The True Story of Purple of Cassius

THE BIRTH OF GOLD-BASED GLASS AND ENAMEL COLOURS

L. B. Hunt
Johnson Matthey & Co Limited, London

For the past 300 years the literature on gold, on glass and on ceramics has ascribed to Andreas Cassius the credit for discovering the purple preparation of colloidal gold and stannous hydroxide that bears his name and that is still in use as the most effective means of producing enamel colours ranging from pink to maroon. But not only was it known and described more than 25 years before its publication by Cassius; it had already been successfully used to produce a beautiful ruby glass.

Reference to any text-book or technical encyclopedia dealing with the chemistry of gold, with glass and ceramics or with colours and pigments will reveal, under the heading "Purple of Cassius" an opening sentence that runs, with very little variation from one source to another:

> Purple of Cassius was discovered by Andreas Cassius of Leyden in 1685 and described in his work *De Auro*.

But the preparation that has borne his name for so very long was not in fact discovered by him, he was not especially associated with Leyden except as a student, and by the year 1659 a detailed method of preparing the purple compound of gold had already been published, while by about 1679 it was in use in the glass factory at Potsdam in the manufacture of ruby glass.

Moreover there was not just one Andreas Cassius; there were two of the same name, father and son. It is quite possible that the elder did in fact devise a process for making the purple precipitate although some years after its first preparation, but if so he remained silent on the subject; it was the son who wrote *De Auro* in which he described the procedure but in the book he made no mention of his father.

That compounds of gold could impart a red colour to glass had been known for many centuries. Egyptian manuscripts from the Greco-Roman era make reference to it. The great metallurgist Agricola knew of it, as did Paracelsus, in the first half of the sixteenth

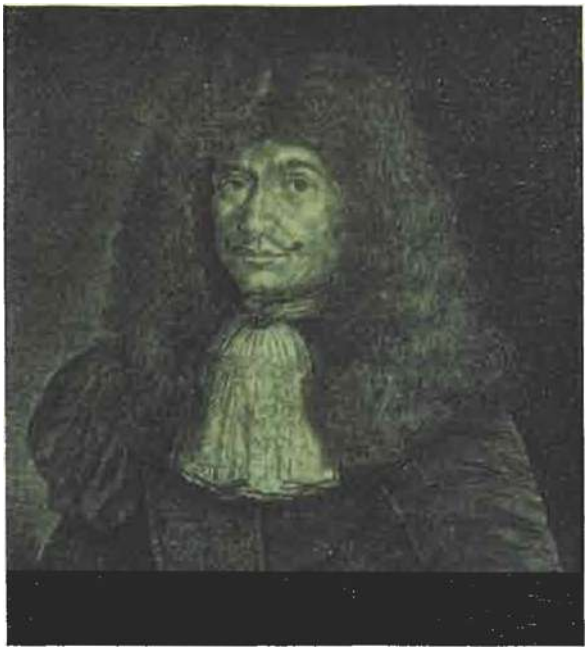
Johann Rudolf Glauber
1604–1670

Born at Karlstadt am Main, the son of a barber-surgeon, Glauber had a chequered career and a wandering life. He was a skilful practical chemist and a prolific author of works on chemistry. A quarter of a century before Cassius he described the preparation of the colloidal complex of gold chloride and stannous hydroxide. The inscription round the portrait, by the Dutch artist Anthonius Santvoort, reads: True Portrait of the Honoured and Highly Esteemed Herren Johannis Rudolphi Glauberi, Noble Chemist and Experimenter at Kitzingen in Franconia: 1654. A.S.

Courtesy of the Deutsches Museum, Munich.

Johann Kunckel
1630–1703

The son of an alchemist to the Duke of Holstein, Kunckel first entered the service of the Elector of Saxony, Johann Georg II, at Dresden. He later lectured in chemistry at the University of Wittenberg, moving in 1678 to Berlin to take charge of the Potsdam glass factory of the Elector Friedrich Wilhelm of Brandenburg until the death of the Elector in 1689. Kunckel then moved to Sweden as Minister of Mines to King Charles XI, who created him Baron von Loewenstein



century, while Benvenuto Cellini at about the same time refers to a transparent red enamel discovered by an alchemist who was also a goldsmith.

Andreas Libavius, the German alchemist who wrote the first real text-book of chemistry, *Alchemia*, in 1597 says:

> "From the red coloured tincture of gold dissolved in liquid or oil it is possible without much difficulty to make red crystal."

while a little later, in 1612, there appeared the first treatise on glass making, written by the Florentine priest Antonio Neri. His *L'Arte Vetraria* assembled a great deal of information he had acquired during his visits to Venice and Antwerp—both then active centres of glass making—and he makes a passing reference to "a wonderful red obtained from gold".

But none of these early writers refer to the purple preparation of gold with a tin compound. They generally appear to have used a straightforward precipitated gold powder, heated until it acquired a purple colour and sometimes incorporated with "liquor of flints" (potassium silicate) as a means of imparting a red colour to their glass.

A near approach to the discovery of the purple precipitate is however recorded in the so-called Bologna manuscript, a work entitled *Segreti per Colori* written in Italianate Latin in the early part of the fifteenth century and now in the Convent of San Salvatore in Bologna. This includes a formula for dissolving tin oxide in a crude form of aqua regia and adding golden marcasite (auriferous iron pyrites) to yield "a beautiful purple".

Kunckel produced ruby glass in great quantities at Potsdam between 1679 and 1689, and many examples survive today. This silver mounted tea-pot shows the red colour obtained by Kunckel using the purple preparation of gold chloride and stannous hydroxide later to be associated with the name of Andreas Cassius

It is to Johann Rudolph Glauber that belongs the credit for the initial discovery of the much more effective and economical means of obtaining the desired red colour. Glauber was really the first industrial chemist in that he made a living from the sale of his medicinal preparations—including solutions of gold and of course his famous *sal mirabila*, sodium sulphate—and he was a very skilled manipulator and a designer of new types of stills and furnaces.

In 1648 he left his native Bavaria to settle in Amsterdam where most of his many books were published. The long religious conflict, afterwards to be known as the Thirty Years War, had just ended, leaving the Germanic states ravaged and impoverished, and Glauber conceived a burning ambition to see an economic and industrial revival based upon his chemical and metallurgical ideas. To this end he compiled a large work, in four parts, entitled *Des Teutschlandts Wohlfahrt* (The Prosperity of Germany) which was published simultaneously in German and in Latin (*Prosperitatis Germaniae*) in the years 1656 to 1660. In this he appealed to his countrymen to develop their national resources and to make fuller use of their minerals and raw materials, using their wood and sand, for instance, to produce glass such as was made in Venice and in France.

Glauber was familiar with several means of precipitating gold from its solution in aqua regia, and he is the first to mention that it can be precipitated with a solution of a tin compound. After a preliminary description of the reaction in Part IV of this work, published in 1659, he goes on:

> "N.B. The tin should be pure, and the whiter and harder, and the better its ring, so much is it better for this work or composition, and you can make use of these weights: Take 1 loth of fine gold powder, dissolve it with 3 or 4 loth of strong rectified Spiritu Salis; to the solution add 12 or 15 loth of pure water and put in a small piece of tin weighing 2 loth. Put the vessel on a warm sand bath and let it stay warm for 1 or 2 hours but do not boil it, and the gold will precipitate from the solution in the form of a brilliant purple-coloured powder" (1).

(There is an apparent anomaly here in that normal spirits of salt—hydrochloric acid—will not attack gold; Glauber was well acquainted with aqua regia, but he had also found that by distilling a concentrated solution of zinc chloride over sand and adding the distillate to hydrochloric acid he could readily dissolve his gold. This he referred to as "strong spirits of salt".)

There is no evidence that Glauber made use of his purple precipitate for the colouring of glass; his experiments in this direction were based upon the older procedure of adding "liquor of flints" to a solution of gold in aqua regia, but his account of the purple precipitate, written a quarter of a century before the publication by Cassius, was undoubtedly utilised by another distinguished contemporary chemist.

This was Johann Kunckel, the son of an alchemist and an alchemist himself, but also a man well versed in the glass technology of his time, and in his later years a genuine chemist. After teaching practical chemistry for a short period at the University of Wittenberg he entered the service of Prince Friedrich Wilhelm of Brandenberg, the "Great Elector", in 1678 and was given charge of the glass factory the Elector had sponsored in 1674 near to his new palace at Potsdam. He had just then published his *Ars Vitraria Experimentalis, oder Vollkommene Glasmacherkunst*, which incorporated the older work of Neri already mentioned and the observations added to this by the Englishman Christopher Merrett who had translated Neri into English in 1662, together with much of Kunckel's own material. This work remained a standard treatise on glass technology for many years, and it is here that are found somewhat veiled references to the production of ruby glass by the use of the purple precipitate described later by Cassius.

In discussing Neri's proposed method of colouring glass red by means of gold powder he says he has tried this more than once but it is no good after one or two pieces have been made as the colour disappears. He goes on:

> "I should like to describe a better method and to show in detail how to make a red or ruby glass if it were not considered such a special rarity by my worthy Prince and Lord. Whoever does not want to believe that I can make it can come and see it in my workshop. The truth is it is still too rare to make it known." (2)

And again, commenting on Neri's formula:

> "This dear and expensive method has certainly been tried by many but it has brought joy to few; it would be better to put the gold into it in such a way that it imparts red tincture to the glass . . . and the author would have been nearer the mark if one could suppose that he had done this or could do it."

Kunckel's successful use of the purple precipitate to produce the ruby glass, often referred to as Kunckel glass, was not revealed until the publication some years after his death of his *Collegium Physico-Chymicum Experimentale, oder Laboratorium Chymicum*, as will be seen a little later.

Meanwhile, there is one other publication to be mentioned before we come to the *De Auro* of Andreas Cassius the younger. This was a tiny little book written by Johann Christian Orschall with the title *Sol Sine Veste*—Gold Unclothed—published in Augsburg in 1684, one year earlier than *De Auro*. Its cumbersome sub-title runs: "Thirty Experiments to Extract the Purple from Gold, which in Part

One year before the publication by Cassius of his *De Auro*, a small book by the metallurgist Johann Christian Orschall recorded a number of his attempts to produce the purple precipitate. The title, *Sol Sine Veste*, Gold Unclothed, is followed by a subtitle reading: "Thirty Experiments to Extract the Purple from Gold, which in Part Proposes the Destruction of Gold, with Instructions for Preparing the Long Sought After Ruby Flux or Red Glass at its Most Perfect; Disclosed from Personal Experience."


SOL SINE VESTE.
Oder
Dreyßig
EXPERI-
MENTA
Dem
Gold ſeinen Purpur
außzuziehen/
Welches theils die Deſtru-
ctionem auri vorſtellet/
Mit angehängtem Unterricht/
dein ſchon längſt verlangten
Rubin-Fluß
Oder
Rothe Glaß/
In höchſter Perfection zubereiten/
Ans Licht gegeben aus eigener
Erfahrung von
J. C. O.
Augſpurg/ gedruckt bey Jacob Koppmayr/
Anno 1684.

Proposes the Destruction of Gold, with Instructions for Preparing the Long Sought After Ruby Flux or Red Glass at its Most Perfect."

Orschall was a metallurgist who had secured an appointment as Inspector-General of Mines to the Landgrave of Hesse-Cassel at Frankenberg on the basis of a promise, by his skill and experience, to make the mines the best and most efficient in Europe within two or three years. This he was unable to achieve, and he was discharged in 1687. There were other accusations against him, including drunkenness and even polygamy, although it seems likely that his new approaches to mining and metallurgical practices brought about an intrigue against him by the more conservative mining officials. He wrote a text book on metallurgical operations, *Ars Fusoria Fundamentalis Experimentalis* (3), published in Cassel in 1687, but then disappeared from view and is thought to have died in a monastery in Poland.

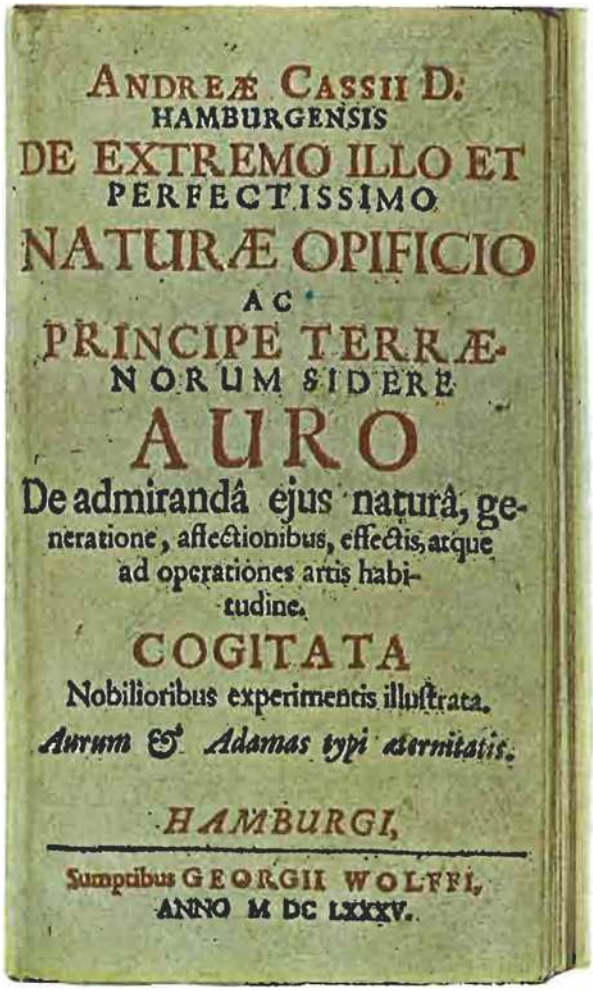
Orschall was something of an alchemist, and he was trying to show that there were means of changing gold in such a way that it could not be turned back into gold again. He had already found by chance that a solution of gold in aqua regia when poured into a pewter wash basin—"I having no other empty vessel handy at the time"—coloured it red, but until he had a discussion with Dr Cassius (presumably the younger one as the father died in 1673) he was not able to prepare the really effective precipitate:

> "This led me to further labours in the hope of obtaining the beautiful ruby flux that is in such demand everywhere but hard as I tried it was all in vain and I saw that I could achieve nothing except by destroying the gold. But it happened that the well known Dr Cassius who was the true inventor of this red glass was willing to discourse with me. He recommended not only how to precipitate the gold to the deepest red but to destroy it to such an extent that it would never again be possible to reduce it to its body. When I later told him what had happened with the tin basin he was amazed and then disclosed his secret to me." (4).

Thus while Glauber first discovered the purple precipitate made from a gold chloride solution and tin, he was unaware of its immense colouring power and sensitivity, and while Kunckel succeeded by his great efforts in finding the correct procedure for producing ruby glass consistently and in quantity by its use, some credit must remain to one or other of the men named Andreas Cassius.

In his *Laboratorium Chymicum* already mentioned, written in Stockholm in about 1700, edited by his friend Johann Caspar Engellender thirteen years after Kunckel's death, and published in Hamburg in 1716, Kunckel described his work on ruby glass:

> "It began in this way. There was a Doctor of medicine called Cassius who discovered how to precipitate Solis cum Jove [gold with tin]; I believe that Glauber may have given him the idea, or so it seems to me. Dr Cassius tried to introduce it into glass, but when he tried to form glass from it or when it was taken from the fire, it was as clear as any other crystal and he was unable to achieve a stable red. . . . As soon as I heard of this, I immediately took it up, but only I know what trouble I had to find the composition, to get it right and to obtain a durable red." (5).


ANDREÆ CASSII D.
HAMBURGENSIS
DE EXTREMO ILLO ET
PERFECTISSIMO
NATURÆ OPIFICIO
AC
PRINCIPE TERRÆ-
NORUM SIDERE
AURO
De admirandâ ejus naturâ, generatione, affectionibus, effectis, atque ad operationes artis habitudine,
COGITATA
Nobilioribus experimentis illustrata.
Aurum & Adamas typi æternitatis.
HAMBURGI,
Sumptibus GEORGII WOLFFI,
ANNO M DC LXXXV.

The title page of *De Auro* by Andreas Cassius junior. Published in Hamburg in 1685, it is often quoted as the source of the first reference to Purple of Cassius. The full title reads:

"Thoughts Concerning that Last and Most Perfect Work of Nature and Chief of Metals, Gold, its Wonderful Properties, Generation, Affections, Effects and Fitness for the Operations of Art; illustrated by Experiments."

Kunckel, earlier in the book, gives his own recipe for the purple precipitate:

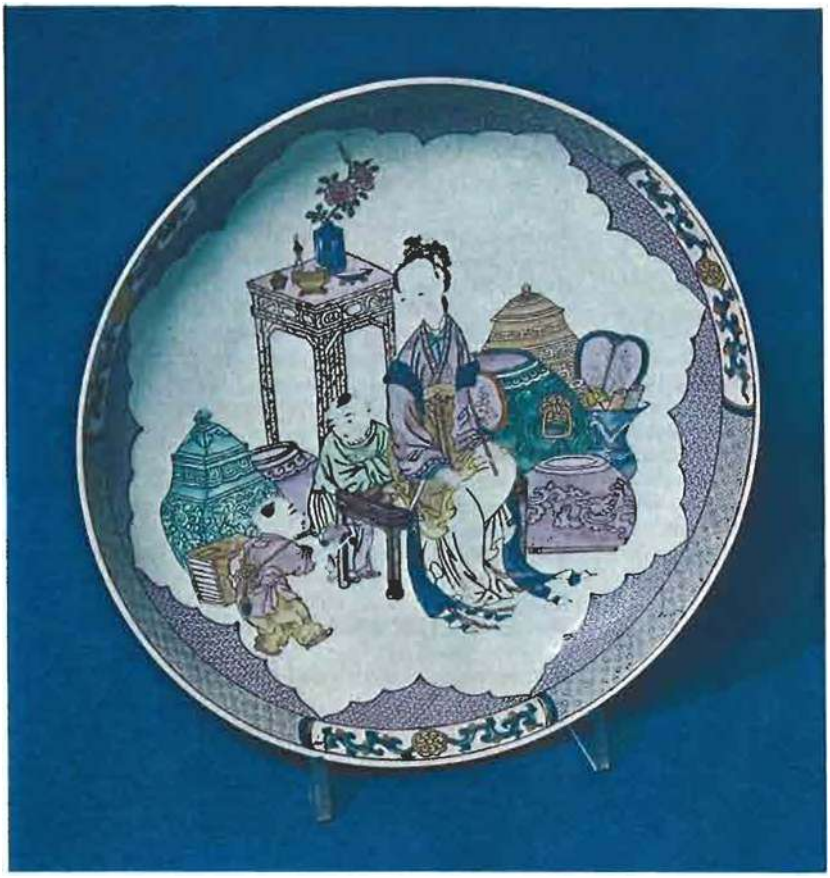
> "I take two parts of good aqua fortis and one part of spirits of salt, or failing this some strong salt water. When these are mixed throw in from time to time a little of the purest tin so that it does not heat up but dissolves slowly. . . . With this solution the gold can be precipitated in such a beautiful colour that it cannot be more beautiful, and thereby can crystal glass be given the finest ruby colour if the gold has previously been dissolved in three parts of aqua regia and one part of spirits of salt." (6).

So we come finally to the two men named Andreas Cassius. The elder, who was born in Schleswig in about 1605, took his M.D. at Leyden in 1632 and became physician to the Duke of Holstein and to the Bishop of Lübeck. He died in Hamburg in 1673. His son, born in Hamburg in 1645, took his M.D. at Gröningen in Saxony in 1668 and practised as a physician in Lübeck, where he died at about the end of the century. He wrote on several medical subjects and in 1685 published *De Auro*. This is basically an alchemical work, as will be seen from the wordy sub-title, and makes frequent references to the "salt" and the "fixed sulphur" of gold. It is in his Chapter 10, "De Operationibus Circa Aurum Chymicis" (Some Experiments in the Alchemy of Gold) that he gives the famous recipe, after saying that the sulphur of gold is extremely difficult to separate:

> "There is, however, another method which has been kept secret until now, by which by a single precipitation of gold with a solution of tin its fixed sulphur is elegantly produced. Thus first English tin, the purer the better, is totally dissolved in aqua regia so that the solution becomes completely yellow or like red wine. You will produce this result by gradually throwing the tin into the mixture so that it is dissolved by the corrosive liquid, and by thus throwing it on again and again until, as it continues to dissolve the tin it has become viscous. Let this solution be left in the open air for a few days to allow the gas sylvestre [the name given to carbon dioxide by Helmont in 1648] to escape, and let it be fed each morning with new tin until the corrosive parts no longer seethe but react smoothly on the sulphurous parts and dissolve the texture of the tin without crackling and tinge themselves with a delicate golden or rather red colour, as though as a sign of a golden precipitation now perfectly worked out. When this has been done, secondly make a solution of one drachm of gold in aqua regia in the usual way. Thirdly, pour a large quantity of ordinary water into a fairly capacious glass with a wide mouth. Pour into this some of the tin solution, and a little later the same amount of the solution of gold and immediately you will see a most curious precipitation of gold in that spring water, exhibiting the three cardinal colours that are found in gold, yellow of course, blue and black, which a little later when the air has got at them turn to a beautiful reddish purple, with a little cloud of salt swimming on the top."

After describing this as "a most noble experiment . . . most fitted to many uses in other chemical and mechanical labours" Cassius goes on to say:

> "By its application, indeed, colours of every kind are enhanced and are preserved better in its viscous substance. This was noted not many years ago in an outstanding work on the art of colouring, with the result that now not a few dyers have learned to reproduce the most beautiful reddish purple (in the way that other artists make gold ruby glass) simply by its means. So I say nothing about how powerful it is in colouring stones, crystals and likewise in producing purple enamels. You cannot expect it



By the early seventeen-twenties the secret of Purple of Cassius had reached China and been put to excellent use in the production of the famous *Famille Rose* porcelain. This plate is an early example from the Yung Chêng period beginning in 1723

Courtesy of the Victoria and Albert Museum

> even from gold without dexterity and good manipulation, for unless you handle the matter in a certain way, the purple of gold returns to its own yellow colour by a process of digestion and is reconcentrated into gold. But to be willing to betray all this would be the act of a fool and injurious to the labours of famous men who have not gained a knowledge of such things without long experience and after much tiring work."

Thus Cassius junior was well aware that the purple precipitate, whether or not the formula for its preparation had been devised by his father, had been used well before the publication of his book to produce ruby glass and red enamels. Orschall, in fact, states that Dr Cassius (the son) "succeeded in making a very fine ruby flux and sold the secret of this in various places for a certain sum so that it is to be seen here and there, and even today some of it is still made at Freysing although it is kept very secret". Only Kunckel, by his special knowledge of chemistry and of glass making, succeeded in producing ruby glass consistently and on a large scale, but it was clearly Glauber who preceded both Kunckel and Cassius in devising the colloidal precipitate that was and still is the most economical and effective means of obtaining the red colour.

Its use soon spread farther afield. By 1719 at the latest it was employed in the decoration of porcelain in the new factory at Meissen and a note-book compiled by Samuel Stöltzel, preserved in the archives at Meissen, gives essentially the same recipe (7). It must also have been used by enamellers on metal work, and it was by this route that the secret reached China, almost certainly conveyed by Jesuit missionaries trained in the arts and crafts, so that by about 1723 it formed the basis of the famous *Famille Rose* Chinese porcelain (8).

Its use in modern ceramic colours persists and grows, but an account of the preparation and properties of these enamels, ranging from pink to maroon, and of modern views on the constitution of Purple of Cassius, must form the subject of another article in this journal.

References

1 J. R. Glauber, "Des Teutschlandts Wohlfahrt", Amsterdam, 1656–61, Part IV, pp. 35–36

2 J. Kunckel, "Ars Vitraria Experimentalis", Frankfurt and Leipzig, 1679, p. 192

3 This was translated into French as "Oeuvres Metallurgiques de M. Jean-Christian Orschall", Paris, 1760, by the Baron d'Holbach, whose preface gives the story of Orschall being deprived of his office by the intrigues of his enemies.

4 J. C. Orschall, "Sol Sine Veste", Augsburg, 1684, pp. 18–19

5 J. Kunckel, "Collegium Physico-Chymicum Experimentale, oder Laboratorium Chymicum", Hamburg, 1716, p. 650

6 J. Kunckel, *ibid.*, p. 382.

7 M. Mields, "Aus der Jugendzeit des Europäischen Porzellans", *Sprechsaal*, 1960, **93**, 391

8 Sir Harry Garner, "The Origins of *Famille Rose*", *Trans. Oriental Ceram. Soc.*, 1967/69, **37**, 1–16