Gold-Based Enamel Colours

THE CONSTITUTION AND APPLICATIONS OF PURPLE OF CASSIUS

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The most effective means of producing enamel colours ranging from pink to maroon is still based upon the purple preparation of colloidal gold first devised three hundred years ago. This article discusses the many conflicting views that have been expressed on its constitution and goes on to describe modern methods of production and use.

The manufacture of colours for use on pottery and porcelain and in vitreous enamels involves a number of metallic oxides and compounds, but to achieve the highest quality in colours ranging from pink to maroon reliance has been placed for some three hundred years upon the preparation of colloidal gold and stannic hydroxide known as Purple of Cassius.

The discovery of this rather unusual combination by Johann Rudolph Glauber in 1659 and its early exploitation by Johann Kunckel in his glass works at Potsdam in 1679 have already been described in this journal (1). Its use in the pottery and porcelain industry has continued to the present day and it remains the most effective means of achieving brilliance of hue with consistent strength and stability in its particular range of colours.

By 1719 Purple of Cassius was being prepared and used in the first porcelain factory to be established in Europe, the Meissen works set up by Augustus the Strong some ten years earlier, and an entry in a note-book compiled by one of the colour chemists, Samuel Stöltzel, illustrated here, gives a detailed recipe for its preparation. This reads simply enough, but over the years many difficulties and uncertainties have been encountered, and great care is still needed in the method of production.

Only a few years later the secret reached China to form the basis of the famous *Famille Rose* decoration on porcelain (2).

A page from the note-book of Samuel Stöltzel, one of the colour chemists at Meissen, compiled in 1731. It reads in translation:

'The finest purple is prepared from gold

1 Take 3 loth of best aqua regia and dissolve in it $\frac{1}{2}$ a gold ducat, and the liquid will turn yellow.

2 Then take 4 loth of English tin and dissolve this in as much aqua regia as is necessary. It will likewise produce a fine tincture.

3 When both solutions are ready, add a few drops of each simultaneously to a quart glass of pure water — if it is bigger it is even better — and continue until all has gone in, when a red tinge will appear and the purple will fall to the bottom.'

Photograph by courtesy of the Archive Department of the National Porcelain Factory, Meissen

A Meissen jug, made in about 1740, and showing one of the earliest applications of gold-based enamels in the decoration of porcelain to achieve a maroon effect

Photograph by courtesy of the Victoria and Albert Museum, London

In 1738 the Vincennes porcelain works was established — later to become the well known Sèvres factory under the patronage of Louis XV and Madame de Pompadour — and here the distinguished chemist Jean Hellot, appointed in 1751, concerned himself, among other activities in colour making, with the production of a pink enamel. In 1757 he finally succeeded in producing the so-called Rose Pompadour, a beautifully fresh colour based upon Purple of Cassius, and many records of his early attempts and his recipes survive in the archives at Sèvres. (The name Rose Pompadour was never in use at Sèvres; it was coined by connoisseurs and dealers, mostly in England.) This colour was at its best in Hellot's lifetime; after his death in 1766 it was less successful and a reference by his successor Pierre Joseph Macquer in his *'Dictionnaire de Chimie'*, published that very year, shows the uncertainty that prevailed (3):

'Purple Powder of Cassius

This precipitate of gold may be made by several methods, but which of these is the best has not yet been decided. The cause of this uncertainty is that the preparation requires delicate management and is uncertain in its result, the beauty of the colour seeming to depend on some small circumstances not yet discovered.'

Despite these difficulties, pink enamels based upon Purple of Cassius were soon being introduced at Worcester and Chelsea among other early porcelain factories.

In the 1760's the Comte de Milly, a soldier turned chemist, on the conclusion of the Seven Years' War spent several years in the service of the Duke of Württemberg who had established a porcelain works at Ludwigsburg. Here he secretly studied the methods of production and on his return to Paris in 1771 he presented a report to the Académie des Sciences, the

The most successful early use of Purple of Cassius to produce an exquisite rose-pink enamel occurred at the Sèvres porcelain factory just outside Paris. This tea-set and tray, made in 1757 and now in the Victoria and Albert Museum, show the delightful effect obtained, the production of the enamel being in the hands of the distinguished chemist Jean Hellot

intention being to assist the Sèvres factory in its technology. In this report he refers to Purple of Cassius:

'The dissolution of the tin demands great attention because the success of the red colour produced by the precipitation of the gold depends absolutely on the manner by which this solution is combined with water.' (4)

The properties and usefulness of Purple of Cassius were already well known to chemists. Professor Joseph Black, for example, in his lecture notes at Edinburgh University in the academic year 1767/8 writes:

'The precipitate of gold with a solution of tin in Aq Regiae produces a purple colour and the gold gradually subsides. None of the precipitations of gold have been more attended to than this as its colour stands the fire.'

And in a later reference:

'This precipitate is valued, and very much used, as a fine purple for enamel colours. It has the advantage of enduring the fire without undergoing any change of its colour to which many other enamel colours are liable.'

The Constitution of Purple of Cassius

The nature and constitution of Purple of Cassius presented scientists with a problem which, throughout the whole of the nineteenth century, was

attacked by some of the most distinguished chemists of the time, often with quite a degree of vociferous argument.

One of the first to study the precipitate — and one who came closest to the right answer well ahead of his time — was Jeremias Benjamin Richter, well known for his law of chemical proportions and for the concept of stoichiometry. Richter was appointed a colour chemist at the Berlin porcelain works in 1797, and his conclusion on the nature of Purple of Cassius was:

'Nothing but an intimate mixture of extremely finely divided gold with tin calx.' (5)

In 1806 Proust, then working in the royal laboratory in Madrid, considered that the precipitate consisted of a chemical compound of metallic gold and tin oxide (6) although he agreed with Macquer that too little was known of its exact nature. Émile Oberkampf, the son of Napoléon's friend, the well known manufacturer of textiles at Jouy-en-Josas outside Paris, disagreed. In a paper published in 1811 he concluded, after referring to the variable nature of the precipitate and its importance in the porcelain industry, that while it was most difficult to ascertain its constitution, the gold was not entirely in the metallic state (7).

Five years later Vauquelin presented his considered opinion:

'It is probable that the precipitate of Purple of Cassius is not entirely of metallic gold but more a mixture of oxide of gold, oxide of tin and a little metallic gold.' (8)

In 1829 N. W. Fischer, professor of chemistry at Breslau, had no doubt that the precipitate comprised 'gold sub oxide' and tin oxide (9), while P. J. Robiquet, professor at the École Polytechnique, held the same view (10) in opposition to an unknown young

Richard Zsigmondy
1865-1929

Born in Vienna, Zsigmondy studied there and in Munich and in 1897 joined the famous Schott glassworks in Jena. Here he investigated gold-ruby glass and ceramic colours based on the finest dispersions of gold. Following a hundred years of intense debate on the constitution of Purple of Cassius, he was able to demonstrate that it consists of very finely divided gold adsorbed on colloidal stannic acid and for this work he was later awarded the Nobel Prize in Chemistry

Photograph by courtesy of the Bundesarchiv, Koblenz

Examination of Purple of Cassius by transmission electron microscopy shows the black particles of finely dispersed gold on the surface of the colloidal stannic acid. Particle size is critical to the successful development of colour, too large a size giving a weak enamel x 100 000

chemist, Alphonse Buisson, who was the personal assistant to Alexandre Brongniart, the director of the Sèvres factory. Buisson, encouraged by his chief and by the colour chemists at Sèvres, embarked on a long investigation on Purple of Cassius and its method of preparation, and dismissed the existence of an oxide of gold, maintaining that the precipitate contained finely divided gold in the metallic state (11). He argued his case most ably in correspondence in the *Journal de Pharmacie* of 1830 (12), refuting Robiquet as well as others.

In the following year, the great Berzelius entered the argument on the side of the oxide school of thought and of the existence of a chemical compound of gold (13), while Gay-Lussac, in 1832, considered that Purple of Cassius was a true compound of gold and tin oxide (14).

Some twelve years passed without further discussion, and then, in 1844, G. L. Figuier of Montpellier presented a very long paper to the Académie des Sciences (15) in which he recounted some of the researches already carried out on the nature of Purple of Cassius, listing no less than seven different interpretations put forward over the years, and concluded that the precipitate was a definite combination of 'protoxide of gold' and tin peroxide.

In 1857 Michael Faraday delivered his Bakerian Lecture to the Royal Society, 'Experimental Relations of Gold (and other Metals) to Light' (16), and in almost a throw-away line said that:

'I believe the Purple of Cassius to be essentially finely divided gold associated with more or less of oxide of tin.'

A review of all these studies — and of several more, but enough has been said — was prepared in 1866 by J. C. Fischer of Munich (17), and he was able to draw up lists of six distinguished chemists who held that the gold was in metallic form against twelve who believed that it was present as an oxide.

One who later came a little closer to the truth, however, was Henri Debray, lecturer on chemistry at the École Polytechnique, who suggested in a paper to the Académie des Sciences (18) that Purple of Cassius

consisted of finely divided gold that had been absorbed by stannic acid and that it should be likened to a lake such as is produced when soluble organic dyestuffs are absorbed by textile fibres and become insoluble.

Not until the turn of the century was the true nature of Purple of Cassius elucidated. Richard Zsigmondy, a Viennese chemist who had spent some years studying gold colours and had joined the Schott Glassworks in Jena in 1897, soon began to publish his researches on colloidal golds. Together with an optical physicist at Jena, Heinrich Siedentopf, he developed the slit ultramicroscope for the detailed examination of colloids, an instrument capable of resolving 'gold particles down to a diameter of one ten millionth of a millimetre'. Zsigmondy successfully synthesized Purple of Cassius from a deep red colloidal gold and showed conclusively that it consisted of very finely divided gold with colloidal stannic acid and that a mixture of colloidal substances is capable of behaving like a chemical compound (19). For this classical investigation he was awarded the Nobel Prize in Chemistry in 1925.

Modern Methods of Production

A large number of factors can cause variations in the hue and the strength of colour of Purple of Cassius. The result is that despite the many years

over which it has been known and studied, its preparation remains one which is difficult and sensitive to control. Two distinct stages are involved, first the formation of a gold sol and then its stabilization.

The first stage is a redox reaction in which the addition of a stannous chloride solution to an auric chloride solution results in the formation of particulate gold:

It is most important that particle growth should be controlled during this reaction, which proceeds very rapidly. Transmission electron microscopy of enamels coloured by good quality Purple of Cassius indicates as the optimum a gold particle size in the region of 10 to 15 nanometres, particles larger than this yielding weaker enamels of bluish tinge. As students of precipitation will know, there are several factors which affect the size of the particles formed under conditions such as these. The most important are temperature, concentration, agitation and the presence of trace ions. Careful control of these will yield particulate gold in the desired size range.

The reducing system used in practice is not a simple solution of stannous chloride, but a combination of both stannous and stannic forms of tin. The ratio between these latter is important if a stable Purple of Cassius is to be obtained. Historical methods for its production, still used, require the dissolution of tin in aqua regia, a mixture of hydrochloric and nitric acids. The resultant stannic chloride is then reduced to produce the required stannous to stannic ratio by a further addition of tin metal. The final reducing solu-

tion, which takes about twenty-four hours to produce, is deep brown in colour owing to the presence of dissolved oxides of nitrogen. Current-day trends are towards the replacement of this variable process with the use of pure stannous and stannic chlorides, whereby the ratio of the two forms of tin can be precisely controlled.

In the second stage to be distinguished in the formation of Purple of Cassius, the gold sol is stabilized by adsorption onto a colloidal base, which is then flocculated. Under adverse conditions, particle growth can again take place during these operations, leading in extreme circumstances to total decoloration. It is thus essential when isolating Purple of Cassius to keep the gold particles discrete. Colloidal stannic acid formed by hydrolysis of the stannic salt in the reaction mixture performs this function well because of its high surface area and when it flocculates the adsorbed gold particles are precipitated with it in dispersed form. In practice, and because of the sensitivity of the particle size of the gold to the conditions under which it is precipitated, it is usual to limit batch sizes to no more than half a kilogram of gold. This is treated in 1 000 litre vats fitted with high-speed agitators.

In using this flocculent precipitate of Purple of Cassius to produce enamels, it is first dewatered and then wet milled with flux. Dewatering of the precipitate can be carried out by several means. The older technique, slow but effective, is by gravity filtration through fine calico cloth, which yields a slurry of the order of 15 to 20 per cent solids content. Modern techniques, more rapid in production, make use of ultrafiltration and centrifugal methods. The

This modern design, by Paula Dromgole, incorporates a brown enamel, a gold pink and a gold purple as well as a metallic gold. All were applied by silk screen transfer
 Photograph by courtesy of Matthey Printed Products Limited

precipitate is not dried, but is milled in the wet condition with the flux, since experience has shown that if it is dried beforehand it loses its colour because of shrinkage of the surface of the protective stannic acid colloid and consequent growth or coalescence of the gold particles.

Milling with the flux is carried out in conventional ball mills, although modern continuous bead mills are proving useful with pre-ground fluxes. The type of flux used is dependent upon the end use of the enamel and can have a marked effect on the properties of the final product. In the milling process, the gold and the stannic acid are thinly distributed over the large surface of the flux, and by grinding to a surface area of $1.0 \text{ m}^2/\text{g}$ a product can be obtained with a gold content of up to 1 per cent by weight. Some modification of the colour towards the red end of the range can be achieved by the addition of precipitated silver to the mill charge. The shift in hue is probably due to some interaction of the silver with the flux and a range of colours may be obtained by varying the constitution of the flux. Reducing its sodium borate content produces a bluer colour while increasing its lead content produces stronger and redder materials.

Once it has been milled in this way, the preparation can be filtered and dried without loss of tinctorial properties. A more homogeneous distribution of gold can

however be brought about by a subsequent calcination and wet milling. Careful control of these steps is necessary to produce an enamel of the correct surface gloss and consistent high quality.

Applications of Gold-Based Enamels

As stated earlier in this article, gold-based colours have been used for very many years in the earthenware, china and porcelain industries. They have been used in a wide range of processes, including ground laying, banding, hand-painting and spraying, but they are now mostly applied by screen printing methods. Direct screening on tableware and ceramic tiles is one method of application, but the main demand is now from the transfer industry. The older type of lithographic transfer for the decoration of pottery and porcelain uses specially prepared and coated powders to promote good adhesion during the printing process, while the manufacturer of screen printed transfers, with their richer enamel deposit, employs pre-dispersed pastes in oil-based media ready for the printing process.

The alternative and less expensive colours based on chrome-tin do not offer the same range of hues and also give a more opaque finish compared with the excellent translucent effect obtained with the gold-based enamels. These also withstand a higher temperature

Gold based enamel colours can be applied by several methods. In this illustration, direct screen printing is being used in a single-head flatware screening machine. Other colours are applied in sequence with complementary designs of screens

during the firing of the colours than the cheaper base metal enamels.

Another field of use is in the colouring of glass — an application going back to the very first usage of Purple of Cassius — for electric light bulbs, cosmetic containers and reflectors, as well as in the decoration of glassware by screen printing.

Despite their high cost, therefore, gold-based enamel colours will continue to find a place alongside the many other enamel colours used in industry on account of their qualities of strength and cleanness and their very appealing tones that no other colours can reproduce successfully.

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An alternative method of application is by offset printing. Here the colour is applied to an etched copper plate, the white silicone rubber pad descends and picks up the entire pattern of colour, and then moves onto the china or earthenware plate to be decorated, giving a perfect reproduction of the pattern