates samples were kept in the solution for more 12 hours. In the end the samples were placed in the solution of ferric chloride for an hour. All the samples were carefully rinsed and dried.

In addition, we tried to color heat treated agate with purple stamp paint. The samples were placed in the paint for 20 minutes and thoroughly washed, degreased, rinsed and dried. In the result we got amethyst like agate with alternating deep purple and lilac stripes.

In the result of the experiments we can make the following conclusions.

The hot method of coloring was much more effective than cold. In a shorter period of time (less than a day) were obtained richer blue colors in all the samples. This can probably be explained by the appearance of numerous tiny fractures after heat treatment and better penetration of red blood salt solution during boiling. Such method requires large amounts of electricity for heat treatment, but the time of treatment is significantly reduced, and what is the more important, it provides deeper color of agates. For better shades, it is necessary to place the samples in the solution of red blood salt, then in the solution of chloride or ferric sulfate, not vice versa.

Rapid and intense coloring can be achieved using aniline dyes, like purple stamp ink. But the colors in the result will be too bright and unnatural. Moreover, the color may bleach by exposure to sunlight and the effect of cosmetics.