

Platinum in the Decoration of Ceramic Wares

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Ancient methods of producing lustre effects are briefly described as a background to the introduction of platinum for this purpose. There follows a short history of the uses of platinum for producing bright and matt-surfaced decorations on ceramic glazes.

The first use of platinum for the decoration of ceramics was as a so-called silver lustre over a brown earthenware body. Although it was only discovered in the middle of the eighteenth century, sufficient was already known about the properties of platinum for it to come into commercial use as a ceramic decorating medium by the end of that century. This took place in the English Potteries of Staffordshire.

The silver lustre thus produced was seen at once to have great commercial usefulness. It was not subject to tarnishing, like true silver, and when applied all over an article of pottery it provided a cheap substitute for sterling silver or Sheffield plated tea-pots, cream jugs, sugar basins, candlesticks and the like. When electroplating appeared in the 1840s the use of silver lustre for this purpose gradually declined (1).

The phrase silver lustre, having been in use for one and a half centuries, is likely to continue but it is not strictly accurate. The preparation contains no silver and this word applies only to its appearance when fired.

An early nineteenth-century English coffee pot, now in the Victoria and Albert Museum, showing the use of silver lustre (bright platinum) on earthenware as an inexpensive substitute for silver

Nor do the liquid preparations of gold, platinum and other metals, now referred to as lustres, bear any relation to the much older process of producing lustres on pottery by means of a reducing atmosphere in the kiln. The newer process might be more accurately described as metallised pottery.

The Original Lustre Process

Means of producing lustre effects—a metallic or nacreous iridescence—on ceramics were known in the Near East before A.D. 900 (2). Egyptian and Syrian potters soon mastered the technique, which spread thence to Persia and to Moorish Spain, where



the magnificent large dishes of Valencia were produced before A.D. 1400. Italians imported the Spanish wares via Majorca—whence their term *Majolica*—and by the beginning of the sixteenth century were themselves masters of the art of *madreperla* or giltwork, as they also called it (1). No later products have equalled the beautiful yellow lustres, produced from a silver stain, of Deruta or the coppery reds of Gubbio (3).

The lustre was produced by painting the tin glaze, already fired on the ware, with a clay paste containing oxides of reducible metals such as copper and silver and then firing it in a reducing atmosphere. Armfuls of gorse branches or broom sprinkled with turpentine were thrown into the mouth of the furnace, producing a dense smoke. The compounds painted on to the ware, deprived of oxygen, tended to return to their metallic state and at this point the process of remetalisation was abruptly arrested by raking out the fire and sealing up the kiln. After removal from the kiln the ware was polished with wood ashes and lustre effects were then revealed of a quality still unsurpassed. A great element of chance was involved and many pieces were spoiled, but the good results were so much admired that for some time Italian potters of the renaissance found it worth while to decorate and fire a hundred pieces of ware in order to produce six good ones (4). By 1550, however, they had given up the use of lustre and confined themselves to the painting of elaborate compositions on white glazed grounds which could be fired in more stable conditions.

The Invention of English Lustre

In more recent years, towards the end of the nineteenth century, the art of lustre staining was rediscovered by William de Morgan and William Burton but its principles have remained unchanged.

English lustres were originally made either from gold or from platinum. The gold lustre applied over a brown body produced a dark copper effect or, over a white body, various

shades of pink, lilac and purple with a golden iridescence. Platinum produced the steel and silver lustres.

It is not certain who first invented English lustre. It may have been John Hancock who, writing to the *Staffordshire Mercury* in 1846, at the age of 89, claimed to be “the original inventor of lustre, which is recorded in several works on Potting, and I first put it in practice at Mr. Spode’s manufactory, for Messrs. Daniels and Brown” (5). Or it may have been John Gardner who was also later employed by Spode.

An early writer on the subject, Simcon Shaw (6), whose *History of the Staffordshire Potteries* was published in 1829, says:

“The general voice of the district is in favour of Mr. John Hancock . . . a person of no mean talents as enameller . . . having first produced the lustre. . . . The lustre of our day is a good red clay body with a fine brown glaze, upon which is laid, for gold lustre, a very thin coating of a chemical mixture containing a small quantity of gold in solution; also of copper, for copper lustre. The Steel lustre employs oxide of Platinum in the same mixture instead of gold; and when Silver Lustre is made, a further coating of platinum in water only, is laid on the steel lustre. . . . The first maker of the Silver lustre properly so called, was Mr. John Gardner (now employed by J. Spode, Esq.) . . .”

Further evidence is in William Evans’ *Art and History of the Potting Business*, published in Hanley in 1846; here it is stated that “Mr. Hancock . . . who subsequently invented the lustre; which was improved to imitate silver by John Gardner, Stoke, and gold, by William Hennys, Burslem . . .” (7).

Formulae for Silver Lustre

The earliest printed formula for lustres is given in Lakin’s book (8) published in 1824. His formula for gold lustre was:

30 parts muriatic acid
10 parts nitric acid
5 parts grain gold

The gold was added to the aqua regia and dissolved in about two hours. It was recommended that 5 per cent of metallic tin on the weight of the gold be added to the acids at the same time. Separately 30 parts of balsam

A nineteenth-century jug in silver resist lustre (bright platinum) also in the Victoria and Albert Museum



of sulphur and 20 parts of spirits of turpentine were gently heated over a water bath until of a homogeneous consistency. The acid gold solution was then poured into the diluted balsam. With this preparation only about 3 per cent of the completed lustring mixture consisted of gold.

Similar receipts occur throughout the nineteenth century, one of them stipulating that small amounts of iron should be included when a more bronzed effect was required.

The same procedure was employed for platinum lustre except that the acid solution of the metal was mixed with 135 parts of spirits of tar and the whole heated gently over a water bath until completely homogeneous. For silver lustre the diluent appears always to have been spirits of tar rather than the balsam of sulphur used in gold lustres. Spirits of tar was a pine tar thinned with turpentine whose resinous content would carbonise during the firing process and assist in the reduction of the platinic chloride to a metallic film.

The best silver lustre was that applied over a red-brown body, as for gold lustre, but two applications of lustre were necessary. The first firing of the lustre solution produced a

steely-grey colour, referred to as steel lustre. The full silver effect is said to have been produced by a second coating, using platinum oxide—not chloride—and a second fire in the enamel kiln. According to W. D. John and Warren Baker in *Old English Lustre Pottery* (9) the platinum oxide was obtained as an orange-coloured powder by the addition of excess of salammoniac to the acid-platinum solution.

For silver lustre decoration on a white body or for resist patterns this second coat was not used.

Many of these old formulae bring smiles to the cheek of a modern chemist and it would seem from the statement just quoted that the old terminology implied something different from its present meaning. At best the products of these early formulæ were most unstable and the solutions had to be used as soon as they were made up.

Current Types of Silver Lustre

The more scientific and stable preparations now in use are more correctly referred to as liquid bright platinum. These consist of a platinum resinate in certain essential oils such as rosemary or lavender; they are true solutions of uniform character. The rather darker

and heavy colour given by platinum on its own, coupled with the high cost, has led to the incorporation of gold and various other metals of the platinum group, resulting in improved whiteness of the metallic film and a less expensive product.

There are thus now available a number of liquid bright platinum solutions varying as regards tint, price, viscosity and suitability for different types of glaze. It is possible to adjust these still further for application to ceramic wares by means of screen-printing, spraying, rubber-stamping, engraved-plate printing or mechanical banding. On account, however, of possible high wastage factors it is most usual to apply silver lustres by hand with a brush and the product is generally adjusted to have optimum handpainting qualities. It is applied to ware that has been previously glazed and fired and, when dry, the lustre is fired in an oxidising atmosphere at temperatures ranging from 680°C to 830°C according to the type of glaze over which it is applied.

Resist Lustre

Almost contemporary with the first use of silver lustre as an all-over covering was the decoration known as resist lustre which is still produced by some potteries such as Josiah Wedgwood & Sons and A. E. Gray & Company.

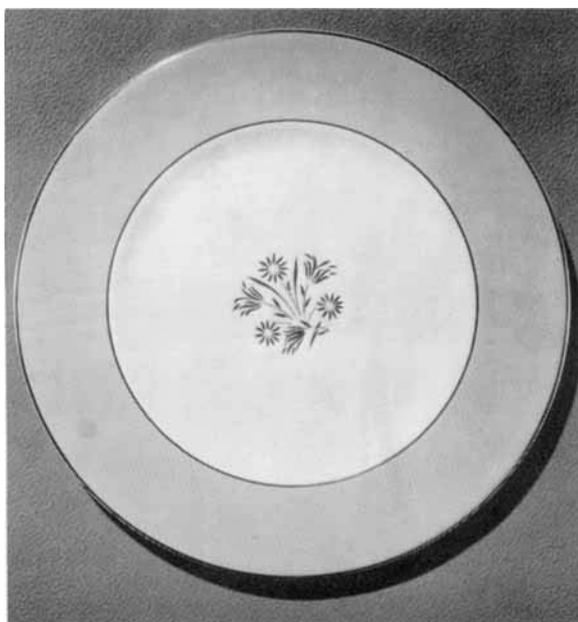
To obtain this result a decorative pattern was painted on to white ware with a water solution of gum, sugar, size, honey or sugar and glycerine—in fact almost any medium that painted well and could be detached by immersion in water. Colouring matter was

added to make the design more easily visible. When the painted pattern had sufficiently set, the article was immersed in the platinum solution up to the top edge and then reversed and dipped to a depth of one-quarter of an inch inside the top. When thoroughly dry it was immersed in water which released the painting medium and the platinum solution upon it. The pattern thus “resisted” the platinum, and when fired it showed up as a white design on a silver ground.

For current types of silver lustre a much-used resist is Chinese white water colour tinted with crimson lake, which makes the design on a white glaze more easily visible to the worker. When dry, this is painted all over with the lustre solution and fired in the normal way. After firing the scurf formed by the resist and the lustre on top of it is washed away, leaving a clear-cut white design against a non-tarnishing metallic background.

Matt Platinum Decoration

The difference between platinum decorations with a bright metallic surface and those with a matt surface that required further burnishing after it was fired was in the first



Dinner plate by Doulton Fine China Ltd., with central design and finishing lines in matt platinum



Vase and beaker in modern silver resist lustre (bright platinum) painted by Colin Haxby, 1958

place less sharply defined than it is today. The modern liquid bright platinum, or silver, as it is still frequently called, is a homogeneous solution which needs no further treatment after firing. In liquid matt platinum the precious metal is only partially dissolved, the remainder consisting of very fine particles suspended in the solution and therefore needing agitation before use. After firing the platinum needs to be scoured, or burnished, with fine round-grained sand in order to produce its characteristic silvery sheen.

It is apparent from a paper by Professor Klaproth, of Berlin (10), that some such result was produced as early as 1802. The following is a description of Klaproth's method of applying platinum to porcelain.

"I dissolve crude platina in aqua regia and precipitate it by a saturated solution of sal-ammoniac in water. The red (*sic*) crystalline precipitate thence produced is dried and being reduced to a very fine powder is slowly brought to a red heat in a glass retort. As the volatile neutral salt, combined with the platina in this precipitate, becomes sublimated, the metallic part remains behind in the form of a grey, soft powder. This powder is then subjected to the

References

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| 3 | M. L. Solon | | A History and Description of Italian Majolica, London, 1907 |
| 4 | Cipriano Piccolpasso | | Li tre Libri dell'Arte del Vasaio, circa 1556 (Original MS in Victoria and Albert Museum, London. English translation by Bernard Rackham and A. Van de Put, 1934) |
| 5 | Anon. | | <i>The Staffordshire Mercury</i> , 1946. (Quoted by John Haslem, <i>The Old Derby China Factory</i> , 1876) |
| 6 | Simeon Shaw | | History of the Staffordshire Potteries, Hanley, 1829 |
| 7 | William Evans | | Art and History of the Potting Business, Hanley, 1846 |
| 8 | Mrs. Lakin | | The Valuable Receipts of the late Mr. Thomas Lakin, Leeds, 1824 |
| 9 | W. D. John and Warren Baker | | Old English Lustre Pottery, Newport, 1951 |
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same process as gold; that is to say, it is mixed with a small quantity of the same flux as that used for gold, and being ground with oil of spike is applied with a brush to the porcelain, after which it is burnt-in under the muffle of an enameller's furnace and then polished with a burnishing tool."

Little commercial use seems to have been made of matt platinum decoration before the beginning of the present century, but in our own time it has come into vogue for the finishing of fine quality china and porcelain, particularly for tea and dinner-ware.

We thus see platinum first appearing on pottery as a lustre, a cheap ceramic substitute for sterling silver or combined with coloured enamels to decorate "peasant" wares for sale at country fairs.

Today its cost is such that matt platinum is seldom seen as more than a narrow band or line, the final luxury of finish on costly services, while platinum lustre is mainly confined to resist decoration on pieces made solely for their ornamental value.

Hydrocracking on Platinum Isomerisation Catalysts

A COMPARISON OF ALUMINA AND SILICA-ALUMINA BASES

Catalysts used in pentane or hexane isomerisation processes require two types of reaction site – the platinum sites where dehydrogenation and subsequent hydrogenation occur and acid sites, provided by the supports, where isomerisation of the dehydrogenated product takes place. An undesirable side-reaction, hydrocracking to lower molecular weight paraffins, has been studied by C. G. Myers and G. W. Munns, Jr., of the Socony Mobil Oil Co. Inc. Their results are published in a recent paper (*Indust. & Eng. Chem.*, 1958, 50, (12), 1727-1732).

The hydrocracking of *n*-pentane, -hexane and -heptane was studied using isomerisation catalysts comprising platinum on alumina and platinum on silica-alumina. The hydrocracking of *n*-pentane can be correlated with the dehydrogenation activity of the catalyst – a function of the platinum sites – but is not directly related to the nature of the acidic support. The products of the cracking reaction are evenly distributed over the range C₁-C₄ hydrocarbons and this distribution is not affected by altering the catalyst support. However, the change in pentane hydrocracking activity per unit change in dehydrogenation activity is less for platinum-alumina than for platinum-silica-alumina catalysts, with the result that the hydrocracking activity

is in general less for platinum-alumina when the two catalysts have the same dehydrogenation activity. This may be explained by chemical interaction between platinum and the siliceous support. These results suggest that hydrocracking of *n*-pentane is catalysed by the platinum sites.

Hydrocracking of *n*-hexane and *n*-heptane does not give rise to an even distribution of cracking products but to a higher proportion of hydrocarbons derived from cracking at the centre-bond. This is a characteristic of cracking at acid sites. It is shown conclusively in the case of *n*-heptane that the more acidic silica-alumina support favours centre-bond cracking to a greater extent than the alumina support.

The results obtained indicate that on dual-function isomerisation catalysts two types of cracking can occur depending on the chain length of the hydrocarbon. Platinum-catalysed hydrocracking, giving an even distribution of reaction products, occurs alone in *n*-pentane and together with acid-catalysed cracking in *n*-hexane. Acid site hydrocracking alone occurs in *n*-heptane. It is suggested that platinum-catalysed hydrocracking occurs via the olefin intermediate produced in the isomerisation reaction by dehydrogenation at the platinum sites.