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ECOLOGICAL RED GLASS

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ABSTRACT
The interest in glasses of the copper ruby type is re-actualized due to the present general tendency to avoid the fabrication and the use of products with a content of toxic or potential pollutant substances. Copper gives a red color as a result of some subtle redox processes doubled by thermal treatments. Although a great volume of practical experience was accumulated many aspects of ruby formation mechanism remained still insufficient elucidated and the rigorous control of numerous parameters influencing the color quality is still difficult or even impossible. In the present work some results are communicated, obtained in the frame of a study following both the more deeply and correct understanding of copper ruby formation processes and the accumulation of data about the role and the influence of technological parameters.

INTRODUCTION

Although in glasses can be obtained a great variety of colors and nuances in the case of red color the situation is special, the possibilities being more restrained. The electronic transitions of the usual coloring ions need, as a rule, energies corresponding to the middle of the visible spectrum towards red or to UV, the transmitted trough glass light having yellow – green – blue colors.

The transmission of yellow – red – IR radiations is possible by means of different mechanisms, preponderantly through light diffusion on colloidal aggregates nano or micro crystalline. In this aim most frequently are used cadmium sulphide, cadmium selenide and sulfo-selenide. On the basis of a similar mechanism one may obtain beautiful red colors by means of colloidal aggregates of Au, Ag or Cu [*Balta P.,* 1984; *Balta P. et al.* 2001].

In the last years glass industry was affected by the tendency, manifested throughout the world, to avoid the use of potential dangerous or pollutant substances. Such a new problem is contoured related to glasses with cadmium content, toxic for human body and pollutant for the environment.

The copper ruby seems to be a possible alternative. Because the implicated subtle redox processes and thermal treatments the obtainment of reproducible colors and nuances at an industrial scale is difficult. In this some results contributing to a more deeply understanding of the redox processes mechanisms and of the peculiarities of technological parameters are presented.

COPPER RUBY

The strong dispersed during melting metal atoms does not color glass. It is needed a developing, striking, thermal treatment to obtain the colloidal aggregates. The red ruby color is obtained when the colloidal aggregates reach dimensions of the order of 50 nm. The coloring mechanism is based preponderantly on the diffusion of light on colloidal particles.

The light diffusion intensity I_D may be evaluated by means of the Rayleigh's equation:

$$I_D = \frac{\pi . V^2}{\lambda^4 . r^2} . \varepsilon_r^{\ 2} (\Delta \varepsilon_r - 1) \sin^2 \alpha \qquad (1)$$

where V is the particles volume, λ the wavelength of the incident light, ε_r the dielectric relative permittivity, r the distance from the particle to the point light intensity measurement and α the angle between the diffused light fascicle and the incident one. It may be remarked the fact that, beside of some parameters related to the measuring conditions, diffusion is strong influenced by the wavelength of the incident light.

Diffusion is more intense when the wavelength is shorter, i.e. in UV – blue – green domain. Thus, through glass pass preponderantly the wavelengths corresponding to domain of yellow – red. The particle concentration has a strong influence too but at their increase, or at the increase of particle dimensions, glass become opalescent or even opaque [*Balta P.,* 1984; *Balta P. et al.* 2001].

THE WORKING MANNER

The copper ruby study followed particularity the redox processes both on simple glasses used as a kind of models and on the industrial type glasses. The model glass was chosen in the system Na_2O-B_2O_3 (10wt%Na_2O). Was used an organic reducing agent (saccharose) but also metallic Sn. Copper was introduced as CuO,Cu_2O or even Cu. Melting was made in an electric furnace, in ceramic or platinum crucibles, at 1000^{0}C for borate glasses or 1450^{0}C for silicate ones, in normal atmosphere. The samples having shapes of discs with a diameter of 25 mm and a thickness of 1-2mm were obtained by pressing molten glass in a metallic form. They were annealed and thermal treated in different conditions. Absorption spectra were recorded by means of a two-beam spectrophotometer Shimadzu UV-160A, in the domain 400-1100 nm, sometime beginning from 200 nm, in comparison with the same glass but without Cu.

COPPER RUBY IN BORATE GLASSES

In a first series of glasses copper was introduced as Cu_2O with the aim to check the opinion of some research workers according to that the colloidal aggregates are formed by cuprous oxide and not by elementary Cu. Even in the absence of the reducing agent the red color must appear [*Capatina C*., 2001]. After melting glasses were colorless and remained so even after long heath treatments. The Cu^+ presence was evidenced the charge transfer absorption in far UV specific to this ion and by means of chemical analysis.

The conclusion was that, at least in this glass, cuprous oxide did not form colloidal coloring aggregates. Introducing an organic reducing in glasses containing Cu_2O or CuO, red colored glasses were obtained. In Fig. 1 are presented the electronic spectra of glasses initially containing CuO. The spectra interpretation seems to be quite simple. After a quart of hour of melting the peak at 590 nm has the maximum amplitude indicating the presence of a great quantity of colloidal aggregates but it can be observed also a small maximum at 800 nm corresponding to some not yet reduced CuO.

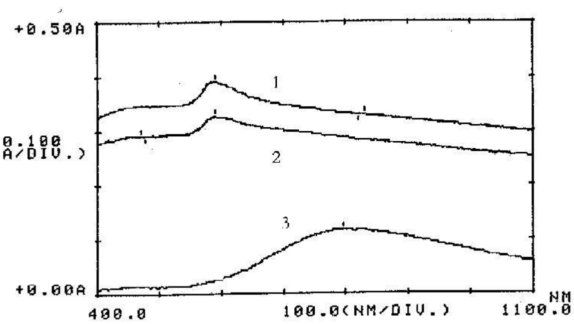

Figure 1. Electronic spectra of borate ruby glasses. Copper was introduced as a CuO and was used an organic reducer. Melting duration: 1 – 15 min., 2 – 30 min., 3 – 60 min.

After 30 minutes the peak at 590 nm is practically unchanged but that of Cu^{2+} totally disappeared. After 60 minutes the peak at 590 nm is not more visible but, in exchange, that at 800 nm is very pronounced.

The high absorption level showed by ruby glasses spectra over all visible is due to the presence of carbon resulted by organic compound decomposition. Following the carbon disappearance the necessary oxygen quantity was calculated resulting that the main oxygen source is the surrounding atmosphere. An apparent difussion coefficient of oxygen in borate melt at 1000 ^{0}C of the order of 10^{-4} – 10^{-5} cm^2s^{-1} was estimated [*Capatina C.,* 2000]. The very high value for this kind of glasses can be explained by the convection contribution, determined by gas bubbles elimination during the organic reducer burning.

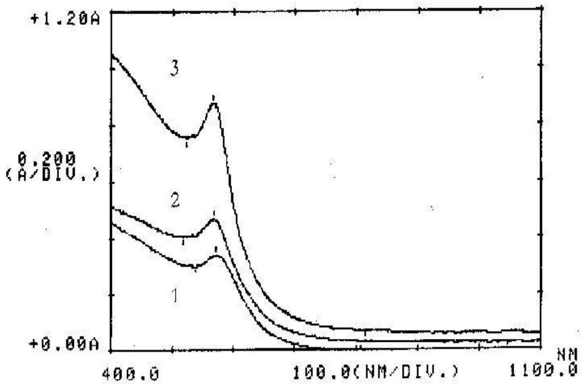

Figure 2. Electronic spectra of borate ruby glasses with copper from a Cu-Sn alloy. The heath treatement duration was: 1 – 120 min., 2 – 210 min.,   3 – 240 min.

An usual soda-lime-silica glass was experimented using as a source of Cu and Sn the same alloy. The melting was made at 1450 ^{0}C in normal atmosphere. The striking treatment was made at temperatures and durations. Some of the recorded spectra are presented in figure 3.

Inspired from the Professor's Cristea and his collaborators works, in a series of borate glasses copper was introduced in the form of a Cu-Sn alloy [*Cristea V. et al*., 1975]. The thermal were performed at 500 ^{0}C. The color appeared only after about 25 minutes. In figure 2 spectra obtained after longer treatments are presented.

At least three differences may be remarked comparing with ruby glasses obtained with organic reducer [*Ram A., et al.,* 1974].

1. the absorption due to carbon resulted by reducer burning is missing
2. a large window is present from about 568 nm up to IR
3. the peak amplitude increases apparently exponentially with time.

It may observe a strong absorption at about 566 nm due to copper colloidal aggregates, a sharp absorption limit a uniform transmission towards IR. The longest melting duration results in the apparition of a very small peak at about 800 nm specific for Cu^{2+} singaling the total oxidation of Sn. In this way a saturation is evidenced related to the end of Sn oxidation process and the beginning of the copper oxidation up to Cu^{2+}. The presence of this copper ion alters the ruby quality and represents the upper time for the good quality ruby glass elaboration process.

The striking temperature and time have a synergetic action the 566 nm peak amplitude depending linearly on temperature but logarithmically on time. These are the main technologic parameters determining, together with copper concentration, the nuance and the intensity of copper ruby glass color.

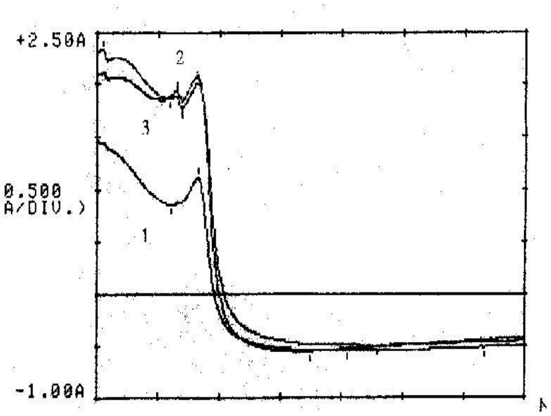

Figure 3. The electronic spectra of the industrial type ruby glasses with alloy, maintained at the melting temperature: 1 – 90 min., 2 – 150 min., 3 – 210 min
Copper ruby in industrial type glasses

Another important achievement consists in the fact that the glass composition has a low influence on the copper colloidal aggregates absorption peak position. Passing from silicate glass to borate and phosphate glasses the peak position modification is very small, inside of some 23 nm [*Weyl W.A.,* 1967].

CONCLUSIONS

Due to the actual tendency to avoid the use of cadmium in red glasses were explored the redox mechanism and the technology of cooper ruby, which seems to be a reasonable alternative.

Using a sodium – borate model glass were melted and studies containing Cu_2O, CuO or Cu^0, using an organics reducer and also Sn from a Cu-Sn alloy. The sodium – borate glass with Cu_2O content did not exhibit a red color. The advantage of using Cu-Sn instead of other copper sources and of the organic reducer was evidenced.

The copper obtainment in an industrial type glass was studied achieving some new information concerning a saturation phenomenon related to Sn quantity, the synergetic influence of striking temperature and time and the low influence of glass composition upon the colloidal aggregates absorption peak position.

The accumulated results contribute to the more deeply understanding of redox processes mechanism at copper ruby obtainment and the influence of some technological parameters. Now it is possible to imagine experiments at an industrial scale to establish the conditions for copper ruby glass obtainment in large quantities.

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