

TRANSPARENT LEADED ENAMELS APPLIED TO COPPER AND SILVER



- by -

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1. INTRODUCTION

This document brings together specific reports written previously by the author. The aim is to highlight some of the factors that affect the quality of transparent enamels laid on copper and silver, and thereby to assist those enamelling for perhaps the first time. Some of the information derives from experiments carried out by the author in seeking to achieve satisfactory results. The observations supplement the more comprehensive information available in books and articles on enamelling which cover various specialist techniques such as Champlevé, Baisse Taille, Cloisonné etc. Hence the scope of this document is to simply deal with the basic principles of metal selection and the preparation, application and firing of transparent leaded enamels on a flat metal base.

The use of transparent enamels is far more demanding and requires much greater attention than opaque enamels. The colour and appearance of opaque enamels is dominated by their surface layer, but with transparent enamels light passes through the whole depth of several enamel layers. Thus imperfections at any level and on the metal surface itself will affect the quality of the finished piece. As a result, beginners should not be too disappointed if their first attempts do not come up to expectation. Hopefully this document will assist in achieving acceptable results using leaded transparent enamels on copper and silver.

2. THE METAL SUBSTRATE

Leaded, powdered, glass enamel can be applied successfully to a range of metals including copper, silver, and gold. It is important to recognise that these metals exhibit different characteristics when heated, and the fusing of an enamel to a particular metal surface may not be straightforward, and bubbles, pits, cracks and lack of adherence might result. Thus the individual characteristics of an enamel/metal combination need to be understood. Even small variations in the composition of some metal alloys can have an influence. The message is clear - consider every distinct enamel/metal combination as unique, and follow the proven procedures in order to achieve success. That this document deals solely with copper and silver and leaded transparent enamels is a further indication of the importance of this message.

2.1. COPPER

Copper presents a problem for transparent enamels applied to it, namely the rapid and significant oxidation that takes place when it is heated to enamelling temperatures. One might conclude it is virtually impossible to achieve results quite as good as those on silver. This may be true, but, by the use of enamel flux, one can significantly mitigate the discolouration of transparent enamels caused by the black/red copper oxides that develop on the surface of the metal.

There are some advantages to using copper, not least being the much cheaper cost compared to silver. The higher melting point of pure copper (1083°C) compared to

silver alloys is also less restricting when seeking to use a high firing temperature. Again, although the reflecting properties of copper are less than silver (67% as compared to 98%) one of the consequential features is that transparent enamels applied to copper have a warmer glow as opposed to the somewhat colder appearance of enamels applied to silver. In view of the above it is understandable why copper is widely used for enamelling, although silver retains its pre-eminence for high quality, high value items.

Although not considered in this document, it is worth mentioning an alloy of copper that is used by a number of professional workers particularly in the badge industry. This is gilding metal, an alloy formed by the addition of a small percentage of zinc to pure copper, (5%). This alloy does not oxidise on heating as significantly as pure copper and hence its attraction. High firing temperatures must be avoided, (not above 790°C), to stop the zinc coming out of the eutectic. It is not easily obtainable to the correct standard in small amounts in the UK, and some products described as gilding metal may contain up to 20% of zinc. This percentage can result in poor adherence with some leaded enamels. Even 5% zinc can cause problems and coupled with the thermal contraction of gilding metal being 4% higher than copper, some low contraction enamels can crack or even detach from the metal.

2.2. SILVER

Fine or pure silver is an attractive metal for enamelling owing to its intrinsic value and because it possesses high reflecting properties, allowing transparent enamels to be shown to best advantage. Although pure silver does not oxidise significantly at the temperatures needed to fuse the enamels, it can impart a very slight yellow tinge to some transparent fluxes and red, orange and yellow enamels.

However, pure silver is a very soft metal and thus impracticable for pieces that require some degree of strength. Its melting point is 962°C, which is sufficiently high to enable the fusing of all enamels, but to be on the safe side long firing times at high kiln temperatures are best avoided. The thermal compression coefficient of pure silver is slightly higher than copper but its yield strength is much lower, (65%). As a consequence, flat pieces can permanently extend after repeated firings depending on the hardness and thickness of the applied enamel. The consequential stress on the enamel is, however, reduced.

2.3. SILVER ALLOYS

Because of the low tensile properties of fine silver, an alloy in common use is standard or sterling silver. It is widely used in the production of items of jewellery, boxes, plaques etc etc. The addition of 7.5% of copper with the remainder silver increases the strength and hardness, but it lowers the maximum firing temperature of sterling silver, (800°C). The reason for this is discussed in Appendix 1. Minor oxidation of the copper and silver components in the alloy during heating can cause some transparent enamels to slightly discolour. They are mainly red, pink, orange and yellow enamels depending on the particular formulation. Nevertheless, there

are well established techniques to enable enamel clarity and colour to be of a very high order.

Britannia silver (with a minimum silver content of 95.8% and the remainder largely copper) is less widely used, but is especially suited for taking stamps and dies. The maximum firing temperature is higher than that for sterling silver (870°C) and again Appendix 1 contains more information. Its mechanical characteristics lie between those of fine silver and sterling silver and many enamelists consider the enamel colours are truer when fired on this alloy due to its reduced copper content.

A recent development in tarnish-resistant silver alloys is argentinium silver alloy. Argentinium silver 935 is a modern sterling silver alloy, containing 93.5% silver, in which the traditional alloy is modified by removing some of the copper and adding the metalloid germanium. A new argentinium alloy containing 97-percent-silver is reported to take transparent enamels very well, with no colour shifts. Argentinium silver is outside the scope of this document.

Some enamels are more susceptible than others to developing cracks that may appear after firing. This depends on a number of factors, notably thermal contraction and yield strength of enamel and metal. In this respect, copper is well suited to the application of most leaded enamels. More information is contained in Appendix 5. The thermal contraction coefficient of sterling silver is about 10% higher than that for copper, and its yield strength is also higher. Depending on the shape of a silver alloy piece, some low contraction enamels can exhibit cracks after firing. Again Appendix 5 discusses this in more detail and also the use of counter enamelling to avoid the bowing of a metal that can occur under certain conditions.

3. OBTAINING COPPER AND SILVER FOR ENAMELLING

Copper is manufactured with different additives depending on the application. The ideal for enamelling is electrolytic, high conductivity copper since it produces no products that, on heating, might cause an excess of bubbles and pits in the fired enamel. Small amounts of silver and phosphorus may be present and also oxygen depending on the method of production. A high phosphorus content produces loss of adherence.

Most suppliers of copper blanks for enamelling purposes are aware of the need for low phosphorus and oxygen content, and items purchased from these sources should be entirely satisfactory. If purchasing sheet copper from a copper stockholder, it is useful to know that the European EN grades of copper that contain low percentages of phosphorus and oxygen and little silver content, and are therefore acceptable for enamelling, are CR004A up to CR007A. Other grades of copper would need testing for enamelling suitability. Picking up scrap copper, perhaps from roof cladding or copper utensils, may seem attractive from a cost point of view but, based on the foregoing remarks, they could well cause problems, and are best avoided.

It is desirable to purchase sterling or britannia silver alloy that is in the annealed condition and that has been manufactured in an inert atmosphere to exclude the development of oxidation products, principally copper oxides. Sometimes zinc is added as a deoxidiser and sterling alloys may also contain germanium and trace amounts of the elements selenium and tellurium, which occur naturally in silver ore. As little as 5 parts per million combined of these latter elements can prevent enamel adhesion. If possible, choose alloys that are either zinc-free or contain very low zinc concentrations, typically less than 2 %.

4. THE TRANSPARENT LEADED ENAMELS

Glass is made out of silica, which has a very high melting point. It is an amorphous material, ie non-crystalline, so that it does not have a precise transition between solid and liquid phases. There is, however, a temperature band where the material becomes sufficiently mobile to flow and spread. Pure glass has a flow temperature too high for fusing to most metals and to lower the flow temperature soda ash (a mixture of sodium oxide, and sodium carbonate) and limestone are added as fluxes. Other additions might include lead oxides, lead carbonates or borax/borax oxides. Coloured transparent enamels are produced by the addition of metal oxides. These are the main constituents of vitreous enamel for jewellery.

The temperature and firing time at which a particular glass enamel powder becomes sufficiently mobile to form a smooth layer and adhere to a metal substrate is achieved by altering the proportions of the above constituents. Thus enamels can be classed as soft, medium or hard. Hard firing enamels take a little longer to reach maturity, i.e. to flow sufficiently to form a smooth layer, than medium firing enamels. Soft firing enamels take a little less time. In general, most coloured transparent enamels for application to copper and silver will achieve a gloss finish at around 750°C. The enamel will be like wet sugar as it starts to reach maturity, then has the appearance of orange peel before smoothing to a gloss. The glass manufactured and referred to as flux has a composition that enables it to absorb oxides forming on metals during a first firing. Flux for use on copper is hard firing and that for use on silver is medium firing. There is another factor that can influence the time it takes for an enamel to mature to a smooth finish and that is the size of the grains making up the powdered glass. Coarse grains may need to be fired a little longer than fine grains when fired at the same temperature.

The addition of lead in the manufacture of enamel has been used extensively for many years, as it provides a clarity and sparkle to the fired enamel. Health and Safety legislation has precluded its continued use principally in the USA where unleaded enamel is now dominant. However, leaded enamels are still readily available in the UK from a number of enamel suppliers, and provided sensible precautions are adopted when preparing the enamel for use, there should be no health issues. In any event, some oxides added to provide a particular colour are

also somewhat toxic and so one should treat all powdered enamel with care and avoid inhalation.

It is important to recognise the different physical properties exhibited by soft, medium and hard enamels. One is the thermal contraction coefficient which, as already mentioned, is a significant factor in determining whether cracks develop due to the different contraction of enamel compared to metal. Hard enamels tend to have a lower contraction coefficient than soft enamels and the consequence is that there is a greater stress imposed on the enamel. It may be a surprise to learn that the contraction coefficient of some blue transparent enamels, for example, can be up to 30% less than some green enamels. There are many other factors involved, but it is well to be aware of this potential problem, (see Appendix 5). If a hard firing enamel is laid over an already fired soft enamel, there will be a tendency for it to sink into the softer lower layer. This can produce some interesting effects but, if not desired, then always lay soft enamels over hard.

5. OBTAINING TRANSPARENT LEADED ENAMELS

There are a number of UK outlets that sell transparent leaded enamels. In the main they source the products from manufacturers either in the UK, Europe or Japan. Enamel is normally sold having been ground to pass through a specified size of mesh or sieve. The most common is 80 mesh enamel which means that the enamel grains pass through a sieve that has 80 openings per inch. This corresponds to enamel particles that are smaller than 0.177mm, (177 μ m). Appendix 2 lists different sieve sizes and the particle size opening on the mesh. The actual proportion of grains that are just less than 177 μ m in size and those that are much finer can vary from supplier to supplier. In general, there should be a good mix of grain sizes and not too many that are so fine, (30 μ m and less), that they are unsuitable for enamelling.

Enamel in lump form is available from a few sources and is preferred by dedicated workers. There are probably two reasons for this. Firstly, one can grind the lump enamel down to a grain size that is best suited for a particular application. Secondly, powdered glass is subject to a corrosion process caused by reactions between it and gases in the atmosphere. Moisture is a known degrading agent. The amount of degradation for a given enamel grain is inversely proportional to its size, so very fine grains will potentially exhibit more deterioration under storage conditions than the same volume of large or coarse grains. Over the years there have been significant advances to make vitreous enamels more resistant to attack. Even so, purchasing enamel in lump form is the ultimate for the purist, and if it is ground just prior to use, there should be negligible deterioration.

Assuming that most workers obtain pre-ground enamel powder from a supplier, it is good practice to store it in a dry atmosphere for the reason stated above. Ideally, the as-received ground enamels should be stored separately in sealed glass jars. For ultimate protection from moisture, several of the jars could be placed in a larger sealable container that contains a desiccant of silica gel. After time, when the silica

gel turns pink, it can be taken out and heated in an oven to drive off the moisture, at which stage the silica gel reverts to its deep blue colour. Even with the above precautions, it is necessary to grind enamel in a pestle and mortar before use - see Section 8.

6. PRIMARY METAL PREPARATION

The surface of a metal as purchased may have grease marks, be tarnished with oxide, and/or be somewhat work hardened. Applying an opaque enamel directly to such a surface and then firing it might be satisfactory from an adhesion point of view and yield an acceptable visual appearance, but it is not good practice.

In respect of transparent enamels, however, metal surfaces prior to laying enamel should be free of all contaminants and oxides. It is beneficial that the metal should also be in an annealed condition so that there are no internal stresses that could be released on heating and that could cause distortion. It may be necessary to heat treat the metal more than once if it is to be formed into shapes. Even grease marks from hand contact should be avoided or removed prior to applying enamel. The copper or silver will then be in the best condition for transparent enamelling. Some primary preparation methods for the as received metal are as follows.

If copper or silver has been work hardened and the surface contains grease or oil from hand contact as well, then the most effective method is heat treatment. The oils will burn off and the metals will be annealed. Annealing is the process of softening metals by heating them to above their recrystallisation temperature, maintaining that temperature for a few minutes, and then cooling them. Heating may be by torch or in a kiln, but beginners may find it easier to use a kiln set to a temperature that will not overheat the metal, particularly silver. Metals such as copper, silver and brass may then be quenched in water a short time after the heating and they will then be fully softened. An advantage of quenching copper in this way is that much, if not all, of the black oxide will shed from the surface.

The removal of remaining surface and sub-surface oxides following annealing is by acid treatment. Different methods are used for copper and silver alloys and this is covered in the next sub-sections.

Removal of just tarnish or surface oxide can be done at any stage by pickling, but care is needed once an enamel has been fired on just part of a metal surface because the pickle can degrade some enamels. Alternatively, mechanical abrasion using carborundum cloth, abrasive pad etc can be used.

Oil or grease at this stage can be removed from metal surfaces without the use of a torch or heating in a kiln. Pickling in dilute acid will not remove them, but there are numerous cleaning agents designed to remove greases from surfaces. An example is using alkali or soaps. Non-ionic surfactants are part of the domestic cleaning scene and they are the modern way of removing grease and oils. A toothbrush or similar can be used to scrub the surface with the product and then the surface must

be washed well with water. Other methods include using a scouring pad and pumice powder made into a slurry and again the piece should then be washed thoroughly. The water should shed from the surface reasonably well and not form globules. If the metal surface has been touched just prior to laying enamel, applying acetone with a soft brush will remove any oily deposit. Acetone can be purchased in 50ml bottles from chemists. It is miscible in water and so a subsequent quick, final wash in distilled water should suffice. A few notes particular to copper and silver follow in the next two sub-sections.

6.1. COPPER

Copper blanks and copper sheet are normally supplied in the half-hard condition rather than fully annealed. The surface may also be lightly oxidised and contain grease from hand contact. To soften the copper and also remove greases, it should be placed in a kiln heated to around 600 – 700°C for a few minutes. An undesirable consequence of the annealing is that all surfaces are converted to black cupric oxide, CuO, and below it, red cuprous oxide, Cu₂O. The general term for these oxides is firescale. After removal from the kiln and allowing the metal to cool for about half a minute, it should be plunged into a large container of water. This rapid cooling should cause much of the cupric copper oxide to shed from the metal. Then, transfer the copper to a pickling solution to remove the remaining oxides.

A cheap, effective pickle is sodium bisulphate, (sold in 7kg containers by swimming pool specialists, or in smaller quantities by craft suppliers). Around 100 grams is added to 1 litre of water. If the solution is heated to about 40°C, it will speed up the reaction. After this, neutralise with a soda solution followed by rinsing thoroughly in water and drying using a lint-free cloth. The annealed copper may then be domed, formed into bowls, fittings added etc. The copper may again work harden and so may need to be annealed and pickled several times after hammering and shaping.

6.2. SILVER

Pure silver is normally supplied in the fully soft condition, but if it has been work hardened subsequently, it can be annealed in a kiln at around 600°C and then left to air cool. Silver oxide forms on heating, but in free air it decomposes above about 200°C, and so there should be no surface discolouration, just a dull matt finish. Because pure silver is so soft, the amount of work hardening produced when, say doming the metal, may be so slight as to not require annealing.

In the case of sterling and britannia silver alloys, the addition of copper as an alloying element introduces a degree of complication that requires some attention. As already mentioned, it is desirable to purchase these alloys of silver in the annealed condition, and manufactured in an inert atmosphere to exclude the development of oxidation products.

Appendix 1 deals with the necessity of not heating silver alloys beyond their solidus temperature (800°C for sterling and 870°C for britannia), to ensure these alloys remains chemically stable. Even so, one needs to consider the metallurgical

changes that result from heating a silver alloy prior to applying the enamels and firing them. The heating may be because the silver alloy has been work hardened when forming it into various shapes, and heating to restore the softness may be part of that process. Fittings may need to be soldered on the reverse, and so heat will have had to be applied.

The surface of the silver alloys will, after heating at around 650°C, exhibit a light grey appearance due to the oxidation of the surface copper, more so with sterling silver and less so with britannia silver. It is also often referred to as firescale although the amount of surface oxide is far less than that which forms on pure copper. It can, nevertheless affect the colour of some transparent enamels and so should be removed. Oxidation will also have extended below the surface of these alloys of silver due to the high porosity of silver to oxygen at the annealing temperature. This is referred to as firestain. There are various opinions on both the nature of this particular oxidation and how to deal with it, and this is discussed in more detail in Appendix 3. It is not effective or sufficient to simply pickle a silver alloy in the same manner as described for copper. Even so, if for other reasons it is desired to pickle silver and silver alloys in sodium bisulphate, the solution should be reserved for this metal only because pickling in the solution used for copper will cause copper salts to deposit on the silver. What is set down below is one method of dealing with the oxidation products that form during the annealing process that restores silver alloys to their virgin state.

The procedure is brief immersion in 59% concentrated nitric acid. There are three hurdles to clear: - acquiring the acid, storing it, and using it. New government regulations in the UK require a prospective purchaser to obtain an EPP licence and photo ID in order to collect 59% nitric acid from a supplier. This is a daunting prospect for non-professional enamellers and membership of a club or guild is likely to be the most expedient way of acquiring the small quantity needed. Having done so, it should be kept under lock and key to ensure that it is not stolen or misused by a third party. A COSHH safety cabinet is ideal but expensive. However, some form of lockable cabinet is desirable and it has the advantage of providing storage for other somewhat less hazardous chemicals such as sodium bisulphate for pickling copper. When using concentrated nitric acid, the recommended practice is to wear protective gloves and apron and to work in a well-ventilated area, as the fumes are noxious.

A silver alloy that has been annealed is briefly dipped in the acid and it will turn 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. It is stressed that the silver alloy should not be left too long in the concentrated acid otherwise it will be progressively etched away. Needless to say, the piece must finally be washed thoroughly to remove all traces of the acid. The silver alloy now has a dull, matt appearance. This procedure of nitric acid dipping is also useful to

check that an as-purchased sterling or britannia silver sheet was manufactured in an inert atmosphere, especially if wanting to enamel on it without it having been heated beforehand. The metal, dipped in the acid, should not turn grey or black.

An alternative approach to deal with silver alloy that has to be heated prior to enamelling is to restrict the oxygen attack by coating the metal surfaces with a borax based flux prior to heating. Perhaps not so effective as the nitric acid treatment, but it avoids having to acquire, use and store concentrated nitric acid. Depending on the shape and area of silver alloy to be subsequently enamelled, removal of the surface layer of the oxidised metal alloy by abrasion to a depth that exceeds the extent of the sub-surface oxides can also be effective. The grey/ purplish stain of interior oxidation should gradually disappear.

7. SECONDARY METAL PREPARATION

The matt surface that is produced after a primary surface treatment, of both copper and silver, as outlined in Section 6, will not reflect sufficient light to show a transparent enamel to best advantage. One simple method is to abrade the surface with say a glass fibre brush or a fine wire brass brush. In the case of silver and its alloys, engraving or engine turning on silver is often used by professional workers to create a bright surface that will enhance a design and one that will reflect the light when viewed from different angles. Following this, surfaces should then be further de-greased. Apart from acetone, human saliva applied using a clean cloth is reported as being effective.

Copper is not an especially reflective metal. In addition there is generally the need to use a flux layer on copper, which can further slightly reduce the reflection of light through transparent enamels. If the surface of a metal, prior to enamelling, is lacking in sparkle, then so will be the final result.

One method of further brightening a copper surface is to use a burnishing tool. This will make the surface very smooth and hence light will be reflected from it much like a mirror. There are pros and cons. On the positive side, the surface area thus created is very close to the nominal area, meaning that there are virtually no peaks or depressions. Hence the amount of copper oxide that develops on heating is the minimum possible and so it is more readily dealt with than would be the case with rougher surfaces. On the negative side, there is evidence that very smooth surfaces reduce the adhesion between the metal and the fired enamel, and in the ultimate the enamel could detach from the metal surface. Experiments with difficult metal/enamel combinations have shown this can occur. Any imperfections in the fired enamel such as trapped bubbles have maximum visibility and as a consequence burnishing creates a rather unforgiving surface. Having said that, it should be noted that curved surfaces, eg bowls, or flat surfaces that have been slightly domed, will tend to obscure any milky appearance caused by an overabundance of fine bubbles trapped in the enamel.

Alternatively, if the copper is engraved or etched to produce recesses or cells for filling with enamel, the surface can also be quite reflective and in addition, tend to obscure imperfections such as bubbles in the fired enamel. The surface of the metal, now much rougher, means there is more copper oxide produced on heating. This should not be a problem if the techniques for applying and firing copper flux outlined in Section 10 are followed. Silver, engraved or etched, will be especially reflective and a rougher surface does not require special attention. There are other distinct forms of surface profiling that can yield excellent results.

To illustrate the visual effect created by some fairly basic surface profiling on copper, a 50 x 25mm test sample was marked into four quarters. Each quarter was given a different surface profile.

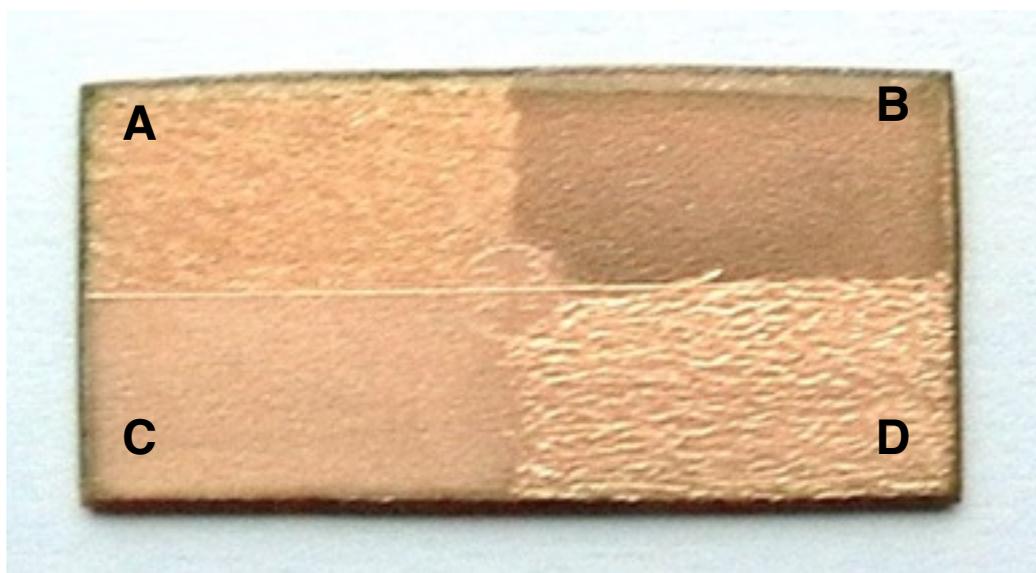


Figure 1. Surface Texturing

A was profiled using a high speed drill with a cylindrical grinding stone, B was polished using a rotary burnisher, C was cleaned by hand using a fine abrasive block and D was profiled with a cylindrical cutter. A 150/325 enamel flux for copper (see Sections 9 and 10) was then sieved over the whole area and slightly under-fired, (930°C for 90 seconds). Quarters A and D 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°C for two minutes. All quadrants were now clear, but with some interesting differences. 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). Microscopic examination revealed bubbles comparable in size and number in all quadrants. Small blemishes in B and C do tend to show and although bubbles were small in size and number, a slight milky cast is seen when the sample is 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.

A further comparison between a conventional glass fibre abraded surface and a textured surface is shown in Figure 2. The sample had been fluxed, fired and then covered with two thin coats of a green transparent enamel, firing between each coat. 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.

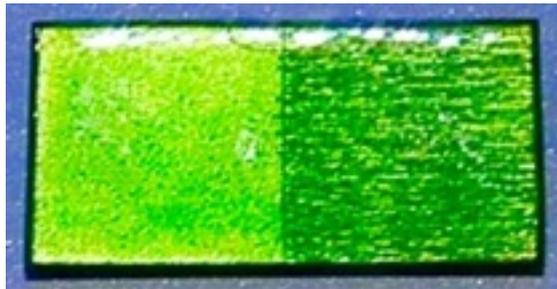


Figure 2. Visual Effect Produced by Two Textured Surfaces

During tests on the surface texturing of copper, some rather unsatisfactory results were obtained using carborundum cloth grade 600. Significance bubble entrapment was observed and this is described more fully in Appendix 4. As this phenomenon has not been reported elsewhere, the result should be treated with caution.

Although it is important that attention is paid to ensuring metal surfaces are bright and reflective in order to show transparent enamels to their best translucency, there are designs using copper as the base metal that favour applying and firing an opaque white layer over the bare metal. Coloured transparent enamels fired over this base of white will produce a truer colour because there is no reflected colour from the copper. Although there is less sparkle and vibrancy, some prefer the more pastel colour produced by firing on a white base. This technique is not considered further in this document.

8. ENAMEL PREPARATION – GENERAL PRINCIPLES

Using any transparent enamel powder straight from the supplier will rarely be satisfactory. As already mentioned, perhaps, the most significant reason is that some chemical deterioration of the surface of enamel grains may well have taken place depending on the date of manufacture and the method of storage prior to use. The surface can adsorb moisture depending on air humidity and this will react with the glass enamel. Some enamels are quite resistant to this deterioration, but others may not be. Again, as already mentioned, very small sized grains are more susceptible than large grains to deterioration because of their greater ratio of surface area to volume.

Even if many enamels being manufactured today are more resistant to moisture deterioration, the surface of the grains will still have a chemically absorbed film. When such an enamel powder is wet laid or sifted dry on the metal, there will be grains lying on top of other grains, and when they fuse under the action of heat in the kiln, there is the potential for trapping water vapour released from the grains. Again very small sized grains will be packed closer together than large grains making the trapping more likely. Of course, the gaps between unfired grains will be air and this can be trapped as bubbles in the same way. The outcome is that extremely small sized grains have the greatest potential for causing cloudiness or lack of transparency, be it due to deterioration or the trapping of many small bubbles.

It is clear from the above that for good transparency, these extremely small particles, (commonly referred to as fines), should be removed from the mix of enamel grains prior to enamelling. It is also a general rule that enamel grains should not be laid too thickly as this will also increase the probability of trapped bubbles. The smaller the grain size, the thinner should be the application. In addition to removing the fines, it is important to grind the enamel in a pestle and mortar to create fresh, uncontaminated surfaces to all grains. Enamel supplied in lump form will have to be ground anyway to produce particles of the desired size.

Two somewhat different techniques are deployed by enamellers in this preparation process of removing the fines and grinding the enamel. By far the most common method is to place a quantity of the as received enamel in a mortar and to cover it with water. It is then ground until all the grains have been reduced in size, thus creating fresh uncontaminated enamel. Over-grinding should be avoided otherwise there will be a preponderance of very small sized particles. The ideal is to purchase the enamel in lump form and to grind this down under water to the consistency appropriate to the application. This is discussed later. Experienced enamellers will know when to stop this grinding, but beginners will have to learn by instruction or trial. The water turns milky in appearance due to the release of surface oxides and the fines in suspension, and it is poured off. More water is added, slowly rinsing the enamel, and this is repeated until the water runs clear. The final washes should be in purified or distilled water. Some enamellers recommend that 2-3 drops of concentrated nitric acid be added to the penultimate rinse to ensure absolute clarity. However, this practice can deteriorate some enamels and so it is of dubious benefit. The wet enamel should be applied to the metal surface without delay to avoid possible further moisture deterioration. It is reported that enamel that has been freshly ground can be kept in good condition under distilled water, say overnight, without deterioration as, like the rusting of iron, the exclusion of oxygen inhibits the degradation process.

If the enamel is kept overnight under water, it is still prudent to make a test strip to be sure the enamel is satisfactory. If the intention is to apply the ground enamel dry using a sieve, the washed enamel should be dried straight away. A glass dish to

contain the wet enamel is ideal, placed on the top of a heated kiln. A cover with small holes will stop dust particles settling on the enamel while allowing the moisture to escape.

An alternative approach to the above, is screen separation. In this method the enamel powder or lump enamel is ground dry. A face mask must be used to avoid inhalation of any fine particles and a cover should be put over the mortar, with a central hole for the handle of the pestle to protrude through. This will ensure as far as possible that the grinding does not cause the larger particles to be ejected from the mortar, and it will also restrict the amount of glass dust entering the atmosphere.

The dry, ground enamel is then poured into a coarse sieve, say 80 mesh, which is stacked above one of 325 mesh. A top lid and bottom cup are fitted. After repeated shaking, those grains that pass through the 325 mesh (44µm and less) and into the bottom cup are the fines that are most likely to contribute to opacity. These can be stored for other purposes or disposed of safely. A small coin placed in each of the two sieves will assist in keeping the mesh clear and help particles to pass through. The grains still lying in the 80 mesh sieve are too large for most purposes and they can be re-ground to provide more smaller sized grains. This enamel, sitting in the 325 mesh, is then referred to as 80/325. The method can be extended to the use of stacked sieves of different opening sizes so that, if desired, it is possible to select a range of grain sizes the enamelist finds most useful.

Having removed the fines as much as possible by this dry grinding method, it is good practice to then swill the remaining enamel in purified water as a small amount of the fine powder may not have passed through the 325 mesh or may have adhered to the other grains. Experience has shown that a single wash will be sufficient, as compared to the many washes needed when grinding under water. Again, if the intention is to apply the enamel grains dry, the enamel should be dried straight away.

Grinding under water is the most widely used method and is free of any risks of inhalation. Dry grinding and then screen separation is more economical in producing enamel for use of a particular range of grain sizes. In summary, the ideal is to purchase enamel in lump form, keep it dry, and then grind it and wash it and use it straight away. The least desirable situation is to purchase an enamel powder that is susceptible to degradation, store it for a long time in the open, and to either not grind it before use or grind it less than diligently and then to leave moist enamel a while before applying it. The chances of getting a satisfactory result are very low. Section 10.1 contains more information about the grinding of enamel to produce the best results.

9. THE FIRST LAYER OF ENAMEL

The first layer of enamel laid on a metal surface and then fired to achieve adherence and a smooth glassy finish is perhaps the most important for transparent

enamels. There will be a chemical reaction involving any oxides formed on the metal when heated, and the oxides present in the vitreous enamel. Depending on the particular metal and also the composition of the enamel, the partial absorption of the metal surface oxides can result in colour changes in the enamel and also a reduction in transparency. Subsequent layers of enamel will be less affected if at all, particularly if a softer enamel is laid over a harder base coat. If an enamel is over-fired by excessive temperature and time in the kiln, its colour can also change independently of the metal substrate and ultimately it will be degraded irrevocably.

Apart from the above, there is a physical effect that influences the colour of both the first layer of enamel and all subsequent layers. This is the colour of the prepared metal surface. A particular transparent colour will appear somewhat differently on different metals due to the additive colour of the metal. The white colour of silver will influence the transparent enamel colour less than the more pinky or golden colour of copper. This is not necessarily a disadvantage as an enamel fired on copper can appear warmer in tone.

In the case of copper, although a few coloured transparent enamels fired directly onto the metal are able to absorb the copper oxides formed on heating with little detriment to their colour and transparency, most do suffer in this respect. Because the enamel grains laid on the surface of the copper restrict somewhat the access of oxygen, the metal oxide that forms is predominately red cuprous oxide, Cu_2O . Nevertheless, many transparent enamels will darken since, at the normal firing temperature and time for transparent enamels to mature, the surface copper oxides can react with the metal oxides in the enamel. Hence they become an additional colourant. If a coloured transparent enamel is fired higher and longer to try and absorb the copper oxide, its own colour can degrade. The chemistry is far more complicated than this, but it is the copper oxide that can make a transparent enamel less pure in colour than when the enamel is applied to silver. Red and pink enamels are particularly affected and also some greens and blues. Many manufacturers provide colour images of their transparent enamels laid and fired on different metals, and one can observe which of them are susceptible to discolouration when applied directly to copper.

The recognised procedure to cope with enamel discolouration due to copper oxide is to firstly apply a clear enamel, called flux. Correctly applied and fired, it will absorb the copper oxide and still remain colourless. The proportions of the basic constituents making up this enamel flux are chosen by the manufacturer for this purpose. It is sensible to use a flux formulated specifically for copper as it will also provide a good hard base for the subsequent application of coloured transparent enamels. The flux must be fired for a sufficient time and temperature for the copper oxide to be fully absorbed. If the firing time or temperature is too low, there will be a red or pink cast. If fired too high or too long, a green cast or blackening will result. Producing a clear flux layer prior to then laying a coloured transparent enamel is

especially important for copper. Imperfections at this first stage are almost impossible to rectify later.

Apart from possible problems with cracking of an enamel, (discussed in Appendix 5), thin rectangular metal pieces can become bowed after firing, again due to the differential thermal contraction forces of metal and enamel. The solution is to apply enamel to the reverse of the metal and this is called counter enamelling. Ideally, the counter enamel should be applied before the first firing and have a similar coefficient of thermal contraction to the enamel on the front. A thin coherent layer of fine grained enamel either wet laid or sieved on the underside should not fall off when it is turned over to enable enamel to be applied on the front. A small amount of gum can be used if necessary. To prevent the counter enamel from adhering to the wire mesh support when the assembly is fired in the kiln, a layer of mica or ceramic sheet should be interposed between the wire mesh and the enamel piece. The need to counter enamel a particular item is not always easy to judge but from the information presented in Appendix 5 it is clear that thin flat pieces of copper or sterling silver, laid with a fairly hard enamel, will be most likely to require a counter enamel. Some enamellers who work almost exclusively with copper are inclined to use a counter enamel regardless, because the copper oxide scale that would normally form on the underside is absorbed by the counter enamel. The overall appearance is improved and cleaning the underside after firing is avoided.

In respect of alloys of silver, the combined effect of silver and copper oxides formed during heating is relatively small, but they can react with some transparent red, pink, orange and yellow enamels causing them to discolour. Although it is stated that silver oxide does decompose at firing temperatures, the presence of the enamel appears to restrict this decomposition with the result that even fine silver will affect the above colours, although to a much lesser degree. As a result, if tests show that a particular enamel discolours when laid and fired directly on silver or silver alloy, a prior flux coat for use on silver is needed that will absorb silver and copper oxides. It should then provide a suitable base for such enamels. Advances in formulation have enabled, for example, some makes of red transparent enamels to be laid direct without becoming discoloured. If possible, all other transparent coloured enamels should be laid direct on silver and its alloys because the flux layer can slightly affect the brilliance and transparency.

10. THE APPLICATION OF ENAMEL FLUX TO COPPER

The following observations major on the application of enamel flux to copper, as it is an essential procedure for producing a clear reflective layer for subsequently laying transparent coloured enamels. It is important to use a flux specified for copper as it will have been formulated to absorb copper oxide. Section 10.3 contains information on a suitable firing temperature and time to ensure the copper oxide is fully absorbed. Some fluxes are more sensitive to firing time and temperature than others. Finishing fluxes are unsuitable since they will soften and flow before an overlaid enamel becomes molten, with the result that the latter can sink into the flux

thus creating a patchy effect. There are a number of copper fluxes on the market and it is sensible to select one that the user finds works consistently well.

10.1. THE IMPORTANCE OF GRAIN SIZE

The percentage of coarse, medium and very fine grains in purchased fluxes can vary quite a lot - see Section 5. Although the use of the word grains might imply spherical or oval shaped particles, they are more polyhedral in shape. Maybe a few more of such particles will be trapped in a given sieve size or might fall through it, than spherical grains, but it seems reasonable to classify them as if they are spherical.

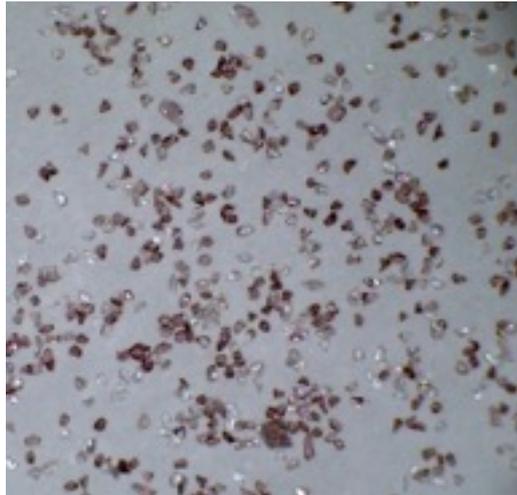


Figure 3. Enamel Grains

Grinding enamel in a pestle and mortar as already described will reduce the size of all grains. It is variously stated that the ideal is to grind enamel flux to the consistency of very fine sand. Although somewhat imprecise, one may conclude that the ground particles will lie in the size range of $125\mu\text{m}$ to $65\mu\text{m}$, (see Appendix 2). The fines which were present in the mix before grinding, and are swilled away, are probably less than 20 to $30\mu\text{m}$. If grinding dry using the screen separation method, the 325 mesh sieve will eliminate particles smaller than $44\mu\text{m}$ and an 80 mesh sieve on top will exclude particles larger than $177\mu\text{m}$.

An overabundance of coarse grains in the flux ($125\mu\text{m}$ and greater) will take them longer in time to fire to maturity than finer grains, meaning that more copper oxide is produced before the enamel fuses to seal off the surface. Coarse grains laid on copper are also prone to pits forming, and they can have large bubbles trapped, (typically 0.15 mm diameter). Large bubbles impart a grainy look to the fired enamel. Figure 4 is a microscope view of a fired enamel that contained a significant number of coarse grains, (80/250). The diameter of view is 1mm and there is a bubble of about 0.1 mm near the bottom and others of smaller size distributed over the area of view.

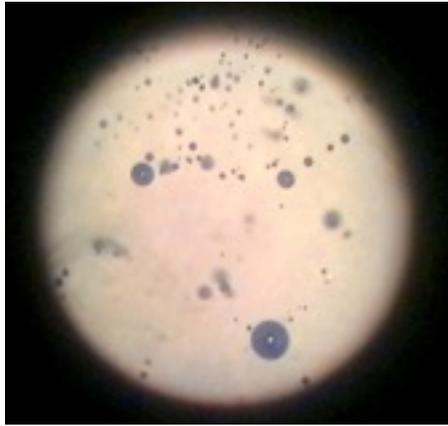


Figure 4. 80/250 Enamel Showing Trapped Bubbles

In contrast, a medium and fine grain mix of particles will pack closer together, reducing the tendency to form pits, they mature quicker thus sealing off the copper against further oxidation, and any trapped bubbles will, in general, be less than 0.05mm. On the other hand, there can be more of these small trapped bubbles than with coarse grains and, if excessive in number, they can cause the fired enamel to appear cloudy. However, if the enamel is laid thinly, the number of trapped bubbles will reduce and they have the potential to migrate through the melt if the enamel/metal combination is fired at a reasonably high temperature.

As a result, a mix of medium and fine grains is most suitable for laying the flux, and this, using screen separation, is 150/325. The particles are in the size range of 100 μ m to 44 μ m and corresponds well with the very fine sand consistency advocated when wet grinding. The major disadvantages of using coarse grains for enamel flux can be summarised as follows:-

- ★ Takes longer to achieve maturity and hence has to absorb more surface oxide
- ★ The more porous structure also allows more surface oxide to form and pits can develop
- ★ Large bubble entrapment can impart a grainy look unless fired at low temperature for a longer time
- ★ When dry sieving, grains can bounce off the surface
- ★ Grains can slide off non-horizontal surfaces unless a holding gum is used
- ★ The compressive strength of a high fired layer of coarse grains is likely to be less than that of a fine grain layer due to the larger occlusions

Grinding enamel under water is the most common method and beginners may be uncertain whether they have produced particles in the desirable size range as suggested above. As a one off experiment, they could grind some enamel flux under water, dry it thoroughly, and pour it into a 150 grade sieve over a 325 sieve.

After shaking for a minute, if there is an excess of grains lying on top of the 150 sieve it would indicate the grinding was insufficient. Equally if most grains pass through the 325 sieve, the enamel was over ground. The experience gained should enable the inexperienced to wet grind enamel flux to a good consistency.

10.2. THE THICKNESS OF APPLIED ENAMEL FLUX

Applying the enamel to the metal surface can be by wet laying or using dry enamel in a sieve. The latter method is advantageous for covering large areas, but is impracticable for recesses such as cells created by etching or engraving.

If sieving is employed, the dry ground enamel should be placed in a 100 mesh sieve. The sieve is held a short distance over the metal and lightly tapped to release the grains. A coarser sieve than this does not allow much control over the release. A thin uniform covering is needed, paying particular attention to covering the metal edges. On curved surfaces, such as steep-sided bowls, it is common practice to apply a thin spray of holding agent, (gum), to the copper to hold the enamel in place. When using the fine mix of particles advocated in this document, the need for this is less than if coarser particles are used. In any event, the gum should be used sparingly as it can reduce the transparency of the fired enamel.

When wet laying, the moist enamel, scooped from the mortar, is normally placed in a small porcelain container. A favoured method of applying the enamel to the surface is using a goose quill. Alternatively a plastic drinking straw, with the end sliced off at 45 degrees, is effective. Others use a fine paint brush or even a small palette knife. The enamel flux should not be so wet that it runs when applied, or so dry that it tends to form in lumps. Although frowned on by purists, a wetting agent can assist the enamel grains to flow and form a uniform layer. Adding just one drop of a washing up liquid, (one with minimal additives), to 50 ml of purified water will provide a liquid with low surface tension that can then be used both as the final enamel wash and when wet laying. It has been stated that wet laying will result in a closer packing of grains than that obtained by dry sifting. Hence, there will be fewer trapped air bubbles. To take advantage of this, the metal is gently tapped at intervals when wet laying. The grains will settle and this is evidenced by water being displaced from the mix of grains and rising to the surface. This excess water can be removed by a paper tissue just touching an edge. Tapping when grains are dry will simply displace the grains laterally and will upset a uniformly applied layer. Hence when wet laying, ensure all the grains are still moist before tapping.

If, by wet laying or dry sieving, too much enamel flux has been applied, an excessive number of small bubbles will be trapped in the melt. The fired enamel then looks milky. This is illustrated in Figure 5 which shows a 50mm by 25mm copper strip, dry sieved using 150/325 enamel flux. It was fired at the correct temperature and time, (see Section 10.3).



Figure 5. A Thick Application of Enamel Flux

On the other hand, if the application is too thin, pits may appear and over saturation by the absorbed copper oxide will result in a green colouration, (see Figure 6). The edges can be particularly affected as there is more access for oxygen, and black cupric oxide will form. These edges are then commonly referred to as being burnt.

Unfortunately, although pits may be repaired, any green cast and milkiness remains

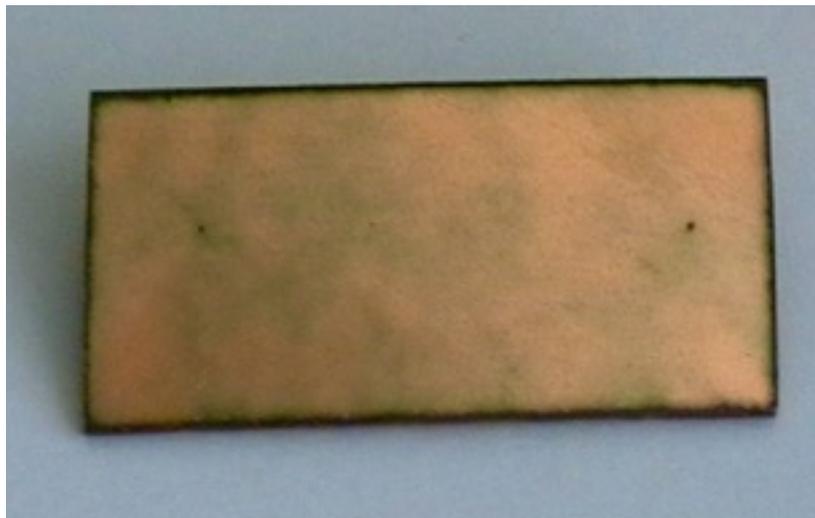


Figure 6. A Thin Application of Enamel Flux

and are more difficult to remedy. Grinding back or starting again may be the best option. Experience in laying enamel to a thickness that is neither too thick or thin is the answer. Appendix 6 contains more suggestions and information that may assist the beginner. Very narrow cells wet laid with enamel can become suffused with copper oxide discolouration. This is because the vertical exposed copper edges of the cell dominate the rest of the surface. Hence, it is best to avoid narrow cells when designing a copper piece for transparent enamels.

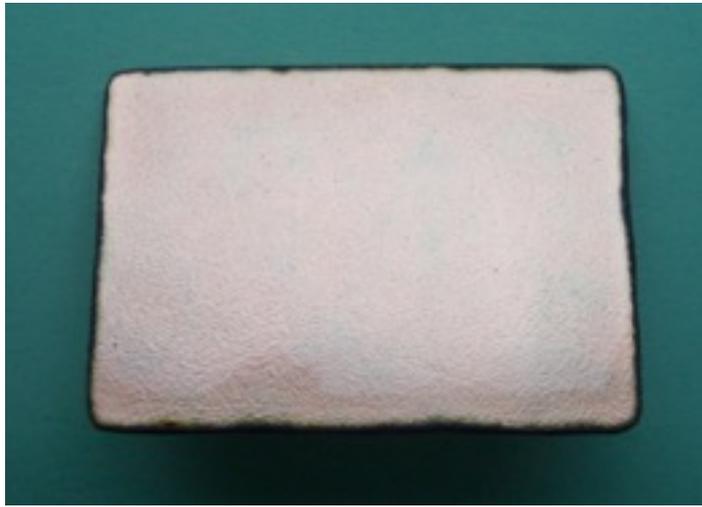


Figure 7. A Satisfactory Application of Enamel Flux

10.3. OPTIMUM FIRING TEMPERATURE AND TIME

Firstly a note about electric kilns for firing enamels. There are over thirty different models on the market in the UK that will run off a domestic supply socket. They range in internal size from around 11 x 13 x 7 (width by depth by height in cm) to around 30 x 30 x 30. The corresponding power consumed is from 700W to 3kW. All except the very smallest kilns can reach a temperature of 1000°C.

A beginner might not wish to spend too much on a first purchase and so a small, low-power kiln may suffice. However, it is desirable that there is some control over setting the kiln temperature and for the actual temperature to be displayed. Without temperature control the kiln will overheat unless the door is opened at intervals. Some idea of kiln temperature can be gained by observing the colour inside the kiln - cherry red corresponds roughly to 750°C, orange red to 850°C and yellow/white to 950°C and above. It is not a good idea to repeatedly peer into a high temperature kiln as the infra red radiation will damage the eyes. The use of protective goggles is recommended. However, it is better if the kiln temperature is displayed on a meter. The operator will then know when the kiln is up to temperature and also when it has recovered to the set value after firing an enamelled piece. Placing a substantial metal piece in a small size kiln will cause a significant drop in temperature, which then slowly recovers to the set value. Hence, if possible, purchase a kiln that has sufficient size and power to cope with the objects that will be enamelled most frequently.

Although many workers suggest setting a kiln to operate just slightly above 750°C when firing flux for copper and then extending the firing time to 3 - 5 minutes, a higher temperature is much more effective in enabling the flux to fully absorb the copper oxide. Indeed, for best results, most fluxes for application to bare copper will need to reach a temperature of at least 870°C and preferably up to 950°C. Although some fluxes will clear at slightly lower temperatures than this, a high firing temperature is the best guarantee that the copper oxide will be fully absorbed. It is actually desirable to operate the kiln at a high temperature (say around 950°C to

1000°C) so that the enamel flux reaches its molten state in the shortest time, thus sealing the metal surface as quickly as possible. This minimises the amount of copper oxide to be absorbed. As already mentioned, the advantage of using flux that has a preponderance of fine grains is that they will coalesce more rapidly than coarse grains.

To provide more experimental confirmation, some 50mm by 25mm copper strips were prepared, and a layer of 150/325 hard enamel flux was sieved on each sample. Each individual strip was then fired in the kiln for a set length of time at a recorded kiln temperature. Figure 8 shows the samples laid out on a card graduated with a vertical axis of kiln temperature (750°C to 950°C) and horizontal axis of firing time 0 to 6 minutes. (The photograph reproduced here is for illustration only as it does not show the colours clearly, nor the surface finish).

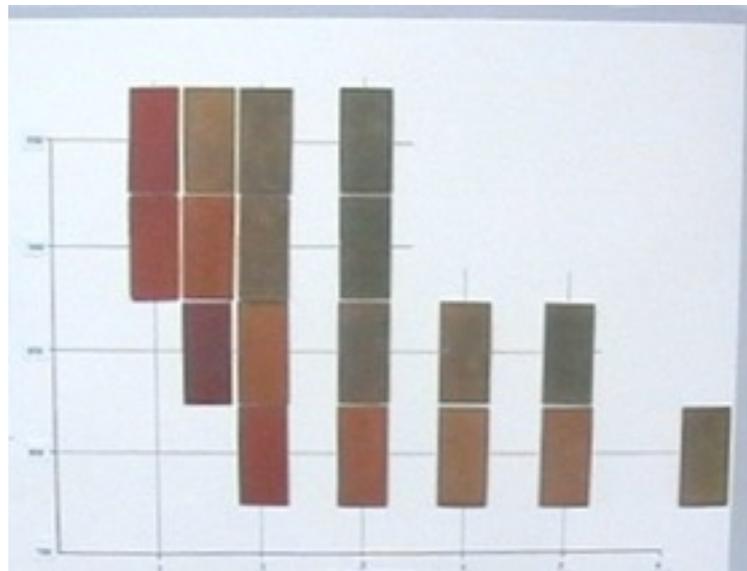


Figure 8. Test Samples After Firing

Visual examination showed that at firing times below about one minute, regardless of temperature, the enamel flux was only partly fused and was sugary in appearance. This is because, at these short firing times, the test samples have nowhere reached the kiln temperature. Then, between about one minute and extending to several minutes, the enamel exhibited one of three characteristics as illustrated in Figure 9 overleaf.

This diagrammatic figure was constructed by examining the colour changes in Figure 8. In the area to the left of the red line, little or no fusion or bonding takes place. 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 forms presumably because the enamel powder restricts the amount of oxygen access to the metal surface. It is only partially absorbed or dissolved in the enamel flux and

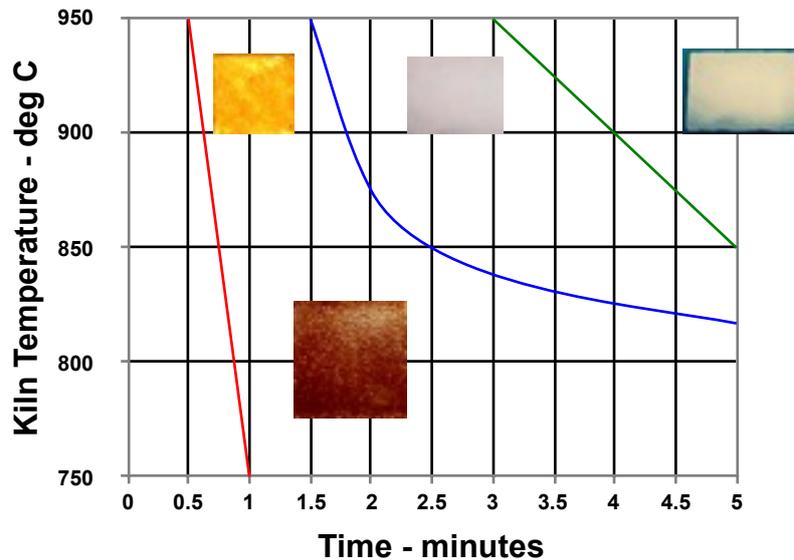


Figure 9. Typical Characteristic of Enamel Flux on Copper

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. 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 particular copper flux that was used in this series of tests, when firing at 950°C, the enamel was clear after about 90 seconds but there was a green cast after about 3 minutes. At 850°C, the firing time to clear was around 2.5 minutes and the green cast at around 5 minutes.

As regards the time a sample is in the kiln, withdrawing it briefly to examine its condition is the normal method of judging completeness of firing. The above evidence suggests that there is little point in examining a fluxed copper piece until it has been in the kiln for at least 1½ minutes. These observations are a simplification as very thin pieces of copper may mature somewhat quicker, and thicker pieces may require more time in the kiln. In addition, a rough copper surface will have an actual surface area larger than a smooth one of the same nominal area. This means more copper oxide, and hence a longer firing time is needed for the flux to absorb it. As mentioned, it is inadvisable to keep peering into a hot kiln to check on completeness of firing due to the significant infra red radiation affecting the eyes. It is much better to quickly withdraw the sample from the kiln after say 1½ minutes and to return it if the surface is not glowing white.

When a piece is removed from the kiln, be it copper or silver, it is good practice to cool it slowly, as rapid cooling will encourage cracking. One method is to sit the metal on its support on top of the kiln and to place a foil tent over the piece. This will protect it against foreign particles and also slow the rate of cooling significantly. After a few minutes the piece with its foil tent can be set down on a heat resistant surface to complete the cooling.

10.4. A SECOND LAYER OF ENAMEL FLUX

From the observations in section 10.3, it is evident that firing temperature and time are quite critical factors in achieving a bright, clear, fluxed surface, free from imperfections. Applying a second layer of flux offers the opportunity of a bit more flexibility in these factors of time and temperature. This is to lay the first coat of flux and to fire it for a slightly shorter time with the kiln still set at around 1000°C. This should avoid the development of a green cast and over-saturation of edges, and bubble formation should be low due to the thin layer and relatively high temperature. The piece after firing may have a slight brown appearance due to incomplete absorption of the oxide. At this stage, if enamelling a large surface area, there is some advantage in lightly abrading this first fired layer to improve layer adhesion and to remove any slight excrescences. There will, if sifting the enamel dry, also be less tendency for the grains to bounce and move around if the surface has been lightly abraded. This can be achieved using silicon carbide wet and dry paper or a diamond pad, both grade 1000, and both being used under water. Large imperfections should be ground out and refilled, and if any edges of the piece are black they can be abraded to remove the copper oxide so formed.

A second coat is then applied and fired for a similar or slightly longer period of time (up to 2 minutes) to allow the first coat to completely absorb the oxide. The finished surface should then be bright and clear. The contribution of this second layer in achieving consistently good results is open to debate. It may simply act as a protection against further possible ingress of oxygen through to the first layer. If the first coat of enamel flux is fired too long and a green cast does develop, adding this second layer might not then significantly dissolve out the green colour. If indeed the case, this is because the second layer probably does not significantly interact chemically with the first layer but is somewhat separate and distinct. Nevertheless, two thin layers of enamel flux will be superior to one thick layer in respect of milkiness and freedom from possible cracks. Typically a single layer of flux when fired is 0.1mm in thickness. So, when preparing copper for laying in cells, allow for 0.2mm depth to be occupied by two flux layers. Also, when wet laying in cells, apply a little more at the cell boundaries as the enamel tends to pull to the centre when fusing. Appendix 7 contains a summary of the factors and procedures for achieving a bright, clear surface prior to the application of transparent enamel colours to a copper piece.

Inevitably, there will be occasions when a fluxed sample has one or more pits that disfigure an otherwise satisfactory layer of transparent flux. Various workers have

stated how important it is to really open up the pits (eg using a diamond burr) to produce shallow-sided depressions. This enables one to fill them with enamel flux and to re-fire. If this is not done, the enamel grains can sit over the pits and trap air. The result shown in Figure 10 below is a milky spot that is still visible as a defect.

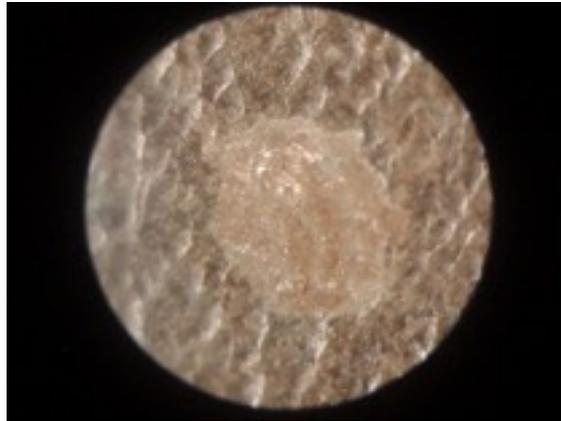


Figure 10. Magnified View of Pit Inadequately Repaired, (1mm Field of View)

11. ENAMEL FLUX FOR SILVER AND SILVER ALLOYS

It should be emphasised that the need for a transparent flux on silver and its alloys is very much less than for copper and is restricted to those enamel colours that are affected by the minor oxidation products that form when the metal/enamel combination is fired in a kiln. The preparation of silver alloys, e.g. by using the nitric acid treatment (see Section 6.2) is important in ensuring there is no sub-surface oxidation prior to the application of enamel.

As already mentioned, it is some transparent red, pink, orange and yellow colours that are normally fired over a flux specified for silver, while other transparent enamels can be laid directly on the silver/silver alloy surface. The grain size of the flux should be the same as for copper. The thickness of application can be a little less, as the nature and extent of oxide formation has far less influence on the clarity of transparent enamels. Increasingly, there are some newer red enamels formulated so they can be laid direct on silver and its alloys without discolouration.

The discolouration of sensitive enamels when fired direct may be due to impurities in the metal, or more likely a reaction with oxides. Since pure silver can also cause discolouration of some fluxes and some reds, pinks, oranges and yellows, it is likely that silver oxide does contribute to such discolouration. This oxide forms at temperature and it is presumed that it does not totally dissociate when under a layer of enamel. So when such fluxes are fired over pure silver, a slight yellow tinge may be apparent particularly at exposed edges. Sterling and britannia silver alloys contain a small amount of copper and oxidation of these alloys at temperature can cause an additional discolouration.

It is fortunate that the oxidation products associated with pure silver and especially sterling silver can be fully absorbed by an enamel flux without having to fire at the high temperature needed for a copper piece. Indeed care should be taken not to over-fire transparent fluxes on silver. As discussed in Appendix 1, sterling silver should not exceed 800°C in temperature and britannia silver 870°C. Many authorities recommend limiting sterling silver to 750°C to be sure that the silver/copper eutectic remains stable.

Silver fluxes are less hard firing than those for copper which is also advantageous bearing in mind the above temperature limitation. In addition, silver items will heat up more quickly than copper due largely to the lower specific heat of silver compared to copper. An approximate calculation suggest that for the same thickness of metal, silver will reach its optimum temperature in 75% of the time that it would take copper to reach the same temperature. The consequence is that if the enamelling kiln is set to the above relatively low temperatures, the firing time for a silver flux to mature on a silver base will be around 1¹/₂ minutes. Even so this relatively long time can result in the enamel flux developing the yellow tinge just described and particularly so at exposed edges. If a second thin coat of flux is then applied and fired for the same length of time and temperature, the yellowness does reduce significantly or disappear. This might suggest that the second coat does play a part in the chemical adsorption, but again it may just be restricting the ingress of oxygen to the surface of the metal.

Beginners may be advised to adhere to this low temperature firing to ensure the silver alloys never reach the solidus temperature. However, a high rate of firing technique has advantage, and this method of approach is further developed and described in the next section. It is helpful, when using a coloured transparent enamel on silver or silver alloy for the first time, to make a test sample with and without a prior layer of flux in order to see if the flux layer is necessary for improving clarity and colour.

12. USING AND APPLYING THE TRANSPARENT COLOURS

The starting point is the laying of coloured transparent enamels on an already fluxed surface, or on a bare silver/silver alloy surface if a flux layer is not needed. Much of what has been described in respect of preparing the enamels and then laying them thinly so that bubble entrapment is minimised can be applied to the laying and firing of the transparent colours. Applying a thick layer also has the potential for cracks to develop in the enamel. Hence colour intensity is built up by laying and firing several thin layers. As in the case of applying a second layer of flux, it can be advantageous to abrade large areas of fired enamel to ensure uniformity in texture. It will also improve the adhesion of a subsequent applied enamel layer. Where possible, when applying a layer containing different colours, it is best if they are from the same firing groups. They will mature at roughly the same time and no one colour will be under or over fired. If, for example, it is desired to use an enamel that is much softer than all the other colours in a layer of coloured

enamels, it could prove beneficial to lay it at a later stage to avoid it being over fired.

12.1. APPLICATION TO COPPER

At first sight there is potentially more freedom of choice when laying transparent colours over a fluxed copper surface as regards the size of the grains and the firing temperature and time. This is because, with a firm, clear base of hard enamel flux now established, there is no obvious necessity to use fine grains and to fire them high and long, as there is now no copper oxide to contend with. There is one situation where copper oxide can still be a problem and that is when laying enamels in narrow recesses. The base of a recess is covered in flux but the sides may be only partially so. If the recess is narrow, a transparent enamel laid in it may become saturated with copper oxide and discolour. The answer, as already mentioned in Section 10.2, is to avoid narrow recesses as much as possible but if unavoidable to use an enamel colour that is less susceptible to discolouration and to use fine grains. In the ultimate, a final high temperature fire may be needed.

Thus, some of the disadvantages of using a coarser mix of grains for enamel flux on copper outlined earlier are not so relevant when wet overlaying transparent colours. They are still disadvantageous if applied dry by sieving because of bouncing off the surface. However, a somewhat coarser mix of grains, when fired, will have a greater colour intensity than medium and fine grains for the same applied volume. Thus, fine grains will be much weaker in colour, which is not necessarily a disadvantage, but more layers will need to be applied and then fired if an intense colour is desired. Many workers use fine grains to produce delicate colour gradations that are not possible if coarser grains are used.

It is surmised that the reason why the finer grains produce a less intense colour when fired is that, when enamel grains fuse under the action of heat, they coalesce to a large degree, but boundary lines remain and some bubbles will be trapped in the melt. This can be observed under a microscope. Both these factors cause some of the light to be reflected, not through the coloured glass, but from the boundaries between grains and through bubbles that have no colour. Fine grains have far more boundaries than coarse grains and the number of bubbles can be much greater, albeit smaller in size. Hence the observed weaker colour. So a coarser mix of grains can produce the most vivid colours and fine grains will enable delicate shades of colour to be produced. Such a slightly coarser mix of grains than that hitherto used by fine grinding/ screen separation could be used if a more intense colour is needed. Some tests have shown that a 100/200 mix of grains is effective, provided the layer is not so thick as to trap the larger sized bubbles. However, when blending colours it may be preferable to continue to use the finer mix of 150/325 grains for best shading and for avoiding a salt and pepper effect. Blending colours is also most effective when the wet laying technique is used and it can be advantageous if the enamels are laid a little wetter to achieve a smooth gradation from one colour to another.

In the interest of minimising the size and number of trapped bubbles, particularly if wishing to use a coarser mix of enamels for intense colour, some tests have been made to see if it is possible to increase the packing density of grains by mixing fine grains with rather coarse grains, This has been investigated in Appendix 8 where it is concluded that this is not practical and not effective in reducing bubbles.

12.2. APPLICATION TO SILVER

The main difference between laying transparent enamels on silver and its alloys as opposed to copper is that, apart from some red, pink, orange and yellow transparent colours, the remainder can be laid direct without a prior coat of flux. Using a rather coarser mix of grains for colour intensity is not so attractive when applied to silver alloy and particularly sterling silver, since the coarse grains take longer to reach maturity and the firing time might need to be extended as a consequence. Although this can be accommodated when using a kiln set to 800°C or lower, the strategy proposed in the next sub-section is most favourable when the finer mix (150/325) is used.

12.3. FIRING RATE FOR TRANSPARENT ENAMELS

At this point it may be helpful to clarify what is meant by low firing and high firing of enamels. Particularly in the case of silver alloys, it is clear that the metal should not exceed the temperature at which it becomes unstable. Hence many workers will set the enamelling kiln to run no hotter than 800°C for sterling silver, although britannia silver can be allowed to go to 870°C. This is a low firing strategy and depending on the thickness of the metal, the hardness and average grain size of the enamel, the firing time to maturity of the enamel could be approaching 1½ minutes, see Figure 11.

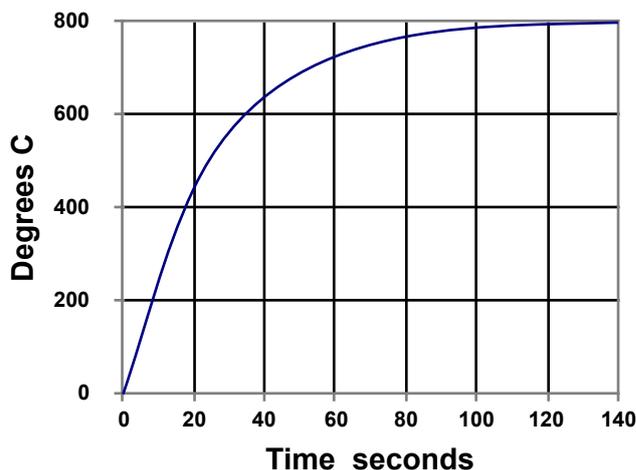


Figure 11. Heating Curve of 0.9mm Thick Silver, Kiln Temperature 800°C

This shows the rise in temperature of a silver piece with time when the kiln temperature is set at 800°C. It should be noted that apart from the variables mentioned above, the size and bulk of the supporting trivet or mesh will also affect the heating time of the piece. As a result, this graph is no more than a rough guide to the heating of this particular silver strip. Also, throughout this discussion, it is

inferred that the rise in temperature of enamel grains follows that of the metal underneath. Some tests using the fine grain mix and observing the stages of coalescing of the grains, developing orange peel and then gloss, support this assumption. It is conceivable, however, that much coarser, hard firing grains could lag behind the above curve thus extending the time to reach maturity.

Since most enamels, ground finely, produce a smooth gloss finish at around 750°C, the graph shows it will take nearly 80 seconds to achieve that temperature, at which point the sample could be withdrawn from the kiln. Copper has a thermal conductivity some 7% lower than silver which means it will heat up a little slower and in the present example it might reach 750°C in around 100 seconds. Because the kiln is set at 800°C, there is no danger of a silver alloy reaching an unstable condition even if it remains in the kiln for a longer time than necessary to fuse the enamel. In this example, the coloured transparent enamel, be it laid on a fluxed copper or a silver base, will have been in the kiln for around 80 to 100 seconds for the enamel to reach the gloss state. When laying and firing several layers, the first layer can be fired to orange peel and subsequent layers to gloss. This is quite an effective strategy since, by withdrawing the first firing of a transparent coloured enamel from the kiln when at the orange peel state and noting the time, it provides information on the subsequent firing times for achieving gloss. Now, we consider the effect of setting the kiln to a much higher temperature of 1000°C and again plot the heating curve for the same silver strip.

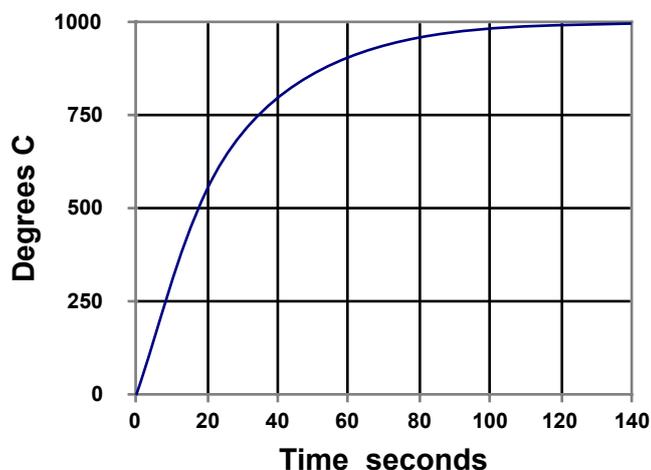


Figure 12. Heating Curve of 0.9mm Thick Silver, Kiln Temperature 1000°C

This graph shows that it will take just under 40 seconds to achieve 750°C at which point the sample should be withdrawn from the kiln to avoid a sterling silver alloy exceeding 800°C and becoming unstable. A copper sample will take a little longer but, in this case, it could be allowed to remain in the kiln somewhat longer because there is no eutectic to cause instability. However, the edges of an enamelled copper piece can blacken and some coloured enamels could start to deteriorate. The above strategy is what is referred to as a high firing rate and is not to be confused with what may be termed high firing where a copper piece is deliberately placed in a very hot kiln for several minutes. This extended firing, normally using opaque

enamels, can produce many interesting effects and it is needed when employing the technique of scrolling where the enamel must be very mobile to enable the scrolling tool to move easily through it.

Many workers consider that a high firing rate produces clearer and brighter colours than a low rate of firing, despite the disadvantage of having to be extra diligent about the timely withdrawing of items, particularly silver alloys, from a kiln operating at around 1000°C. Beginners should be re-assured that it does no harm to take a piece out of the kiln and to check if it has reached maturity. If not, then to put it back for a short time until the enamel is molten. Alternatively, if wearing approved kiln goggles, the object can be viewed in situ by quickly opening the kiln door. The next section reports on the results of some tests on transparent coloured enamels in which the two different firing strategies are compared.

13. SOME TEST RESULTS ON TRANSPARENT ENAMELS

The main thesis is that the transparent enamel coloured pigments, being metal oxides, can degrade in the presence of air and particularly when heated. It is surmised that there is a critical period where the enamel grains could start to degrade before they then fuse to be protected against further ingress of oxygen and hence further degradation. It follows that it should be advantageous to bring the enamel grains to a molten state in the shortest possible time. Figures 11 and 12 indicate that the high rate of firing produces molten enamel in about half the time of the low rate of firing. Some evidence that this shorter heating time does indeed produce superior results now follows. No doubt some makes and colours are more resistant to this degradation than others but the presumption is that bringing a transparent enamel to maturity in the shortest time and then withdrawing it from the kiln will yield the best results.

Considering firstly transparent enamels applied to a fluxed copper piece, Figure 13 shows the increase in temperature with time of a 1mm thick copper strip, (supported on a metal mesh), when placed in a kiln.

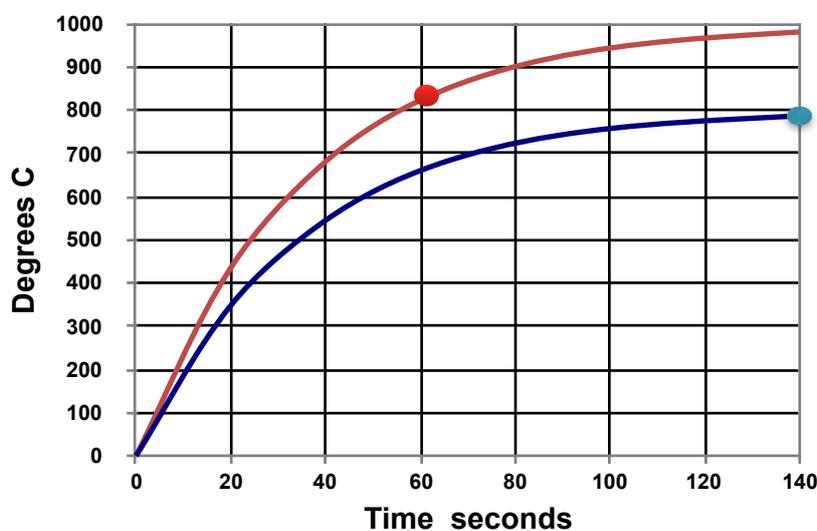


Figure 13. Heating Profile for 1mm Thick Copper Strip

The blue curve is with the kiln temperature at 800°C and the red curve is with the kiln at 1000°C. After about 120 seconds, the copper has nearly reached kiln temperature and is at a constant value at 140 seconds. The red curve represents the situation when firing the first layer of an enamel flux on copper which requires the piece to be fired high and fairly long and this corresponds to a firing time of 90 to 120 seconds for a 1mm thick copper piece. For the subsequent firing of transparent colours, this copper sample can be withdrawn from the kiln after no more than 60 seconds firing time, (at the point marked with a red blob). It is assumed that the applied enamel is made up of a mix of reasonably fine grains and not very coarse grains as the latter will take longer to mature if fired at the high rate. In addition large bubbles may be trapped in a coarse grain layer. Alternatively, with the kiln temperature at 800°C, the piece would only be removed from the kiln after some 120 to 140 seconds, (see the blue blob).

Figure 14 shows a test sample with one make of red, yellow, green and blue transparent leaded enamels having been fired over a flux base. As regards the grain size, a useful approach was to use the medium mix of grain sizes, 100/200, to check that they come to maturity in a reasonably short time and are not impaired by trapped bubbles. The upper colours, red, yellow, green and blue were fired for 50



Figure 14. Transparent Enamels on Fluxed Copper

seconds with the kiln at 940°C. This temperature was near the maximum achievable with this particular kiln. Three thin layers were wet laid, firing between each application and the sections were examined after each firing. The same colours were then applied in the same way to the lower half and fired for 120 seconds with the kiln at 800°C. Thus the upper colours had been subjected to these three further firings, albeit at this lower temperature. Their visual appearance, however, was unchanged. It was evident, from a close visual examination, that brighter colours were obtained when firing at a high rate. Lower rate firing produced more subdued, pastel shades of colour. There were no visible defects in any of the segments. When examined under a microscope, a few bubbles were evident on all sectors but of small size, 0.03mm and less. However, there were imperfections

showing in the low fire rate colours and there were black bits, albeit small in size. Figures 15 and 16 below are microscope photographs taken of the two yellow sectors, the field of view being 1mm.

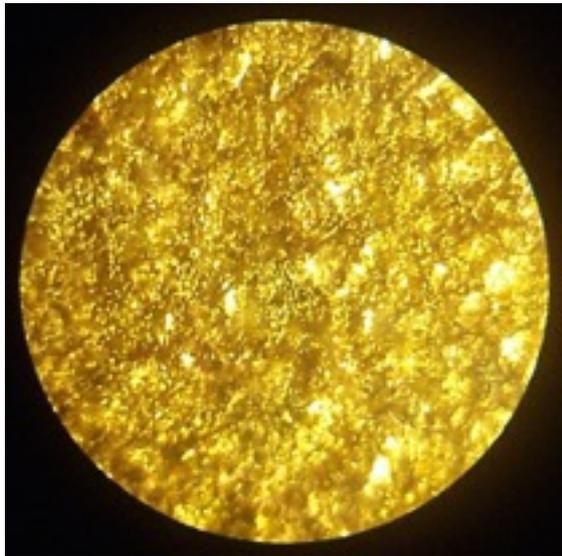


Figure 15. High Firing Rate

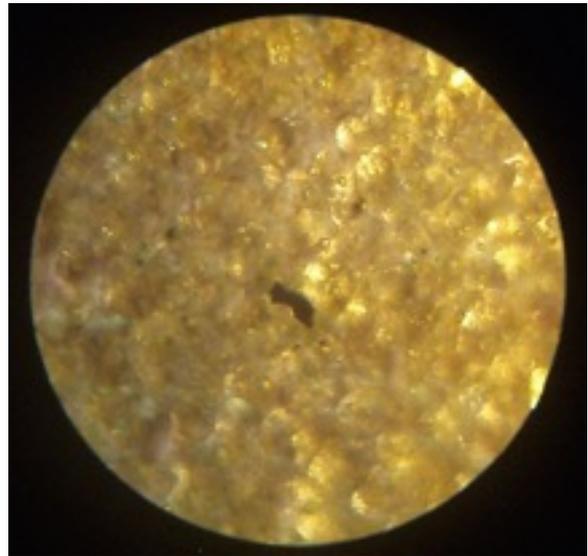


Figure 16. Low Firing Rate

The presence of black bits, seen in the centre of Figure 16, and the generally muddy appearance indicates some deterioration has taken place when this leaded enamel was fired low and long. Of course these observations are specific to the enamels tested and the grain mix. However, other workers have supported this limited evidence in concluding that firing transparent colours in a kiln at around 1000°C and withdrawing them as soon as they mature will produce good bright colours. Sometimes, despite following best practice, a transparent enamel, when fired, can show evidence of deterioration not associated with trapped air bubbles. This underlines the wisdom of making a test strip of any enamel intended for use but not tested previously. In Figure 17 below, is an example of a small opaque particle in an otherwise satisfactory green transparent enamel. Where there are many such particles, they can appear as visible blemishes. Now to consider the



Figure 17. Magnified View of Imperfection in a Green Transparent Enamel

firing of silver alloys using the high firing rate. Clearly, the solidus temperature

limitation means a silver alloy piece must be watched closely while it is in the kiln and then quickly removed before the onset of instability. For example, a small sterling silver item with its support, placed in a kiln at 950°C, took 47 seconds to reach 790°C. If this piece had been left in the kiln for a further 10 seconds, it would then have reached 850°C. There is more latitude in time with the high rate firing of britannia silver and this combined with its lower copper content is advantageous. The low firing rate test on britannia silver reported on in Appendix 3 (see the lower image in Figure A.2) shows a reasonable green transparent but the red transparent has yellowing at the edges. A repeat of this test but with the kiln at 940°C and a firing time of 40 seconds yielded a much clearer and brighter green, and the red transparent had no yellowing at the edges. A further sample using sterling silver fired at the high rate showed that the green and flux were not quite so true, but the differences were slight and only observable under a bright light and close scrutiny. The table below summarises these latter results.

Sample	Kiln Temp. °C	Firing Time Sec.	Final Appearance of Enamels
Britannia Silver	760	105	Green is transparent, Flux is clear, Red on flux is red except at edges where it is yellow
Britannia Silver	940	40	Green is bright and transparent, Flux is clear, Red on flux is red with no yellowing at the edges
Sterling Silver	940	40	Green is not quite so bright and transparent, Flux is slightly less clear, Red on flux is red with no yellowing at the edges.

Some further transparent enamel tests on britannia silver using the high rate of firing are illustrated in Figure 18.



Figure 18. Transparent Coloured Enamels on Britannia Silver

The left hand half was laid direct with the transparent coloured enamel (150/325) and the right hand half was laid with an enamel flux for silver. After firing at 940°C for 40 seconds, a second coat of transparent coloured enamel was laid on both halves and fired. In these examples, it is evident that the transparent yellow enamel needed a flux undercoat.

Figure 19 shows the same colours plus a red enamel, laid on pure silver without a flux undercoat and fired at the high rate.



Figure 19. Transparent Enamels on Pure Silver

Undertaking sample tests such as those shown in Figure 18 is good practice when using a particular coloured enamel for the first time. In this way, a library of test results can be built up that will enable the selection of colours for a particular design. It will also identify those transparent colours that, for whatever reason, do not yield results that the user finds acceptable. It should also be noted that occasionally a manufacturer finds it necessary to alter the formulation of a particular enamel and this can affect its performance and colour, necessitating a new sample test.

14. FINISHING

Having fired the final layer of transparent enamel on a copper or silver piece, the surface, although bright, is invariably uneven. It can have dips and bumps and waves and to make it smooth the surface needs to be abraded. This can be accomplished by hand tools or by using motor powered discs. Beginners will probably be content to start with hand abrasers. The abrasives commonly used for this task are composed of silicon carbide, and more recently diamond. The former is the main constituent of wet and dry paper and carborundum stone. The diamond abrasives are available in thin strips with a velcro backing or as diamond hand pads in various grades of roughness. The main advantage of using diamond is that, being

nearly three times harder than silicon carbide, it lasts some forty times longer and produces less of its deposits on the material being abraded. However, it is more costly to purchase.

Most abrasives are available with different surface roughnesses, generally categorised as coarse, medium and fine, but they are also obtainable in a much wider range - see Appendix 9 for more information. There are three golden rules when abrading enamel. The first essential is to use a copious amount of water as a lubricant when abrading. Wet and dry carborundum papers and diamond pads can be used under water and mechanical abraders have a water supply constantly drip feeding onto the surfaces. This also assists in conveying away the products of the abrasion. Secondly, it is important not to start with too coarse an abrader as it can create holes and grooves in the enamel surface. Coarse abrasion will also create deep scratches in any surrounding metal that will need to be polished out at some stage. It is best to start with an abrader that corresponds to a grit size of no greater than 35um, (400 to 600 grit). The aim, at this stage, is to produce a smooth, matt surface. Where pits and other deficiencies do appear, they need to be ground out, re-filled and the piece re-fired. Use of a fine abrader should then render the surface smooth and ready for the next stage. The third rule is not to exert too great a pressure on the piece when abrading it, as there is a danger that the stress could cause the enamel to crack. If this occurs, the enamel will need to be re-fired and hopefully the crack will have sealed invisibly.

There are basically two ways of proceeding further to achieve a smooth glossy finish to the enamel. The first is to flash fire in a hot kiln (1000°C) so that the top surface flows just sufficiently to become glossy. Prior to this, it is important to thoroughly wash the abraded surface using a glass fibre brush, or to use an ultrasonic bath so that there are no loose or slightly embedded particles remaining after the final abrasion. The piece should be kept under water if firing is delayed and then dabbed with a cotton cloth to dry it. Cotton is preferred to paper tissue as the latter can leave fibres of cellulose on the surface. Firing times must be sufficiently short to just produce a glossy surface, and it is better to remove a sample from the kiln, say after thirty seconds, and to quickly examine it rather than to leave it in the kiln for a longer period of time before removal. If the piece has not glossed, it can be re-inserted in the kiln for a little longer. The disadvantage of anything longer than a flash fire is that the bulk enamel becomes more fluid and it can draw away from any metal edges that might contain enamel, with the result that the enamel surface becomes slightly convex - this is commonly referred to as "balling" and is the natural tendency for liquids to try and form into a shape of minimum surface area.

After flash firing, the metal edges of a piece such as Cloisonné or Champlevé might still be slightly proud of the enamel contained in the cells. If significantly so, it will be necessary to use a fine abrader to smooth the surface again and to re-fire. There are situations where enamels of markedly different hardness have been used side

by side on a piece. If so, it can prove impossible to flash fire successfully without the softer enamels “balling” before the harder enamels have glossed. Sometimes in this same situation a harder enamel might crack on heating and again it can only be healed at the expense of over-firing the softer enamels. The moral is to look at one’s choice of enamels and to select those with a closer firing range. However, a second method of approach can overcome the problem, albeit in a rather more tedious way.

This method is to continue with the abrasives in several stages by using progressively finer grits. So, if hand abrading with wet and dry papers or diamond pads, having started with 400 or 600 grit, then to continue with 800, 1000 up to 2500. There is no flash firing and the final result with the 2500 grit should produce a similar glossy finish. At each stage the piece should be thoroughly washed out and the aim is to remove the scratches produced by the preceding coarser grit. Best practice is to abrade in one direction and then to use the next finer abrader at right angles and so on. Mechanical aids will speed up the process. One benefit is that any surrounding metal will be free of oxide, or of firestain in the case of silver alloy.

Having deployed either of the two methods described, the traditional next step deployed by many workers is to use pumice grade 240 made into a slurry with water. For maximum effectiveness and speed this is applied using a motor driven felt mop running at slow speed. A substantial vessel containing the slurry is positioned below the mop to recharge the surface with the slurry and to catch the residues. The main action of the pumice is to remove marks and any oxide from exposed metal, residual scratches from the enamel and it will take down enamel to a level surface removing any bumps or minor depressions that are left after the last fire. Using the pumice slurry by hand with a felt pad is very tedious and messy and unlikely to produce a result as good as that obtained by mechanical means. There are other soft abrading/ polishing agents on the market which can be applied using smaller rotary felts or mops and the beginner may find these will achieve the same result as the pumice slurry.

APPENDIX 1. SAFE FIRING TEMPERATURE OF SILVER ALLOYS

That one should not heat pure silver or its alloys to melting temperature is obvious, but there is a further consideration that is particular to silver alloys containing copper.

In the cold annealed condition, both sterling and britannia silver contain a mix of two discrete constituents. Depending on the rate at which the alloys had been cooled, this mix is composed largely of silver crystals, with a copper-rich solid existing either at the grain boundaries or scattered more uniformly through the silver crystals. We now refer to the phase diagram for these two alloys.

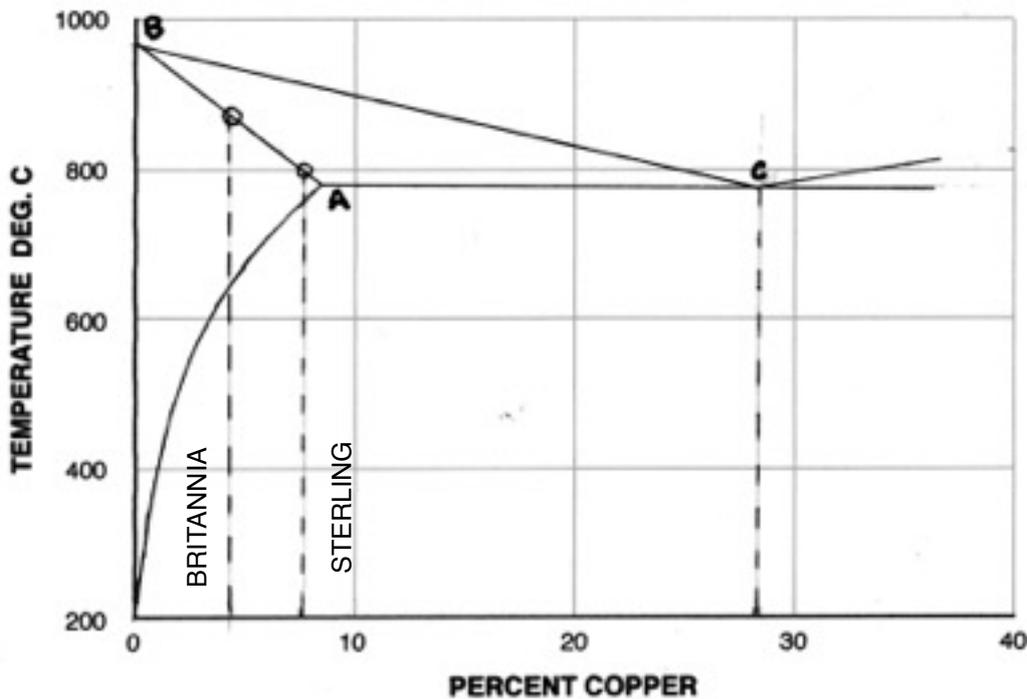


Figure A1. Phase Diagram for Silver /Copper Alloys

This is quite a complex picture of the phases that silver/copper alloys pass through when heated. For the present, we concentrate on conditions at the temperatures for firing enamel, i.e. around 800°C. In the diagram, the line AB forming part of the triangle ABC is called the solidus. As its name implies, below this line the silver alloys are solid and stable. So, tracing the dotted line for sterling silver, (7.5% copper), at a temperature just below 800°C, the alloy is indeed secure for enamelling. At this point all the copper rich crystal content has been completely absorbed within the solid mass of silver crystals. If the temperature is raised further so the dotted line is now inside the triangle ABC, a percentage of the silver now separates out of the solid and becomes molten with some of the copper. The higher

the temperature, the more of the silver becomes molten with copper. The triangle ABC is a realm of increasing mushiness and if the temperature is raised still further so the alloy is above the triangle area, it is then a fully liquid mix of silver and 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 line, are fully liquid at the melting point, and in between are in a transition or “mushy” state. It is interesting to note that an alloy containing 28% copper, (point C on the diagram), is called the eutectic composition because it passes from solid to liquid at the eutectic temperature of 780°C without any transition phase.

The region above the solidus line is clearly one of metallurgical change, and this explains why silver alloys should not be allowed to exceed the solidus temperature. So for sterling silver, a safe limit is shown by the small circle at 800°C. The corresponding safe value for britannia silver is again shown ringed at around 870°C. Thus, 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. The information derived from the phase diagram is shown in the table below.

Type	Melting Point °C	Solidus Point °C
Fine Silver	962	962
Britannia Silver	930	870
Sterling Silver	910	800

Table A1. Temperature Characteristic of Silver Alloys for Enamelling

APPENDIX 2. SIEVE SIZES

SIEVE SIZE	ENAMEL GRAIN SIZE - μm	FINE SAND	VERY FINE SAND
60	250		
80	177		
100	150		
120	125		
150	100		
200	74		
325	44		

APPENDIX 3. PREPARATION OF SILVER ALLOYS FOR ENAMELLING

Section 6.2 has outlined the use of concentrated nitric acid in preparing sterling and britannia silver alloys prior to the application of transparent enamels. This treatment is the removal of surface forming oxides following the application of heat. The heating is when soldering findings, and/or when annealing following work hardening. As will be seen below, the nitric acid also removes sub-surface oxides that form if silver alloys are heated in air. The metal, after this acid treatment, is that of the original alloy, i.e. it contains the crystalline mix of silver and copper. If the alloy has not been subjected to heat prior to enamelling, then the nitric acid treatment is not necessary.

There is a technique that is more widely used for removal of surface oxides and which is purported to create a surface layer of pure silver devoid of copper. The technique clearly merits examination and discussion. It uses cycles of heating and sodium bisulphate/sulphuric acid pickling.

At this point of the discussion, it should be pointed out that the metallurgy of silver alloys, when they are repeatedly heated to annealing temperature and then pickled, is a complex subject. The writer's own understanding is imperfect, despite trawling through the scientific literature. It is, therefore, left to the reader to decide if the following explanation best fits the results of subsequent experiments made by the writer in comparing the two methods of preparing silver alloy, prior to laying on enamels and then firing them in the kiln.

It is well known that the grey/slightly black surface colour that appears after a first heating at say a temperature of 600°C and up to 780°C is predominately a thin layer of copper oxide, CuO. Its extent is less with britannia silver than sterling due to the lower copper content of the former. By then pickling in hot, dilute sulphuric acid and washing, the grey/black deposit is dissolved and the surface appears a little whiter. The process is variously described as depletion silvering because the exposed copper at the surface has been depleted or partly so. The following table shows the relative solubility of the primary components of a silver copper alloy in two acids. In respect of removing oxides of copper, both acids are equally effective.

Metal/Oxide	Hot dilute sulphuric acid	Cold concentrated nitric acid
Cupric oxide CuO	32	25
Cuprous oxide Cu₂O	4	3
Copper	0	160
Silver	0	1

Now, the practice with the depletion method following the first cycle of heating and then pickling in hot, dilute sulphuric acid is to repeat the cycle, maybe three times,

although some workers suggest six or more times. The pickled surface is often lightly abraded when washing the surface prior to the next cycle of heating. The stated objective is based on the presumption that any copper still remaining at the surface is completely depleted by its conversion to copper oxide. The oxide is then dissolved in the pickle. The visual evidence that supports this is that the surface appears progressively whiter and matt with each heating and pickling cycle and it is thus reasonable to suppose that it has been depleted of copper to leave pure silver.

There is evidence, gleaned from a few scientific papers, that suggests this may not be an accurate explanation of the depletion process. Firstly, although the silver component at the heated surface forms little or no oxide, because it is unstable above around 200°C, such is the propensity for atmospheric oxygen to diffuse through it at high temperature that, below the surface, it is able to interact with the copper that is held in the silver crystal structure. Workers who have studied this internal oxidation conclude that the oxidation products are a complex combination of the two copper oxides. These oxides begin to form just under the surface during the first heating cycle, and grow with time at temperature.

The amount of this oxidation follows a parabolic law in which the oxide layers develop rapidly at first and slow subsequently. As an example, heating sterling silver for 3 minutes at 700°C, yields an oxide thickness of 6 μm which grows to 26 μm after twenty minutes at this temperature. Some workers call these oxides firestain and the initial surface copper oxidation as firescale. If the surface is lightly abraded after pickling, the grey/purplish stain of interior oxidation is revealed.

It is further stated that the silver on the surface following heating and pickling is not totally coherent and one scientific paper shows micrographs that seem to indicate there are a complex combination of oxide products on the surface that remain after pickling. Their porosity is such that they have the visual soft white surface appearance normally associated with silver. So this evidence suggests that the depletion silver technique is successful in clearing the grey/black copper oxide on the surface in the first heating/pickling cycle but not the more complex copper oxide combinations that form when the silver alloy is heated repeatedly.

That there might be some substance to this assertion that the resulting surface layer after heating is not pure silver is supported by some tests undertaken by the writer. Firstly a britannia silver sample 0.9mm thick and surface area 350 sq. mm was immersed in cold concentrated nitric acid. This silver alloy had been manufactured in an inert atmosphere to exclude the development of oxidation products. The sample turned a light straw colour and, after removal from the acid and washing in water, the surface was white.

Then, another britannia silver test sample was heated in air to 650°C for 90 seconds, pickled in hot sodium bisulphate to remove any surface oxides, washed and then dipped in the concentrated nitric acid. It immediately turned black but cleared quite quickly. To confirm that the oxidation is progressive with time and

temperature, this experiment was then repeated with two more samples. One was heated for 15 minutes at 700°C, and the other for two minutes at 800°C. Both turned black in the nitric acid and took many tens of seconds to clear with constant brushing with a feather.

This appears to indicate that, while both the heating/sulphuric acid pickle method and the nitric acid treatment dissolve any first formed surface layer of copper oxide, only the latter treatment will dispose of more complex oxidation products generated by repeated heating. From an enamelling point of view, one may ask do they react with and degrade enamel? One way to find out is to try both methods of surface preparation and to visually compare the results when the samples were enamelled.

So, two transparent enamels with markedly different characteristics were selected. One, a hard firing green that can be laid directly on silver alloy, and the other a medium firing red that required a flux undercoat. Firstly, some 35mm x10mm britannia silver test pieces, 0.9mm thick, were scribed into three equal sections. Samples 1- 5 were then prepared using the heat and pickle method, (650°C for 90 seconds), and pickling in hot sodium bisulphate. After each pickle, the surface was lightly abraded with a soft brass brush using plenty of water and detergent. Sample 5 was not abraded at any stage of the anneal and pickle process. The following table shows the number of anneals made for each sample.

Sample	1	2	3	4	5
No. of Anneals	3	3	10	10	10

Two other samples, 6 and 7, were prepared using the nitric acid treatment and abraded after the nitric acid dip. Sample 8 was also prepared in this way but it was left matt and not abraded.

The right hand end of all samples was then wet laid with the green enamel, and the remaining two thirds were laid with a flux specified for silver. After a 1¾ minute firing of two coats of green on this right hand third, and two coats of flux on the remainder, the red enamel was then wet laid on the left hand end and the sample fired again. A further coat of red was then laid on this third and fired. Thus, one could observe, all on one test piece, the performance of the green enamel and the flux on bare silver alloy, and the red enamel over the flux. The following table summarises the visual appearance of the eight samples.

Sample	Kiln Temp. °C	Final Appearance of Enamels
1	760	Green is slightly opaque, Flux is slightly yellow, Red on flux is reddish-brown
2	860	Green is slightly opaque, Flux is almost clear, Red on flux is reddish-brown
3	760	Green is slightly opaque, Flux is yellow-grey, Red on flux is brown
4	860	Green is rather opaque, Flux is dark brown, Red on flux is muddy brown
5	760	Green is very slightly opaque, Flux is slightly yellow, Red on flux is reddish-brown
6	760	Green is transparent, Flux is clear, Red on flux is red except at edges where it is yellow
7	860	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	760	Green is transparent, Flux is clear, Red on flux is red except at edges where it is yellow

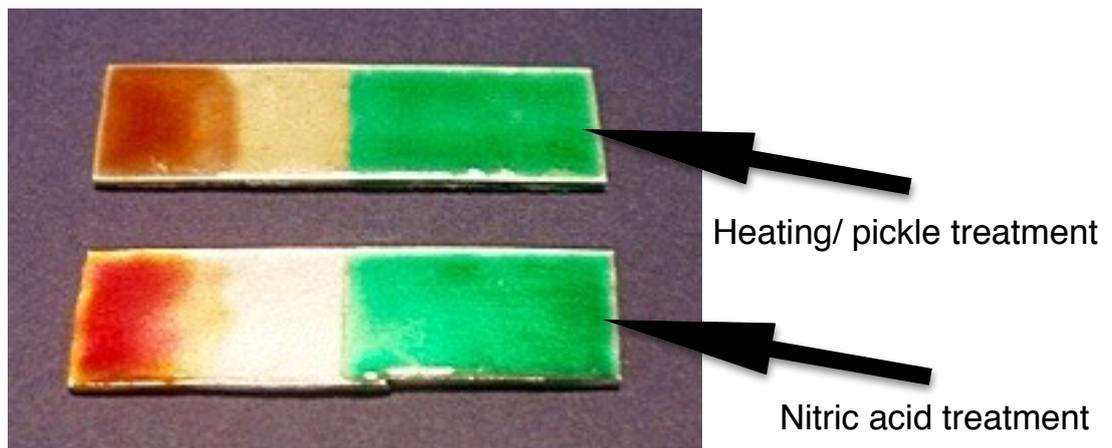


Figure A2. Visual Comparison

The following conclusions are drawn from the visual appearance of the enamels:-

1. 10 cycles of annealing and pickling produces inferior results compared to 3 cycles if samples are lightly abraded after each pickling treatment.
2. Even if light abrasion is avoided, results with multiple cycles of heating and pickling are inferior to those prepared by nitric acid dip.
3. Abrading a sample after treatment with nitric acid had no deleterious effect.

These conclusions suggest that heating a sample and pickling it does not produce a coherent silver surface, since the visual appearance of the transparent enamels is unsatisfactory. Even mild abrasion after pickling appears to influence the surface

conditions to a degree that causes repeated cycles to be increasingly disadvantageous. For these reasons, the writer favours the nitric acid treatment as the most effective method of secondary metal surface preparation for silver alloys.

Reference: Hall, Jon, A, High Temperature Oxidation of Sterling Silver (1981). <http://scholarworks.rit.edu/theses/1324/>

APPENDIX 4. BUBBLE ENTRAPMENT

A further example of surface preparation on copper is shown in Figure A3. The right hand half was abraded with carborundum cloth grade 600. The left half was burnished with a rotary steel burnisher. After dry sifting and firing two thin coats of copper flux, (150/325), there was a significant difference in the visual appearance of the two halves.



Figure A3. Rotary Burnisher v Emery Grade 600

This picture shows that the sample needed to be fired a little longer to completely absorb the copper oxide. This is very evident on the right half of the sample where the flux has not completely absorbed the greater volume of copper oxide produced by the rougher surface. Hence the darker appearance, in contrast to the almost clear burnished half. When examined closely, the carborundum abraded half had an overall milky appearance indicating the presence of a significant number of bubbles. Different firing times and temperature had little effect on the number and size of bubbles. Further tests were done with 240 grade carborundum paper and also 100 grade. These coarser grades showed some improvement in reducing the number and size of bubbles. Far more tests would need to be done to determine if indeed there is a critical surface roughness that produces more bubbles.

To consider this further, it is recognised that the abrasion of a surface creates peaks and troughs in which the heights and widths are determined by the grade or coarseness of the abrader. Of particular interest then is the milky effect observed with the 600 grade preparation. The abrasive particles are of order 0.026mm diameter,(26 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 these grains are laid on the 600 grade abraded surface, the grains in contact with the surface will sit across several surface peaks. It is conceivable that, as the grains soften and coalesce, air

is partially trapped in the troughs or furrows thus creating the milky effect. These air bubbles and those between grains might rise to the surface and escape depending on the thickness of the enamel layer and the time and temperature of firing.

Nevertheless, if the surface is less rough, the peaks and troughs are smaller and the air spaces are correspondingly less. Equally, the surface roughness produced by 100 grade carborundum is produced by particles of around 150 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 less trapped air to escape. Surface profiling as shown in quadrant D of Figure 1 (Section 7) produces troughs far greater still. All the above is hypothesis and there may be another explanation for the milky effect observed with the particular finish produced by 600 grit carborundum paper. If nothing else, these remarks reinforce the virtues of wet laying enamel grains. By gently tapping them they have a greater chance of packing into surface troughs than is achievable by dry sifting.

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

APPENDIX 5. MECHANICAL FORCES ON THE ENAMEL AND METAL

The topic of mechanical stresses on enamelled pieces and the possibility of cracks developing in the enamel, and/or bowing of the metal, is complex and subject to a number of variables. In this Appendix an attempt has been made to identify the major influences and hence how best to avoid undue stresses on both enamel and metal substrate. The use of a counter enamel on the reverse side of flat pieces to eliminate possible bowing is also discussed.

If a layer of enamel is laid on a flat piece of metal and the piece is then placed in a hot kiln, the enamel grains eventually become mobile and fuse to the metal surface. At this stage there are no mechanical stresses on the piece. It is important to note that a flat piece of annealed metal such as copper or pure silver is very soft and so it should be well supported in the kiln to stop it sagging when heated. This applies particularly to large, thin items of flat metal, and a wire mesh can provide a better overall support than stilts.

When such an assembly on its mesh support is then removed from the kiln, and starts to cool, the enamel initially contracts faster than the metal. On further cooling, below a critical temperature of around 450°C to 500°C, the enamel is becoming more rigid and, because its coefficient of thermal contraction is now significantly less than that of the metal, it is increasingly under compression. The metal is subject to a corresponding tensile force or stress. So, when fully cool, the thermal stresses on enamel and metal are a maximum.

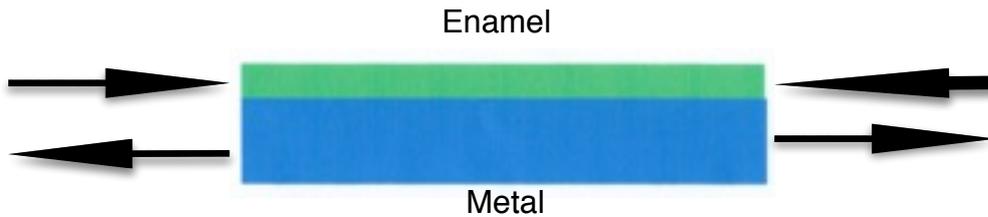


Figure A4. Thermal Stresses on Enamel and Metal

The arrows in the above picture show imaginary external forces applied to the enamel and metal that simulate what happens when two materials have different coefficients of thermal contraction and are therefore under mechanical stress.

Although the ideal situation, throughout cooling, would have been for both the enamel and metal to be stress free, this is not possible because of their different rates of expansion and contraction. Below the critical temperature, vitreous enamels contract less than metals such as copper and silver and so they will be in a state of compression when fully cool. However, one should note that this is not normally a problem, as properly prepared enamels have a compressive strength sufficient to withstand most thermal forces generated when such an assembly cools. If an enamel were to contract at a faster rate than the metal, (a coefficient of thermal contraction greater than that of metal), it would be subjected to a tensile force or stress. The tensile strength of vitreous enamel is some 15 to 20 times less than its strength in compression, and it is doubtful if one could enamel successfully without cracks and splits appearing if significant tensile forces were to exist. Cooling should be done slowly to ensure both enamel and metal cool at the same rate to avoid the possibility of localised, enhanced stresses developing sufficient for cracks to appear.

Having stated that enamels have a good resistance to the compressive force generated when a piece is cooled from a high temperature, it is evident that the strength is far less than solid glass due to the imperfections and bubbles that exist in a non-uniform solid. The compressive strength of typical vitreous enamels after firing has been measured to be between 500 and 800 MPa, (MN/m^2), although lower values have been recorded. Hence, if the compressive force in a particular set-up approaches 500 MPa, there is the danger that cracks might develop in the enamel. Very occasionally an enamel piece will develop cracks after some long time, and it is supposed it had been near the limit of maximum acceptable compressive stress and finally failure occurred. In this situation, it has been found that atmospheric moisture plays a prominent role in the time- dependent weakening of glass. It should also be noted that, in practice, many geometries are more complex than flat sheets and enhanced stressing could occur at edges sufficient to cause localised chipping or cracking.

Throughout this discussion it is assumed that the enamel is sufficiently bonded to the metal so that it can withstand the shearing force generated at the interface due to the opposing forces shown in Figure A4. In the majority of situations when using transparent enamels on copper and silver, the adhesion of enamel to metal is more than adequate. An example of what could happen in an extreme case is illustrated below.



Figure A5. Unsatisfactory Bonding of Enamel to Metal

Here the metal substrate was gilding metal and the enamel was fairly hard. As a result the difference in coefficients of thermal contraction was quite high. In addition the metal surface was very smooth. Much like friction effects, the smooth surface of the metal reduces the adhesion and a rougher surface would be preferred. It is also possible that the molecular bonding of enamel to gilding metal is not as high as copper. As can be seen, the enamel has detached from the metal over a large central area.

Now, considering again the compressive stress on a vitreous enamel layer, there is a recognised formula for determining this.

$$\mathcal{Q} = E_e \times \Delta t \times \Delta A / \{ 1 + (t_e / t_m) \times (E_e / E_m) \}$$

where, \mathcal{Q} = compressive stress on the enamel, MPa

E_e = Young's Modulus of the enamel, MPa x 10³

E_m = Young's Modulus of the metal, MPa x 10³

Δt = temperature difference between onset of compression and ambient, °C

A = coefficient of thermal contraction, x 10⁻⁶/ °C

ΔA = difference in coefficient of thermal contraction of metal compared to enamel, x 10⁻⁶/ °C

t_e = thickness of enamel layer, mm, t_m = thickness of metal, mm

To calculate the compressive stress on an enamel layer and to see how it varies with type of metal, e.g. copper or sterling silver, and also the characteristics of the enamel, values have been selected for the quantities in the formula. Most are based on fairly limited, published data, and so the results can be no more than a rough estimation of the compression stress. The following tabled values have been used.

ITEM	COPPER	STERLING SILVER	SOFT ENAMEL	HARD ENAMEL
E_e			50	90
E_m	115	75		
Δt	480	480	480	480
A	17	19	11	8

Using these values in the formula, the following graph has been produced by plotting the compressive stress created on both a soft and hard enamel with the substrate either copper, (shown in red), or sterling silver, (shown in blue).

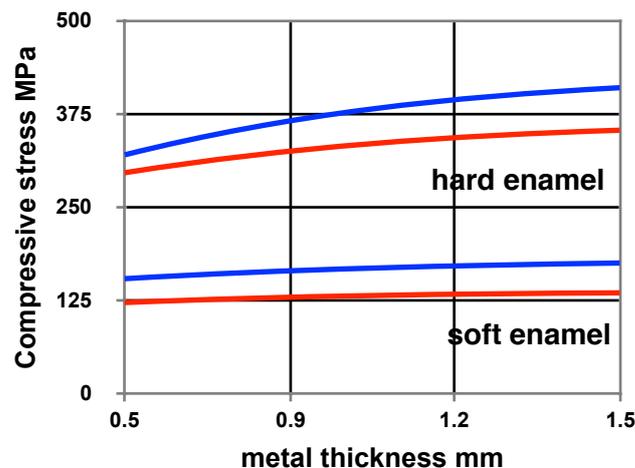


Figure A6. Compressive Stress on 0.2mm Thick Enamel After Firing

The most significant observation is that the compressive stress on the hard enamel is some three times greater than on the soft enamel due to the former having a higher Young's Modulus and lower coefficient of thermal contraction. However, the values lie below the level where compressive fracture might occur, although the margin of safety in respect of the hard enamel is not large and will depend on the limiting compression strength of the particular enamel and how it has been prepared. Enamels for use on copper and silver are specified to have a medium contraction coefficient to suit these metals, and so the contraction forces are generally containable. The compressive strength of an enamel will also depend on the size of the prepared grains and how thickly they have been laid. As previously

stated, the enamel grains should be small in size and then laid closely in contact with each other and thinly on the metal. This will minimise the occlusions that can reduce the strength of the enamel layer. Perhaps wet laying is advantageous in this respect.

The difference in mechanical properties of the two metals, copper and sterling silver does not appear to be overly significant. Although the formula would indicate that a thicker layer of enamel reduces the compressive stress on it, this is not generally borne out in practice and it is presumed that a thicker layer will have a lower compressive strength than a thin layer due to the greater number and size of occlusions.

It is equally important to determine the corresponding tensile stress that is imposed on the metal substrate when it has cooled to room temperature. If excessive, the metal could be stretched beyond its yield point. This is where the elastic limit of the metal has been reached and thereafter it will be permanently deformed and will not recover to its original size. This is particularly noticeable with pure silver which has a very low yield strength and pieces have been known to extend progressively with repeated firing in the kiln. The formula for determining the tensile stress on the metal is the same as already stated, but replacing the parameters for enamel with those for the metal. The result is shown below for an enamel 0.2mm thick.

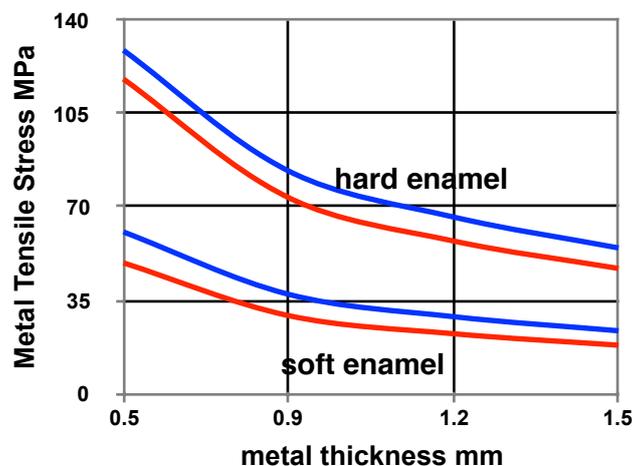


Figure A7. Tensile Stress on the Metal

Now, the yield strength of pure annealed copper is around 60×10^3 MPa and that of sterling silver around 125×10^3 MPa. So, considering just the hard enamel situation, it can be seen that copper of 0.5mm thickness will have been stretched well beyond the elastic limit and sterling silver just about on the limit of remaining elastic. If faced with such a situation in which a piece has permanently extended to a degree that causes fitting problems, then the solution is to use a thicker piece of metal.

There can be an additional stress imposed on the enamel coat and the metal because a bending couple or force is also produced. This could cause the enamel/

metal combination to bow in the manner shown below when it is cooled to room temperature.



Figure A8. Bending of Rectangular Strip

The bowing shown above might occur in the case of a flat metal strip in which the length is at least twice the width. The elastic modulus in bending approximates to the values previously used for uniaxial tension and this applies to such a strip which has a low rigidity. This is probably the most extreme situation and other geometries such as bowls and vases have a greatly increased resistance to bending. Circular or oval discs are often domed to increase their rigidity. It is also suspected that articles which are effectively ribbed, (Champlevé) or have metal additions, (Cloisonné), will be more rigid than flat plates totally covered by enamel. As a consequence, it is the flat, rectangular shape which will be most bowed by the bending forces.

Some idea of the possible deformation or deflection is shown in the following graph for an enamelled piece 50mm long by 25mm wide. The formula is complicated, but relies on the same parameters listed previously.

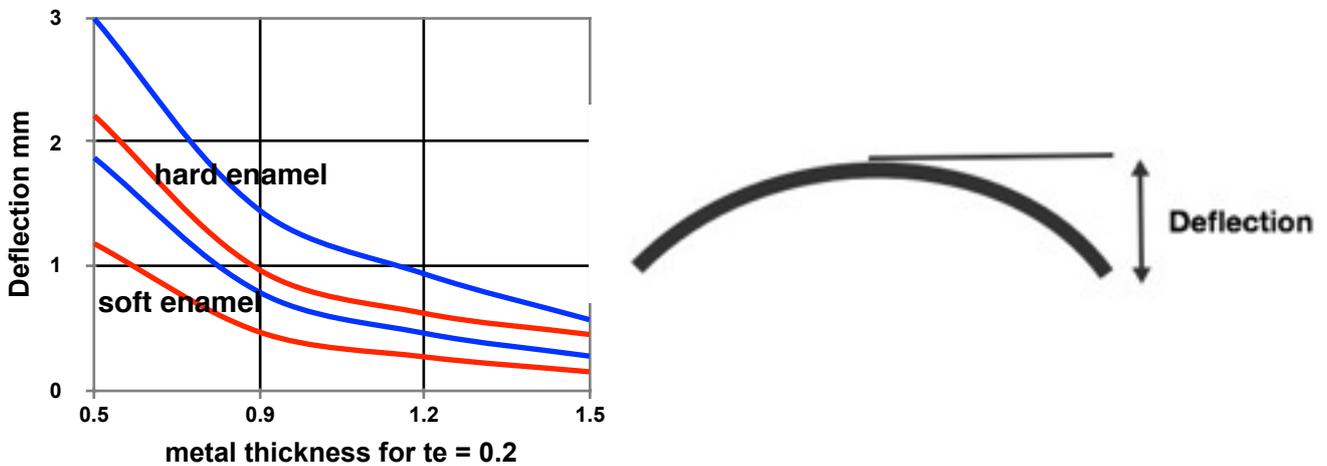


Figure A9. Deflection Due to Bending Couple

The deflections shown are significant and would be quite noticeable when the metal, be it copper or silver, is less than about 1mm thick. Even a soft enamel results in some bowing. Pieces that are bent in this way create other stresses on the enamel. The upper surface of the enamel is being stretched and hence has a tensile stress imposed on it and the lower surface is under a compressive stress as shown in Figure A10.

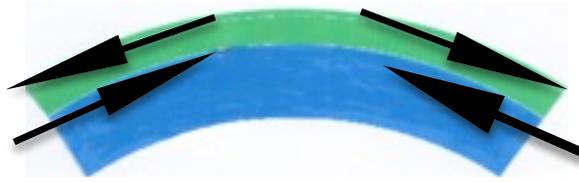


Figure A10. Additional Forces Due to Bending

We have previously shown that an enamel is subject to a compressive stress when in a cooled state. This stress is uniform across the enamel thickness. Now if the geometry of the sample is such that it becomes bent into a convex shape as shown above, the upper surface compression stress is reduced by an amount dependent on the bending produced. The lower surface has an enhanced compressive force. The calculations become even more complex and it is perhaps sufficient to conclude that enamelled pieces that have bowed after firing in the kiln are potentially at risk of cracking due to the extra bending stresses imposed, which might cause tensile failure at the upper surface or undue extra compressive force at the enamel surface in contact with the metal.

Fortunately, there is a technique that can eliminate or significantly reduce the tendency for bowing. This consists of coating the reverse side with enamel, (counter enamelling). This balances the bending couple on the top surface so that there is no net force to cause bending. Section 9 deals with how to apply the counter enamel so the bowing is reduced or eliminated. The application of this thin enamel layer on the reverse side should also reduce the compressive stress on the enamel shown in Figure A6, (for a single layer 0.2mm thick). Figure A11 has been plotted for a total enamel thickness of 0.4mm to simulate a layer of counter enamel, also of 0.2mm thickness. If we compare the compressive stress values in Figure A11 with that in A6, there is a reduction in compressive stress of around 12% as a result of counter enamelling.

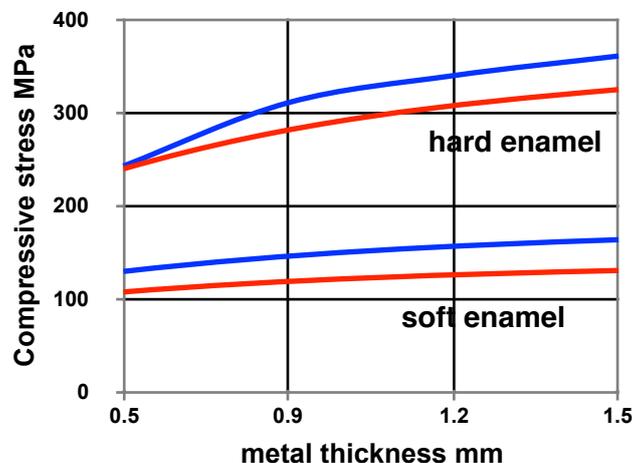


Figure A11. Compressive Stress on Enamel Due to Counter Enamelling

Reference: McKinley, K, Evele, H, Baldwin, C Analysis of Fracture in Porcelain Enamels, www.iei-world.org

In summary, some suggestions are presented below :-

- ★ To maximise the adhesion between metal and enamel, a rough metal surface is preferred to a very smooth surface.
- ★ The maximum compressive strength of an enamel is best achieved using fine grains, laid thinly and closely packed. Wet laying is probably superior to sieving in achieving a layer with minimum occlusions.
- ★ Hard firing enamels are more susceptible to cracking than medium or soft enamels because of their lower coefficient of thermal contraction, and higher Young's Modulus. Choose enamels that are specified for use on copper and silver.
- ★ Thin sections of copper and pure silver e.g. 0.5mm with a hard firing enamel could extend plastically. Repeated firing will cause further extension to a degree that could make fitting in a bezel or frame difficult.
- ★ Having removed an enamel piece from the kiln, allow it to cool gradually.
- ★ Flat, thin, rectangular pieces of metal covered all over with a hard enamel are most liable to become convex after firing and hence will be stressed non-uniformly on the upper and lower surfaces. This could lead to cracking. Use thicker metal and/or counter enamel applied to the reverse side prior to a first firing.
- ★ By doming a flat piece the rigidity and hence resistance to bending forces is enhanced.
- ★ Sharp recesses can act as stress raisers and hence may cause localised cracking.

APPENDIX 6. THICKNESS OF APPLICATION OF ENAMEL FLUX FOR COPPER

Those with experience of wet laying or sieving will know just how much enamel flux to apply to avoid results like those shown in Section 10.2, Figures 5 and 6. To assist beginners, some further experiments were made using different amounts of 150/325 enamel flux applied to a flat copper piece of a known area, A_c mm². The samples were fired at 950°C for two minutes and then the results examined. Below a certain amount, V_{ml} , of enamel applied to the surface of the copper, there was a significant green cast and some pits formed. An amount some three times greater than this resulted in a milky cast but no pits or green cast. An amount just under twice V_{ml} produced a clear result, free from the above deficiencies. From this, a simple formula was arrived at for determining the amount of enamel flux to apply to a specific area of metal. The process is as follows:-

Firstly, estimate the area of copper (A_c) in mm^2 to be covered by enamel flux. For the rectangle shown in Figure 2, it is simply the length in mm multiplied by the width in mm. Circles and ovals are also easy to calculate but some more complicated areas such as etched cells need to be traced onto paper, which is then cut out and re-assembled to form a recognisable shape. One may question the tedium of doing this for complicated shapes and prefer to make an estimate of the area.

Then, an amount of dry 150/325 enamel is measured out in ml that equates to $A_c/4000$. This will result in a layer of enamel powder that when laid uniformly, by wet laying or dry sieving, is around 0.25mm in depth. The grains are stacked about three high. This is neither too thick nor too thin.

As an example, the rectangular strip shown in Figure 2 is 50mm by 25mm. Its surface area is thus 1250mm^2 . The amount of flux needed is $1250/4000 = 0.31\text{ml}$. Because final swilling in water will remove some residual fines, add 10% to the above to give 0.34ml. This technique is economical in the use of material, especially if wet laying, since none is left over to possibly deteriorate. If dry sieving, collect the powder that has fallen around the edges of the piece and return it to the sieve to ensure all the powder is applied to the copper.

To measure out the required amount, one needs a graduated hollow tube and a small funnel. The transparent outer case of a ball point pen can, for example, be used when suitably calibrated and marked on the outside in 0.05ml graduations. Alternatively a graduated plastic pipette can be purchased. This technique of measuring a specific amount of enamel flux is proposed simply to help beginners achieve a clear, transparent layer over the copper substrate. When applying coloured transparent enamels over this layer of flux, thin layers do not suffer from pitting or a green cast and so there is less need to pre-determine how much to apply. Experience in this case is the best guide to not applying too much enamel so that bubble density is low and hence clarity is not compromised.

APPENDIX 7. SUMMARY ABOUT THE APPLICATION OF FLUX TO COPPER

- Getting a clear flux layer prior to laying transparent coloured enamels is important and unique as the flux has to absorb the copper oxide. Imperfections at this stage are almost impossible to rectify later.
- A dull copper surface will not reflect well and small imperfections can show. Create a textured surface that will provide interest, mask minor imperfections and show the beauty of transparent colours to good effect.
- Use a hard firing flux specifically formulated for absorbing copper oxide. It will also form a good base for the softer transparent colours without pull through.
- Coarse enamel grains should be avoided as they take longer to fire to maturity than fine grains, they can have bubbles trapped when fired at the high temperature needed to dissolve the oxide and they are more prone to pits forming. When

sieving, they can bounce off the surface and make uniform coverage difficult, especially at edges.

- Grind enamel flux under water to the consistency of very fine sand. Alternatively grind dry and use sieves to select enamel that is 150/325.
- Wash the flux thoroughly until the water runs clear and use straight away.
- If dry sieving, dry the 150/325 flux on top of the kiln with a metal foil tent over to speed drying and to protect from foreign bodies.
- When sieving or wet laying flux, applying too much can result in a milky effect when fired. Applying too little flux can result in a green tinge or pocks and over saturated (burnt) edges.
- A useful rule of thumb for beginners is to calculate the area to be fluxed, A_c in mm^2 , and to divide it by 4000. The value obtained is the volume of flux to measure out and then apply.
- Operate the kiln at 950°C to 1000°C , and, for copper 0.5 – 1.2mm thick, place the piece in the kiln for $1\frac{1}{2}$ minutes. For 1.6 mm thick copper, extend the time to $1\frac{3}{4}$ minutes.
- Allow the piece to cool slowly under the metal foil tent. Grind out any small imperfections and clean up edges.
- Measure out another quantity of flux and repeat the laying procedure.
- Fire the second coat for slightly longer – around two minutes. The flux should have dissolved the copper oxide formed on heating and be clear.
- If slightly brown, another firing at the same temperature should clear it.

APPENDIX 8. PACKING FACTOR

When enamel grains are wet laid or dry sifted on a solid surface, they do not pack so closely together that there are no air gaps between them. Even if the grains were completely spherical in shape, they could not be packed together without air gaps being present. The best that can be achieved is a close cubic arrangement where the ratio of the sum of the volume of the individual grains divided by the volume they occupy when packed together approaches 75%. This packing factor decreases for a more random arrangement of spheres and is around 50% for a cubic lattice arrangement.

It is, therefore reasonable to expect that enamel grains, which are hardly spherical but more rectangular in shape, will have air gaps that probably occupy at least half of the total volume that is laid on the surface. It should be noted that for grains that are more nearly spherical, the packing factor is independent of the size of the grains. Thus coarse grains will trap the same total amount of air as fine grains. The difference is that the size of the individual air gaps will be considerably less in

a fine mix than a coarse mix, but the number of such gaps is correspondingly greater. Tests undertaken to measure the packing factor of coarse, medium and fine grains of vitreous enamel all yielded results of 45% +/- 2% and these are consistent with what might be expected from the previous observation. They are also in line with the fact that the thickness of an enamel layer after it has been fired in the kiln is around half that of its thickness prior to firing.

It has been suggested that the size of any bubbles that might be trapped in a fired enamel could be reduced by first adding some fine particles to a coarser mix. These finer grains might be expected to fill the gaps between the larger particles and hence reduce bubble size. This appears to be a dubious proposition because, when dry sieving enamel grains, the finer particles tend to be deposited first and are overlaid by the coarser grains. When wet laying, perhaps the separation of coarse and fine grains is less, although repeated tapping may produce the same result. Then one needs to consider the size of those fine grains that would be able to nestle in the gaps between the coarse grains. If we select a coarse grain mix of say 80/100, this will yield grains between 0.177mm and 0.15mm in size. A fine grain mix of 250/325 will yield grains between 0.075 mm and 0.044mm. The ratio between the coarse mix and the fine mix is thus about 3:1. Calculations then indicate this ratio is barely big enough for all the fine grains to fit in the gaps between the coarse grains. If so, the packing factor would not be expected to increase by a significant amount. Experiments made by adding measured proportions of the fine grain mix to the 80/100 grains showed the packing factor could in fact increase from around 45% for all coarse grains to around 60% for an equal volume mix. However, this increase in packing factor did not make a significant difference (when viewed through a microscope) in the number and size of trapped bubbles after the mix has been fired.

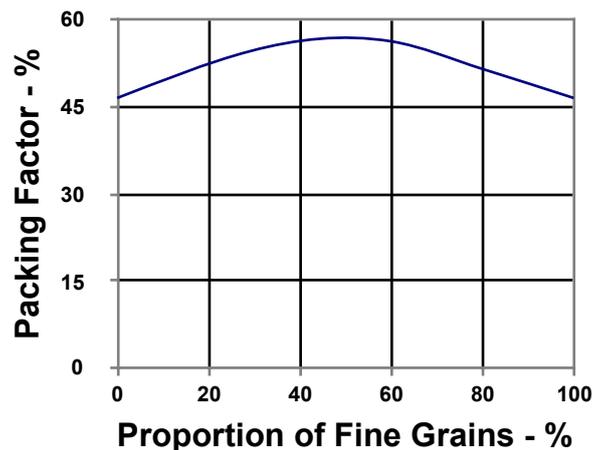


Figure A12. Packing Factor of Enamel Grains

APPENDIX 9. TYPES OF ABRADER AND MICRON SIZES

Silicon carbide has largely replaced emery (aluminium oxide) as the material bonded to sheets and used as wet and dry paper for rubbing down hard materials including enamel. Diamond grit in the form of pads or grinding discs is increasingly popular due to its long life and hardness as a cutting agent.

Considering the silicon carbide papers, although the coarser grit sizes (down to around grade 250) are produced by the use of closely sized screens to produce grains of a particular average size, finer grains are separated by hydraulic flotation and sedimentation or by air classification. The following table shows the grit size in microns corresponding to the finer wet and dry papers generally available in the UK.

GRADE	AVERAGE GRIT SIZE - μm
320	46
400	35
600	26
1000	18
1200	15
2000	10
2500	8

Diamond pads are also available in the grades shown in the table. These pads are colour coded to enable the user to identify the grade corresponding to the above table. However, there appears to be no international agreed colour for each grade of pad and so reference should be made to a particular supplier's information.

As stated in Section 14, it is advisable to start the abrading process using a silicon carbide paper or diamond pad of grit size no greater than 35 μm (400 grit) to avoid the possibility of deep scoring. In both cases plenty of water should be used to lubricate the surface and to carry away the enamel particles removed by the abrasion.