

STUDY ON THE STATE OF DISPERSOID IN THE COLLOIDAL COLOURED GLASS

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INTRODUCTION

The understanding of the correct mechanism of the coloration of the ruby glass is a long-standing problem. The ruby glass covers the whole type of colloidal coloured glasses such as gold ruby, copper ruby, etc. Along with that the glasses coloured by Ag and Pt need be studied because they belong to the same class of ruby glass but they are of different colours. In course of the preparations of the above glasses, two operations are required: (1) preparation of colourless transparent glass, and (2) development of colour by heat-treatment.

All workers are unanimous that the coloration of the glass is due to the fine suspension of the metal. But there is much controversy regarding the state of existence of metal in colourless glass. Zsigmondy (1909), Weyl (1945), etc., believe that metals like Au and Pt exist in atomic form or in a form of nucleus in the colourless glass while Silverman (1931), Stookey (1949), etc., believe that the metal exists in oxidised state in the above glass. In the present paper the above problem about the state of existence of the metal in the colourless glass has been studied in borate and sodasilica glass where the solubility of metal is appreciable in comparison with usual silicate glass. Along with that the effect of concentration of the dispersed phase and heat-treatment on the size of the metal particle has been studied. It is worthwhile to mention here that as the size of the particle increases, the scattering of the incident light comes into prominence. Although some works have been done in the above direction, yet it is expected that the above investigation will give some valuable information about the different stages of the dispersed phase during the development of colour in above glass specimens. Use has been made of both chemical and physical methods so as to study the following problems: (1) the state of existence of the dispersoid in colourless glass specimen, (2) to study the effect of heat-treatment on the colour and the size of the suspensoid, (3) the relation between the concentration and the size of the suspensoid in the glassy matrix, (4) to determine the size of the suspensoid by the X-ray method, (5) to study the effect of concentration of the dispersoid on the characteristic diffraction pattern of the original glass base.

CHEMICAL STUDY OF COLOURLESS GLASS SPECIMEN

Glass specimens of $M\text{-B}_2\text{O}_3$, M-borax and M-Lindemann and M-soda-silica glass (where M stands for Au, Pt or Ag) were prepared in the Pt-crucible in an electric furnace and in complete absence of any reducing agent. In all these glass samples M can be dispersed to an appreciable extent as for example, Au can be dispersed in borate and soda-silica glass with 25% soda content to the extent

of 2.45% and 0.20% respectively. Colourless transparent glass was obtained by rapidly quenching the melt in a low temperature, but in course of that operation it is observed that some high M (especially Au) content specimens exhibit coloration even when rapidly quenched. However, some colourless specimens of each series were prepared. All the borate glass specimens are moderately soluble in water and the solubility of soda-silicate glass in water is quite appreciable. In colourless specimens in order to find out whether M can exist in atomic or ionic form or can form a compound with the glass-solvent, the aqueous solution of 2 gm. of 0.5%M content borax and B_2O_3 glass and that of 4 gm. of 0.1%M content of soda-silica glass were subjected to the following chemical reaction.

With NaCl solution, a precipitate of AgCl was obtained from a clear solution of silver glass and that indicated the presence of Ag ion in solution. Again with the addition of dil. HNO_3 to the filtrate after the separation of AgCl, a further precipitate of AgCl although very small in amount was obtained and that indicated the presence of Ag in the elemental state. Whereas in a clear solution of gold and Pt-glass no evidence of metal in the ionic state was found when the respective solution was treated with specific test for Au^{+++} ion such as alkali iodide in alkaline solution and the above operation indicated absence of metal in the oxidised state. But in the solution of Au or Pt-glass in aqua regia, when treated similarly as above, evidence of metal in the ionic state was obtained and that indicated the presence of elemental metal in glass. Thus it is obvious from the above operation that Ag remains in the glass in both elemental and ionic state whereas Au and Pt exist only in the elemental state in glass. Further it has been corroborated by the fact that up to this time any borate or silicate of Au and Pt is not known, while Ag can form both borate and silicate.

THE EFFECT OF HEAT-TREATMENT ON THE SIZE OF THE DISPERSOID

It has been stated before that during the heat-treatment of colourless specimen, the coloration of glass takes place. The duration of heating and temperature of heat-treatment vary with the nature of glass composition. It has been suggested by Zsigmondy that the development of coloration in glass is controlled by the relative rate of two distinct processes: (1) nucleus formation, (2) the speed of crystal growth where nucleus is a colourless discrete particle containing a number of atoms just sufficient for the thermodynamic stability and the crystal growth is a process in which additional material deposits on this particle causing it to increase in size. These two functions are independent of changes of temperature, both of them having maxima, more or less pronounced at different temperatures, and they cause crystallisation of the dispersed phase. The above process of crystallisation of the dispersed phase is quite distinct from the devitrification.

The relation between the concentration and the size of the suspensoid

In connection with the size of the dispersoid of different coloured glasses, having the same or different metallic colourant, of different glass compositions, but of same or different thermal history, the size of the dispersoid has been determined by the X-ray method. The present investigation also includes some specimens of AgCl-borax glass. During the course of our study of different glass specimens, we have found that the width of the line of the dispersed phase in the X-ray picture decreases gradually with the rise of concentration of the dispersed phase, and that is due to the increase of particle size and the details of the particle size measurement have been discussed in the following sections.

Particle size of suspensoids in colloidal coloured glass

The relation between the particle size and the width of the diffraction line at half maximum intensity was proposed by Scherrer (1920) on the assumption that the radiation was parallel and the sample was transparent by the following equation—

$\beta = \frac{k\lambda}{L \cos \theta} + b$, where β = the breadth of diffraction interference at points of half-maximum intensity, expressed in radians.

λ = wavelength of X-rays.

L = the edge length of the crystal considered as cubic.

θ = the angle of diffraction.

b = the natural breadth of the Debye-Scherrer diffraction line which is a constant depending upon the particular apparatus, size, and absorption of the specimen.

k = a constant, the value of which is 0.9. It must be pointed out that the above two assumptions of Scherrer are difficult to realise in practice.

An equation similar to Scherrer was derived by Seljakov, Bragg, Laue (1926), etc. Laue derived an equation which in its most general form permits the size evaluation in different directions on the assumption that the radiation was purely divergent. The general form of that equation is as follows:—

$$\beta = \frac{\pi \frac{w}{n} \left(\frac{r}{R} \right)^2 \cos^3 \theta}{\sqrt{1 + \left(\frac{wr}{nR} \cos^2 \theta \right)^2} - 1}$$

β = absolute corrected value of the breadth in angular measure.

θ = angle of reflection.

w = a constant (0.55).

r = specimen radius.

R = radius of camera.

n is a quantity related to the particle size by a complex expression which, for cubic crystals, reduces to

$$n = \frac{\lambda}{4\pi\Delta}$$

where Δ = edge length of the particle. Later on Brill (1928), Brill and Pelzer (1931) and a few other workers published some interesting accounts of the limitation of the above equations and suggestions of some new equations and procedure considering the nature of the experimental specimen.

It is worth while to mention here that in the case of colloidal coloured glass specimens, we are confronted with some difficulties such as weak lines, the presence of diffuse bands of glass which in some cases superimpose on strong lines, absorption factor of glass base, etc., and some of the details of X-ray photographs have been given in our previous paper (1953). The particle size of the dispersoids of some glass specimens has been measured in the usual process. The X-ray pictures were photometered on a Moll's recording microphotometer. The angular width at half-maximum intensity is measured from the curves after converting the above curves into densities with the help of a standard wedge in the usual process. Again, in the evaluation of the particle size, broadening due to instrumental factor has

been considered. The average particle size of some dispersoids is given in the following table :—

TABLE I

Glass composition.	Sample No.	Concentration of dispersoids.	Average particle size.
Pt-borax ..	1	0.75%	89 A
Pt-borax ..	2	0.975%	120 A
Pt-borax ..	3	1.63%	228 A
Pt-B ₂ O ₃ ..	4	0.80%	124 A
Pt-B ₂ O ₃ ..	5	1.62%	243 A
Pt-Lindemann ..	6	0.61	60 A
Pt-Lindemann ..	7	0.75%	100 A
Pt-Lindemann ..	8	1.75%	243 A
Ag-borax ..	9*	0.50%
Ag-borax ..	10	1.50%	115 A
Ag-borax ..	11	3.50%	275 A
AgCl-borax ..	12*	0.45%
AgCl-borax ..	13	1.20%	86 A
AgCl-borax ..	14	3.20%	139 A

* Lines of the dispersoid are too weak for the correct evaluation of half-width.

Thus it is quite evident from the table that the concentration of the dispersed phase decides the ultimate size of the particle and the size of the particle increases with concentration in the same series, when other factors such as glass composition, thermal history, etc., are the same. The average size of the particle lies within the range of colloidal particle. We may mention here that in transparent coloured glass the amount of colloidal particle does not represent the whole of the dispersed phase, because along with the colloidal form, there is a possibility of existence of atomic form or nucleus form in the glassy matrix. However, the size and the number of colloidal particles will be increased by the diffusion process at the cost of atomic form of the dispersed metal, ultimately by prolonged heat-treatment, the whole of the dispersed phase is precipitated thereby causing a drastic change in colour and transparency of the glass. That has been amply demonstrated by X-ray study of a transparent Ag-borax glass which initially did not reveal the presence of crystalline Ag, but after prolonged heat-treatment for six hours at 550°C. that particular specimen revealed the presence of big crystallites of Ag which was indicated by the discontinuous lines of Ag in the diffraction photograph of glass specimen.

NATURE OF THE GLASS BAND

It is well known that the X-ray diffraction pattern of oxide glass consists of bands only and from the analysis of the diffraction pattern, valuable informations concerning the interatomic distance between the atoms and the co-ordination number of cation are known. In connection with that work the rôle of different cations in the glass composition has been understood with considerable success. Warren and his associates (1938, 1942) have done a considerable amount of work on the above problem. But the colloidal coloured glass deviates from the usual oxide glass by the existence of fine suspensoid of metal in the glassy matrix. During the course of investigation comprising several coloured glasses, it is found that the characteristics of the diffuse band of pure glass remain unchanged in coloured silicate, B₂O₃, borax and Lindemann glass. Only with the rise of concentration of the dispersed phase, there is an increase of diffuseness and lowering of intensity

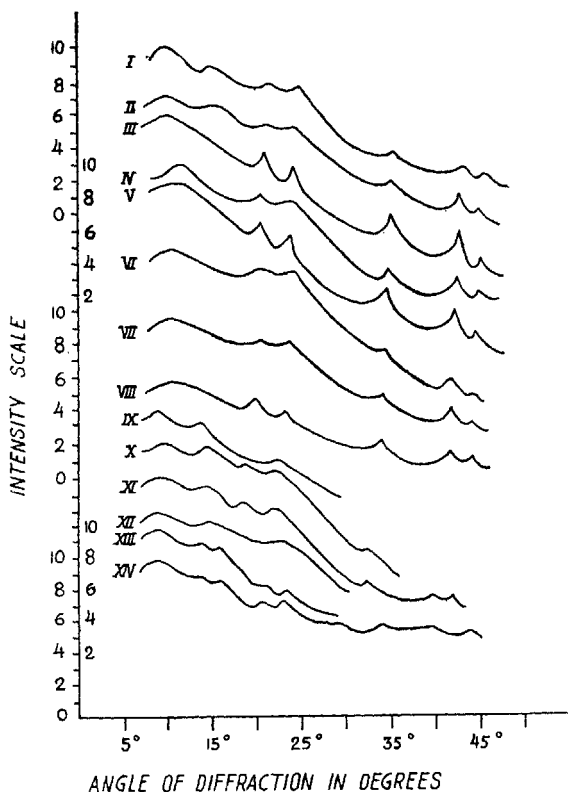


FIG. I.

Maximum of every curve is taken as 10 units. Photometric curves of samples I, IV, VII, XIII and XIV with intensity Units have been shown in the above figure. Details of each sample have been given in Table I.

of the bands (*vide* photometric curves of samples of the same glass base with increasing concentration of solute, for example, Sp. 1, 2, 3; Sp. 4, 5; Sp. 6, 7, 8; Sp. 9, 10, 11; and Sp. 12, 13, 14, in Fig. I) and that is due to the increase of randomness in the respective glass structure in addition to the high absorption coefficient of the dispersed phase. The photometric curves of X-ray diffraction pattern of some glass series are given in Fig. I.

ABSTRACT

This paper comprises the information about the different stages of the dispersed phase during the development of colour in the colloidal coloured glass samples. The nature of the dispersed phase, the relation between the size of the dispersoid with concentration as well as with heat-treatment and the influence of the dispersoid on the characteristics of the diffuse band of the original glass base have been studied. It is found that Ag remains in both elemental and ionic state in glassy matrix while Au and Pt exist mainly in the elemental state.

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