Noble Metals in Photography

PLATINO-TYPE PRINTS OFFER PERMANENCE

The history of the use of platinum in early photography has been described in this journal previously (1). In Great Britain the use of platinum metals in photography virtually ceased at the time of the First World War; however, in the U.S.A. the tradition did not die out completely and it enjoyed a modest revival in the 1970s. The work of American photographers sparked an interest in other countries, including Great Britain. Among those drawn to the beauty and delicacy of platinum prints was Dr. Michael J. Ware, a lecturer in the Department of Chemistry at the University of Manchester. In recent articles he describes how he became attracted not only by the quality that could be obtained, but also by the chemical and practical principles behind the process (2). He found that the techniques being used to produce the platino- and palladio-type prints were virtually identical to those employed in the late nineteenth century, so he set about bringing the technology up to date and understanding the chemistry governing image quality. (3).

The principle of platino- and palladio-type systems involves a first step in which a photosensitive material, normally an oxalato complex of Fe(III), for example ammonium trisoxalato ferrate(III), is photochemically reduced in the presence of ultraviolet light to yield the corresponding Fe(II) species:

$$2\,[Fe\,(C_2O_4)_3]^{3-} \rightarrow 2\,[Fe\,(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2 \quad (1)$$

The Fe(II) complex thus formed is a powerful agent, readily reducing appropriate compounds of platinum, palladium and gold. In practice it is important to use the more labile complexes of the platinum metals to enable the metal image to develop in short times:

$$PtCl_4^{2-} + 2\,[Fe\,(C_2O_4)_2]^{2-} + 2C_2O_4^{2-} \rightarrow Pt^0 + 2\,[Fe\,(C_2O_4)_3]^{3-} + 4Cl^- \quad (2)$$

Choice of paper (high alpha-cellulose) and its absorbency are important factors in producing successful prints. The sensitiser solution, containing the Fe(III) complex and platinum, palladium or mixed palladium/platinum salts, is carefully applied to the paper which is then dried. However, water plays a significant part in the subsequent procedure. If the paper is equilibrated at 80 per cent relative humidity (RH) the image needs no wet development after exposure, while below 50 per cent RH considerable development is required. It is postulated that at 80 per cent RH the paper will contain typically 10 per cent by weight of water which is sufficient to confer limited mobility on the sensitiser ions; thus as the Fe(II) ions are produced by exposure to ultraviolet light of an appropriate wavelength they are able to react with the platinum or palladium ions immediately. However, below 50 per cent RH there is insufficient absorbed water to allow this, and therefore a separate development step is necessary. A particular advantage of the direct "printing out" process is that the print can be examined at intermediate stages of the exposure—particularly if specific effects of tone or texture are sought—then returned for further exposure if this is desirable.

In the second of his two part article in the *British Journal of Photography*, Ware describes the process for people wishing to try platinum-palladium printing for themselves (2).

One advantage of platino-type prints is their permanence, platinum and palladium being more noble than silver. Furthermore, the prints do not contain organic materials such as gelatine which can nourish fungi and moulds. Therefore, use of the process for archival material could be important. D.E.W.

References

1 I. E. Cottington, *Platinum Metals Rev.*, 1984, **28**, (4), 178

2 M. J. Ware, *Brit. J. Photogr.*, 1986, **133**, (6583), 1165; **133**, (6584), 1190

3 M. J. Ware, *J. Photogr. Sci.*, 1986, **34**, (5/6), 13