W. E. S. Turner *) (Sheffield) and H. P. Rooksby †) (Wembley)

FURTHER HISTORICAL STUDIES BASED ON X-RAY DIFFRACTION METHODS OF THE REAGENTS EMPLOYED IN MAKING OPAL AND OPAQUE GLASSES

For several years past the authors have been engaged on a study of the materials used purposely by the ancient glassmakers with the object of producing opal (white) or opaque glasses in various shades of blue, green, turquoise, red and yellow. Our initial studies were taken up in order to examine what foundation there existed for the view commonly expressed by archeologists and writers on the history of glass that opal glasses were produced by the inclusion of tin oxide in the glass making mixture. A close examination of existing analyses of ancient glasses showed that the evidence for such belief was comparatively slender. Not only was there a lack of evidence based on analyses, but experimental meltings showed that it was comparatively easy to dissolve tin oxide in ordinary soda-lime-silica glasses up to a content of 10 to 15% by melting at temperatures as low even as 1050° C[1]). At this stage a decision was made to attack the problem by means of X-ray diffraction methods, and after the examination of a few miscellaneous specimens an investigation by these methods was concentrated on the opal glass overlay of the Portland Vase. The detailed investigation, which was described in 1958, led to the unexpected discovery of the importance in the ancient world of antimony oxide in producing opal and opaque glasses. In the opal glass material partly covering the transparent body of the Portland Vase as much as 8.8% of antimony in the form of Sb_2O_5 was discovered; the highest amount indeed of this oxide hitherto found in any glass[2]).
This discovery induced us to explore more widely the ancient glasses from the earliest specimens available down to modern times and to ascertain what changes in fashion took place over some 3400 years in the use by the ancients of reagents for making opal and opaque glasses. For that purpose thirty seven specimens, spaced in time between 1450 B.C. and the present day, were collected from authorities who could testify to the place and the approximate date of origin. The results were very instructive. It appeared that down to the first or second Christian centuries antimony oxide exercised a dominating position in the production of opal and opaque coloured glasses other than in the sealing-wax red

*) Emeritus Professor of Glass Technology, University of Sheffield, England.
†) Leader of Crystal Analysis Group, The General Electric Co. Ltd., Hirst Research Centre, Wembley, England.

1) Turner, W. E. S. *Antichi vetri opali il supposto effetto opalizzante del biossido di stagno.* Vetro e Silic. 2 (1957), No. 6, pp. 27-30.

2) Turner, W. E. S. *Studies in ancient glasses and glassmaking processes VI: The composition and physical characteristics of the glasses of the Portland Vase.* J. Soc. Glass Technol. 43 (1959), pp. 262-284 T. – Rooksby, H. P. *An investigation of ancient opal glasses with special reference to the Portland Vase.* J. Soc. Glass Technol. 43 (1959), pp. 285-288 T.

opaque glasses. In these the opacifier was red cuprous oxide, Cu_2O, or Cu_2O plus metallic Cu, and in certain cases Cu. It is worthy of note that, when a specimen in which metallic copper had been identified by X-rays was newly fractured, metallic spangles were revealed.

During the Christian era other opal producing substances came into use including tin oxide, SnO_2, phosphates (P_2O_5) and in the eighteenth century arsenic as As_2O_3/As_2O_5 in conjunction with lead oxide. Fluorides were introduced in the second half of the nineteenth century and have remained as the commonest reagent so far in the twentieth.

An account of this work was given at the Munich meeting of the International Congress in July 1959[3]). During the delivery of this paper and in the discussion which followed one of us emphasized the fact that although tin oxide began to be used as an opacifying agent within a few centuries after the beginning of the Christian era, we were unable, because of the lack of appropriate glass material, well spaced in date within the first ten Christian centuries, to determine more precisely at what time it began to appear. We were prepared, given suitable specimens, to endeavour to explore the gap. Dr. T. E. Haevernick who took part in the discussion made a generous suggestion which led one of us (W. E. S. Turner) to pay a visit to the Römisch-Germanisches Zentralmuseum at Mainz to examine the specimens of ancient glasses which over the years had there been collected. The result was that she selected and put at our disposal specimens, small but adequate, of 44 glasses ranging from the Egyptian 18th Dynasty, originating from Amarna and dated about 1370 B. C., down to the ninth century A. D. In addition to these specimens, others were received from archeologists working in various fields. A convenient source of material was mosaic tesserae because, although already known before the Christian era, the use of mosaics for decorating floors and walls was greatly developed in the first ten Christian centuries, glasses of many types and colours being melted from which to prepare these tesserae. Specimens of this type came to us from sources in Turkey, in Sinai, in Cyprus and Spain. These and other specimens arising from fragments of holloware and Arabic coins and weights were subjected to examination prior to those which Dr. Haevernick had put at our disposal.

The results showed that somewhere between the second and the fifth centuries A. D. tin oxide began to be used as an opacifying agent and simultaneously antimony oxide, for some reason which it would be interesting to trace, was ceasing to be employed. Lack of specimens which with certainty can be dated at intervals within these centuries make it impossible to ascertain more precisely when these changes took place; but they are apparently beginning in the first half of the fourth century. Out of five specimens of tesserae dated 330-350 A. D. from a Roman tower at Centcelles, near Tarragona, Spain, kindly put at our disposal by Mr. Ernest W. Hawkins of the Byzantine Institute, Istanbul, two, of yellow colour, owed their opacity to lead antimonate, $Pb_2Sb_2O_7$, thus still main-

3) *Glastech. Ber. 5th International Congress Special Supplement* 1959, Part VIII/17-28.

taining a tradition of some eighteen hundred years in duration; but one, purple-brown in colour, was opaque due to large crystallites of SnO_2 (averaging 20-30 μ in diameter) together with a compound of calcium oxide, tin oxide and silica, $CaO \cdot SnO_2 \cdot SiO_2$*). Spectrographic analysis revealed Sn, Pb, Si, and Ca, as major constituents, with no Sb, but with Cr, Fe and Mn among the colouring agents of low concentration.

After the examination of these numerous specimens we felt it very fitting to deal with those from the Römisch-Germanisches Museum, because they range in date over the period 1370 B. C. to the tenth century A. D., and provided an adequate and independent check over the greater part of the period we had previously surveyed.

Fifteen out of the forty-four specimens available were chosen for examination and the results are summarised in the following table.

Reagents used in Producing Opacity in Ancient Glasses. Investigation based on Specimens in the Collection of the Römisch-Germanisches Zentralmuseum, Mainz

Museum Reference Number	Date	Origin, Colour and General Appearance	Crystalline Constituent Identified by X-rays	Constituent Elements by Spectrographic Analysis	Inference
2414	1370 B.C.	Amarna, Egypt, Small rod, opaque orange-yellow	Lead antimonate $Pb_2Sb_2O_7$	Strong: Na, Si Medium: Pb, Sb	The opacifier in the yellow specimen is the lead antimony oxide compound $Pb_2Sb_2O_7$ found in many yellow opaque glasses of Egyptian and Roman times. Essentially the same substance is present in the green specimens in lower concentration. Copper is also revealed in the green specimens by spectrographic analysis and this may be assumed to be dissolved in the glass matrix, giving it a blue colour; thus the overall colour becomes green. The significance of the presence of tin in the green specimens cannot be explained at present.
2408	1370 B.C.	Amarna, Small rod, opaque green	Lead antimonate $Pb_2Sb_2O_7$, in relatively large crystals up to 30 μ in size	Strong: Na, Si Medium: Pb Weak: Sb, Sn, Cu	
2475	1370 B.C.	Amarna, Small rod, opaque "spring green"	Lead antimonate $Pb_2Sb_2O_7$	Strong: Na, Si Medium: Pb Weak: Sb, Sn, Cu, Ca	
2407	1370 B.C.	Amarna, Small rod, opaque bright blue	Calcium antimonate $Ca_2Sb_2O_7$; crystal size small, *ca.* 1-5 μ	—	—
2410	1370 B.C.	Amarna, Small rod, opaque white	Mixture of two calcium antimonates, namely, $Ca_2Sb_2O_7$ and $CaSb_2O_6$, in approximate ratio 70 : 30	—	—
2467	1370 B.C.	Amarna, Fragments from a vessel of opaque blue	Sodium calcium silicate $Na_2O \cdot 2CaO \cdot 3SiO_2$	—	Opacification attributable to a crystalline soda-lime-silicate, incompletely vitrified, or formed by subsequent devitrification.

*) This comp. is crystallograph. iso-structural with the titania-containing mineral sphene, $CaO \cdot TiO_2 \cdot SiO_2$.

Museum Reference Number	Date	Origin, Colour and General Appearance	Crystalline Constituent Identified by X-rays	Inference
470	c. 450 B. C.	St. Michael, G. B. Adelsberg Krain, Yugoslavia. From the Natural History Museum Vienna. Yellow bead with blue and white superficial "eyes"	Yellow portion: cubic pyrochlore-like compound, lead antimonate, $Pb_2Sb_2O_7$, with a small amount of cristobalite (SiO_2)	These specimens are typical of glasses made up to Roman times, in which the opaque character stems from the presence of compounds of antimony oxide, namely: a) $Ca_2Sb_2O_7$ in white specimens b) $Pb_2Sb_2O_7$ in yellow specimens
1791	c. 450 B. C.	Bologna, Arnoaldi, Italy. From a private collection. Yellow opaque bead with blue and white superficial "eyes"	Yellow area: cubic pyrochlore-like compound lead antimonate $Pb_2Sb_2O_7$ with a small amount of cristobalite (SiO_2)	
2295	5th century B. C.	Kertsch, South Russia. Bright emerald green bead with superficial "eyes" of white, blue and brown	Green portion: no crystalline constituent. White: calcium antimonate $Ca_2Sb_2O_7$	
2437	2nd century B. C.	Dendereh — Upper Egypt Private collection. Opaque white piece for inlay	Calcium antimonate $Ca_2Sb_2O_7$ in relatively high concentration	
1924	2/3rd century A. D.	Assab, Africa. Private collection. Opaque red fragments with transparent inner layers	Metallic copper. No cuprous oxide detectable	Colouring and opaque character stems from the presence of metallic copper.
1145	7th century A. D.	Worms — Alzey district Rheinhessen. Opaque bright yellow bead c. 3 mm diameter	Contains an unusually high concentration of the cubic pyrochlore-like lead tin oxide ($Pb_2Sn_2O_{6+x}$) compound lattice parameter c. 10.7 Å. Average crystal size 20-25 microns, unusually large for this class of glass material	This specimen has an appearance resembling a ceramic preparation rather than a glass. It contains a correspondingly higher concentration of crystalline material than the majority of the other yellow specimens investigated. It has probably been made by a glass-making process, but vitrification has been arrested at an early stage. An interesting representative of lead tin oxide opacified material.

Museum Reference Number	Date	Origin, Colour and General Appearance	Crystalline Constituent Identified by X-rays	Inference
1153	7th century A. D.	Worms — Alzey district Rheinhessen. Opaque bluish-white bead	Tin oxide (SnO_2)	Both these specimens are examples of early glasses opacified with free tin oxide.
1041	8th century A. D.	Koban, Russia. Private collection. Transparent blue glass with white opaque glass in which millefiori eyes of brown, blue and white glass are inserted	White opaque glass contains tin oxide (SnO_2) in high concentration	
1057	9th century A. D.	Koban, Russia. Opaque multicoloured bead, slightly oval in shape (4 × 5 mm) in which four rings of white (inside), red, yellow and green coloured glasses are inserted in millefiori fashion	White: Tin oxide, SnO_2 only Red: Metallic copper Yellow: Lead tin oxide compound $Pb_2Sn_2O_{6+x}$ (lattice parameter c. 10.7 Å) of comparatively large crystallite size, estimated at 20-30 microns Green: Similar to the yellow, but concentration of lead tin oxide compound low	The various glasses are well matched together. The green colour of the outer layer may differ from the yellow in containing copper oxide in solution, as has been suggested by results on other pairs of yellow and green specimens. The red glass is a typical representative of the glass in which the red opaque character is conferred by substantial concentrations of metallic copper.

The results completely confirm those derived from the study of samples reported on in 1959 and others which have subsequently been studied. Thus, it is shown that down to the first, if not the second, century of the Christian era, the sole agent employed in the production of opal glasses and opaque coloured glass other than sealing wax red was antimony oxide. The specimens from the Römisch-Germanisches Museum have assisted us substantially in charting the course in the development in the use of tin oxide. Thus, specimen nos. 1145 and 1153, both of the seventh century A. D., 1041 of the eighth century, and 1057 of the ninth century, all contained tin oxide, the last three in particular owing their opacity to SnO_2 alone. As already stated we have other experimental evidence that tin oxide began to come into the picture during the fourth century A. D.
It is of interest to note that the two specimens of red opaque glass Nos. 1924 and 1057 both owe their colour and opacity to metallic copper and not to cuprous oxide, thus confirming that the red to brown opaque glasses could be produced by Cu_2O, or metallic Cu, or mixtures of the two.

We would like to express our indebtedness to the Director of the Museum and to Dr. Haevernick for so readily and generously putting these specimens at our disposal. It is clear from our own experience that the collection of material at Mainz is of great value in serving the interests of research workers on ancient glasses.

MS. received August 1961.