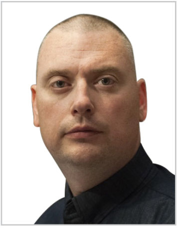

Niello for the Modern Jeweler

Christopher M. Manning
Owner
Silver Hand Studios
Ottawa, Ontario, Canada

Introduction

Niello was an important alloy used by metalsmiths from ancient times until the end of the Renaissance. The low-temperature metal sulfide was commonly used as a high-contrast, fusion inlay alloy. The color permeates the alloy and ranges from dark grey to deep black. It is an excellent choice when making high-wear items where patinas and other surface treatments will wear. It was regularly fused into bronze, iron, silver and gold.

My first introduction to niello came from Cellini's *Treatise on Goldsmithing and Sculpture*.[1] Since first experimenting with niello six years ago, it has become an important material in my art.

Niello was an important alloy in Renaissance Italy and commanded the first chapter in Cellini's Treatise. While the Renaissance was the pinnacle of niello production, its use in decorative metalwork spans from the ancient Egyptians and Romans up to modern-day Russian and Thai jewelers. The Fuller Brooch, located in the British Museum, is one of the finest surviving examples of niello work (Figure 1).

Figure 1 *Late 9th century Anglo-Saxon brooch made of silver and niello*

In my 2017 Santa Fe Symposium® paper, "Niello: An Introduction to an Ancient Material for the Modern Jeweler,"[2] I explored some of the most common historical recipes for making niello. While many of the traditional recipes have withstood the test of time, there are significant toxicity and contamination issues associated with their use. Most traditional recipes include lead to lower the melting temperature of the alloy. This paper explores practical substitutes for lead-bearing niello in order to reduce the health risks for artisans as well as consumers.

Traditional Niello

Various forms of niello have been used in decorative metalwork for thousands of years. Early recipes used silver and copper alloys and were applied primarily to bronze. The early lead-free alloys are difficult to work with. They were primarily silver and copper, which require high melting temperatures for application. The high temperatures can cause the sulfides to break down and can also come close to the melting temperature of the metal into which the niello is being inlaid. By the early Middle Ages, lead was added to the silver/copper alloy to lower the melting temperature. Niello's use on bronze decreased, while its use on silver, gold and iron increased. A number of early niello recipes have survived, including recipes by Pliny the Elder, Benvenuto Cellini and Theophilus. Despite tin being a well-known metal earlier than lead-based niello, there is no evidence that tin was used as an alternative to lead.

While niello recipes have varied dramatically in their proportions, the principle ingredients have not changed. Unfortunately, the lead content in traditional niello makes it dangerous for both the artist and the consumer. Modern consumer protection laws in many countries prohibit lead in jewelry, which makes traditional niello recipes inappropriate for this purpose. Lead also presents a significant long-term health hazard to artisans who prepare and use niello, and it is also a contamination hazard in the shop. A modern alloy of niello is needed for it to be used safely in the modern shop.

Materials Used in Niello

Traditionally, there are four elements used in making niello: silver, copper, lead and sulfur. Increasing the silver content raises the value of the niello, lowers the melting temperature by a small amount, and lightens the color. Increasing the copper content raises the melting temperature and makes the niello blacker. Increasing the lead content significantly lowers the melting temperature. Introducing sulfur to the molten alloy converts it into a metal sulfide, causing it to turn black.

Reducing the melting temperature of niello is crucial. Without reducing the melting temperature of a silver/copper-only alloy, it becomes challenging to apply and the sulfides begin to break down.

In an attempt to find a replacement for lead, I examined other elements surrounding it on the periodic table for their suitability. The primary criteria for selection were these three: low melting temperature, boiling temperature above the melting temperature of the silver/copper alloy and low toxicity.

Gallium

Gallium (Ga) is number 31 on the periodic table. It appears between zinc and germanium, aluminum and indium. It has a melting temperature of 30ºC (86ºF), and a boiling temperature of 2400ºC (4352ºF). Gallium is non-toxic. It is liquid near room temperature, which can make it difficult to measure and handle. Gallium is relatively easy to obtain and has a higher cost relative to the other alternative metals.

Indium

Indium (In) is number 49 on the periodic table. It appears between cadmium and tin, gallium and thallium. It has a melting temperature of 156ºC (313ºF) and a boiling temperature of 2072ºC (3762ºF). Indium is mildly toxic if injected into the blood stream. It is not absorbed through the skin and is not well absorbed by ingestion or inhalation. It is a very ductile metal, which makes it very easy to work with in the shop. It can be easily cut with a knife or scissors. Indium is easy to obtain and has a higher cost relative to the other alternative metals.

Tin

Tin (Sn) is number 50 on the periodic table. It appears between indium and antimony, germanium and lead. It has a melting temperature of 232ºC (450ºF) and a boiling temperature of 2602ºC (4716ºF). Tin does not represent a health risk. It is very ductile and when purchased as sheet, it is easy to cut with scissors. Tin is very easy to obtain and is relatively inexpensive.

Lead

Lead (Pb) is number 82 on the periodic table. It appears between thallium and bismuth, tin and flerovium. It has a melting temperature of 327ºC (621ºF) and a boiling temperature of 1749ºC (3180ºF). Lead does represent a long-term health risk. The primary risk of exposure is through inhalation and ingestion. Exposure is gradual and symptoms are often not obvious until a significant build-up occurs. Because of the dangers of lead exposure, a replacement is needed.

Bismuth

Bismuth (Bi) is number 83 on the periodic table. It appears between lead and polonium, antimony and moscovium. It has a melting temperature of 271ºC (520ºF) and a boiling temperature of 1564ºC (2847ºF). Bismuth has low toxicity and because it shares many physical properties with lead, it has become a common replacement for lead. Bismuth is used in some cosmetics and medicine, and it does not present a significant risk for use in the studio. It is often found in a crystal form and is very brittle. It is easiest to smash into smaller pieces when measuring. Bismuth is easy to obtain and relatively inexpensive.

Experiments and Results

During the experiments with leaded niello recipes for last year's Santa Fe Symposium® paper,[2] I found that the "Modern French" recipe gave the best results. It provided the best combination of black color, melting temperature and flow. The recipe, Ag:Cu:Pb 3:7:5, provided a starting point for experimenting with the new metals. I prepared and tested 20-gram samples of each for melting temperature, color and ease of application. I cast the silver sample disks, then sanded to 600-grit prior to applying the niello. I sanded the gallium-, indium- and bismuth-based samples to 400-grit, and I sanded and polished the lead- and tin-based samples as I would for a finished piece.

I quickly discounted the gallium-based niello as a possible replacement (top right in Figure 2). Despite repeated applications of sulfur to the molten alloy, it would not turn black. It appears as though the gallium resists turning into a sulfide. The resultant alloy is slightly more grey than silver, but not enough to provide a useful contrast to the silver. I did not conduct any further experiments with gallium.

***Figure 2** Experimental results of making niello with (clockwise from top left) tin, gallium, indium, bismuth and lead (center) as the third element in the recipe. The bismuth sample is from the first experiment. All others are from the second.*

The three remaining alloys (indium, bismuth and tin) had very high melting temperatures. All were high enough to be unviable as niello. The indium-based alloy had a melting temperature above 650ºC (1202ºF). The bismuth and tin-based alloys had melting temperatures above 530ºC (986ºF). Based on past experience with niello, I find that temperatures above 430ºC (806ºF) during application are problematic. Above that temperature, the sulfides begin to break down in lead-based niello, and the silver will usually precipitate out. The precipitated silver forms small crystals that look like snowflakes and, in more extreme examples, large areas turn silver. The bismuth- and tin-based alloys held up to the higher temperatures during a single application; however, there were flow issues during application. Since multiple applications are often required, the chance of damage on subsequent applications is high. The indium-based niello required enough heat to cause the sulfides to begin breaking down during the first application.

During the next set of experiments, I changed the initial approach for the recipe. In order to start with as low a temperature as possible, I created a near-eutectic silver/copper alloy with a ratio of Ag:Cu 7:3. Adding five parts of the third metal allowed for dramatic reductions in temperature compared to the initial recipes. based on the Modern French recipe.

The tin-based recipe flowed at roughly 230ºC (446ºF). Once flowing, it filled both large areas and small details nicely. The color after application is a good dark grey. The tin-based sample is top left in Figure 2. A common problem with this formula is the precipitation of silver from the alloy. The effect is exaggerated by the photograph and is not visible at arms' length. When compared to the lead-based niello, this recipe is not as dark, primarily due to the silver crystals that formed on the surface. Without a direct comparison, it would be difficult to distinguish this niello from many lead-based ones.

The bismuth-based recipe flowed at roughly 200ºC (392ºF). This recipe is the closest to the lead-based niello with regard to flow and fill qualities. The alloy does not have a consistent color after application (bottom left in Figure 2) and the surface shows evidence of damage from over-heating. It appears as though the silver is precipitating out in larger amounts than from the tin-based alloy. The black areas are a bit darker than the tin-based alloy.

The indium-based niello requires a higher temperature than the other recipes, roughly 350ºC (662ºF), to begin melting. It does not flow well until heated over 500ºC (932ºF). As a result, there is a risk of sulfides breaking down with this recipe. In addition to the high temperature required, the alloy is not consistent in color. Large areas are affected by silver precipitating from the alloy (in Figure 2 the indium-based sample is bottom right). Due to the melting temperature being higher than is safe for the sulfides, I don't believe it is worth experimenting further with an indium-based recipe.

For comparison, a fifth sample was made using the Modern French lead-based recipe (center sample in Figure 2). This niello flowed comfortably at 175ºC (347ºF). It is very easy to apply and flows well. It is a nice black color and, due to the low melting temperature, overheating (and the associated damage to the sulfides or silver precipitation) is unlikely.

Safety

The recipes presented in this paper were selected with the intention of reducing the long-term health risks to the artist using them. While the elimination of lead from the alloy has removed the most significant health risk, there are still important steps required to work safely with niello.

During the preparation of niello, all normal precautions should be taken while working with torches, high heat and molten metal. The most important safety consideration compared to normal alloying procedures is the sulfur dioxide produced from burning sulfur in air. Sulfur dioxide readily reacts with the moisture in mucous membranes and forms sulfurous acid, a severe irritant. Mild exposure will result in airway restriction, coughing, sneezing and eye irritation. Higher exposure will result in bronchospasms, resulting in an obstructed airway and severe eye irritation.

Sulfur dioxide is heavier than air and will pool in low-lying areas of the shop. Good ventilation is important while preparing niello. If adequate ventilation is not possible in the studio, preparation outside is encouraged. Along with adequate ventilation, a full-face respirator should be worn during preparation. For information on how to build an effective fume hood for preparing niello, see Whit Slemmons' excellent article/tutorial entitled, "Studio Ventilation Tutorial."[3]

Care should also be taken when filing, sanding and polishing niello. Dust can present a health risk regardless of the toxicity of the metals. The dust and particles from niello can also contaminate other work. Pitting can occur during high-temperature operations such as soldering with pieces contaminated by niello particles. Care should be taken to avoid cross contamination with other work.

Preparation

All recipes are prepared essentially the same way, requiring similar equipment and precautions. The silver and copper are first alloyed together. The third metal is added and allowed to mix. The molten alloy is then poured into the sulfur. At that point the niello can be cast into a rod for easy use.

Below is a list of the tools and materials required to perform the above experiments.

- Full mask respirator
- P100 filter for respirator
- Two crucibles
- Graphite stir rod
- Fume hood
- Sulfur
- Copper
- Silver
- Tin, galium, indium or bismuth
- Scale
- Torch
- Steel angle iron
- Mortar and pestle
- Wire mold
- Borax
- Steel spoon
- Ingot mold
- Steel bowl with water

A good fume hood is an absolute requirement for making niello in a shop. The hood must exhaust out of the room, and care must be taken when selecting where the exhaust exits the structure. Be sure to test the draw of your fume hood before you start burning sulfur because the fumes from this process will contain large amounts of sulfur dioxide. Niello can also be made outdoors, as long as there is a reasonable breeze to carry away the fumes (be sure to prepare away from bystanders who are unaware and/or unprotected).

No matter where it is made, everyone in the studio or area must wear an appropriate full-face respirator. A half-face respirator is inadequate for this work as it will not protect the eyes from the sulfur dioxide. The respirator must fit properly and should be fitted with a P100 cartridge. If you are unsure about the respirator or cartridge you currently have, consult with a reputable safety equipment supply house. They will be able to provide you with the correct products to protect against lead and sulfur dioxide.

Wear clothes you are willing to discard. The smell of burning sulfur is invasive, and you should be willing to throw out the clothes you are wearing. Be aware of the dust created when filing, sanding, and polishing niello, as it can also contaminate clothing. The dust can cause issues with other work in the shop.

Figure 3 *The raw materials required for this experiment*

The sulfur must be in a powdered form. It is unnecessary to use chemically pure sulfur. Garden centers are a good source of sulfur, which is sold as a slug deterrent and is typically 92% pure. Despite some historical sources that discuss specific quantities of sulfur, it is difficult to recommend an exact amount. The goal is to saturate the alloy with sulfur. More sulfur is better, and with experience you will get a sense of how much to work with at a time.

The silver should be pure or contain nothing except copper. If it is an alloy such as sterling or coin silver with a known amount of copper, take into account the copper content when weighing all the metals. The silver should be cut into small pieces or used in grain form to help it melt rapidly.

The copper should be pure. Unused copper plumbing tube is a reasonable source. Even though it often contains a very small amount of deoxidizer, I have found that it does not affect the quality of the niello produced. However, do not use pipe taken from an existing plumbing installation as it may be contaminated with solder. Electrical wire can also be used; however, removing the insulation can be tedious. As with the silver, it should be cut into small pieces or used in grain form.

Pure tin can be purchased in several forms. Sheet tin is the easiest to use—a 1-mm thick sheet can be cut easily with scissors.

Preparation is important. Before starting, lay out everything you need so it is easily at hand. Weigh all metals and keep them separate. Making 20 grams of niello at a time is reasonable. Disposable paper cups are useful to keep each of the metals sorted.

Prepare the two crucibles by coating them in borax and firing them. The crucible used for alloying the metals should be pre-heated before adding any metals. The crucible with the sulfur should not be pre-heated. Fill the sulfur crucible with a spoonful of sulfur.

The steel angle iron should be a few feet long and tilted at a slight angle. You will be pouring the molten niello into it and making a long rod of niello. It should be readily accessible and stable while handling the torch and the crucible of molten niello. Prepare the angle iron by coating it with a thin layer of oil and burning it off to create a layer of soot. There is no need to heat the angle iron prior to pouring the rod.

Once everything is laid out and ready, begin by melting the silver with a reducing flame. When the silver is liquid, slowly add the copper. Stir the alloy as necessary to ensure that everything has melted and mixed. When the silver/copper alloy is liquid, slowly add the third metal. It is important to ensure that the third metal has melted and successfully alloyed with the existing metal before pouring it into the sulfur. Roll the molten metal in the crucible to ensure it is all molten and consistent. Temperature is important from this point on, as high temperatures can damage the sulfides you will create in the next step. Overheating the niello can also cause the silver to precipitate from the alloy.

When you are satisfied the alloy has mixed, pour it into the crucible with the sulfur. Stir the mixture and add heat occasionally until all of the sulfur has been absorbed or burned off. Apply short bursts of heat from the torch to keep the niello molten. While allowing the sulfur to burn off, there may be a small amount of cinder on the molten niello. Do not heat the mixture to the point where the cinder is absorbed into the niello. Instead, remove the cinder with the graphite rod. Once the sulfur is absorbed or burned off, slowly pour it into the angle iron to form a long, irregular rod. The rod should be consistent in color throughout and should be brittle. If there is a silver core in the rod, you have overheated the niello or did not add enough sulfur. It is impossible for the niello to absorb too much sulfur. Melt the rod and pour it into another crucible of sulfur. Pour a new rod in the angle iron and check it for consistency.

When you are satisfied with the niello, make it into either rods or powder. If you want to use niello as a powder, melt it and pour it into a bowl of water. Remove the niello from the water, then grind it in a mortar and pestle. Once ground, it should not be stored for long periods of time. A simple wire mold works well for making niello rods for either immediate or later use. Be careful not to overheat the niello when casting into rods or ingots.

Application

Using niello in a piece needs some planning and requires preparation similar to using enamel. All soldering operations must be complete before applying niello. At soldering temperatures, the niello will flow again and the high temperature will cause damage to the sulfides. Niello will also cause significant pitting in silver and gold at soldering temperatures. Even extra easy solder requires too high a temperature for use with niello that has already been applied to a piece. Laser or fusion welding is required to repair a piece after the niello has been applied. All stone setting should wait until after the niello has been applied and finished.

A basic finish should be completed prior to application. I recommend finishing with at least 400-grit sandpaper before. It is best if the area where niello is being applied is flat, or convex, and is easily accessible with files and sanding sticks. All forming should be complete before applying the niello. Do not apply to a flat piece of metal and then try to form it.

Figure 4 *Sample disks cast in Argentium® silver and prepared with sandpaper up to 400-grit*

Niello is opaque once it is more than 0.05 mm thick. It can be applied into deep or shallow pockets or engravings. Be cautious about using very shallow depressions, as it is easy to damage the surrounding piece when sanding and possibly destroy the pattern in the process. I recommend making depressions 0.5 mm deep.

If a flux is required to protect the base piece, use a mixture of alcohol and boric acid. Apply the mixture to the work before applying the niello. Heat the piece until the flux has become liquid. The work is now hotter than the melting temperature of the niello. It can be fed by rod through the flux, displacing it. Depending on the size of the piece, it may be necessary to apply heat to the piece to keep it hot enough to melt the niello. Avoid applying heat directly to the niello.

If flux is not required to protect the base piece, apply heat to the base piece and allow it to melt the niello. Once again, avoid applying heat directly to the niello.

If using niello as a powder, apply it as you would enamel. Over-pack the area to be filled with powdered niello. The piece can either be torch fired or heated in a kiln. Follow the same steps as above when torch firing. If using a kiln to fire the piece, pre-heat the kiln to 700ºC (1292ºF) and use a trivet to support the work. The temperature of the kiln is high enough to damage the niello, so closely monitor the niello to observe when it has melted and remove it once it has flowed. Be careful when removing it as the niello is molten and can be spilled from the depression. The niello may stay liquid for a few minutes. Place the piece on a flat surface to prevent the niello from under filling one side and overfilling another side of the piece.

Regardless of application method, always overfill the area with niello. There is often damage to the top surface of niello, and overfilling will ensure it can be filed and made level with the surrounding surface (Figure 5). If necessary, use a solder pick to pull niello into all areas of the pattern and prevent air pockets. In particular, pay attention to corners and areas of fine detail.

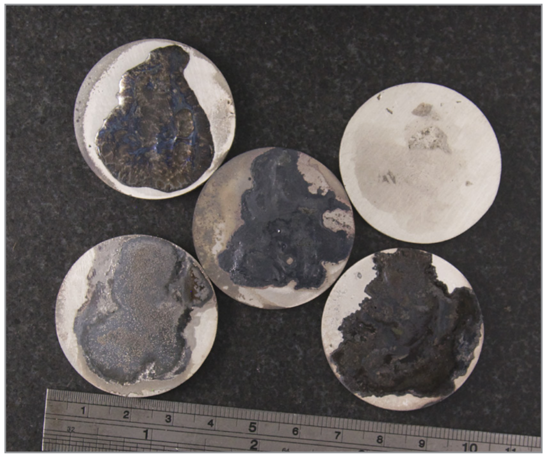

Figure 5 *Sample Argentium® silver disks after the initial application of niello*

When filed flat, a second application may be necessary to fill air pockets or areas without enough niello to reach the same level as the base piece. Slowly heat the piece and watch for the existing niello to melt. Use a solder pick to draw the niello into any air pockets and apply a small amount of fresh niello to overfill the area.

With practice, most pieces can be filled in one or two applications. Be cautious when reheating the piece. It is easy to become impatient and damage the niello with too much heat.

Once applied, niello can be drilled, allowing mechanical fastening of stone settings or other parts. I also commonly use Loctite® to secure parts together where appropriate. Low- and medium-temperature Loctite will provide a semi-permanent bond and can be released with heat below the temperature at which niello will melt.

Finishing

Because niello is a metal alloy, many of the standard finishing techniques used in jewelry will apply to pieces with niello. Files and sanding sticks should be used to complete most of the finishing. Dedicated tools should be used for finishing. All files, sanding sticks and polishing buffs will be contaminated with the low-temperature niello. If they are used on another piece in the future and high temperature is applied during soldering, pitting can occur from the fine niello particles.

As much finishing as possible should be completed with progressively finer sanding sticks. The niello is very soft compared to the surrounding gold or silver. Avoid aggressive polishing to prevent undercutting the niello. Use buffing compounds that are appropriate for the metal of the base piece. The most aggressive buffing compounds should be avoided; instead, prepare the surface as best as possible for final buffing using sanding sticks. After finishing, the niello and base silver should be level, and then polished (Figure 6).

Figure 6 *Taj Mahal pen by author in Argentium® silver and niello*

Conclusion

The purpose of these experiments was to explore alternatives to traditional lead-bearing niello. Some of the alternatives are viable but they are certainly not perfect replacements for historical recipes.

Tin is the most promising replacement for lead. It is not a perfect replacement, primarily because it does not lower the melting temperature of the alloy as much as lead. However, the results show that it is worthwhile to use a lead-free niello as a replacement to traditional alloys.

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