

THE DEVELOPMENT OF IMPROVED GOLD RUBY GLASS.

By H. T. BELLAMY.

It has been a well-known phenomenon for sometime past that gold and copper produce a ruby color in glass which contains certain necessary constituents and which has been given a special heat treatment. The color is universally agreed to be due to the metals in suspension as colloids.

The ability of gold to exist in the colloidal state was first observed by Faraday while experimenting on the volatilization of gold. He found that gold in an atmosphere of hydrogen volatilized quite readily and that the vapor condensed as an intense ruby stain. Mostowitsch and Pletneff¹ have recently reported similar results. They melted gold in an unglazed porcelain boat, in streams of air, carbon dioxide, carbon monoxide, nitrogen and oxygen and held it at various temperatures up to 1400° C for a period of thirty minutes. No loss of gold could be detected. However, when heated in hydrogen the gold began to volatilize at 1250° C and the volatilization increased with temperature and time. The unglazed boat and the heating tube were colored an intense red—due to colloidal gold. It is probable that Au_2H_2 —which is unstable, breaking up into Au_2 and H_2 —was first formed. By heating copper in hydrogen a similar action was observed.

As an example of colloidal phenomena, gold ruby glass has been rather thoroughly investigated and the behavior of colloidal gold in this solid solution appears to be similar to its behavior in aqueous solutions, existing in both instances as colorless, green, red, blue, violet, or brown particles. When ruby glass is at the melting temperature the particles are colorless and when suddenly chilled they remain colorless, but if the glass is re-heated to the softening point, the particles become ruby. Further heating tends to produce other colors.

¹ *J. Russ. Metall. Soc.*, 1915.

Zsigmondy¹ says that at the melting temperature the gold is all in solution but at ordinary temperatures the colorless glass contains gold in two different forms—most of it being present in the supersaturated crystalloid solution and part existing as nuclei, which at higher temperatures serve as centers of growth.

Experimental.

The work which supplied the information for this paper was not undertaken to study ruby glass in general nor as a purely research proposition and on this account an exhaustive exposition of the problem is not to be expected. The manufacture of ruby glass was taken up to reproduce a ruby glass purchased in France, the importation of which had been discontinued since the war. A glass of the exact shade and possessing the requisite working properties could not be obtained from domestic suppliers. The treatment, to which the glass is subjected, is rather severe, as it must not shatter when introduced into a glass blower's flame, it must not discolor when heated to a very soft condition and it should be of such a nature that small lenses can be formed from the heated rod without subsequent annealing. The lenses so formed should be of uniform color, matching an accepted standard; should be free from surface cracks and other visible defects; and when mounted in a brass shell should withstand impacts of three pounds applied at the rate of 115 per minute.

A chemical analysis was made of the imported ruby glass and the molecular formula calculated as follows:

Analysis:

	Per cent.
SiO ₂	38.35
PbO.....	54.48
K ₂ O.....	6.17
Sb ₂ O ₃	0.67
R ₂ O.....	0.70
Gold.....	Present
B ₂ O ₃	Not determined

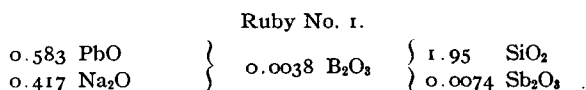
Calculated Formula:

0.791 PbO	}	0.0173 R ₂ O ₃	{	2.05 SiO
0.209 K ₂ O				0.0075 Sb ₂ O ₃

¹ Zsigmondy, "Colloids and the Ultra-microscope."

While this work was being done the scarcity of potash was beginning to be evidenced and although the imported glass was made with a potassium compound, as was to be expected, it was decided to try to substitute a sodium compound.

The first melts were made in a small crucible-type gas furnace, using Battersea crucibles. After making a few trial batches to determine the proper quantity of gold to be added, a glass of the following formula was developed:



The gold, which is not included in the formula, was prepared by dissolving ten karat sheet gold in aqua regia, separating the base melts in the ordinary manner, and diluting the gold chloride so that ten cubic centimeters contained one gram of metallic gold. The requisite volume of gold chloride was added to the sand of the batch and evaporated to dryness.

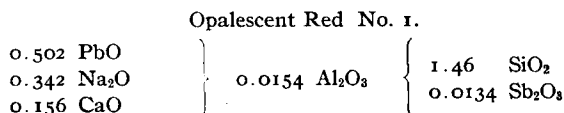
Ruby No. 1 appeared to match the imported ruby in color and preparations were made to melt a larger quantity. A No. 30 open glass-melting pot was used in the same type furnace and a batch eight times as large as the preceding one was prepared. The batch was added gradually and held at approximately 1300° C for fifteen hours when it was ready to work. Rods were made by the ordinary method of forming a bell-shaped gather. Each gathering of glass was allowed to solidify and, as the next coating was added, the previous coating developed the ruby color. After completion, the gather was re-heated in an improvised glory hole and drawn into rods.

It was very difficult to heat the gather sufficiently uniformly so that the rod would be of one color throughout its length. The smaller area next to the punty was usually overheated—showing light blue, purple and rose colors. Furthermore, the consecutive layers of the gather were frequently of different colors and when a lens was formed from the rod and viewed over a light it appeared streaked. The center of the rod showed the greatest tendency to discolor, as was to be expected—since the small initial gather

could readily become over-heated when dipped into the molten metal. However, when proper precaution was exercised in having the metal at a certain temperature, when the gathers were cooled to the proper degree, and when the re-heating was carefully controlled, a certain percentage of rod matching the standard shade was obtained from each gather.

Simultaneously with the development of ruby glass, experimental work was being carried on to produce other colored glasses to match imported glasses not obtainable since the war and also to develop opalescent colored glass of certain requirements which we were unable to procure from either domestic or foreign suppliers. The opalescence required was to be of such a degree that a lens should be of uniform color and opalescence when viewed normally over a light and the diffusion should be such that the quantity of light transmitted normally would compare favorably with that transmitted at 90 degrees from normal. To compare opalescent colored glasses on this basis, the sample lens was set in a tube in front of a small lamp mounted in a suitable revolving support in a photometer.

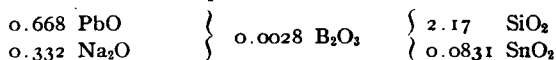
With the above requirements in mind, the development of an opalescent red was begun and after melting a few small batches to adjust the color and opalescence a glass having the following formula was tried out:



Lenses of Opalescent Red No. 1 had the proper color and degree of opalescence but the glass rods shattered while being heated in the glass blower's flame and the finished lenses shattered when subjected to the previously described impact test.

Although the quantity of cryolite used as an opacifier in opalescent red was considerably less than is present in our opalescent white glass, which withstood the impact test extremely well, the brittleness was attributed to its presence and it was decided to substitute tin oxide. After a few trial batches a glass having the following formula was developed:

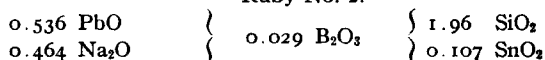
Opalescent Red No. 2.



Opalescent Red No. 2 melted well, was readily worked into rods, and lenses formed from the softened rods fulfilled the requirements previously described. The resistance to impact was equal to that of the transparent ruby and the light diffusion was all that was desired. The opalescent red, being lighter in shade, is not as pleasing to the eye as the so-called ruby.

In developing Opalescent Red No. 2, a much smaller amount of gold was used than is present in Ruby No. 1, but as the concentration of tin oxide was increased to produce opalescence, a dark red glass resulted which in the form of a lens was almost opaque. The gold content was repeatedly reduced until Opalescent Red No. 2 of the desired properties were obtained. However, at an intermediate stage, when the gold content was about one-fifth of that used in the transparent Ruby No. 1, a glass was obtained which was quite similar in shade to Ruby No. 1. A perfect match for this glass and the former standard, the imported ruby, was produced by a slight adjustment arriving at the following molecular formula:

Ruby No. 2.



Lenses molded from Ruby No. 2 did not crack or shatter when subjected to the standard impact test and, unlike the lenses made from Ruby No. 1, were never streaked or off-color. The melting was carried on in No. 30 open glass-pots in a crucible-type gas furnace for a period averaging fifteen hours. The gather for rod drawing was shaped in the usual manner and each successive coating was allowed to cool before the next layer was added. The ruby color developed in the previous gatherings, as was the case when working Ruby No. 1, but always to a uniform color. The gather was re-heated to plasticity and drawn into rods in the usual manner. The rods and lenses made from Ruby No. 2 were always of a uniform ruby color. At first the precautions required in working Ruby No. 1 were followed but it was soon evident that

Ruby No. 2 would always develop the ruby color on re-heating and that the temperature of the glory-hole would not alter this color.

Ruby No. 3.

Quite recently we were called upon to produce a red glass enamel and finely powdered Ruby No. 2 was used with other suitable constituents. The enamel was not sufficiently red for the small thickness which was viewed over a light, and the amount of gold was trebled. The result was a very dark ruby referred to as Ruby No. 3 and which worked exactly like Ruby No. 2. The color developed upon heating to the softening point and it could not be changed except at a very high temperature when the ruby color disappeared, leaving a colorless glass.

The presence of a certain percentage of tin oxide, besides acting in the ordinary manner as an opacifier, apparently reacts to precipitate the gold in the red colloidal state. Its presence may affect the magnitude of the gold particles catalytically and produce this result or it may react to precipitate the gold particles as red hydrosols in the same manner that certain substances aid or retard the precipitation of colloidal gold in aqueous solutions.

Walker¹ states that gold particles may exist so finely divided in solutions that the ultramicroscope not only fails to reveal their presence as individuals, but fails even to detect any scattered luminosity in the solution when a powerful beam of light is concentrated in the solution and, since luminosity can be detected with gold particles of two millionth's of a millimeter in diameter, it is concluded that red colloidal gold particles have dimensions approximating the recognized magnitude of molecules, or approximately one millionth of a millimeter.

Ruby No. 2 and Ruby No. 3 and the opalescent red glasses which we have produced can exist in only two states—the red and the colorless. When at a high temperature, the absence of color is probably due to the fact that the gold is in solution. When colorless at ordinary temperatures, the gold particles, some of which it is assumed have separated out, are too small to be visible. Upon reheating, the gold particles grow until of visible size

¹ Walker's, "Physical Chemistry."

in which form they impart a ruby color to the glass. If the ruby colored glass is heated to the temperature at which the glass regains its solvent action, the red gold hydrosol again goes into solution. These glasses appear to be so constituted that the gold cannot assume the various colors which was noted in Ruby No. 1 and which it is generally believed is to be expected in gold ruby glass.

Conclusions.

It is rather difficult to draw general conclusions from this work regarding the composition of workable ruby glass for, as previously mentioned, this study was undertaken solely to produce glasses with predetermined properties. However, it may be stated that the range of stable red glasses is rather wide as the red opalescent described is quite light and Ruby No. 3 is very dark. The quantity of gold used to produce these shades of red varied from one part in ten thousand to one part in three thousand. The use of tin oxide to stabilize the gold and produce a ruby color with the minimum quantity of gold is new and novel and a patent has been granted. Two definite conclusions are apparent, namely: (1) a stable, reliable, gold ruby glass can be economically produced and (2) the presence of other colors is not a natural phenomenon of gold ruby glass, for when the necessary components are properly proportioned, the gold particles are either red or colorless.

CHEMICAL DIVISION—HAWTHORNE WORKS,
WESTERN ELECTRIC COMPANY, INC.,
CHICAGO, ILL.

COMMUNICATED DISCUSSIONS.

F. CARDER: The paper is very interesting and shows that the author has given the subject careful thought.

The very small lenses which were shown by Mr. Bellamy should not have been difficult to make or match, either for color or for the physical standards set, especially when so high a content of PbO could be used in the batch.

Has Mr. Bellamy tried his Ruby No. 1 after gathering a mass from the pot, and cooling until it was below a red heat and then raising the temperature slowly by heating in a glory-hole? Has

he subjected his various trials to blowing out with the blowpipe or flashing his ruby on a flint base? While the rods or lenses may be good enough in color for the purpose intended, I am inclined to think that upon treating his ruby as suggested, he would find discolorations such as he mentions, *viz.*, blue, purple or brownish streaks which usually occur when gold ruby is subjected to a too sudden transition from the colorless state (or state of solution) to the colloidal or crystalline state.

The proportion of gold to the batch, 1 to 3000, or even 10,000, is, to my mind, excessive. Josiah Wedgewood found that one part gold to 20,000 batch colored glass red.

I was somewhat surprised to note that Mr. Bellamy considers the introduction or use of SnO_2 in gold ruby as an innovation. When gold ruby was discovered it was made with "purple of cassius," which some chemists believe to be a gold stannate. I believe that Kunkel made his first gold ruby with "purple of cassius," samples of which are still to be seen in the art museums in Dresden. Berzelius states that "purple of cassius" contains 28.2 per cent of gold to 64 per cent of tin oxide. To my knowledge tin oxide has been used for a great many years and in my experience in manufacturing glass I have never known any formula worthy the name of gold ruby which did not contain tin oxide. Many other oxides are used to give reds varying from a yellowish red to a purple, such as U_2O_3 , Fe_2O_3 , and CoO .

STUBEN GLASS WORKS,
CORNING, N. Y.

E. C. SULLIVAN: Mr. Bellamy's method of intensifying the red color of gold ruby by means of tin oxide recalls the similar use of tin oxide with copper in making qualitative tests by means of the blowpipe applied to the bead of molten borax glass. In testing for copper, tin oxide is added to the bead to assist in the formation of the color of reduced copper, and a test for tin depends upon subjecting the borax bead containing copper to such a reducing condition that the ruby color of the copper will develop if tin is present, not if it is absent.

CORNING GLASS WORKS,
CORNING, N. Y.

R. L. FRINK: It occurs to me that the author's statement in the last paragraph, last three lines: "The presence of other colors is not a natural phenomenon of gold ruby glass, for when the necessary components are properly proportioned, the gold particles are either red or colorless," is not compatible with the results as found by Zsigmondy and others; that gold, when existing in colloidal solution, or in aqueous solution, irrespective of the components, may produce colors ranging from red to blue.

I also cannot understand how it is possible to obtain patents upon the use of tin, or its salts, to either stabilize or in any manner affect the characteristics of gold in glass, for I had supposed that this was an old, in fact very old, method of producing ruby glass, at least I have heard of it for the past 25 years.

THE FRINK LABORATORIES,
LANCASTER, OHIO.

H. T. BELLAMY: 1. Practically all gold ruby glass described in the literature contains potash as an alkali. In view of the scarcity of potash at the time, soda was substituted, and the resulting glass was equally as satisfactory as ruby glass made with potash.

2. A ruby glass designated as "Ruby No. 1," which matched the imported ruby glass, and like it and other ruby glasses described in the literature, was changed to blue, purple or brown under certain conditions, was developed.

3. An improved "Ruby No. 2" was developed which does not discolor. This result is ascribed to the high percentage of tin oxide. Of course, those familiar with the art, know that "purple of cassius" has been extensively used in making ruby glass and that it contains a certain amount of tin oxide but experience has shown that the ruby glass so made is not stable. The author claims that when sufficient tin oxide is present in a properly proportioned batch, the ruby glass will not discolor, and that this feature is an innovation.

4. Another advantage in using a high percentage of tin oxide is the production of ruby glass with a minimum quantity of gold. While there is no doubt that red glass has been made with one part gold in twenty thousand parts batch, the literature gives

ruby glass formulas ranging from one part gold in one thousand parts batch to one part gold in fifteen hundred parts batch. The usual quantity was being used and the introduction of tin oxide reduced the gold content to one-fifth of its original amount.

It should be borne in mind that this paper is the story of a manufacturing investigation and that the statements made were based on information obtained from a large number of glass batches. The title "Gold Ruby Glass" under which the paper was presented, is no doubt rather broad and it has been revised to "The Development of Improved Gold Ruby Glass." It might appear that the glass described should be restricted to the manufacture of glass rod and small lenses. However, Ruby No. 2 has been successfully made into tubing as well as blown, flashed and pressed parts, and in conclusion the author desires to emphasize that this glass has been subjected to all conceivable temperature transitions and never has a particle of glass been observed which was other than ruby or colorless.