A BEGINNER'S LOOK AT ENAMELLING ON SILVER ALLOY

Common Silver Alloys for Enamelling

Sterling silver (7.5% copper in a minimum of 92.5% silver) is widely used for silver articles including jewellery and for enamelling the same. The copper content increases the strength and hardness.

Britannia silver (a minimum silver content of 95.8% and the remainder largely copper) is less widely used but is especially suitable for taking stamps and dies. Being softer than Sterling silver, it is more susceptible to bowing unless counter enamelled. However, some experts state that enamel colours are truer when fired on this alloy. As to cost, there is virtually no difference.

It is reported that the presence of impurities even at low levels can affect the adhesion of enamels. In particular, Selenium and Teluriam can cause problems. To avoid this potential problem, reputable silver suppliers use only fine silver and pure copper in the initial alloy casting process.

Temperature Characteristics of Silver and Common Alloys

Type	Melting Point ^{0}C	Solidus Point ^{0}C
Fine Silver	962	962
Britannia Silver	930	870
Sterling Silver	910	800

Table 1. Temperature Characteristic of Silver Alloys for Enamelling

Although the melting point of fine silver is precise at 961.93^{0}C, the other values in the above table are probably only accurate to ± 5^{0}C depending on the exact alloy composition and. manufacturing process.

If a molten mass on the kiln floor is to be avoided, the combination of kiln temperature and firing time must be such that the silver nowhere approaches the melting point.

Firing Temperatures for Sterling and Britannia Silver

That one should not fire pure silver or its alloys to melting temperature is obvious, but there is a further consideration that is particular to the alloys. This concerns the solidus temperature (see third column in Table 1), an aspect clearly and carefully explained in the Thompson Enamel Workbook.

In the annealed condition, both Sterling and Britannia silver contain a mix of two discrete constituents: one is composed of pure silver crystals, and the other silver-copper crystals. At room temperature, Britannia silver has around 85% of its mass as pure silver crystals and the remaining 15% are silver-copper crystals. For Sterling silver, 73% is pure silver, and 27% silver-copper.

When these silver alloys are heated and reach the solidus temperature, the silver-copper crystals become liquid. If the temperature then exceeds the solidus, this eutectic is able to absorb more of the pure silver crystals. The higher the temperature, the more silver becomes integrated into the silver-copper eutectic. Finally at the melting point of the alloy, all the silver is in solution with the copper.

Thus, unlike pure silver, alloys of silver-copper change from solid to liquid over a temperature band. They are essentially solid below the solidus point shown in Table 1, are fully molten at the melting point, and in between are in a transition or "mushy" state.

The region above the solidus is clearly one of metallurgical change, and no doubt this explains why Thompson Enamel state that silver alloys should not be allowed to exceed the solidus temperature. Skilled enamellers recognise that the change of crystal structure is gradual, and they have the experience to know just how high they can fire a particular silver alloy. Beginners, however, should limit the alloy temperatures to no more than those shown in the third column of Table 1.

Thompson Enamel, in fact, recommend Sterling silver be taken no higher than 790^0C to allow for inaccuracies of pyrometers and other variables in firing. As a consequence, attention has to be paid to some enamels that are hard firing, as they may not reach maturity easily. Presumably, applying the same criterion to Britannia silver means one should limit the temperature of the metal to 860^0C.

Although the melting temperatures of Britannia silver and Sterling silver are quite close, the difference in solidus temperature is considerable. Perhaps it is understandable why Britannia silver holds an attraction for the relatively unskilled, because the safe working temperature is considerably higher.

Annealing

When enamelling on pure copper, it is common practice to anneal the metal first to relieve stresses and any work hardening and to burn off surface products such as oils and greases. This is done by heating it to about two thirds of its melting temperature and then, after slight air- cooling, it is quenched in water. Apparently, allowing any metal to air-cool will not entirely soften it. An undesirable consequence of the annealing is that the surface is converted to black cupric oxide, CuO, and below it, red cuprous oxide, Cu_2O. The quenching can cause some of the oxide to come away and pickling in an appropriate acid will finally removes these oxides.

In contrast, a silver alloy is normally supplied in an annealed condition using a protective inert atmosphere to exclude any oxidation products. Only subsequent work hardening by the user, which alters the size and boundary composition of the silver and silver/copper crystals, would dictate the need to restore the alloy to its annealed state.

Silver alloys anneal rapidly and one authority states that 650^0C is a preferred upper limit. Although silver oxide forms on the surface when heated, it decomposes above about 200^0C. However, the silver-copper crystals in the alloy mix will oxidise to produce copper oxide at the surface. Because of the low percentage of copper in the alloy, the effect is not as extreme or as visible as when annealing pure copper.

Nevertheless, a dark grey staining will usually appear and this is commonly called firestain. It can be avoided by prior coating of the work piece with a proprietary fluxing compound that restricts the access of oxygen to the metal surface. Alternatively, the firestain can be removed by pickling after the annealing process.

Further Treatment of Silver Alloys Prior to Enamelling

Again, when enamelling on copper, most transparent enamels benefit from being fired over a layer of flux, since cuprous oxide will form under an applied coloured transparent enamel, and will invariably muddy it. The flux layer, if fired correctly, will absorb the oxide, seal the surface against further oxidation, and leave a clear base for laying the coloured enamels.

In the case of silver alloys, the amount of copper oxide that will be produced on the surface, upon heating, is small. Indeed, many transparent enamels can be applied directly to Britannia and Sterling silver without being degraded. Red transparent enamels and some rose and pinks apparently are in a special category that can require the use of a flux layer– more about that later.

Even so, it appears to be good practice to remove, or significantly reduce, the copper content that resides in the silver-copper crystals at the surface and thereby the copper oxide. The aim is to produce a surface that is pure silver. This, presumably, is felt to be a better solution than the use of a pre coat of flux since the final result is never quite so clear or brilliant as a direct application of transparent enamel on silver. In any event, why apply a flux coat if it can be avoided in some way.

The literature mentions two main methods of creating a pure silver layer and there seem to be advocates of both methods. Thus the beginner is faced with a choice. A reading of the literature has produced the following summary of both methods.

(a) Repeated Heating and Pickling

As mentioned earlier, if a silver alloy piece has had to be annealed by the user because of work hardening, the surface layer of silver-copper crystals will already have become oxidised, unless a fluxing compound has been used. This also applies when findings have been soldered to the work piece. The surface oxide can be removed by pickling. An effective pickle is dilute sulphuric acid or a derivative of it. Hot, dilute sulphuric acid is quicker and safer than the concentrated acid in dissolving copper oxides and it does not attack the base metal underneath. If this heating and pickling process is then repeated a few times, it will cause a reduction each time in any remaining surface copper. What remains is a surface that is pure silver and no copper, a condition that would appear to allow maximum clarity to transparent enamels applied without a pre-layer of flux. Some authorities recommend repeating the process up to ten times to be certain the surface copper has been removed by this process of oxidation and pickling. This, then, is one treatment favoured by many in the preparation of silver alloys for enamelling. After washing, the silver alloy has a dull, matt surface that needs brightening in some way. Alternatives mentioned in the literature include the sparing use of a soft brass brush or a glass fibre brush, both being used with plenty of water and detergent.

(b) Nitric Acid Treatment

Another technique is by immersion in concentrated nitric acid. There are three hurdles for the novice to clear: - acquiring the acid, storing it, and using it. One supplier is Walsh's who list 70% concentrated nitric acid in three litre containers. European Directives prohibit sending this through the normal channels and so it must be collected. It should be kept in a locked cabinet in accordance with the COSH regulations. When using it, the recommended practice is to wear protective gloves and apron and to work in a well-ventilated area, as the fumes are noxious.

It is stated that when a silver-copper alloy is briefly dipped in the acid, the metal turns grey or black and slowly fades to light grey/white. The piece is removed from the acid and dipped into hot water to remove the water-soluble by-products of the reaction. The process is repeated until dipping in the acid results in no further blackening. Concentrated nitric acid has a great affinity for attacking copper and so one presumes the action is one of removing any surface copper leaving pure silver. Dilute nitric acid is not so effective, as it will attack the silver in the alloy much faster than it attacks the copper. Nevertheless, it is stressed that the piece should not be left too long in the concentrated acid since the whole silver alloy will be progressively etched away. Needless to say, the piece must then be washed thoroughly to remove all traces of the acid. One method is to first neutralise the acid with a solution of soda crystals (sodium carbonate), followed by rinsing in water. As with the previously described Heating and Pickling technique, the silver alloy now has a matt appearance that can be brightened before enamelling.

So, in respect of creating a surface that is pure silver, both the Heating and Pickle method, and the Nitric Acid treatment appear, at first sight, to achieve the same result. Some authorities even suggest doing both i.e. heat and pickle several times and then dip in the nitric acid.

The respective actions of the two acids can be seen in the following table. The definitive work is by Mr Woodrow Carpenter in the very first issue of "Glass on Metal".

Metal/Oxide	**Hot dilute Sulphuric acid**	**Cold concentrated Nitric Acid**
Cupric oxide CuO	32	25
Cuprous oxide Cu_2O	4	3
Copper	0	160
Silver	0	1

Table 2. Relative Solubilities of copper oxides, copper, and silver in acids

The solubility of silver in cold concentrated nitric acid is taken as the reference point. Thus, this same acid will attack copper some 160 times faster. It is clear that the hot dilute sulphuric acid treatment will remove the surface oxides only and hence it is a safe, time independent treatment. Equally this table shows the nitric acid treatment will eventually attack all elements making up the silver alloy.

Some Initial Tests Using the Nitric Acid Treatment

Having purchased some annealed Britannia silver sheet (0.9mm thick), I made some test samples, 10mm wide and 35mm long. I immersed the samples in the concentrated nitric acid to observe the result. I found it convenient to place the test sample in a plastic sieve with a handle so that it could be immersed easily in the acid. I also found it effective to brush the silver alloy surface with a feather when it was in the acid, rather than swilling the acid over it. This technique results in deposits collecting in the acid. They seem to do no harm, but ultimately the acid will become exhausted and need replacing. I then lifted the sieve out of the acid and transferred the sample to a hot water rinse.

To my surprise, when placed in the acid, my samples only turned a light straw colour and after subsequent washing in the water, the surface was reasonably white. The absence of any blackening was puzzling. After delving into the literature again, I discovered a fact about silver and its alloys that seemed to provide an explanation.

When silver or its alloys are heated in air, silver oxide forms on the surface. Above about 200^0 C, this oxide decomposes. There is, however, the potential for oxidation below the surface. This is because silver is porous to oxygen when it is heated, and so the underlying material will also oxidise. In the case of pure silver, silver oxide forms, although it is not clear how much, if any of it, decomposes when it is below the surface. In the case of the silver alloys, both silver oxide and cuprous oxide will be produced. Certainly the latter does not decompose at temperature. It is reported that the oxygen can penetrate to a depth in excess of 0.02mm if a sample is held at annealing temperature for an excessive time (say one hour). If such a sample were then to be pickled in sulphuric acid, any surface oxidation that might be present is removed, but not oxides below the surface. However, subsequent dipping in concentrated nitric acid, will eat away the surface, exposing any sub-surface oxides which themselves will be dissolved away. The blackening indicates the presence of copper oxide (Cu_2O).

Despite much searching of the literature, I have not been able to determine the precise nature and extent of these oxides that form below the surface when silver or its alloys are heated, or the chemical reaction of the nitric acid upon them.

Nevertheless, from the above observations, it would seem that the Britannia silver I purchased was supplied in an annealed condition, using a protective inert atmosphere to avoid any possible sub-surface oxidation products. The nitric acid is attacking the metal alloy but there are no oxides to react with and cause blackening.

To investigate this a little further, I took another of my Britannia silver test samples, heated it in air to 650^0 C for 90 seconds, pickled it in sulphuric acid to remove any surface oxides, washed it and then dipped it in the nitric acid. It immediately turned black but cleared quite quickly. I measured the amount of silver alloy that had been etched away by the nitric acid – 0.005mm. To confirm that the oxidation is progressive with time and temperature, I then repeated this experiment with two more samples. One I heated for 15 minutes at 700^0 C, and the other for two minutes at 800^0 C. Both turned black in the nitric acid and took many tens of seconds to clear with constant brushing with the feather. In the former case, 0.02mm had been removed by the acid and in the latter case 0.015mm.

This all seems to indicate that, while both the Heating/Sulphuric acid Pickle method and the Nitric Acid treatment convert the surface layer of a silver alloy to pure silver, only the latter treatment will dispose of sub-surface oxidation products. From an enamelling point of view, one may ask is this important? The only way to find out is to try both methods and compare the results.

Enamels Tested Using the Alternative Preparation Methods

To gain an insight into any major differences between preparing a silver alloy by heating and pickling or by the nitric acid treatment, I selected two transparent enamels with markedly different characteristics. One, a hard firing green, (Soyer 50), that, it is said, can be laid directly on silver alloy, and the other a medium firing red, (Soyer 8) that requires a flux undercoat. According to Thomson Enamels, any silver oxide that forms on heating silver or silver alloys, and which does not decompose, will react with most transparent reds causing them to turn orange or brown. As a consequence, a prior flux coat is needed that is not discoloured by silver alloy oxides. It should then provide a suitable base for the reds. Thus simply removing the copper content from a silver alloy is not sufficient for the direct laying of red enamels.

There are many such fluxes that are formulated for use on silver. In particular, Thomson advocate the use of their 2020 as it does not "yellow" on silver if a sufficient amount has been applied. Another flux, Schauer 2A (ST17), is also mentioned frequently in the literature as being an effective base for red transparent enamels. I note, in more recent publications, that Ninomiya N1 flux is an alternative, and then there is Soyer3 flux for silver and Blythe medium flux C1.

So, I firstly took some of my 35mm long Britannia silver test pieces and scribed them into three sections. Half the samples were then prepared using the heat and pickle method (see below), and the remainder were prepared using the nitric acid treatment. Following this, the right hand end was wet laid with the green enamel, and the remaining two thirds were laid with Schauer 2A flux. After firing two coats of green on this right hand third and two coats of flux on the remainder, I then wet laid the left hand end third with the red enamel and fired the test piece again. A further coat of red was then laid on this third and fired. Thus, I could observe the performance of the green enamel on bare silver alloy, the flux, and the red over flux all on one test piece.

As to firing times and temperatures for the enamels, I was conscious of the information about the solidus temperature and I decided to set the kiln temperature well below it, (760^0 C), and to fire for 1¾ minutes. I also did some tests at a higher kiln temperature, nearer to the solidus temperature for Britannia silver (860^0 C for 1¾ minutes).

Results Using the Heating and Pickle Preparation

The heating of these samples was done at 650^0 C for 90 seconds followed by pickling in hot sodium bisulphate (pool acid). After each pickle, the surface was lightly abraded with a soft brass brush using plenty of water and detergent. After the first anneal, the surface had turned grey (firestain). At least two further anneal/pickle operations were done and the surface was now matt, with hardly a hint of grey. I presumed the surface was now sensibly free of copper.

The following table summarises the test conditions and the final appearance of the enamels.

Sample No.	No. of Anneals	Kiln Temp. ^{0}C	Firing Time Sec	Final Appearance of Enamels
1	3	760	105	Green is slightly opaque, Flux is slightly yellow, Red on flux is reddish-brown
2	3	860	105	Green is slightly opaque, Flux is almost clear, Red on flux is reddish-brown
3	10	760	105	Green is slightly opaque, Flux is yellow-grey, Red on flux is brown
4	10	860	105	Green is rather opaque, Flux is dark brown, Red on flux is muddy brown
5	10*	760	105	Green is very slightly opaque, Flux is slightly yellow, Red on flux is reddish-brown

* This sample was not abraded at any stage of the anneal and pickle process

Table 3. Enamel Tests on Britannia Silver Prepared by Heating and Pickling

Across the range of test samples, the green Soyer 50 enamel was acceptable but not very transparent. Its opaqueness was apparent from the first firing onwards. It was slightly clearer (sample 5) when the surface was left untouched ie not abraded after the pickle. This suggests that even slight abrasion damages the pure silver layer exposing the copper. It is also possible that the removal of pickle deposits allow easier access of oxygen.

The flux ranged from almost clear to dark brown and the red over the flux was generally disappointing. The flux discolouration was also apparent from the first firing onwards. As regards the red, the first coat was nearly always yellow. After firing the second coat of red, the colour either became more reddish, (samples1,2,5) or became brown (samples 3,4).

Increasing the number of heating/pickle operations from 3 to 10 was not beneficial. The implication here is that there is more extensive oxidation below the surface and that this does degrade the enamels. In respect of the green enamel, I suspect it is the copper oxide component in the silver alloy. In the case of the flux and red enamel, it may be a combination of both copper and silver oxide.

I found, from subsequent tests, that even very modest mechanical cleaning of the surface does have a deleterious effect. However, as shown by test sample 5, even if the top surface is undisturbed, the flux and red enamels appear to be affected by the presence of sub-surface oxides.

Results Using the Nitric Acid Treatment

The samples were first cleaned with a soft brass brush and liquid detergent. They were then immersed in the acid and brushed with a feather for about thirty seconds. The samples were transferred to a warm water bath and subsequently washed well using a detergent/ammonia wash. After this, the surface had a somewhat milky

appearance, lacking the normal reflectivity of silver. Although the previous tests, using the heating and pickling method, had shown that the enamel quality was adversely affected by even light cleaning, I nevertheless decided to finally clean up the surface by light abrasion with a soft brass brush to produce a silvery matt appearance. I did this because this method of brightening the surface is widely advocated in the literature. I was also interested in a direct comparison with the heating and pickle samples. Table 4 summarises the results.

Sample No.	Result of Acid dips	Kiln Temp. ^{0}C	Firing Time Sec	Appearance of Enamels
6	Went slightly yellow	760	105	Green is transparent, Flux is clear, Red on flux is red except at edges where it is yellow
7	Went slightly yellow	860	105	Green is less transparent, Flux is clear, Red on flux is red but more yellowing at edges and enamel is pulling back from edge
8*	Went slightly yellow	760	105	Green is transparent, Flux is clear, Red on flux is red except at edges where it is yellow

* This sample was not abraded

Table 4. Enamel Tests on Britannia Silver Prepared by Nitric Acid Treatment

These results show a significant improvement on the heated and pickled samples of Table 3. The green is transparent, although perhaps lacking in sparkle. The brass brush imparts a satin finish to the silver alloy and this may be the reason for the subdued colour. The flux is clear and it was possible to achieve a reasonable red colour. The yellowing at the edges is an indication of oxygen accessing the silver surface at this point resulting in excessive silver oxide being taken into solution of the flux and red enamel. Perhaps enamelling in a cloisson or on silver with a raised edge would reduce this effect. Although abrading samples No 6 and No 7 may have damaged the upper silver layer, there is no evidence of degradation of enamel colours because of this. Perhaps this is because there was not the significant sub-surface oxidation that results from prolonged prior heating that might otherwise interact with and degrade the enamels.

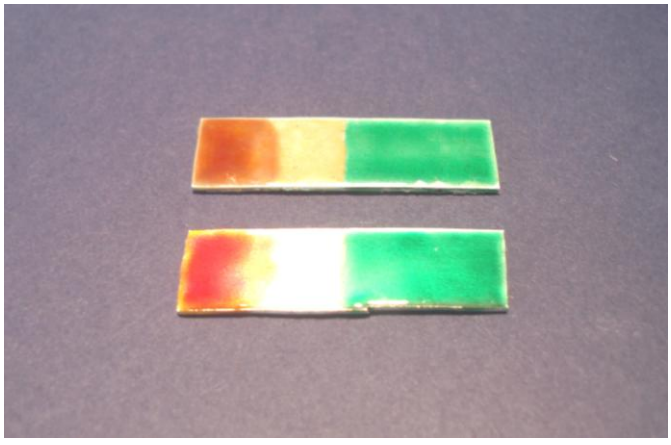


Figure 1. Comparison of Sample 4 (top) and Sample 8 (bottom)

Figure 1 shows (within the limitations of photographic reproduction) the better result obtained by nitric acid dip as compared to heating and pickling.

I cannot escape the conclusion from these tests that prolonged heating of a silver-copper alloy in air prior to laying transparent enamels, and particularly red enamels, is deleterious. The porosity of silver to oxygen at temperature creates oxide products that degrade the enamels. The sulphuric acid pickle can only remove surface oxides. If it is necessary to relieve work hardening by annealing, these oxide products can be removed by a nitric acid treatment or the surface protected by a fluxing compound. As a consequence of my test results, I decided to adopt the nitric acid treatment for the pre-enamelling treatment of the silver/copper alloys.

Comparison of Some Fluxes for Use with Silver Sensitive Enamels

The red transparent enamel that I tested confirmed the need for a flux undercoat.To compare the Schauer 2A flux tested with three others that I had to hand, I cut out a piece of Britannia silver 40mm long by 30mm wide and scribed it into four equal strips. It was given the nitric acid treatment as already described and finally gently abraded with the soft brass brush using plenty of detergent and ammonia solution. The fluxes tested were the Schauer 2A, Ninomiya N1, Soyer 3 and Latham T232. There was no blackening of the silver during the acid treatment and this is consistent with the previous findings.

All four fluxes were ground to 150/325, swilled with distilled water until clear, and wet laid. The test piece was then fired at 760^0C for two minutes. Although some straw colour was evident with the 2A and N1 fluxes, after firing a second flux coat, all four fluxes were clear. The 2A flux was quite gritty to wet lay and grainy when fired. I subsequently purchased some fresh lump 2A, ground it and found that, after firing, the grittiness and grainy appearance was no longer evident. Clearly my original powder stock had degraded. I then laid a thin coat of the red Soyer 8 enamel over the bottom half of the test piece and fired it as before.

With one coat of red enamel, all sections had some yellowing particularly at the edges. I applied a further three thin coats, firing each coat, and the yellowing progressively reduced. The final result on all fluxes, see Figure 2, was a reasonable red, albeit with a slightly brownish tinge. From this test, I concluded that there was no significant difference between the four fluxes when they were fired to a low temperature.

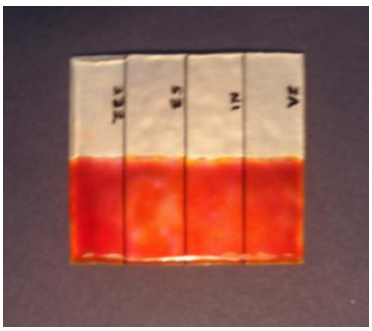


Figure 2. Fluxes and Red Enamel on Britannia Silver

Further Considerations – Firing Rate

It seemed to me that any difficulties in achieving clear transparent enamels, particularly the reds, is associated with oxides that develop on heating silver and its alloys. The logical outcome is to minimise the extent of any such oxidation. The ideal would be to lay down the enamels in such a way that the metal does not oxidise when heated, or, if this is not possible, to at least restrict the amount of oxidation.

As regards the former possibility, an inert gas atmosphere, enamelling kiln would be an attractive proposition. Unfortunately, I have not found a kiln of this type that would be justified, economically. It remains a goal of mine to investigate this further.

Thinking then about restricting the surface and sub-surface oxides, it should be beneficial to minimise the time that the metal is at temperature. Thus, if the enamel powder can be brought to maturity in the shortest possible time, it will be least affected by oxidation of the metal. In fact, I note that some experts consider that a short, sharp firing results in brighter, clearer enamel colours. The effect may indeed be associated with minimising the amount of metal or oxide absorbed by enamels. It might also be an intrinsic property of all enamels that they fire better when brought to maturity in the shortest possible time.

Whatever the reason, the advocates of high, rapid firing recommend setting the kiln to around 1000^0C, and to remove the piece from the kiln when the enamel has reached maturity or just beyond. If the piece is a small jewellery item, this strategy means it must be watched closely while it is in the kiln and then quickly removed or else the silver alloy, and particularly Sterling, will significantly exceed the solidus temperature. For example, a particular small Sterling silver item with its stilt, placed in a kiln at 950^0C, took 47 seconds to reach 790^0C. If this piece had been left in the kiln for a further 10 seconds, I calculated it would then have reached 850^0C.

My present strategy had been to set my kiln to around 760^0 C and to allow my Britannia silver samples to slowly reach maturity. Perhaps 1¾ minutes is rather a long time, but at least the kiln temperature was such as to not allow the silver to exceed its solidus temperature. Now, I am about to embark on the rather more adventurous, high rate of fire approach. Regarding the enamel powder itself, I had already been using 150/325 grains and these lie closer together and reach maturity much quicker than coarser grains.

With my small kiln, 950^0 C was about the maximum temperature that I could achieve. I calculated that my 10mm by 35 mm by 0.9mm thick Britannia silver alloy test piece on its small trivet support would have a time constant of around 25 seconds. It is then possible to construct two heating curves for this piece – see figure 3.

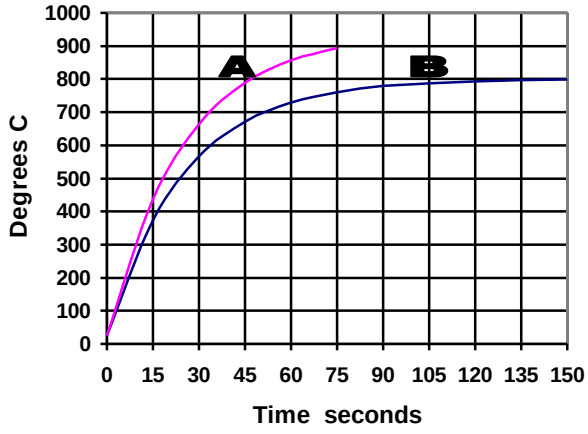


Figure 3. Heating Curves for 35x 10x 0.9mm Silver Strip

This shows heating curve B for the silver alloy when the kiln temperature is set at 800^0C. This corresponds to the test results reported thus far in which the samples were withdrawn from the kiln after 105 seconds. Heating curve A is with the kiln set to 940^0C, and it can be seen that the high rate of firing means that such samples should be removed after 45 seconds if they are not to exceed 800^0C.

If there is a critical period, it is where the silver alloy starts to oxidise rapidly and before the enamel fuses to shut off the oxygen supply to the surface. If we assume this to be between about 200^0C and 750^0C, then it may be deduced from the figure that a high rate of fire sample, (curve A), is exposed for around 33 seconds. A low rate of fire sample, (curve B), is exposed for around 62 seconds – nearly 100% longer. I needed to see whether this difference in exposure time is significant for enamel clarity.

High Rate of Fire Tests

First of all, I did some sample enamel tests using Soyer 3 flux for silver to see if the firing time of around 45 seconds, deduced from my high–rate heating curve (A), was of the right order. Samples were put in the kiln, (set at 940^0C), for 35, 40 and 45 seconds respectively. At 35 seconds, the enamel was just past the crystalline stage, at 40 seconds it was just past orange peel, and at 45 seconds it was smooth. This seemed reasonable confirmation that a 40 to 45 second firing time was appropriate.

Accordingly, I made up some more samples, similar to those reported on in Table 4. The surface of the Britannia silver was not abraded but cleaned with an ammonia and detergent solution using a toothbrush. It was somewhat dull as a consequence. I used the Soyer 3 flux as an undercoat for the red enamel, the kiln was set at 940^0C and the firing time was 45 seconds. After firing the enamels and upon examination, the flux was clear and the green was a rich, brilliant colour and superior to the twenty or so previous results. After firing the first coat of Soyer red over the flux, it was pinky red with some yellow at the edges. After a second coat was fired, I had a good red and only slightly orange at the edges. I subsequently repeated these tests using the Schauer flux with comparable results.

These very limited results do perhaps suggest that the high rate of firing produces a superior result for the green laid directly on the silver alloy. The flux, when it was fired quickly, was also very clear. Of course, with large pieces on corresponding bulky stilts, the time taken to reach maturity will be much longer than that reported here, but one can understand why it would still seem sensible to fire for the shortest time that is possible. Despite this, as I am somewhat cautious in my approach, I remain rather apprehensive about firing Sterling silver at a high rate for fear of exceeding its rather low solidus temperature.

Surface Treatment after Acid Dip and prior to Laying Enamels

The action of the nitric acid on the Britannia silver results in a dull and sometimes streaky finish that remained after neutralising the acid and washing the silver. If there is no subsequent, prolonged heating of the silver alloy in air, then, using the brass brush to brighten the surface prior to laying the enamels did not seem to affect the final result. Nevertheless, I wondered if there was another way of brightening the surface other than by mechanical means. If so, it would remove any concerns I might have about over vigorous use of the brass brush in exposing the copper component of the silver alloy.

I eventually settled on a cleaning agent for silver, (Hagerty Silver Foam). I applied this using a moistened soft toothbrush and the resulting surface finish was very similar to that achieved using the brass brush. Whether the action is entirely chemical, or there is a very mild abrasive in the cleaning agent, is not clear. I then washed the surface thoroughly as before. This is a method of brightening the surface that I am more attracted to rather than gentle abrasion with a brass or glass fibre brush.

Application to Sterling Silver Alloy

Having established, to my satisfaction, a procedure for preparing Britannia silver and then a firing regime for the transparent green and red enamel, I wanted to see how they worked on Sterling silver, the latter having a higher copper content. I purchased some 1mm thick sheet and used the same size samples as before. I also obtained some more Britannia silver, (1.1mm thick), to compare with the previous results. I used the same procedure of nitric acid treatment, subsequent brightening using the silver foam, and firing at a high rate (940^0C for 40 secs). The result is shown in Table 5.

Sample	Result of Acid dips	Kiln Temp. ^{0}C	Firing Time Sec	Appearance of Enamels
Britannia Silver 0.9mm	Went slightly yellow	940	40	Green is bright and transparent, Flux is clear, Red on flux is red with no yellow at edges
Britannia Silver 1.1mm	Went slightly yellow	940	40	Green is bright and transparent, Flux is clear, Red on flux is red with no yellow at edges
Sterling Silver 1.0mm	Went slightly yellow	940	40	Green is not quite so bright and transparent, Flux is slightly less clear, Red on flux is red with no yellow at edges. Sample is significantly bowed.

Table 5. Enamel Tests on Britannia and Sterling Silver Prepared by Nitric Acid Treatment and Using a High Rate of Fire

Although these results indicate that the green and flux are not quite so true when fired on Sterling silver, the differences are slight and only observable under a bright light and close scrutiny. Other colours may show up differently and further tests would be needed to determine this.

I did find, however, that the sterling silver developed a pronounced bowing and I suspect that I had taken it above the solidus temperature and it had softened. Nevertheless, I feel happy to use the Sterling silver as an alternative to Britannia silver, albeit with rather more care about firing rate, and I decided to use this alloy when I came to do a few more tests on different red transparent enamels.

Back to the Heat and Pickle Method

Having decided to adopt the nitric acid treatment, I had, on the way, found out about high rate of firing and perhaps not to abrade the surface if possible. Would these latter procedures have improved the results shown in Table 3? So, I repeated the test shown as sample 1 in Table 3, but with no abrasion after pickling and using silver foam to brighten the surface. I also fired the enamels at the high rate, (940^0C for 40 secs).

The green was marginally less opaque than sample 1, the flux almost clear and the red was somewhat less brown. Notwithstanding this, the enamels were still not quite as good as when the nitric acid treatment was used. It confirmed to me that significant sub-surface oxidation is detrimental to the appearance of these enamels laid on silver alloy.

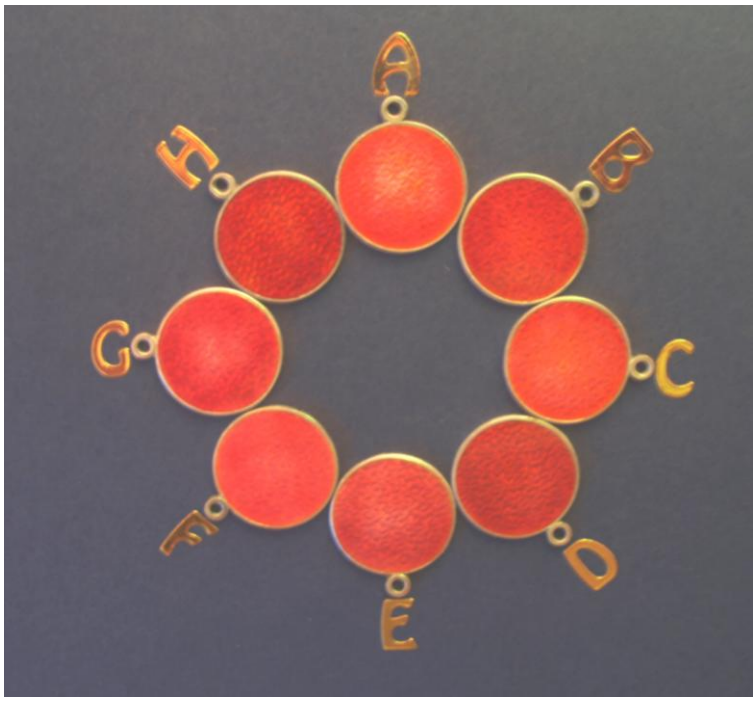
Some Further Tests on Red Enamels

There is little doubt that my investigations have been dominated to some extent by trying to produce a good red using the Soyer 8 transparent enamel. It made me wonder if, using the procedures here, I could achieve acceptable results with other makes of red transparent enamels. So, I obtained a representative selection of seven other red enamels for testing. They were as follows :-

Soyer red 39, Soyer Light red 41, Schauer Ruby red 8, Schauer Ruby red 1216, Blythe Red A31, Latham Cherry red 236, Kujaku Ruby red 105A. The latter enamel is relatively recently available in the UK and is claimed to not require an undercoat of flux. Sarah Wilson has already reported on Kujaku reds, (GOE Winter Journal 2000) and found them very satisfactory with and without a flux undercoat.

I purchased some circular Sterling silver stampings that had a retaining edge. I used the nitric acid treatment without any prior annealing and as expected the stampings turned a light straw colour and no blackening. I cleaned them with the silver foam and applied two coats of Soyer 3 flux using the high rate of firing previously described. The Kujaku enamel was applied directly to the metal without any prior flux coats.

The results are shown in Figure 4.



A Soyer 8

B Soyer 39

C Soyer 41

D Schauer 8

E Schauer 1216

F Blyth A31

G Latham 236

H Kujaku 105A

Figure 4. Tests on Some Red Transparent Enamels

Due to the photographic limitations, the Figure does not do justice to the nice clear colours obtained with all the enamels. There was no yellowing of flux or red and the result with the Kujaku 105A was particularly impressive since it was laid direct on the sterling silver without an underlying flux layer. Perhaps because of the retaining edge, and the geometry of the discs, there was no bowing of these samples.

Conclusion

When I look back at trying to understand the process of enamelling on silver alloy and my attempts to translate that into a working procedure, I realise it was not quite as straightforward as I had imagined. Perhaps the most revealing conclusion is the fact that silver and its alloys are porous to oxygen at enamelling temperatures. If oxides are allowed to form, they can affect the clarity of transparent enamels. The nitric acid treatment is an effective method of ensuring the metal is best prepared for the subsequent application of such enamels. There should be no prolonged heating of the silver prior to the laying of the enamels.

R.L. Jackson August 2007