AN INVESTIGATION INTO USING ENAMEL FLUX ON COPPER

-by-

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Introduction

As a relative beginner in the craft of enamelling, I find myself especially attracted by transparent enamels. They yield their true beauty when light is reflected through them from the metal substrate beneath.

Copper, being much cheaper than silver, is a popular metal base for enamelling. However, the copper oxides that form at the high kiln temperatures necessary to fuse the enamel to the metal can both colour the enamel and reduce the transmission of reflected light. Some transparent enamels are little affected but most appear somewhat opaque and dark. As a consequence it is generally good practice to first apply a colourless enamel flux. This flux is formulated to more easily absorb the copper oxide. The result should be a clear and bright surface onto which coloured transparent enamels can then be applied.

The proper application of enamel flux is thus an important first step in achieving reflective enamel pieces with copper as the base metal. In contrast, silver presents problems only for specific enamels (eg some reds and oranges) and the flux layer is correspondingly less necessary.

Through my inexperience and understanding of the factors involved in achieving transparency with enamel flux, my enamelled pieces were rarely clear or bright, and more often they were muddy, or cloudy.

I decided, therefore, to embark on a series of experiments aimed at finding and controlling the factors that determine the clarity of enamel flux applied to copper. These experiments deal with the sieving of dry enamel flux powder on copper. Most of the results, however, are also relevant to the technique of wet laying of enamel flux.

This report describes those experiments that have subsequently led me to achieve a consistent and acceptable enamel flux base coat.

The information is presented in the hope that other beginners may find it useful. It owes much to various excellent publications that provide background information on the fluxing of copper.

The Grade of Copper

It is reported in the literature, Thompson[1], that oxygen free, high conductivity copper (OFHC) is the ideal grade to use for enamelling. Less pure forms of copper can apparently cause bubbles in the enamel and in extreme cases affect the adherence of the enamel/metal interface.

Reviewing various enamel suppliers, it is noted that American outlets positively specify the copper they sell as being OFHC. In the UK, there is generally a more relaxed view about the need for the purest copper and not all suppliers indicate the grade of copper they sell for enamelling purposes.

Nevertheless, in order to eliminate any variability that might result from unknown sources of copper, I used OFHC copper for all the experiments. The European specification for this grade is EN CR007A but it is often referred to in the UK by the designation C103. A cheaper and more readily obtainable alternative is EN CR004A or C101. This contains slightly more impurities than C103 (up to 0.03% of other elements) but is reported to be entirely satisfactory for enamelling.

Choice of Enamel Flux

When I first started enamelling, I paid no great attention to which make or type of flux to use on copper. Now, embarking on a more controlled approach, I needed to decide which flux to use for the main body of the experiments. The intention would then be to try other fluxes when the fundamentals had been established.

Pat Johnson[2] has published a table comparing the performance of a few fluxes. For a base coat under transparent enamels on copper, those particularly suitable include T200 normal flux manufactured by Milton Bridge of Stoke-on-Trent, and Soyer1 flux manufactured by Cristallerie de Saint-Paul in France. Many more fluxes are available from various sources and are, no doubt, equally suitable.

The T200 flux is of medium hardness with a normal firing range of 760 – 820^{0}C. The Soyer1 is a hard firing flux with a normal firing range of 840 – 900^{0}C. I decided to use the Soyer1 flux since its hardness provides a secure base coat for all subsequent transparent enamels. It is appreciated that special effects can be produced using a soft or medium firing flux over which harder transparent enamels are then fired.

Temperature and Time

The first objective was to determine the effect of firing temperature and firing time when applying the Soyer1 flux to copper. In the literature, remarks such as "fire at 790 – 840^{0}C for 3-5 minutes or until all copper oxide is dissolved" or "fire at 1000^{0}C to orange peel", are somewhat contradictory.

As regards actually measuring the temperature, many enamellers rely on the colour of the heated kiln to judge how hot it is. I was not sufficiently confident to use this approach especially as the colour looks different when viewed under various external lighting conditions. Further, there has been a suggestion not to look too long and closely in the kiln window unless special goggles are worn to remove IR and UV radiation – Goldman[3]. I therefore invested in a thermometer probe with meter read out of temperature. A particularly good arrangement is a kiln control unit[4] that automatically holds the temperature of the kiln at a pre-set value.

To measure the firing time, I timed the period my test samples were in the kiln. In normal practice, precise timing how long a sample should be kept in a kiln at a given

temperature is generally regarded as of dubious value. Perhaps this is because the point at which any enamel softens and then fuses to the base metal varies in time depending not only on the enamel composition but also on the bulk of the metal sample and the support it is on. The size ie heat capacity of the kiln will also influence the time needed to bring a sample to maturity. Withdrawing a sample briefly from the kiln to examine its condition is the normal method of judging completeness of firing. However, precise timing is necessary for my experiments in order to assess how firing time affects the finished result.

I did, in fact, experiment with various sizes of metal to see how long they take to reach a set temperature. The results are reported in Appendix 1. In the author's opinion, they indicate that accurate timing is useful on a routine basis for ensuring the flux layer is correctly fired.

Test Details

50mm by 25mm test strips of C103 copper were cut from 18 gauge (1.2mm) sheet, annealed for a few minutes at 650^0C in the kiln and then pickled in warm sodium bisulphate solution to remove the copper oxides. After thorough washing of the copper, a glass fibre brush was then used to brighten the surface prior to applying the enamel flux. Counter enamelling the reverse side to equalise thermal stresses was deployed on some samples.

The Soyer 1 flux, (supplied to pass through 80 mesh), was swilled in distilled water. The resulting milky water was then poured away. This was repeated a number of times until the water ran clear. This removed the ultra fine particles that can otherwise reduce the clarity of the fired enamel flux. The flux powder was then dried and stored under silica gel dessicant to minimise medium to long term degradation by moisture attack. When sieving this powder on the copper test strip, I found it was difficult to get good coverage particularly at the edges of the strip due to the larger grains bouncing off the surface. Holding agents, such as specially formulated gums, are often used on metal surfaces prior to sieving to reduce the bounce and provide adhesion prior to kiln firing. However, I chose not to use them here as they could perhaps reduce the ultimate clarity of the fired enamel.

So, I ground the flux powder more finely in a pestle and put it in a 150 size mesh container. After vigorous shaking, that which passed through the 150 mesh was then washed and dried for use. In order to provide greater control of application, a corresponding fine sieve was used, (100 mesh), to sift these finer grains onto the copper. Uniform coverage was now achieved. A benefit of using finer grains is their ability to pack more tightly so that they resist sliding off sloping surfaces such as bowls.

A question of some importance is how thick to lay these150/ flux grains. This is particularly so for a beginner who has not the experience to know just how much to apply. The general advice seems to be to cover the surface until the copper base is not visible and then to apply just a little more.

To quantify the amount more exactly, a small measuring cylinder was made using the outer plastic tube from a ball- point pen cut to a length of 50mm and sealed at one

end. This was then graduated with marks registering 0.25ml, 0.5ml, 0.75ml and 1.0ml. The enamel powder was fed into the tube using a small funnel. By tapping the tube to consolidate the grains, consistent amounts of enamel powder could be measured out each time. For the present, an amount of enamel powder corresponding to 0.3ml was used to sieve over the 50 x 25mm area of copper. From an approximate calculation, the enamel grains would then be stacked about four high.

Later in this report, I look at different thicknesses of enamel application. When sieving the enamel powder, that which fell outside the copper area was gathered up and sieved again to ensure the stated amount of powder was applied to the test piece.

Individual copper strip samples, with the sieved Soyer1 flux were then fired in the kiln for a set length of time at a given temperature. Tests ranged from 750 to 950^{0}C and for durations around one minute to over five minutes.

Figure 1. Test Equipment

The above figure shows some of the test equipment. In the background is the kiln and to the right of it, the temperature gauge and timer. In the foreground are the various items used to prepare the flux and copper, (in practice these were placed on a separate bench well away from the kiln). From the left, is the Soyer flux container and a piece of lump flux, then the 150 sieve, the measuring cylinder and funnel, the pestle and mortar, and pickle solution. At the front is the copper test strip, the 100 mesh sieve used to apply the enamel powder and the glass fibre brush used to brighten the copper surface.

Results

The test samples after firing are shown in Figure 2. They have been laid out on a card graduated with a vertical axis of kiln temperature (750 to 950^{0}C) and horizontal axis of firing time (0 to 6 minutes).
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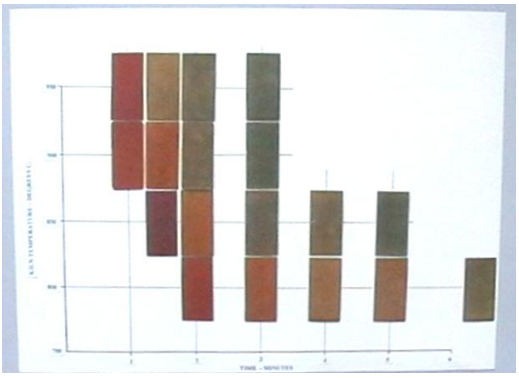

Figure 2. Copper Strip Samples after Firing

At firing times between 0.5 minutes and one minute, depending on kiln temperature, the enamel flux was only partly fused and sugary in appearance. Then, from this pre-fusion time and extending to several minutes, the enamel exhibited one of three characteristics as illustrated in Figure 3. This figure was constructed by examining the colour changes in figure 2.

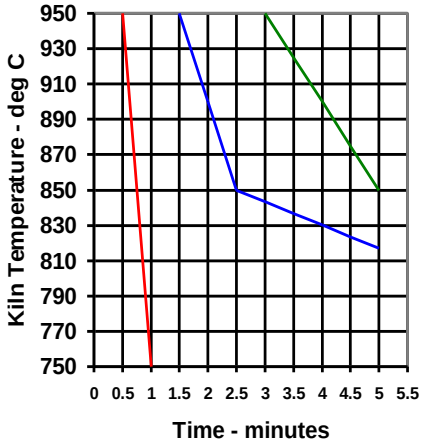

Figure 3. Characteristic for Soyer Flux on Copper

As just mentioned, in the area to the left of the red line, little or no fusion or bonding takes place. This is because, at these short firing times, the test samples have not reached the temperature necessary for fusion and are well below the kiln temperature (see Appendix 1). In the middle region bounded by the red line and blue line, the enamel is fused or starting to fuse and is coloured red, brown or pink by degrees of cuprous oxide that remain unabsorbed by the flux. Cuprous oxide, rather than cupric oxide, is formed because the enamel powder restricts the oxygen access to the metal surface. The oxide is only partially absorbed or dissolved in the enamel flux and hence the colouration.

In the region bounded by the blue line and the green line, the enamel is clear, having absorbed all the oxide. Both a sufficient firing time and high enough temperature are required to achieve this. In the area to the right of the green line, a green cast appears and the edges of the enamelled sample are noticeably black. The green colouration becomes more pronounced with increased time and temperature.

The conclusion from this test series is that the firing temperature must be above a certain level in order to fully dissolve the copper oxide. Thus, if an enamel piece does not clear, despite a long firing time, the temperature needs to be higher. This explains why some of my enamelled pieces were muddy in appearance – a higher firing temperature would no doubt have improved matters.

The firing time should then not be so long as to produce a green cast and the edges looking rather "burnt". At the highest temperatures, the latitude in firing time between fusion, clear and then green cast can be quite short. At a slightly lower temperature it is somewhat longer. For the thickness of Soyer 1 flux that was used in this series of tests, (0.3ml), when firing at 950^0C, the enamel is clear after about 90 seconds but there is a green cast over about 3 minutes. At 850^0C, the firing time to clear is around 2.5 minutes and the green cast appears at around 5 minutes.

The results of this particular investigation into the firing characteristics of Soyer 1 flux have enabled me to avoid under or over firing and given greater confidence in knowing how far to fire to fully absorb the copper oxide. It is presumed that other fluxes will have the same general pattern of performance but the actual temperatures and times will differ.

Effect of Grain Size

In the tests reported on so far, the enamel used was 150/- which means that only grains finer than about 0.1mm were used. Although the use of the word grain might imply spherical or oval shaped particles, examination under a microscope reveals that they are polyhedral shaped pieces of glass. The washing process removes the extremely fine particles that can contribute to opacity in the fired enamel due to trapped air bubbles, Helwig[5]. These very small particles may also have deteriorated significantly due to attack by moisture.

It is further reported[1] that optimum transparent enamel clarity is achieved if particles smaller than would pass through a 325 mesh screen are also removed. This presumably is a further measure to reduce bubble entrapment. As a consequence, I now slightly changed my enamel preparation by grinding and then sieving the enamel first through the 150 mesh and then through a 325 mesh. The enamel remaining on the 325 mesh is then 150/325 material. This was washed to remove any finer dust that might otherwise remain adhering to the particles. The resulting material is smaller than 0.1mm but greater than around 0.05mm (50 microns).

So, by eliminating particles less than 50 microns, greater clarity should be achieved and by eliminating particles greater than 100 microns, a better overall coverage is possible.

There are bound to be some air bubbles in the fired enamel even with the removal of the very fine enamel particles. Numerous small bubbles can create a milky effect and very large bubbles may be seen as individual imperfections in an otherwise clear glass. These bubbles are distinct from the gassing of impure copper and are caused by the entrapment of air between enamel particles as they fuse. Two factors appear to be of importance, - the mix of particle sizes and the thickness of application of the enamel powder. I first investigated the particle sizes by seeing if the 150/325 enamel

flux is indeed better than say 80/250 sized enamel notwithstanding the fact that the latter will cause more problems in sifting due to particle bounce.

Both 80/250 and 150/325 Soyer1 flux mixes were prepared and separately fired over a range of temperatures and times. The enamel powder was sieved on uniformly to avoid as far as possible any variability due to enamel thickness. In order to examine the bubbles more easily, glass slides were used as the substrate rather than copper. By firing the enamel on the slide, bubble size and number could then be measured using a transmission microscope. Good edge coverage was difficult with the 80/250 grains due to the bounce effect mentioned previously but this was not a problem since only a small central area was viewed through the microscope.

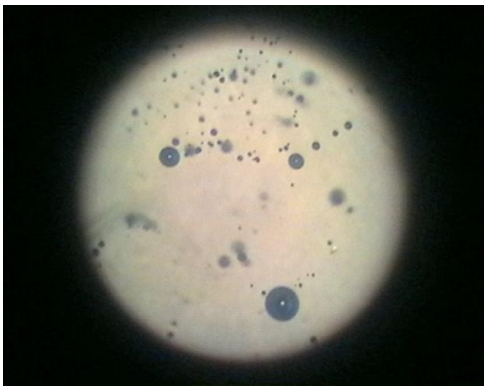

Figure 4. Enamel viewed under Microscope

In Figure 4, the diameter of view is 1mm and there is a bubble of about 0.1mm near the bottom and others of smaller size distributed over the area of view.

The examination revealed that 80/250 enamel samples had bubbles ranging in size from 0.15mm to 0.03 mm in diameter. The 150/325 enamel samples had bubbles from 0.05mm to 0.02mm and less. An isolated bubble, 0.15mm diameter, is visible to the naked eye as an imperfection.

The results also showed that, with the 80/250 sized enamel, the fewest number of bubbles occurred when the enamel particles were fired for a long time at low temperature. Presumably there is time for air to be released from the relatively open structure as the particles slowly fuse together. In contrast, firing the enamel at a high temperature would appear to trap large bubbles in the melt (typically 50 or more over an area of 1 mm^2) and these can impart a grainy look to the final result.

The finer grain samples fired at low or medium temperature, (850^0C), produced many small bubbles that tended to show as a milky cast, particularly when viewed at an angle to the surface. The flux particles are more tightly packed together and hence the opportunity for gas escape is less. When these particular samples were re-fired at a higher temperature, (950^0C), the number of small bubbles reduced significantly and likewise the milky cast. It would suggest that small diameter bubbles can migrate to the surface if the enamel is fluid enough. When a fine grain sample was given one firing at high temperature, again there were a few small bubbles.

I consider these observations to be quite significant for the application of enamel flux on copper. It is noted, (Figure 3), that a sufficiently high firing is needed to fully absorb the copper oxide. Now, if a coarse mix of grains is fired high, there is the possibility of trapping large visible bubbles, whereas high firing the finer grain mixes tends to result in a few small-sized bubbles. It is noted that there are other reasons for not using predominately larger particles. They take more time at temperature to soften and flow and the surface oxidation of the copper is thereby increased. This produces more discolouration and the tendency to produce pits is increased. This observation is particular to the application of flux onto copper. Indeed, I repeatedly found that pitting is a marked feature of firing enamel flux containing coarse grains.

The merit of using coarse grains and firing them at low temperature for a long time must not be overlooked for other enamelling applications. For example, in Reference 1, it is stated that 60/150 mesh enamel allows the greatest clarity of transparent enamel in the technique of plique á jour. Hence the selection of a particular sized enamel is very much determined by the application.

One feature of the microscopic examination of some of the samples was the presence of a few black particles. It perhaps indicated the need to be meticulous in keeping the enamel powder clean and free from foreign particles at all stages. I, subsequently, spread the 150/325 enamel powder thinly over a clean white sheet of paper and removed all the visible foreign particles using a fine moistened brush. I also used the smallest size of metal trivet that would support a given test piece of copper in the kiln. Metal trivets can throw off foreign particles unless care is taken to keep them clean. If the trivet overhangs the test piece significantly, the possibility of contamination also increases.

Thickness of Enamel Application

Apart from grain size, it is clear from the literature that too thick an application of enamel will also trap bubbles and inhibit their migration to the surface. The enamel then looks milky in appearance – Figure 5.

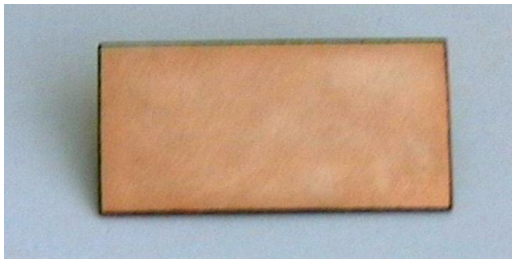

Figure 5. A Thick Application of Flux

On the other hand, if the application is too thin, pits may appear and over saturation by the absorbed copper oxide is likely to give a green discolouration – Figure 6.

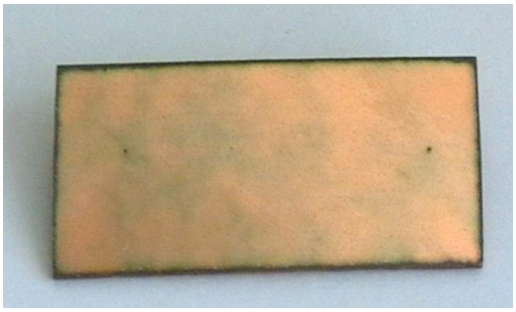

Figure 6. A Thin Application of Flux

In the tests reported on so far, I used 0.3ml over the area of 1250 mm^2 without encountering real problems of either milkiness or pitting or a green cast.

However, I felt it would be useful to find out what is the optimal amount of enamel powder that can be applied which avoids all the aforementioned deficiencies. There is also the consideration of applying a further coat of enamel flux after firing the first coat.

Using the graduated measuring cylinder, a specific volume of powder was sieved on the 50 mm by 25 mm copper test pieces. To make the results more meaningful when applied to other areas of copper, the measured volume was then converted to mm depth of enamel over the given area. For example, a volume of 0.3ml applied to the test piece area of 1250 mm^2 translates to a depth of enamel powder of 0.25mm (0.3 x1000/ 1250).

Thus, if after examination of the fired samples, *X* mm is an acceptable depth of enamel powder to use, then for an area of *A*mm^2, the cylinder would need to be filled to *X* multiplied by *A* divided by 1000 ml and sieved on uniformly over the whole area.

A number of test pieces were assembled each covered with a different thickness of the Soyer 1 enamel powder. They were all fired at 950^0C for two minutes. At a thickness of 0.15mm and below, there was a significant green cast and some pits were developing below around 0.13mm. A thickness of around 0.2mm produced a clear result without pits. At about 0.3mm, there was a slight milky cast but only when viewed at an angle. At 0.4mm and thicker, the milky cast was increasingly evident.

I concluded, for the Soyer 1 flux, that a thickness of application of around 0.25mm would be satisfactory and, perhaps fortuitously, this was what I had been using in the tests to date. Out of interest, I did sieve some 150/325 flux powder onto copper using the maxim of covering the copper until it was not visible and then applying a little more. I measured this amount and it corresponded to a depth of 0.16mm. The grains would be stacked approximately two to three high and, for the application of flux to copper, my tests show this to be rather too small an amount.

Interestingly, the air that is in the spaces between the enamel grains prior to firing occupies about the same volume as the grains themselves. Thus, when the enamel is fired and the grains coalesce, the final thickness of fused enamel is correspondingly about half the measured thickness of the enamel powder. So, if 0.25 mm of enamel powder is sieved on, the final thickness of the fired enamel flux is of order 0.125 mm.

Although around 0.25 mm application seemed to be optimum, the margin for error is quite small in that temperature, time and sieved enamel thickness need to be closely controlled. Figure 3 has already shown the precision needed at high temperature. Many references advise multiple firing of two or more coats with the first coat fired for a slightly shorter time. This is perhaps a way of overcoming the need for precision. The slightly shorter fired first coat reduces the potential for a green cast but it will have a slight brown appearance due to incomplete absorption of the oxide. Bubble formation should, however, be low due to the thin layer and high temperature. The second coat is then applied and fired for a similar or slightly longer period of time to complete the dissolving of the oxide. The greater overall thickness of enamel flux should extend the time before the dissolved oxide produces a green cast.

Further tests were therefore made in which the first coat of 0.25 mm thickness was now fired for 1.5 minutes and a similar thickness second coat for a full two minutes. If anything, these samples appeared clearer and brighter than the single application and it is a technique that I now adopted. It has the further advantage that if any minor pitting is evident after the first firing, it can be ground out and the second layer will hopefully repair the imperfection.

Knowing precisely how much enamel to apply to the surface is a benefit when counter enamelling the underside. Exactly the same amount of counter enamel can be applied and this minimises the stressing and warping of the enamelled copper caused by differences in thermal expansion of metal and enamel.

Sometimes the enamel flux has to be wet laid rather than sieved. An example is the technique of Champlevé where part of the copper has been carved or etched away. These recessed areas need to be fluxed if transparent enamels are subsequently to be applied. By working out, either the total recessed area or each individual area, the amount of flux needed can be determined and then wet laid as uniformly as possible. It is perhaps useful to note that two coats of enamel flux will be 0.25 mm final thickness and so the amount of carving or etching has to be perhaps at least twice this depth for a copper Champlevé piece with transparent enamels.

The use of the fine particles of enamel flux, sieving on a specific amount, firing to a high temperature, and using two coats was now resulting in fluxed samples that were consistently clear.

Surface Preparation

Thus far, the surface of the copper had been annealed, pickled and then abraded using a glass fibre brush. This produced a matt reflecting surface for the fired enamel flux. I now tried other treatments to the copper surface. Incidentally, I found from experience how important it is, after pickling, to wash the copper thoroughly to remove all traces of chemical. One effective treatment is a light scrub with a toothbrush dipped in ammonia to which has been added a few drops of detergent. I followed this by washing in hot running water until the water no longer formed droplets but shed from the surface.

I now modified this process further having studied the article by Carpenter[6] on metal preparation. After the pickling to remove the oxides after annealing, I dipped the samples in a warm 25% solution of bright dip or aqua fortis for two to three minutes. This removed any trace of remaining oxide and initially attacked the copper itself. This made the copper brighter, a little more yellow in colour and according to Carpenter produces a smoother surface with the grain boundaries not very evident – see Figure 7.

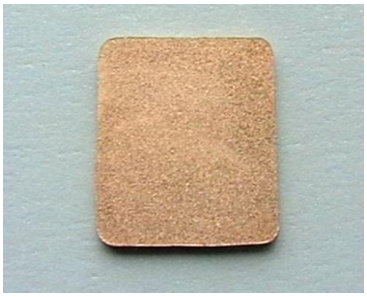

Figure 7. Fine Grain Structure Produced by Bright Dip

Needless to say, thorough washing then followed. I found this bright dip treatment very effective in producing a bright surface, free from surface scale marks and grain boundaries, and I used it on all subsequent copper test pieces prior to further surface preparation. Aqua fortis is an aggressive chemical and I kept the concentrated liquid in a small, labelled, lockable safe to avoid accidents. I would advise others to do the same.

Now, as an alternative to the glass fibre brush, I experimented with a fine abrasive pad. This also resulted in a matt appearance similar to the glass fibre brush. A fine wire brass scratch brush produced a more silken finish. These surface treatments, prior to the application of enamel flux, resulted in broadly similar results that were satisfactory although, to my mind, somewhat lacking in the reflective sparkle that should enhance the subsequent application of coloured transparent enamels.

Further test samples were then prepared using a steel burnisher rubbed over the surface followed by the ammonia/hot water clean. The surface appeared brighter and it yielded a good reflective surface under the fired enamel flux. Burnishing by hand can be tedious, especially on large pieces of copper and I invested in a small high speed drill with a steel burnisher attachment. This was certainly quicker and a slightly superior shiny finish was obtained using this tool. Chemical polishing the surface was a disappointment in that parts of the final fired test piece were muddy and grey. I attribute this to my not removing all traces of chemical from the surface.

It has been stated that creating too smooth a surface for enamelling could cause lack of adherence. I did not experience this in my tests on copper but some tests on gilding metal demonstrate it probably does reduce the interfacial adhesion of glass to metal.

As a further experiment, I abraded one half of a 50 x 25mm test piece with an emery cloth grade 600 to produce a fairly rough surface. The other half was burnished with the rotary steel burnisher as described. After firing, there was a surprising difference in the visual appearance of the two halves – see Figure 8.

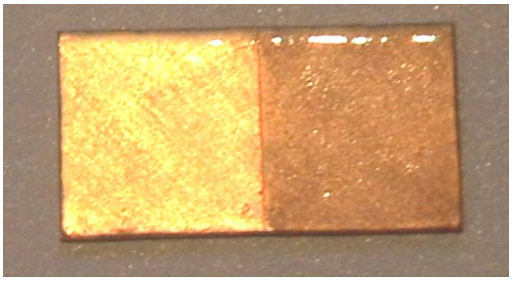

Figure 8. Rotary Burnisher v Emery 600

The left hand, burnished half, was clear and bright as expected and, when examined through a reflection microscope, the number and size of the air bubbles were small (about 25 bubbles of 0.03mm diameter and 60 bubbles less than 0.01mm diameter over an area of $1mm^2$). In contrast, the emery abraded half had a few bubbles visible to the naked eye and there was an overall milky effect (about 13 bubbles of 0.1mm diameter, 20 of 0.04mm and 40 of 0.01 mm diameter). Expressed another way, the bright sample had less than 2 % of its area occupied by bubbles, whereas the abraded sample had almost 15%. Different firing times and temperature had no effect and it was noticed from the colour of deliberately under-fired samples that the amount of copper oxide remaining with the rough surface was greater than the smooth surface. Further tests were done with emery grade 240 and also grade 100. These even coarser grades, in fact, showed some improvement and the number and size of bubbles reduced. The burnished surface however remained far superior. A possible explanation for these phenomena is given in Appendix 2. It was a salutary lesson that simply by changing the surface preparation technique can lead to an unexpected and, in this case, unsatisfactory result.

There are other distinct forms of surface profiling such as engraving or engine-turning (Guilloche) that are widely used and that yield spectacular results, albeit normally with silver as the base metal. It is presumed that the depth and width of these profiles are sufficiently large so that the enamel particles lie closely together in the grooves and recesses and hence bubble entrapment is not significant. Certainly as far as silver is concerned, transparent colours can, by and large, be applied directly to the surface and there is more flexibility in choice of the enamel thickness, firing time and temperature in order to minimise air entrapment.

However, the situation with flux applied to copper is different, and to test the performance of some fairly basic surface profiling on this metal, a 50 x 25mm test sample was marked into four quarters. After the annealing, pickling, bright dip etc, each quarter (top left *A*, top right *B*, bottom left *C*, and bottom right *D)*, was given a different surface profile. Using the high speed drill, *A* was profiled using a cylindrical grinding stone, *B* was polished using the rotary burnisher previously tested, *C* was simply cleaned by hand using a fine abrasive block and *D* was profiled using a cylindrical cutter.

The 150/325 enamel flux was then sieved over the whole area to a depth of 0.25mm, and slightly under-fired, (930^0C for 90 seconds). Quarters *A* and *D* both appeared mid brown to light red in colour while *B* and *C* were light brown. The deep profiled surfaces *A* and *D* are greater in actual surface area than the smooth surfaces B and C and result in a correspondingly greater amount of copper oxide. Another coat of flux

was then applied and fired at 950^0C for two minutes. All quadrants were now clear, but with some interesting differences - see Figure 9.

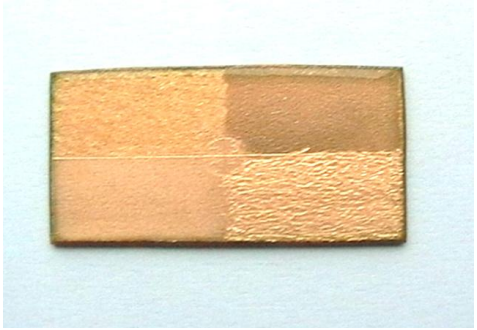

Figure 9. Effect of Different Surface Profiles

The smooth surfaces were visually as expected, with the burnished quadrant *B* brighter than the matt appearance of *C* (the photographic reproduction does not do justice to the actual sample result). Small blemishes do tend to show and although air bubbles were small in size and number, a slight milky cast was seen when the sample was tilted at an angle to the main source of light. However, the profiled surfaces *A* and *D* appeared bright when viewed at all angles due to the multiple reflections, and any blemishes were totally masked by the dominant background profiling. Microscopic examination revealed bubbles in size and number in all quadrants much as previously reported for burnished surfaces. Hence the significant bubble entrapment observed particularly with 600 emery abraded samples was not a feature of these profiled surfaces. It is inferred that there is a critical relation between enamel particle size and surface roughness that will influence the number and size of bubbles and that may be sufficient to visually impair the finished result.

A further comparison between a conventional glass fibre abraded surface and a textured surface is shown in Figure 10. This sample had been fluxed, fired and then covered with two thin coats of Soyer green transparent enamel, firing between each coat. .

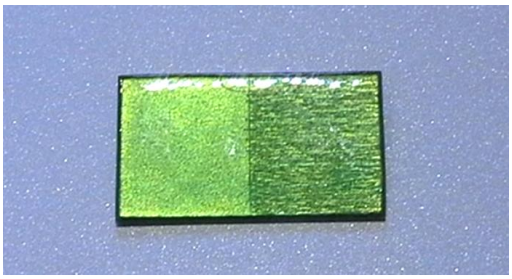

Figure 10. Green Transparent over Fluxed Copper

Although they both show the rich green reflective enamel to good advantage, there is an added sparkle to the right hand textured surface. Again, due to the limitations of the photographic reproduction, the picture does not bring this out very clearly

Copper pieces that are oval or circular in shape are often domed to minimise the warping that results from the different thermal expansions of glass and metal. The doming also affects the way in which any bubbles are seen when the piece is tilted. A flat sample can appear very slightly milky when tilted but not when viewed overhead. By doming a piece, it appears quite brilliant and clear when viewed at all angles.

Incidentally, I found that when sieving the fine particles of flux, (150/325), on to a domed copper surface good coverage was achieved without the need for a holding agent.

In summary, there are a number of ways of preparing the copper surface prior to enamelling, some of which are more effective in providing a good reflective background for the transparent enamels. Sometimes the size and nature of the piece reduces the choices available. For myself, I find the burnished or surface profiled finishes show off transparent enamels to good effect. At the end of the day, it is a matter of personal preference and selecting the surface finish that pleases and enhances the finished piece.

Tests using other Fluxes

All the results reported on so far used Soyer 1 enamel flux powder. I now undertook a limited number of tests on some other enamel fluxes. Although a wide choice is available, I restricted my tests to just a few. They were samples I had purchased from time to time but not used to any extent. There is no suggestion they are superior to the many other excellent enamel fluxes that are on the market, simply that they were easily to hand and provided an opportunity for testing. The fluxes are listed below:-

Soyer
Soyer 1 flux for copper (repeat tested for comparison)
Soyer2 flux for gold
Soyer3 flux for silver

Milton Bridge
T200 normal flux
T232 silver flux
T700 diamond flux

Enamel Shop
EST 300 flux

The percentage of coarse particles and very fine particles in the various as received fluxes varied quite a lot. By grinding, washing and particle sizing to 150/325, as previously described, consistent batches for sieving were produced. 50 x 25 mm copper test samples were annealed and pickled and the rotary burnisher used to create a reflective surface.

The technique of now applying more than one layer of enamel flux was adopted with a thickness of each application of 0.25mm. The firing time and temperature remained the variables that I needed to investigate. After testing a number of samples of each flux, I arrived at the values shown in Table 1. The temperatures shown here are those recorded at the end of the firing time. The kiln temperature had been set about 30^0C higher than this to allow for the drop in temperature when the 18 gauge copper was heating up in the relatively small kiln.

Flux	1st Layer		2nd Layer	
	^{0}C	Mins	^{0}C	Mins
Soyer 1	950	1.5	950	2
Soyer 2	900	1.5	900	1.5
Soyer 3	900	1.5	900	1.5
T 200	875	1.5	875	2
T232	850	1.5	850	1.5
T700	950	2	950	2
EST 300	900	1.5	900	1.5

Table 1. Firing Times and Temperatures for 18 Gauge Copper

Clearly other combinations of temperature and time are possible within the bandwith of acceptability. However, I have found this table a useful tool when wishing to fire different fluxes.

With the exception of T700, good clear results were consistently obtained for the six fluxes with the firing temperatures reflecting the manufacturer's specified hardness. With T700, the flux seemed to be especially sensitive to firing time and temperature. Thus the bandwidth for achieving a clear result (with complete dissolving of the oxide but no green cast) was quite small for this flux. T700 produced a gold reflective surface in contrast to the pink surface of all the other fluxes tested.

Summary

After testing a hundred or so samples, I have gained a better insight into the application of dry sieved flux on to copper and then how to fire it to give a consistently clear and good base for transparent enamels. Those already well versed in the craft will no doubt view some of my procedures as tedious and in parts perhaps unnecessary.

However, for those who, like myself, have experienced difficulties and inconsistencies, the findings may be of some assistance.

In the first place, a final pickle of the copper in aqua fortis (bright dip) produces a surface free from scale marks and visible grain boundaries.

Subsequent treatment of the copper surface has a significant effect on the resulting reflection of light through transparent enamels. Profiled surfaces can produce attractive and interesting backgrounds and may mask small blemishes in the enamel. Doming a surface is also effective in masking the visible effect of bubbles. Caution is needed since some roughened surfaces can trap bubbles and appear milky as a result.

Care is needed to avoid foreign particles in the enamel. They should be removed from the enamel powder prior to sieving. Supporting stilts can be a possible source of contamination if they greatly exceed the size of piece being fired.

By grinding the enamel flux to a relatively fine mix of sizes, (150/325), a uniform, closely packed layer can be applied to the copper. The ultra fine particles are removed by washing in distilled water. The fine mix is of benefit in the absorption of the

copper oxide, reduced pitting and improved clarity. A sieve of 100 mesh size provides good control in the sieving of these fine grains.

Knowing the firing characteristics of a particular enamel flux will indicate how long and high to fire it to ensure the copper oxide is absorbed without producing a green cast.

In particular, the firing temperature has to be sufficiently high to both absorb the oxide and allow the many small bubbles to migrate through the melt.

Timing how long a piece is kept in the kiln will enable a consistently clear flux layer to be obtained. Ideally, some knowledge is needed about the characteristics of the kiln and the thermal time constant of different metal gauges.

The thickness of application of flux is important. Tests have shown that a thickness of 0.25 mm over a given area will balance the demands of freedom from pitting and avoidance of too many trapped bubbles. By knowing the area to be covered, this thickness determines the volume that can then be measured out using a graduated measuring cylinder.

Being precise about the amount of enamel flux sieved on the top copper face can be used to advantage when counter enamelling. Equal amounts on both faces minimises the thermal stresses on the enamel/metal interface and any consequential warping.

Two applications of flux minimises the chances of over-firing and the resulting burnt edges and green cast.

One may then ask how do these summarised procedures on small test strips translate to the more realistic sizes of copper used for enamelling? I have, subsequently, fired a number of transparent enamelled copper pieces using these techniques. A brief mention of one such example may further illustrate the method used.

A 80mm by 80 mm square of 18 gauge C103 copper was selected to make an enamelled piece using transparent enamels. The copper was annealed and pickled in sodium bisulphate to remove the copper oxides.

A hard fire counter enamel was applied to the reverse side. It was ground fine and a selected amount was put in a sieve, grade100 mesh. The amount was calculated as follows. 80mm by 80 mm of copper surface is 6400 mm^2. Two coats of flux, each 0.25 mm thick are going to be used on the front face. The total is 0.5mm and the volume needed is, therefore, 0.5x 6400/1000 ml = 3.2 ml. This quantity of counter enamel was sieved on the reverse and then fired in the kiln.

The piece was significantly warped, as expected. The gross oxide on the front face was removed by pickling and it was then transferred to 25% bright dip solution at 38^0 C. After a few minutes, bubbles started to form on the copper surface. When the whole surface was emitting bubbles uniformly, the piece was removed and washed thoroughly as previously described.

For the effect I was seeking, the rotary burnisher was used over the whole piece until it was bright. It was then washed again until water shed uniformly. It was dried and covered until ready for fluxing.

Soyer 1 flux was ground dry in a pestle and mortar and sieved through a 150 mesh sieve. The resulting powder was then sieved through a 325 mesh and that remaining on top of the mesh was washed several times in distilled water. It was then dried on a hot plate and the measuring cylinder used to measure out 1.6ml (a single coat 0.25 mm thick). It was spread out on a sheet to remove a few dark particles that were in the mix.

A sieve, grade 100 mesh, was then used to coat the copper surface with the 1.6ml Soyer 1 flux.
The kiln was raised to 980^0 C and the 80 x 80 mm copper was placed inside. The temperature was around 930^0 C. after 1.5 minutes. The sample was removed and allowed to cool. The warping was reduced but still evident. The surface was very light brown all over with no evidence of pitting or green cast. The edges were blackened and a carborundum stick was used to clean them.

A second coat of 1.6ml Soyer 1 flux was sieved on and fired for two minutes. The final temperature was 940^0 C. After cooling, the piece was completely flat and bright and clear. I was pleased that the final fluxed result was as anticipated.

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APPENDIX 1

Heating Time of Copper Samples

When a copper piece, supported on a steel mesh or trivet, is placed in an enamelling kiln, the kiln temperature drops and then recovers while the copper gradually rises in temperature until it approaches the kiln temperature.

For most of the experiments in this report, the copper samples were 50mm x 25 mm x 1.2mm thick. The small kiln was left to soak at the set temperature for about 30 minutes before use. Even so it dropped about 30^0C in temperature shortly after inserting a sample. As a result, the kiln was raised in temperature by this amount prior to inserting the test sample to ensure that, over the firing period, the copper reached the temperatures listed in Table 1. Larger capacity kilns would drop less in temperature for the same size of copper. The firing times also listed in Table 1 are, strictly speaking, applicable to this copper sample size supported on the given steel support and it is not obvious what firing time is needed for other sizes of copper. For enamel flux, the firing time is just as important as temperature if the oxide is to be absorbed without extending into the green cast region.

To try and answer this question, I purchased a fine thermocouple with glass bead insulation. This was connected to a digital voltmeter scaled in degrees centigrade. This temperature measuring device responds very quickly to changes in temperature and so was ideally suited to measuring how quickly different sizes of copper heat up in the kiln.The thermocouple was secured to a stainless steel mesh on which lay the copper test strip and the sensing bead was bent so that it contacted the copper surface under positive pressure. The assembly could be inserted in the kiln and the door closed with the measuring leads coming out through a crack in the door.

Figure 11 shows the heating curve of the copper strip with the kiln temperature set to give 800^0C as the equilibrium temperature.

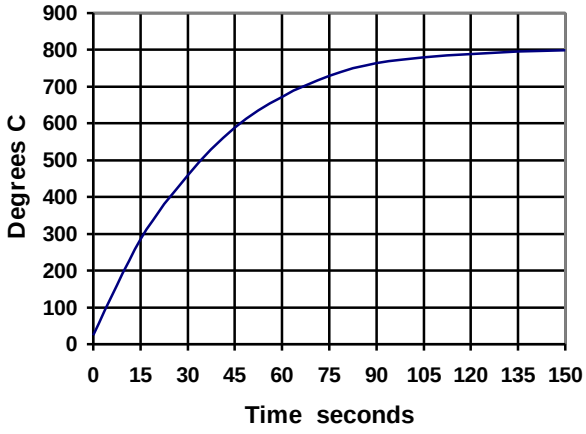

Figure 11. Heating Time of 50x 25x 1.2mm Copper Strip

It took longer than 60 seconds to approach the fusing temperature of the enamel flux and nearer 120 seconds to reach the final temperature. For those familiar with the concept of Thermal Time Constant (T_c), it is the time to reach 63.2% of final temperature. T_c in this example is 38 seconds. After 3 time constants, ie 114 seconds, the sample reaches 95% of the equilibrium temperature of 800^0 C.

Heating curves were obtained for other areas of 1.2mm thick, (18gauge), copper up to a size of 75x 75 mm. Within the limits of experimental error, the curves were identical to that shown in Figure 11. Thus the firing times in Table 1 apply equally to larger and smaller samples of 18 gauge copper.

With larger samples still, which would occupy most of the small kiln area, there can be an excessive temperature drop and also the temperature gradient from back to the front of the kiln can cause incomplete firing of the enamel flux. A larger kiln would then be indicated.

The time constant and hence heating time for the copper pieces of 18 gauge material was also found to be the same for different kiln equilibrium temperatures. Thus it will take no longer for samples of this thickness to reach say 900^0C kiln setting than to reach 800^0C setting.

Overall, it is clear that a firing time for Soyer 1 enamel flux will be a minimum of around 1.5 minutes using 18 gauge material. This knowledge, coupled with familiarity with one's own kiln avoids the need to keep withdrawing a fluxed sample from the kiln to check for completeness of firing. This information may be of value even to those who rely on visual inspection because it indicates there is little point in withdrawing a piece from the kiln before 1.5 minutes have elapsed.
The heating time constant for two other gauges of copper was also measured, (0.56mm or 24 gauge and 3.0mm or 11 gauge). The results for all three gauges are as follows:-

24 gauge copper	T_c = 32 sec, 3xT_c =94 sec
18 gauge copper	T_c = 38 sec, 3xT_c =114 sec
11 gauge copper	T_c = 47 sec, 3xT_c =141 sec

Thus, copper of 24 gauge reaches kiln temperature some 20 seconds sooner than 18 gauge material. 11 gauge copper takes some 27 seconds longer. The logic is that the firing times in Table 1 can be adjusted up or down by interpolation depending on the gauge of copper used.

APPENDIX 2

Surface Finish and Grain Size

The abrasion of a copper surface with emery paper creates peaks and troughs in which the heights and widths are determined by the grade or coarseness of the emery. The actual surface area is greater than the nominal area by an amount depending on the surface roughness. Hence the total amount of copper oxide formed on heating is likewise greater. A given amount of enamel flux has thus to absorb more oxide on a rough surface than a smooth one.

Of particular interest in this report is the milky effect observed with the 600 grade emery preparation. These emery particles are of order 0.01mm (10 microns) and the surface troughs and peaks created by these particles are presumed to be of the same order of magnitude. The enamel grains (150/325), are between 50 and 100 microns in size. When this enamel powder is sifted on the surface, each grain will lie across several surface peaks. The suggestion is that, as the grains soften and coalesce, air is trapped in the troughs or furrows thus creating the milky effect.

If the surface is made smoother, the peaks and troughs are smaller and the air spaces are correspondingly less. On the other hand, the surface roughness produced by 100 grade emery is caused by emery particles of around 175 microns in size. The enamel grains are now tending to fall into the troughs rather than straddling across several troughs and it is surmised there is greater opportunity for the air to escape.

All the above is hypothesis and there may be another explanation for the milky effect observed with the particular surface finish produced by 600 grit emery paper. It does not alter the fact that the use of this abrasion method with 150/325 enamel flux is an unsatisfactory combination. It is conceivable that other combinations of enamel particle size and surface roughness might be equally undesirable.

Sources of Supply

Some of the items used in this investigation are perhaps less well known to beginners in the craft of enamelling and so their source is listed.

OFHC copper C103 in 1.2m x 0.6m sheets
From Smiths Metal Centres. Tel: 01403 261981
Stock No CUC103HHSH62037

Mesh Screen 325 mesh
95/5 Gilding Metal
From jgoldman@hetnet.nl Tel: 070 3607916
Or direct from www.thompsonenamel.com

Bright Dip
From H.S. Walsh & Sons Tel: 0208 778 7061
hswalsh@dial.pipex.com
Stock No T221066

Burnishers and Engraving Tools
From Cookson Exchange Tel: 020 7400 6500
www.CooksonGold.com

Fast response Thermocouple
From TC Direct Tel: 01895 855555
www.tcdirect.co.uk
Product Code D 409-010