



## RESIN CASTING: A COLLECTION OF HYPOTHESES

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### INTRODUCTION

A cursory Google search reveals a plethora of methods, tips and tricks for casting jewelry with resin parts. However, the sheer quantity of information belies a painful truth. Our beliefs on resin casting must be wrong. At best, they are incomplete.

We have tried to educate ourselves on resin curing and investment strength. We have experimented. We have developed bulletproof protocols. We've shared them in detail with our friends, and we've wondered why they struggle.

We've also had our confidence eviscerated by a simple pendant with inset lettering. The truth is our success is situational. The "what" dictates our success more than the "how."

This paper is about the "why." It will challenge the prevailing wisdom on curing and investment strength by treating them as inconsequential—a byproduct of the process. Instead, it will introduce and investigate new concepts that underlie our success and failure.

### INITIAL RESEARCH

When this investigation began in 2014, the predominant reasons stated for casting failures fell into three categories: ash, thermal expansion and the reaction of investment to resin parts. While most of the discussion in the jewelry community revolved around thermal expansion and investment reaction, ash was shown to be the most problematic.

Many more factors contributed to the production of ash than initially thought. Ash is also to blame for much confusion. The presentation of ash defects can mimic those of virtually any other defect including investment breakout.

### Ash

Ash is created when resin suffers incomplete combustion in the mold. The primary solutions recommended were a slow burnout, a fast burnout and a burnout that used high temperatures. The results of initial testing with each method varied considerably. It was apparent that the rate of heating and the temperatures used by a burnout program were less of a factor than thought.

The inconsistency of tests led to the evaluation of resins in isolation. Casting crucibles and other ceramic dishes were used to observe their physical changes during heating. The clay proved to be a better analog than nonporous vessels. Some of the findings include:

- None of the resins tested produced a visible flame during a slow burnout. They all thermally decomposed, leaving behind ash. Most resins left a small quantity of ash along with a globular residue that adhered to the dish. Others yielded a large volume of light, fluffy ash that resembled those from a cigarette ashtray.
- A fast burnout resulted in combustion with a visible flame and left no residue.
- Long holds at 1450°F (788°C) showed no effect. All of the ash appeared stable beyond 1100°F (593°C). A casting torch was used to induce higher temperatures. The dishes were removed from the kiln and heated to a cherry red. Again, the ash showed no change. However, the globular residues glowed white hot and were uncomfortable to view through a #3 shade welding lens.

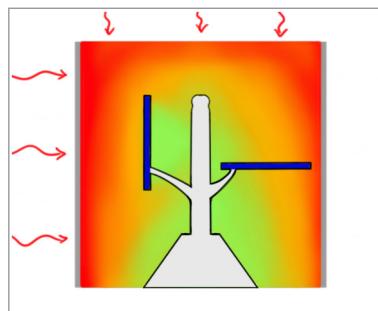
It appeared the only solution to ash was prevention. The goal of further testing was to minimize the duration of pyrolysis prior to combustion. Again, the results varied considerably. Sometimes the castings were flawless. At other times, ash created severe surface defects. The defects were usually located on prongs or at the mid-shank position of a ring (Figure 1). The defects formed in bands running parallel to the flask wall.



*Figure 1 Ash banding defect on an otherwise clean casting*

Patterns emerged as the day-to-day production castings were tracked closely. The following factors were found to influence results significantly:

- Part geometry—Thin parts or thin features of a part, having a higher ratio of surface area to volume, were more prone to banding defects. Typical examples include large, lightweight pendants or long, thin prongs.
- Part position in the flask—Parts performed better when the surface area was oriented minimally toward the flask wall (Figure 2). Large disc pendants would consistently produce ash when oriented vertically facing the flask wall. When laid flat with the disc facing the kiln ceiling, they would burn out cleanly.
- Flask position in the kiln—There was a negative correlation between ash production and the amount of radiant energy received during the early stages of the burnout. Flasks performed best when placed in the rear corners of the kiln. Here they had a direct line of sight to two heating elements. In the center of a full kiln, flasks shielded from the heating elements produced the most ash.
- The kiln load—The casting quality decreased as the volume of investment in the kiln increased. Five 2.5" x 2.5" (61 in<sup>3</sup>) flasks performed satisfactorily while three 3" x 3.5" (74 in<sup>3</sup>) flasks proved difficult.



*Figure 2 Placement is essential when casting resin parts (blue). The flask wall reaches combustion temperatures (red) while water arrests the center cone of investment (green). Orienting a large disk pendant to face the flask wall (left) will interrupt the flow of heat. If oriented horizontally (right), it is spaced too close to the flask wall, and the edge will combust early. Either scenario will produce intense ash.*

Surprisingly, ash played a principal role in another line of inquiry. A dissection study was devised to investigate the interactions between investment and resin. The dissections would use geometries known for a repeatable defect. They were prepared identically and then split into two flasks that mirrored each other in the kiln. At the end of the burnout, one was cast and the other dissected. This allowed the defects in the casting to be correlated with observations of the mold.

Ash was determined to be causal in most of the cases selected for the study. It was clear that ash must be considered as a possible cause when diagnosing any defect. This included defects from investment breakout. It is believed that molten metal causes a rapid off-gassing in the residue. The gasses are trapped by the investment and inrushing metal, exhibiting an explosive force which destroyed delicate features in the mold.

More research is needed here. The reaction observed between residue and metal was not investigated. The focus remained on preventing ash. While the residue did not change in appearance above 1100°F (593°C), higher temperatures may change its chemical structure and prevent this phenomenon.

Higher temperature treatments were also excluded from this study as they lead to increased production of sulfur dioxide ( $\text{SO}_2$ ). It is known that carbon, time and temperature influence the breakdown of gypsum into  $\text{SO}_2$ .<sup>1</sup> Removing carbon with longer holds or higher temperatures is counterproductive.

This inquiry also found an investment designed for resin casting to be problematic. It had a higher concentration of gypsum and, therefore, a higher potential for  $\text{SO}_2$  production. It proved much less tolerant of time and temperature when combined with the carbon remains from resin parts. It is thought that the recommended maximum temperature for high gypsum investments should be 1250°F (677°C) rather than 1350°F (732°C).

## Thermal Expansion

When this investigation began, thermal expansion was the favored explanation for most casting defects. These defects were thought to be caused by the resin as it expanded between 350° and 850°F (177° and 450°C). The expansion force would have exceeded the investment's compressive strength, causing it to fracture.

Possibly due to prior research, visual observations of current resin formulations showed the opposite. The parts would shrink as they heat-cured, then wither away under pyrolysis. Also, the resin was a soft blob of molten plastic at these temperatures.

The methods prescribed in Andy Andrews' 2011 Santa Fe Symposium® paper, "The Quest for the Perfect RP Burnout,"<sup>2</sup> did improve the rate of success. However, it was not found to be a result of the investment's strength. Different qualities of investment, water-to-powder (w:p) ratios, hygroscopic setting, etc. showed no impact. Parts that were likely to fail would do so, regardless of the relative decrease or increase in investment strength.

Prior research agreed with these findings.<sup>3</sup> When appropriately mixed, using a higher (weaker) or lower (stronger) w:p ratio within the manufacturer's recommended range was inconsequential. The change in the investment's properties was marginal. Andrews had discovered something, but it was unclear what that something was.

## Investment Reaction

The final category of failures is the reaction of investment to resin parts. These defects were thought to be caused by residual monomers and free radicals that reacted to and weakened the investment. Many solutions were recommended, such as heat curing, UV curing and microwave curing.

The initial testing of each method showed promising results. However, when checked for repeatability, the results became inconclusive.

The dissection study was used to identify specific defects not attributable to ash. An initial batch of control parts was printed in wax and resin for each geometry. The wax control would demonstrate the castability; the uncured resin control would serve to contrast the effect of a treatment.

Again, the initial results were promising but became inconclusive. Each method worked well on some part geometries but produced consistent defects on others. More interestingly, the uncured resin controls began to perform better with age, surpassing each treatment and ultimately resulting in perfect castings by week three (Figure 3).



*Figure 3 Top: Solidscape control; middle: aged B9v1.2 Emerald control; bottom: B9v1.2 Emerald 12-hour UV test*

It was apparent that another method was needed to quantify the efficiency of curing protocols. Unsuccessful attempts were made to gain access to an FT-IR spectrometer to measure the cross-link density of the test subjects. When a practical stain test was found in a 1988 publication by RadTech International,<sup>4</sup> it was successfully adapted for testing resin parts.

## The Stain Test

The stain test provided a qualitative measure for a curing protocol's efficiency. A solution of potassium permanganate was used to oxidize and stain uncured monomer on the surface. This finally allowed a test subject's cross-link density to be studied in isolation, which significantly improved the feedback loop.

Initial tests were performed with a predetermined exposure interval of 15 minutes. Several treatments were tested, including 12 hours of UV, microwave curing, and heated annealing (Table 1). Each showed a deep saturation, indicating the surface remained uncured. Heat curing (Table 2) appeared to be the only treatment capable of fully curing resin parts.

It was later determined that fixed exposure intervals were inappropriate for this test. The stains were overexposed, making the effect of each treatment indistinguishable. The saturation of the stain did not solely depend on the cross-link density of the part. The length of exposure, pH, temperature and age of the solution were also a factor.

Later tests were done using comparisons. Different protocols were stained together, often with a heat-cured and uncured part used as a control (Figure 4). The subjects were removed from the solution and checked every 30 seconds until a significant contrast in the stain developed. This provided a better comparison of a treatment's curing efficiency.



**Figure 4** Formlabs Castable V2 resin after a 60-second stain test in a heated ultrasonic. Left: fully heat-cured part with crazing, right: uncured control

The potassium permanganate solution was composed of:

- 500 mL distilled water
- 2.50 g sodium hydroxide (lye)
- 1.25 g potassium permanganate (greensand iron filter regenerant)

Lye and a heated ultrasonic bath were used to increase the pH and temperature to accelerate the reaction. Stirring was also required to prevent parts from resting on each other, inhibiting the stain.

A popular explanation for casting defects was that the interior of a part remained uncured. Cross-sections of parts were tested to address this concern. The interior of a part was always found to be more cured than the surface. This can be seen in the uncured part pictured in Figure 3. The surface is a saturated dark blue, while the interior is closer to the light blue of the heat cured part.

It should also be noted that UV treatments of any intensity or duration did not affect the subsurface. The dyes and pigments in a resin exponentially limit the penetration of light waves. This is why they are appropriately named UV blockers.

An interesting idea arose for a purely chemical treatment to prepare resin parts for casting. Once the stain test oxidized the residual monomer, it was left inert. The remaining free radicals could be removed using a reducing solution of ascorbic acid (Vitamin C). Unfortunately, the parts free of both residual monomer and free radicals still showed casting defects.

The stain test demonstrated that the rate of cure is utterly inconsequential. Fully cured parts could produce a casting defect for a particular geometry while aged, uncured parts did not.

## Aged Parts

Others have reported on aged, uncured parts before. Gary Dawson discussed it in his 2013 Santa Fe Symposium® paper, “Direct Casting Photopolymer Resin Models.”<sup>5</sup> There are also numerous anecdotal reports from jewelers. They successfully cast samples obtained from trade shows but struggled with the same, freshly printed geometry after purchasing a printer.

In this study, the only treatment the aged control parts received was a brief cleaning with isopropyl alcohol in an ultrasonic. They were stored in a semi-airtight, plastic tackle box in a temperature-controlled office before casting. At no time were they exposed to direct UV light, only the occasional fluorescent and LED office lighting.

## Current Research

The results from stain testing brought an end to the initial line of inquiry. Weak investment and uncured resin were not to blame for casting defects. A new inquiry was launched based on the questions left unanswered. Why did uncured, aged parts cast without defect? Why did Andy Andrews’ method for casting

resins show a demonstrable improvement? Moreover, why did a fast burnout either leave no ash or create intense bands of carbonization?

## Testing Setup

The initial inquiry used five different resins. It was determined that using a large sample size of a single resin would be more beneficial for this inquiry. While each resin exhibited specific behaviors, the concepts covered here are thought to apply universally. B9 Emerald was chosen for its widespread acceptance across various printers.

The initial inquiry also used two hobby-grade stereolithographic (SLA) printers, one laser and one digital light projection (DLP). This made some tests difficult. It was critical the parts were dimensionally consistent, both across the build plate and over time. A B9 Core 530 (30 $\mu$ m XY) was purchased for its uniform light engine and active management of exposure profiles.

The parts were cleaned by placing them in a disposable plastic bag with 25–75mL of fresh, 91% isopropyl alcohol. The air was removed from the bag, and it was sealed. They were sonicated for three minutes in a heated (43°C/110°F) Elma E30H Ultrasonic. After three minutes, the parts were rinsed with tap water and blown dry with compressed air.

The surface of fresh prints is very delicate, and a fingerprint can sand off detail. A short UV cycle was used solely to enable handling. The dried parts were placed into a \$28 fluorescent UV nail curing unit and left stationary for ten minutes.

All annealing, heat curing and burnout cycles were performed in a Neycraft fiber furnace (9" x 9" x 6.5"). Its four heating elements are embedded in the left, right and back walls along with the ceiling. The kiln was controlled with a Paragon programmable controller, although there was a strong desire for a more accurate PID controller.

Several high-quality, standard gypsum investments were used with identical results. Investments with higher gypsum concentrations were ruled out due to the use of temperatures above 1250°F (677°C).

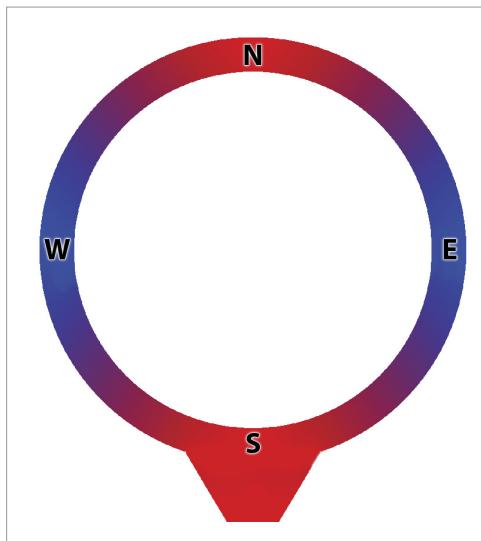
### **HYPOTHESIS #1: NON-UNIFORM DEFORMATIONS ARE CAUSING INVESTMENT BREAKOUT.**

It is not a question of “if” resin parts deform in the mold during burnout. Heat causes the resin to cure, which induces shrinkage. Heat also allows for internal stress to be relieved as it transitions from a rigid to a rubbery state. The question is whether these deformations are uniform or non-uniform.

Uniform deformations are not prone to investment breakout. If the deformation pushes evenly against the mold, it challenges the investment’s superior compressive strength. This is why thermal expansion is an unlikely source of casting defects.

However, investment is weak in shear strength. A relatively weak sliding force can cause it to fracture. Non-uniform deformations, where the resin pushes or pulls in one direction more than another, dramatically increases the possibility of investment breakout.

Evidence for non-uniform deformations was found experimentally, and a conceptual model was derived (Figure 5). Features that were castable at cardinal positions (red and blue) became prone to investment breakout as they approached intercardinal positions (purple). Lettering defects provided additional insight. Letters with horizontal channels seemed to relieve the force responsible for the defects (Figure 6).



*Figure 5 Model of non-uniform part deformation*



*Figure 6 "L" located at an intercardinal position*

Heat-curing treatments were shown to resolve these investment breakout defects. This pre-shrinks and stabilizes the geometry prior to entering the mold. Parts are reduced in volume by 1–2% (depending on resin and printer exposure), becoming denser through polymerization and the volatilization of constituent components. However, shrinkage was not the cause of investment breakout. Full-sized versions of these same troublesome geometries were cast successfully once aged (Figure 3).

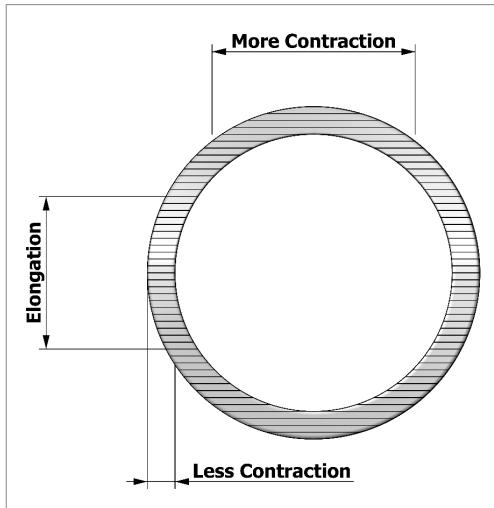
The castability of aged parts was novel, however impractical. We cannot wait three weeks to cast. Attempts were made to accelerate the aging process with heat using an annealing protocol. Annealing plastics is standard practice for the injection molding industry. Otherwise, molded parts would shatter easily.

Heating plastic to its glass transition temperature causes a state change. It becomes a rubber-like material that allows for more internal movement. This ease of movement accelerates the relief of stress. As it cools to room temperature, the transition reverses. It vitrifies, increasing in rigidity by several orders of magnitude. In the glass-like state, it will fracture rather than cut. Exploiting this property will prevent divots during support removal. As with glass cutting, the desired parting line can be scored with a scalpel and wiggled, leaving a clean break.

As goldsmiths, we understand stress in metal. We induce stress through cold-working. The metal becomes rigid and requires annealing. As it is heated, we see the metal move as stress is relieved. The same concept applies with resins, with a differential in cure causing the stress rather than cold-working.

Internal stress is most notable when printing flat on the build table. The initial layers are over-cured for adhesion, which then curl at room temperature. We also see stress from UV treatments. The penetration of light is limited to the surface, increasing stress and rigidity.

What's not noticeable is the stress induced by changes in surface area from layer to layer. The rate of change is highest where we find casting defects at the intercardinal positions. With each layer that gets progressively bigger (or smaller), the stress is compounded (Figure 7).



*Figure 7 Non-uniform deformation caused by changes in layer surface area*

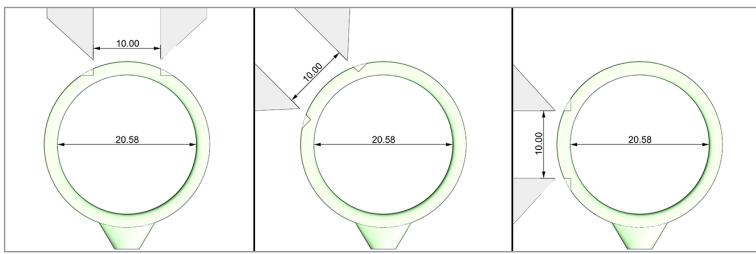
It is thought that lower levels of stress are relieved slowly at room temperature since rapid deformations are observed with higher levels. This is a possible explanation for the success of aged parts.

The deformations from internal stress proved difficult to isolate. Casual observations of aged parts showed no change while the heat from annealing induced some curing shrinkage. More importantly, this information was useless by itself. It was the deformations that occurred in the mold which caused the investment breakout.

A new series of tests were devised to address these issues. While accurate measurements of deformations could be taken before investing, no measurements could be taken after. Instead, these deformations were estimated through the use of an analog.

## Testing Setup

Three test geometries were used. They contained caliper mating points across a 10 mm span at a 0°, 45°, or 90° angle (Figure 8). Measurements were taken with a set of Mitutoyo 500-170-30 calipers. Parts were measured only once as it was observed to influence future measurements. The accuracy of the measurements was further increased by visually determining contact under a Leica A60 microscope.



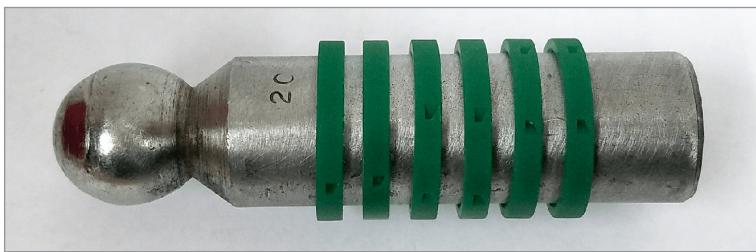
**Figure 8** 0°, 45°, and 90° geometries

Larger sample sets were used to address a concern over the dimensional consistency of prints. The geometries in Figure 8 were printed in groups of 12, for a total sample size of 36 parts per test. Ultimately, smaller sample sets of 12 or 6 parts were used with repeated testing. Using a professional grade printer eliminated the inconsistencies observed with hobby-grade machines. The average standard deviation for each group of 12 was only 8  $\mu\text{m}$ .

Each test group was exposed to a single or series of treatments including:

- UV cure—10-minute stationary exposure.
- Boiling—Placed into boiling tap water and held at a boil for 10 minutes. The pot was removed from the heat source and allowed to air cool to 150°F (66°C) before removal.
- Annealing—Parts were placed freely into the oven and heated according to the program in Table 1.

Parts underwent treatments as if being prepared for casting before having their measurements recorded. This was the pre-mold shrinkage (or expansion). While these deformations were of interest, the primary concern was how these parts further deformed in the mold. An analog was devised to mimic the primary forces involved (Figure 9).



**Figure 9** Analog for parts constrained by the mold during heat curing

If an invested part is not entirely heat-cured, the first hold of the burnout at 350°F (175°C) will complete the polymerization process. This primarily contracts and shrinks the part. The analog was designed to constrain the shrinkage as if they were in the mold.

Analog parts were friction fit onto a machined dapping punch during heat curing (Table 2). The pre-mold shrinkage was then compared to the deformation of the constrained parts to estimate the stress exerted on the mold.

*Table 1 Heated annealing program*

Fahrenheit Starting at 12:00 PM				
Segment	Ramp	To	Duration	End Time
Cold Kiln		72°F		12:00 PM
Leg 1	150°F/hr or 2.5°F/min	250°F for 00h 30m	01h 41m	01:41 PM
Leg 2	100°F/hr or 1.7°F/min	125°F	01h 15m	02:56 PM

Celsius Starting at 12:00 PM				
Segment	Ramp	To	Duration	End Time
Cold Kiln		22°C		12:00 PM
Leg 1	83°C/hr or 1.4°C/min	121°C for 00h 30m	01h 41m	01:41 PM
Leg 2	56°C/hr or 0.9°C/min	52°C	01h 15m	02:56 PM

*Table 2 Heat-curing program*

Fahrenheit Starting at 12:00 PM				
Segment	Ramp	To	Duration	End Time
Cold Kiln		72°F		12:00 PM
Leg 1	150°F/hr or 2.5°F/min	250°F for 00h 30m	01h 41m	01:41 PM
Leg 2	100°F/hr or 1.7°F/min	125°F	01h 15m	02:56 PM

Celsius Starting at 12:00 PM				
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Leg 2	56°C/hr or 0.9°C/min	52°C	01h 15m	02:56 PM

## Assumptions

It is believed that heat curing is deterministic. Any prior treatment(s) causes intermediate, transitional deformations. In other words, prior treatments do not affect the heat cure. However, parts are permanently affected if constrained during heat curing. Table 3 shows the deformations that occur when a part is prepared for investing using a heat curing treatment. The deformations are relatively uniform with slightly more shrinkage across the 0° angle.

*Table 3 Deformations from a standard heat cure*

	<b>As Modeled</b>	<b>Standard Heat Cure</b>	<b>Shrinkage</b>
<b>0°</b>	10.00 mm	9.88 mm	<b>-1.25%</b>
<b>45°</b>	10.00 mm	9.89 mm	<b>-1.08%</b>
<b>90°</b>	10.00 mm	9.92 mm	<b>-0.84%</b>

When constrained as in Figure 9, the resulting deformations are much less uniform (Table 4). The north and south cardinal positions deform as before, but the east and west cardinal positions show virtually no change. The constraint of the mold is causing the intercardinal positions to slide, which results in investment breakout.

*Table 4 Deformations from constrained heat cure*

	<b>As Modeled</b>	<b>Constrained Heat Cure</b>	<b>Shrinkage</b>
<b>0°</b>	10.00 mm	9.89 mm	<b>-1.11%</b>
<b>45°</b>	10.00 mm	9.95 mm	<b>-0.55%</b>
<b>90°</b>	10.00 mm	9.99 mm	<b>-0.15%</b>

The constrained, heat-cured parts were deemed to be a suitable analog for mold stress. The deformations matched the conceptual model derived from observed casting defects (Figure 4) and agreed with the understanding of internal stress caused by changes in surface area (Figure 5).

## Results

The first test group underwent a simple UV treatment. The surface of the part received a reasonably uniform cure as measured by the amount of curing shrinkage (Table 5). Because the cure was limited to the surface, there was a noticeable increase in rigidity.

The next group received the UV treatment followed by the boiling treatment. This is the minimum recommended treatment to prepare resin parts for casting. The UV increases the durability for handling, while boiling dissolves any investment accelerant(s). The next hypothesis covers accelerants in detail.

Boiling caused some areas to expand while others contracted (Table 6). Several factors contributed to the deformations. The heat from boiling, while not at the glass transition temperature, did have a slight annealing effect. It removed most of the increased rigidity from the UV cure. Resin parts are also permeable and absorbed some water.

The final group received UV, boiling, and annealing treatments. The deformations (Table 7) were of note. The annealing treatment removed stress and reversed the deformations of prior treatments. The parts now showed a slight amount of heat-induced curing.

*Table 5 Deformations after a 10-minute UV treatment*

As Modeled		Post UV	Shrinkage
0°	10.00 mm	9.96 mm	-0.45%
45°	10.00 mm	9.98 mm	-0.25%
90°	10.00 mm	9.97 mm	-0.33%

*Table 6 Deformations after a 10-minute boiling treatment*

As Modeled		Post UV/Boiling	Shrinkage
0°	10.00 mm	9.98 mm	-0.23%
45°	10.00 mm	10.01 mm	0.05%
90°	10.00 mm	10.03 mm	0.25%

*Table 7 Deformations after a 30-minute annealing treatment*

As Modeled		Post UV/Boiling/Annealing	Shrinkage
0°	10.00 mm	9.95 mm	-0.55%
45°	10.00 mm	9.95 mm	-0.55%
90°	10.00 mm	9.99 mm	-0.15%

Controlling the shrinkage from casting, rubber molding and finishing operations is complicated enough without introducing another vector. From that perspective, we would want to avoid the over 1% shrinkage of a heat curing treatment in favor of either a UV or boiling treatment.

However, when we compare the deformations to those of the analog, the UV treatment is least desirable (Table 8). The north and south positions contracted, pulling and elongating the east and west cardinal positions. The shifting of the intercardinal positions explains the treatment's propensity for investment breakout.

The expansion of the boiling treatment allowed for a more uniform contraction in the mold (Table 9). The estimated stress was minimal and corresponds with casting observations. The boiling treatment has proven useful for most geometries. Only marginally castable features, like trademark stamps, continued to show defects at the intercardinal position.

Annealing resulted in the least amount of stress exerted on the mold (Table 10). The only deformation occurred at the north (and south) cardinal position, contracting by just 60  $\mu\text{m}$ . With no shifting or shear forces at the intercardinal positions, the strength of the investment is likely a non-factor.

*Table 8 Stress exerted in the mold by UV cured parts*

	<b>Pre-Mold Shrinkage</b>	<b>Mold Stress</b>
<b>0°</b>	-0.45%	<b>-0.66%</b>
<b>45°</b>	-0.25%	<b>-0.30%</b>
<b>90°</b>	-0.33%	<b>0.18%</b>

*Table 9 Stress exerted in the mold by boiled parts*

	<b>Pre-Mold Shrinkage</b>	<b>Mold Stress</b>
<b>0°</b>	-0.23%	<b>-0.88%</b>
<b>45°</b>	0.05%	<b>-0.60%</b>
<b>90°</b>	0.25%	<b>-0.40%</b>

*Table 10 Stress exerted in the mold by annealed parts*

	<b>Pre-Mold Shrinkage</b>	<b>Mold Stress</b>
<b>0°</b>	-0.55%	<b>-0.56%</b>
<b>45°</b>	-0.55%	<b>0.00%</b>
<b>90°</b>	-0.15%	<b>0.00%</b>

## Further Research Needed

The analog parts were printed, cleaned, and tightly fit onto the dapping punch. There was considerable friction preventing the parts from moving on their own. Somehow they did move during heat curing. They were evenly (although minimally with groups of 12) spaced entering the kiln. When removed, they were found in clusters of two or three. The shrunken heat-cured parts were now frozen to the dapping punch and could not be removed intact.

The only explanation is that the parts expanded when entering the glass transition phase. The irregular base and the weight of the dapping block caused the now loose parts to slide together. More sophisticated equipment is needed to measure this expansion and determine its effect on the mold.

Also, as much as the investment strength appeared to be a non-factor, this was not proven. The geometries that remained prone to casting defects included marginally castable features. They were difficult to cast with injection wax. A larger casting trial is needed to compare annealing and heat-curing treatments, along with stronger 38:100 and weaker 42:100 w:p ratios.

## Discussion

Investment cannot be made sufficiently strong enough to withstand non-uniform deformations. This material has an inherently weak shear strength. Marginal changes in the investment's overall strength are inconsequential. Resin parts will relieve their internal stress during the first hold of the burnout, which presents as a shearing force at the intercardinal positions.

UV treatments should be kept to a minimum with resin parts. Longer or higher intensity exposures do not affect the subsurface of a part. The increase in surface rigidity will prevent investment reaction defects but adds stress in the process. The next hypothesis will discuss a more efficient way for preventing investment reaction without this side effect.

The boiling and annealing treatments use heat to relieve stress before the parts enter the mold. A part's resistance to movement is a function of temperature. At 72°F (22°C), 212°F (100°C), and 250°F (121°C), lower levels of stress can work out of the part over weeks, hours, and minutes, respectively.

The 10-minute boiling treatment sufficiently prepares most parts for casting. High levels of stress with enough force to shear off adequately designed pilot holes are also strong enough to relieve themselves at 212°F (100°C). The controlled cooling of the water after the treatment minimizes the remaining stress. Only parts with delicate, marginal features such as thin, inset lettering require a 250°F (121°C) annealing treatment. The fins of investment created by lettering are easily fractured by the remaining stress that could not overcome the part's viscosity at 212°F (100°C).

A common problem when heating resin parts is cracking, especially in thick sections. This can be prevented by controlling the rate of heating and minimizing the exposure to UV treatments. Plastic is a superb insulator, and heat will move very slowly through the part. A fast heating rate will soften the exterior and allow high levels of stress to burst out of the part.

The boiling treatment was also shown to reduce cracking significantly during subsequent annealing and heat-curing treatments. Water transfers heat to the part much more efficiently and uniformly than air. It also arrests the temperature and, therefore, the viscosity of the part, allowing higher levels of stress to exit the part slowly and safely.

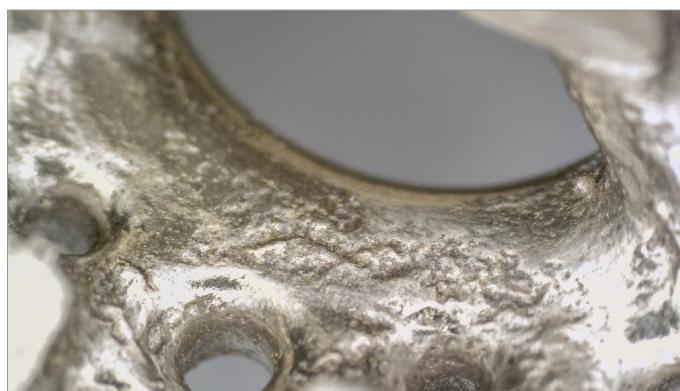
Isopropyl alcohol and especially acetone are also known to cause cracking and crazing. The solvents penetrate the part during cleaning and weaken the polymer. This is especially true when heat is added. The increased kinetic energy accelerates the damage. A three-minute cleaning is recommended using a sealable plastic bag, fresh isopropyl alcohol, and an ultrasonic. Removing the excess air from the bag allows a dozen parts to be cleaned with less than 100 mL of solvent. The parts should be rinsed in water and allowed to dry before exposure to heat.

## HYPOTHESIS #2: THE SETTING SPEED OF THE INVESTMENT IS LOCALLY AFFECTED BY RESINS.

Resins are permeable to solvents. Investment reaction defects occur when the free water in a flask leaches constituent components from resins. The reaction results in a weakened matrix. The mold will contain loose particles of investment that contaminate the cast metal. It can also weaken entire features, such as pilot holes.

UV curing can be used to vitrify or harden the part. A sufficiently hardened surface is much less permeable and limits investment reaction defects. However, the prior hypothesis showed the side effects of these UV treatments. While typical geometries will cast successfully, the added stress increases the probability of investment breakout.

Annealing reverses the surface hardness and stress induced by UV treatments. One such protocol was used in production and survived the holiday season with a 100% success rate. After four months, defects like the one pictured in Figure 10 began to appear. A month-long autopsy revealed a single, insignificant change. The duration of a heated ultrasonic bath had been shortened.



*Figure 10 Underside of a halo contaminated with investment*

Freshly printed parts had always been cleaned in an ultrasonic, but it was never considered part of a treatment protocol. It was not thought to have an impact, nor was it controlled and recorded in casting logs. However, performance returned to normal once the duration of cleaning was extended.

At first, the ultrasonic was considered. Energy, in the form of heat and acoustic waves, was being delivered to the part. Research also showed that ultrasonics cure and improve the mechanical properties of photoinitiated epoxy resins.<sup>6</sup> More research is needed on the effect of acoustic waves on castable resins, but it was not a factor in this case. When the fluid was changed from water to mineral oil, the defects reappeared.

Exposure to water was studied in isolation and found to be the critical factor. It was known that microwave curing in water was used by some casters, while others found it ineffective. This inconsistency was reasoned to be a difference in microwave energy. A pattern emerged when interviews were conducted. If the water was refreshed between heating cycles or used in large volumes, the treatment was effective.

Water, the universal solvent, was dissolving something from the resin. If left to dissolve in the mold, it caused localized weakness in the investment interface.

## Additives in Gypsum-based Investments

Where gypsum is mined and how it is prepared will affect its properties.<sup>7</sup> No two batches of prepared investment are the same. Investment manufacturers closely monitor the raw materials and use additives to ensure consistency.

They maintain a uniform setting speed by varying the quantity of accelerant added to each batch of investment. A number of chemicals are known to either accelerate or retard the setting speed of investment.<sup>8</sup> Boric acid is an accelerant commonly used for stone-in-place casting that can cut the working time in half. Retarders like tartaric acid are not used because the additional time would allow water to separate out of the matrix and stain the castings.

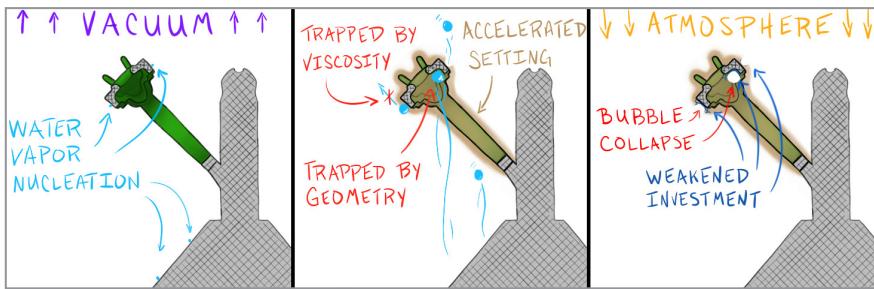
## Resin Additives Affect the Setting Speed

Different geometries were cast without exposure to water to study the defect. They were found primarily on downward-facing surfaces and were most pronounced in cavities. The concave side of a domed ring would show severe metal contamination while the convex outside showed none.

The pH of the resin was considered as the cause. The investment in a cavity was exposed to more surface area of resin and could explain the prominence of the defect. However, it could not explain the directional nature of the defects. A flat surface showed defects when facing the bottom of a flask but not when facing the top.

## Mode of Failure

A conceptual model of the defect was developed (Figure 11). If the resin leached an accelerant(s) into the investment, a skin of thicker investment would develop around the part. The skin would have a shortened working time. Once set, any disturbance would compromise its integrity.



*Figure 11 Cross-section of a flask during vacuuming*

This happens when the flask is vacuumed to remove air. The pressure in the chamber drops and the flask boils. Rising bubbles collect in cavities, filling them with water vapor. The increased viscosity of the skin prevents bubbles from flowing around them. When the chamber returns to atmospheric pressure, these vapor bubbles collapse, causing an inrush of liquid investment.

Bubbles on upward-facing surfaces do not experience as much drag. They are gently displaced to the flask's surface. This is far less damaging than when a large bubble(s), trapped in the bridge of the ring, collapses quickly. The inrush of liquid investment will punch the bridge's skin, causing severe, localized weakness.

## Testing

The first tests proved that a localized accelerant could cause these kinds of defects. Salt (NaCl) was known to accelerate the setting speed by threefold.<sup>8</sup> Parts were placed into a saturated solution and boiled on a gas burner. The location of casting defects was consistent with the conceptual model. They were also much more pronounced.

Subsequent tests proved this to be causal. The setting of the skin was isolated from the setting of the flask via shell casting. A paintbrush was used to coat subjects with a thin layer of investment. While this was not a practical solution (great care must be taken not to disturb the investment after its contact with resin), the castings were free from defect.

Finally, the effect of handling and speed of vapor bubble collapse were analyzed. Three identical parts were cast in separate flasks. The first flask was not vacuumed. It was prepared by wetting and hand mixing the investment for one minute, mechanically mixing for two minutes, and vacuuming the mixing bowl for one and a half minutes before being poured and allowed to rest.

The second and third flasks received an additional two minutes of vacuuming in the flask. The vacuum chamber was modified to allow atmospheric pressure to re-enter quickly via a quarter-turn ball valve or slowly through a needle valve.

Figure 12 shows the results. The delicate zig-zag texture seen was oriented down. The non-vacuumed flask had a five-minute working time and did not exhibit the

defect. The other two flasks were vacuumed, which increased the working time to eight minutes. When the pressure was released slowly via the needle valve, the defects were minimal. The quick-release flask showed a complete disruption of the pattern.



**Figure 12** Top: no vacuum; middle: slow release; and bottom: fast release of vacuum

## Discussion

A boiling treatment has since become standard practice for production castings. This treatment has proven to eliminate all downward-facing defects. Any remaining metal contamination was found to be the result of ash, which mimicked the appearance but not necessarily the placement of accelerant defects. It is recommended that casting trees be analyzed before disassembly to accurately diagnose the cause of defects.

Downward-facing defects should also occur more frequently towards the top of a casting tree. When water boils on a stove, the bubbles are created by heat at the base. Bubbles form in a vacuum from a drop in pressure. The top of the flask may be seen to boil rapidly, but the weight of the investment increases the pressure with depth. There are few bubbles three inches into the flask. In a near vacuum at

72°F (22°C), it is estimated the flask will exceed the vapor pressure and saturation pressure of water at a depth between 5.2"-5.4" and 7.2"-7.4", respectively.

Only two variables are tightly controlled for the boiling treatment: the time held at a roiling boil and rate of cooling. Use of a timer is mandatory. Under no circumstances should the pot be allowed to boil dry. A loose-fitting lid will minimize the loss of water through evaporation.

Ten minutes was found to be a sufficient duration in these tests using tap water at sea level. A large ratio of water to resin parts (250 mL to 1 cm<sup>3</sup>) was targeted but not measured. The differences in local tap water and altitude may require the use of purification or longer hold times.

Rapid cooling creates stress in plastic. The water should be allowed to air cool slowly. Parts may be safely removed at 150°F (66°C), which can take upwards of 45 minutes. To accelerate the process for rush castings, slowly add or remove water over a ten-minute span.

This treatment may not be appropriate for resins containing wax. The wax may soften and bleed into fine details. Extended exposures at lower temperatures can be used, possibly one hour at 125°F (52°C) in an ultrasonic. It is also possible that it is unnecessary. Depending on the resin, it may contain wax in place of an accelerant. The wax could also act as a barrier to water during treatment and in the flask.

It should also be noted that adding wax does not guarantee an increase in castability, but it does complicate every part of the process. If reducing the quantity of monomer was beneficial, then it would be better to print and cast hollow forms.

Although the exact mechanism is unknown, aging was shown to resolve these defects. It is possible the accelerant(s) oxidizes over time, though heated annealing was not shown to be effective. They may also volatilize, which is more likely to happen with vacuum curing.<sup>9</sup> The controlled radiant heating is also ideal for annealing the parts prior to casting. It should be noted that none of the five resins tested were ever observed bonding with the investment during dissection.

### **HYPOTHESIS #3: YOU CAN ONLY PREVENT ASH. ONCE CREATED, NEITHER TIME, TEMPERATURE NOR MECHANICAL PROCESS WILL PREVENT DEFECTS.**

Burnouts that use slow heating rates will produce ash. While every resin has a different thermal profile, most will start to show signs of incomplete combustion, or charring, around 400°F (204°C) before combusting efficiently at 800°F (427°C). A prolonged exposure between these two temperatures guarantees the production of ash.

With traditional wax casting, the majority of the wax melts and exits the mold. The small amount that remains seeps into the pores of the investment. These small pockets of carbon atoms require a significant amount of energy, namely two or more hours at 1350°F (732°C), to be removed.

Resin parts remain in the mold cavity. Incomplete combustion creates ash in the form of very durable and long chains of carbon atoms. Heat is not able to solve this problem. The energy required to shake these chains apart would destroy the mold.

Mechanical processes like vacuuming are also ineffective. The airflow follows the path of least resistance and will bypass many of the ash deposits. When resin parts are observed decomposing in a dish, they remain as a single body. The whole part shrinks into a miniaturized carbon skeleton. The mold does not allow this. The dissection of flasks showed that small features like prongs or inset letters gripped the ash body, tearing it into small pieces.

Some ash deposits were also seen to adhere to the mold. In a ceramic clay dish, there would be a single globular deposit left with the ash skeleton. This bonded with the clay, and a grinding wheel was required for removal. When the ash body is broken into many small pieces in the mold, the same color deposits were found in the investment (Figure 13).



*Figure 13 Stain surrounding possible globular residue on the mold wall*

In short, ash is permanent. Once created, it cannot be removed. The only solution is to prevent ash by minimizing the time spent under pyrolysis. We must proceed from 400°F (204°C) to 800°F (427°C) as quickly as possible. Unfortunately, water makes this a complicated task.

Traditional burnout programs are not suited for resin casting. A non-uniform thermal gradient remains until the second hold at 700°F (371°C). The flask's core temperature is arrested by free (212°F/100°C) or chemical (392°F/200°C) water well into the second hold. Only then does the thermal gradient become linear and uniform.

Many casters prefer the consistent, minimal ash defects offered by a slow burnout over the seemingly random, intense ash defects that can occur with a fast burnout. These defects are commonly blamed on thermal expansion but are produced

when combustion is abruptly halted. Extinguishment is intensely carbonizing, and it is the worst-case scenario for ash production.

With any burnout, a long, thin prong on a ring is often found to have ash defects. This occurs when it is sprued too close to the flask wall. It combusts early and, with little mass, it is unable to propagate combustion to the ring body. Faster burnouts can cover the entire mid-shank of a ring with the same defects (Figure 1). In this case, combustion reached an area of investment several hundred degrees cooler and is extinguished by thermal inhibition.

The flask must be free of water before combustion begins. Water removal takes time because it requires the conduction of a considerable amount of energy through an insulator. Attempting to minimize the duration of pyrolysis further impedes the process by constraining the temperature to below 400°F (204°C).

Water has an exceptionally high heat capacity. A considerable amount of energy is required because water molecules can store a considerable amount of energy. Unfortunately, evaporation cools the mold. Once the molecules have enough energy to become water vapor, that kinetic energy leaves the mold with the molecule.

While water is an excellent thermal conductor, the flask dries from the outside. Once the flask wall is free of water, the insulating investment is left to transfer heat to the wet core slowly. This is why water cannot boil in the mold. The energy transfer is too slow. Water evaporates and either finds a path out of the mold or condenses back into a liquid if the pressure increases.

The goal of these tests is to establish a baseline for water removal and investigate ways it can be accelerated. Each test builds off of the previous, seeing how a change in the burnout program, kiln or investment influences the drying efficiency of the mold.

## Testing Setup

A single 3" x 3" flask was invested without any treed parts. The only thing it contained was a jig holding eight Type K thermocouple probes (Figure 14). The probes, jigs and data logger were color-coded to prevent confusion during setup and testing (Figure 15).

The location of the probes was selected to overlay a typical part geometry (Figure 16). This geometry was not in the flask during testing. The probe readings could then be used to show the part's temperatures as if it were cast with the test protocol (Figure 23).

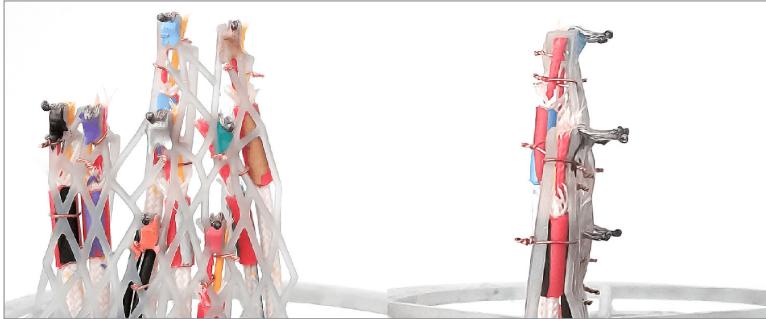


Figure 14 Color-coded jig used to ensure probe placement



Figure 15 Color-coded data loggers

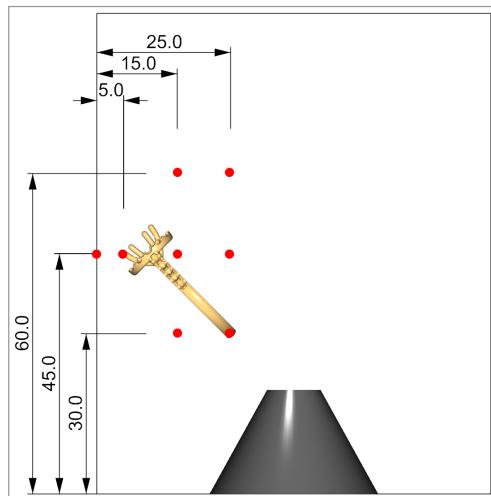


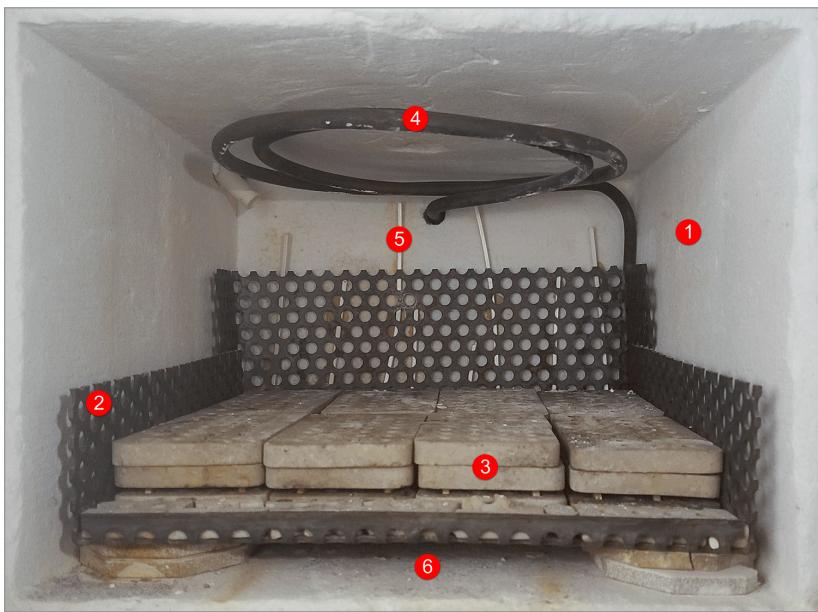
Figure 16 Points for thermocouple probes selected to overlay typical geometry

The row of four points elevated 45 mm from the base of the flask was used to assess the thermal gradient. The first point was in contact with the flask wall. The second point was 5 mm from the wall. This simulated a prong that was sprued with improper spacing. Points three and four were placed 15 mm and 25 mm into the flask, respectively.

The flask was placed in the back right corner of the kiln. It was given 1" of space from each wall. It was oriented with the jig perpendicular to the right and parallel to the rear heating elements. The PID's thermocouple was immediately in front and above the flask.

The kiln was modified for resin casting as seen in Figures 17 and 18. Certain modifications were only employed in specific tests. The full list includes:

1. Location of kiln controller's thermocouple
2. Flasks elevated 1" by a stainless steel tray with one layer of ceramic briquettes (Figure 19)
3. Flasks elevated 1.63" by two additional layers of briquettes
4. Coiled stainless steel brake line to pre-heat forced air and diffuse at kiln floor
5. Eight fine silver, 2.5 mm<sup>2</sup>, L-shaped conductors to transfer heat from rear kiln wall to briquette floor
6. Location of cold air intake



*Figure 17 Interior of kiln*

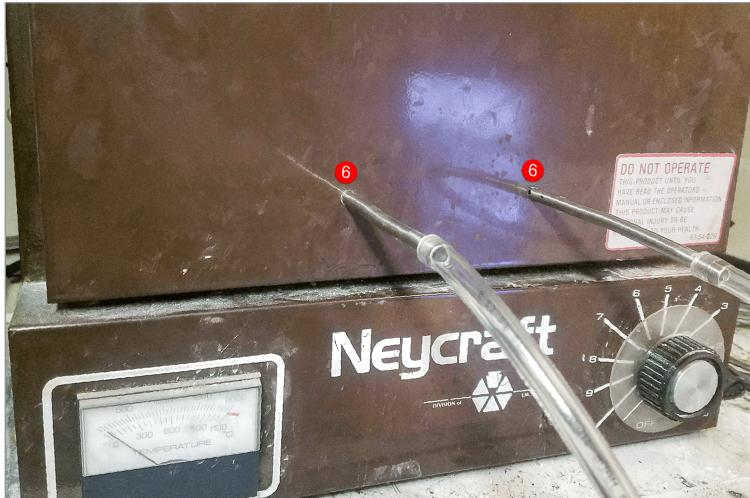


Figure 18 Exterior of kiln



Figure 19 Ceramic BBQ briquettes

Air was pumped into the kiln by an EcoPlus commercial air pump rated at 50 L/min, although the measured airflow was considerably less. An argon flow meter (Figure 20) measured the air, and the entry point to the kiln could be controlled by a manifold (Figure 21). The estimated flow of atmospheric air was 19 L/min for pre-heated and 20 L/min for room temperature air.

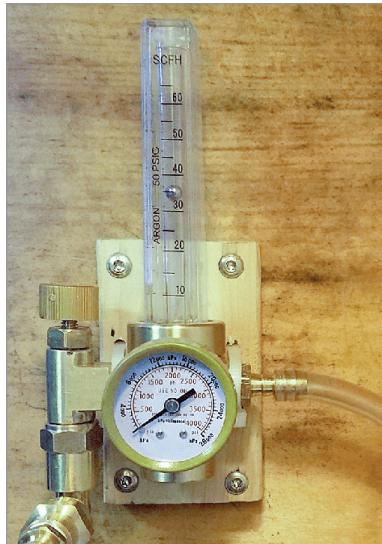


Figure 20 Airflow gauge



Figure 21 Manifold to switch between pre-heated air (top) or cold air (bottom)

The maximum heating rate of the kiln was measured. The speed varied considerably by temperature. This required the programmed ramp rate to be divided into multiple segments (Tables 11–13).

Three burnout programs were used during testing. They all feature a fast ramp rate after the initial hold(s). The first program used a traditional two-hour hold for wax and water removal at 350°F (177°C) (Table 11). The second program increased the initial hold to four hours (Table 12). The final program uses a three-hour hold at 350°F (177°C) before slowly ramping to 500°F (260°C) (Table 13).

*Table 11 Two-hour hold burnout program*

Fahrenheit				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		72°F for 02h 00m	02h 00m	02:00 PM
Leg 1	350°F/hr or 5.8°F/min	350°F for 02h 00m	02h 47m	04:47 PM
Leg 2	1,650°F/hr or 27.5°F/min	625°F	00h 10m	04:57 PM
Leg 3	1,150°F/hr or 19.2°F/min	925°F	00h 15m	05:12 PM
Leg 4	900°F/hr or 15.0°F/min	1,100°F	00h 11m	05:23 PM
Leg 5	400°F/hr or 6.7°F/min	1,250°F for 02h 00m	02h 22m	07:45 PM

Celsius				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		22°C for 02h 00m	02h 00m	02:00 PM
Leg 1	194°C/hr or 3.2°C/min	177°C for 02h 00m	02h 47m	04:47 PM
Leg 2	917°C/hr or 15.3°C/min	329°C	00h 10m	04:57 PM
Leg 3	639°C/hr or 10.6°C/min	496°C	00h 15m	05:12 PM
Leg 4	500°C/hr or 8.3°C/min	593°C	00h 11m	05:23 PM
Leg 5	222°C/hr or 3.7°C/min	677°C for 02h 00m	02h 22m	07:45 PM

*Table 12 Four-hour hold burnout program*

Fahrenheit				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		72°F for 02h 00m	02h 00m	02:00 PM
Leg 1	350°F/hr or 5.8°F/min	350°F for 04h 00m	04h 47m	06:47 PM
Leg 2	1,650°F/hr or 27.5°F/min	625°F	00h 10m	06:57 PM
Leg 3	1,150°F/hr or 19.2°F/min	925°F	00h 15m	07:12 PM
Leg 4	900°F/hr or 15.0°F/min	1,100°F	00h 11m	07:23 PM
Leg 5	400°F/hr or 6.7°F/min	1,250°F for 02h 00m	02h 22m	09:45 PM

Celsius				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		22°C for 02h 00m	02h 00m	02:00 PM
Leg 1	194°C/hr or 3.2°C/min	177°C for 04h 00m	04h 47m	06:47 PM
Leg 2	917°C/hr or 15.3°C/min	329°C	00h 10m	06:57 PM
Leg 3	639°C/hr or 10.6°C/min	496°C	00h 15m	07:12 PM
Leg 4	500°C/hr or 8.3°C/min	593°C	00h 11m	07:23 PM
Leg 5	222°C/hr or 3.7°C/min	677°C for 02h 00m	02h 22m	09:45 PM

*Table 13 Slow to 260°C (500°F) burnout program*

Fahrenheit				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		72°F for 02h 00m	02h 00m	02:00 PM
Leg 1	200°F/hr or 3.3°F/min	350°F for 03h 00m	04h 23m	06:23 PM
Leg 2	100°F/hr or 1.7°F/min	500°F for 01h 00m	02h 30m	08:53 PM
Leg 3	1,300°F/hr or 21.7°F/min	900°F	00h 18m	09:11 PM
Leg 4	800°F/hr or 13.3°F/min	1,100°F	00h 15m	09:26 PM
Leg 5	400°F/hr or 6.7°F/min	1,250°F for 02h 00m	02h 22m	11:48 PM

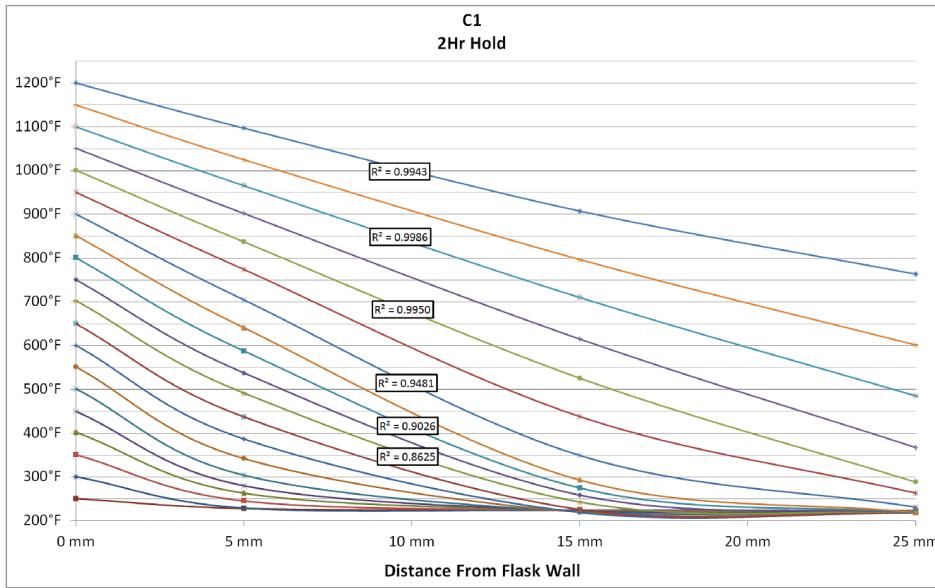
Celsius				Invested At 12:00 PM
Segment	Ramp	To	Duration	End Time
Bench Cure		22°C for 02h 00m	02h 00m	02:00 PM
Leg 1	111°C/hr or 1.9°C/min	177°C for 03h 00m	04h 23m	06:23 PM
Leg 2	56°C/hr or 0.9°C/min	260°C for 01h 00m	02h 30m	08:53 PM
Leg 3	722°C/hr or 12.0°C/min	482°C	00h 18m	09:11 PM
Leg 4	444°C/hr or 7.4°C/min	593°C	00h 15m	09:26 PM
Leg 5	222°C/hr or 3.7°C/min	677°C for 02h 00m	02h 22m	11:48 PM

## Thermal Conductance Tests

Instead of plotting the temperature of the flask over time, each line in Figures 22, 24, 25, 26, 28, 29 and 31 represents a specific moment in time. This shows whether the interior of the flask is able to follow the temperature at the flask wall or is being arrested by water. Straighter lines that are evenly spaced indicate better results.

The flask temperature was plotted for each increase of 50°F (28°C) at the flask wall. Each plot contains the four probes at the 45 mm elevation (Figure 15). A linear regression analysis was performed on these measurements. A coefficient of determination ( $r^2$ ) of 1.00 would mean the thermal gradient is perfectly linear at that moment. The probes could not be positioned with that level of accuracy. The 1200°F plot should be considered when comparing plots from different tests. At this temperature, all of the tests were linear. The difference in  $r^2$  indicates the accuracy of the probes placement.

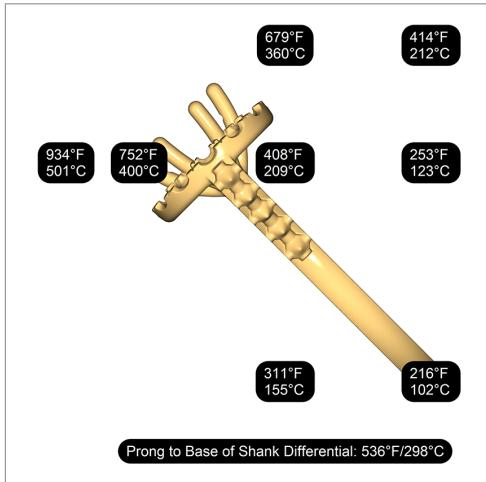
The first test was C1. It demonstrates why a standard burnout program should not be modified with a fast ramp rate (Table 11). The flask was mixed with a w:p ratio of 40:100. The kiln was static; no air was pumped in or circulated. The flask was elevated 1" from the kiln floor, and the two-hour hold was used.



*Figure 22 C1: Fast burnout with a two-hour hold*

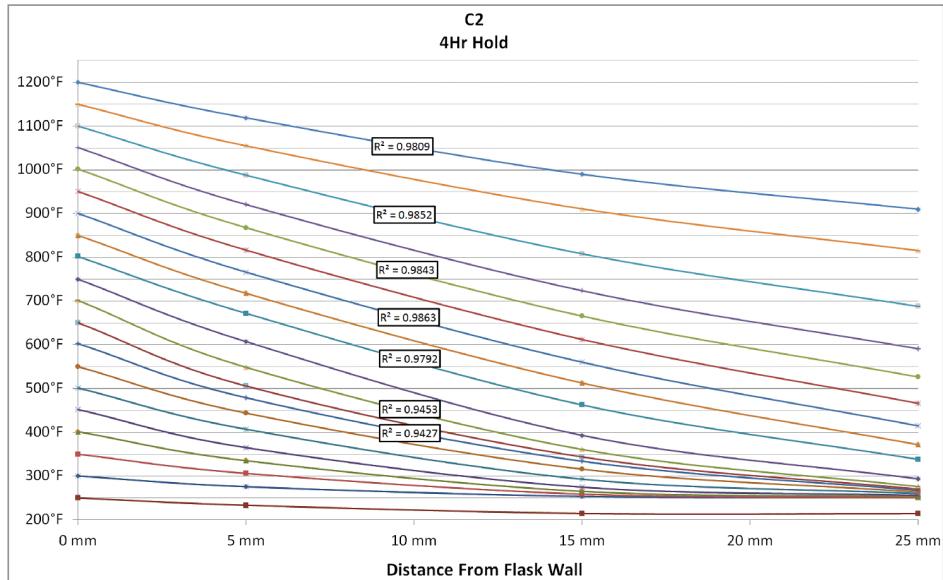
A fast burnout after a two-hour hold induces a significant thermal gradient. The center of the flask remains wet until after the flask wall reaches 1000°F (538°C). Every resin part in the flask would have ash defects.

Figure 23 illustrates this problem. As the prong begins to combust at 750°F (399°C), it does not have enough mass to propagate combustion to the halo with its temperature at 400°F (204°C). Combustion will extinguish and leave an ash deposit on the prong. This intensely carbonizing cycle will repeat at least two more times given the amount of thermal inhibition that is baked into the flask.



*Figure 23 C1: Combustion cannot propagate through the part*

There is one difference between tests C1 and C2. The initial hold of the burnout was increased from two to four hours (Table 12). This showed improvement (Figure 24), but would not work for production casters. They use a wall clearance of 7–9 mm for sprued parts. With C2 being free of water at 900°F (482°C), parts would need at least 15 mm of clearance to burn out cleanly.



*Figure 24 Fast-burnout with a four-hour hold*

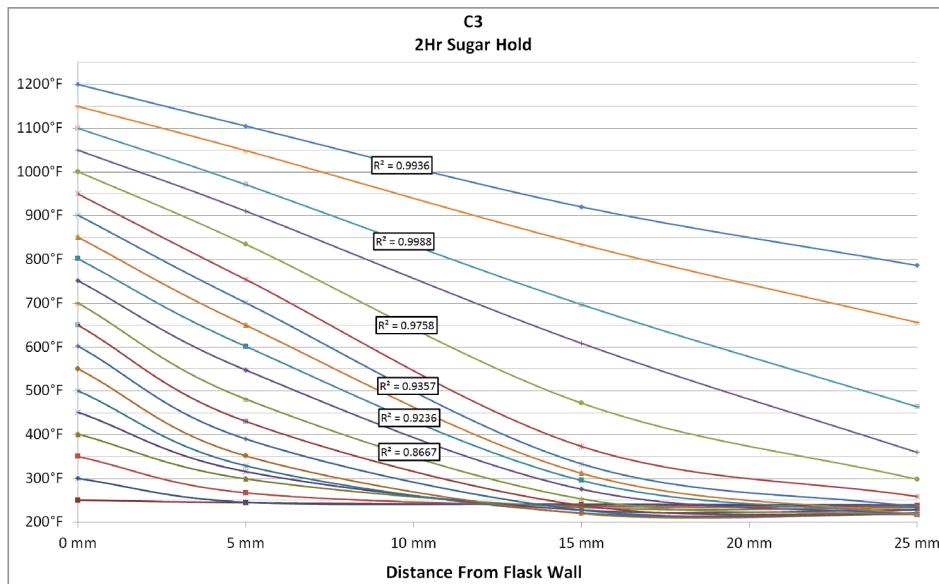
Longer initial holds are imperative when working with resins. This is likely the improvement seen in "The Quest for the Perfect RP Burnout."<sup>2</sup> Andrews held his flasks below 400°F (204°C) for a total of six hours and twenty minutes. This likely eliminated all free water prior to ramping.

Additives were discovered to expedite the removal of water. Sugar acts like a liquid while it thermally decomposes. This increases the thermal conductance of the investment. It also has a high heat capacity. Unlike when water evaporates and cools the flask, sugar makes the heating process more efficient. It stores energy to feed the evaporation rate of water. These increases in conduction and efficiency allow more flasks to be burned out at once.

While additives like sugar are promising, more research is needed before they can be recommended. This investigation's research into sugar is invalid as it occurred prior to the discoveries outlined in the prior hypotheses. Its effect on mold strength needs to be re-examined.

Sugar was added at 3 g for each 100 g of investment, along with the 40 g of water in C3. If a four-hour hold was used with a single flask, C3 would have outperformed any other test. The initial hold was reduced (Table 11) to illustrate another aspect that requires study.

Normally, free water arrests the flask temperature around 212°F (100°C). Sugar increases the arresting temperature to 230°F (110°C). However, if the sugar is exhausted prior to the free water, the temperature of the flask will drop back to 212°F (100°C). This can be seen at the 550°F (288°C) line in Figure 25.



*Figure 25 Sugar increases the thermal conductance until exhausted*

If a ratio of sugar to w:p is found of the appropriate strength, then an initial hold will need to be designed. Given the increased conduction and elevated arresting temperature of 230°F (110°C), a two-stage hold of 250°F (121°C) and 400°F (204°C) would likely delay the decomposition of sugar until both free and chemical water are removed from the mold. This should be independent of the kiln load.

Until more research is done on additives, C4 is recommended for resin casting. It uses a four-hour hold with an additional mode of heat transfer. Anecdotal reports have suggested that gas-fired kilns outperform electric when casting resins. The reason stated is that oxygen is depleted in a static kiln, while the flow of gases creates a more suitable atmosphere for combustion. While gas-fired kilns likely outperform static electric kilns, it cannot be due to oxygen levels.

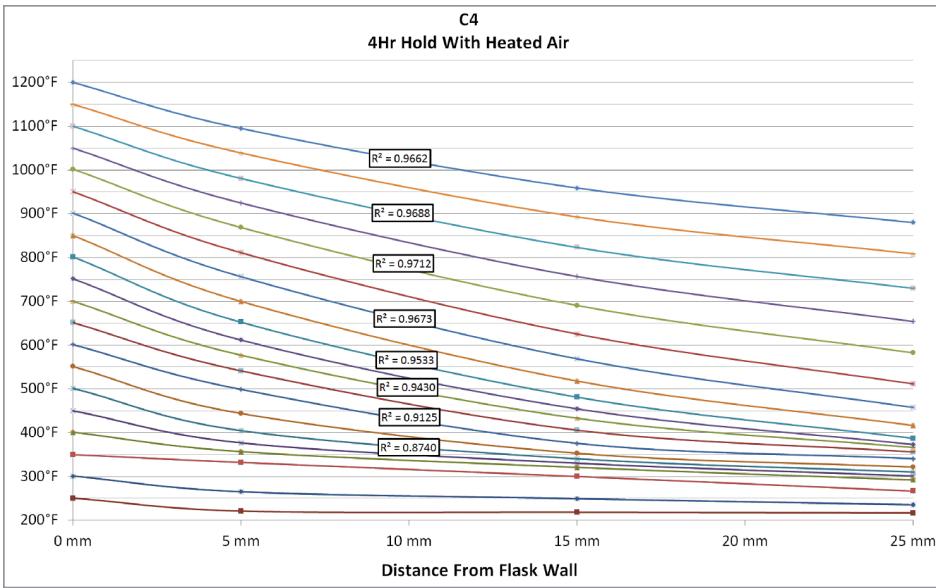
The 2002 Santa Fe Symposium® paper by Aithal, Busby and McCloskey, "Evaluation of Mold Burnout By Temperature Measurement and Weight Loss Techniques,"<sup>10</sup> showed that the ramp in temperature limits oxygen levels in a gas-fired kiln. More oxygen is consumed by the burner as it heats the kiln. The oxygen level fell from 13% to 8% during the period where resin combustion is expected. In the static electric kiln, oxygen levels remained at atmosphere through most of the burnout, only dipping to 18% at the height of wax combustion.

The paper also showed that gas-fired kilns dried the flasks nearly twice as fast. The authors suggest the principal factor was the heating capacity of the ovens. The gas-fired kiln was rated at 125,000 BTU/hour versus the 13,000 BTU/hour of the electric kiln. While this is indeed a significant disparity, both handily maintained a consistent temperature of 300°F (149°C) during the initial hold.

The critical difference between electric and gas-fired kilns is the dominant mode of heat transfer. For an electric kiln, this is conduction at lower temperatures. Gas-fired kilns heat by convection, which is significantly more efficient at transferring energy. Convection allowed the flasks to dry twice as fast during the initial 300°F (149°C) hold.

The only difference between tests C2 and C4 is the addition of convective heating. Approximately 19 L/min of room temperature atmospheric air was pumped into the kiln through a stainless steel brake line. The line was coiled below the upper heating element which pre-heated the air. It then ran to the kiln floor where perforations dispersed the air evenly.

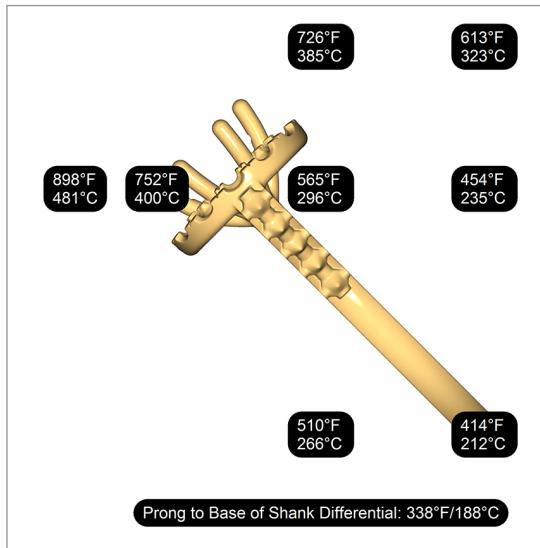
This small amount of convection proved more efficient using the same kiln and burnout program as before (Figure 26). At the end of the four-hour hold, the probe located at the base of our imaginary shank measured 248°F (120°C) in C2 and 288°F (142°C) in C4. The difference of 40°F (22°C) is small but significant.



*Figure 26 Pre-heated airflow removes water fastest*

There are two points where a flask's temperature is arrested, and a jump in temperature can be seen. The first occurs when all of the free water is removed at 212°F (100°C). The second is at 262°F (128°C). This is when gypsum converts from calcium sulfate dihydrate ( $\text{CaSO}_4 + 2 \text{ H}_2\text{O}$ ) to calcium sulfate hemihydrate ( $\text{CaSO}_4 + \frac{1}{2} \text{ H}_2\text{O}$ ). The remaining water has a minimal impact on temperatures and is removed at 392°F (200°C).

C4 performed very well with the fast ramp rate. Figure 27 shows the probe temperatures when it would have entered combustion. Even when our imaginary prong tip is located too close to the flask wall, combustion is likely to propagate through the part. The base of the shank is at 414°F (212°C), while in C2 it was 330°F (166°C). Adequately spaced parts would experience even less thermal inhibition.



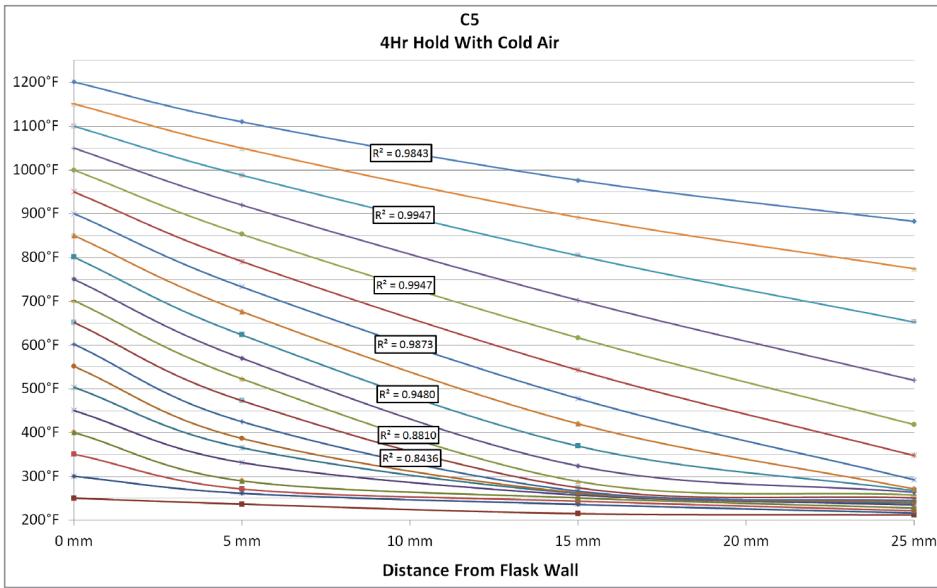
*Figure 27 Pre-heated airflow reduces the thermal inhibition during combustion*

A number of casters add cold, room-temperature air to the base of their kiln. This was known to impact the thermal gradient of the flasks negatively. An attempt was made in C5 to warm the inflow of cold air at the kiln floor.

The airflow was increased slightly from 19 L/min to 20 L/min in C5. The floor was raised by two additional layers of ceramic briquettes, bringing the elevation to 1.63". Fine silver wire conducted heat from the rear wall to the briquettes.

The mitigation showed a slight improvement, but the cooler airflow negatively impacted the mold (Figure 28). The static kiln from C2 outperformed C5 in water removal. However, the airflow did affect the flask. This may improve oxygen levels in the mold.

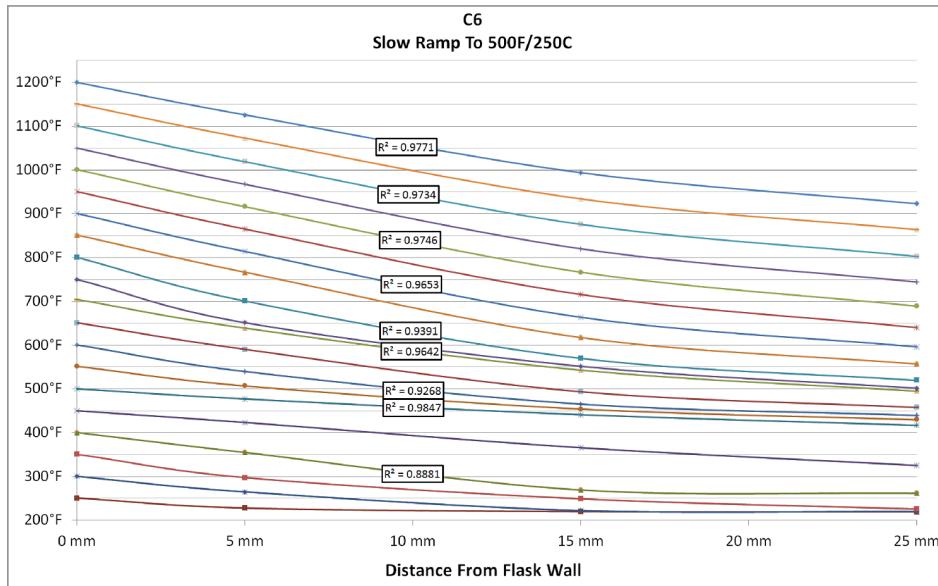
Evidence for this was observed during casting trials. The static kiln used in C1, C2, and C3 produced a noticeable odor that lingered in the casting room after burnout. A lingering odor was not found with the added airflow in C4 through C7. This suggests an overall improvement in combustion. Further study is required on this topic.



*Figure 28 Fine silver conductors and forced cold air*

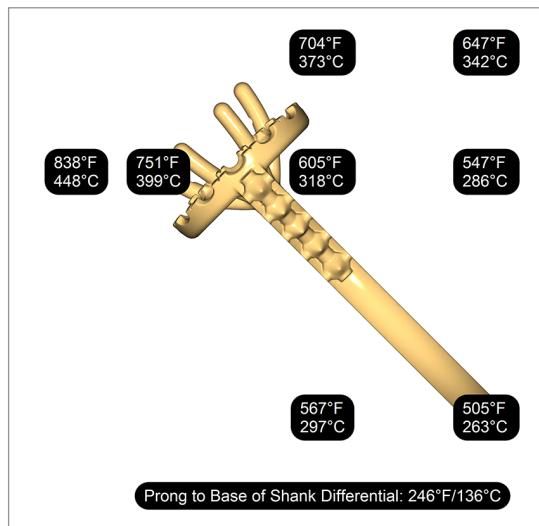
The only change between C5 and C6 was the burnout program used (Table 13). The initial four-hour hold is reduced to three hours, before slowly ramping to 500°F (260°C) for one hour. It is recommended that a slight amount of charring be allowed if the airflow cannot be pre-heated. In exchange, the investment is converted from calcium sulfate hemihydrate ( $\text{CaSO}_4 + \frac{1}{2} \text{H}_2\text{O}$ ) to anhydrite. This frees the mold of all water.

The thermal gradient produced was the most uniform out of all the tests (Figure 29). This arrangement performed exemplary when used in production for six months. The only ash defects found were attributed to an overloading of the kiln.



**Figure 29** Slow ramp to 500°F (250°C) with cold air

Figure 30 shows the temperature profile of the flask when combustion begins with C6. It is very tolerant of typical geometries that are placed too close to the flask wall. It is important to note that this tolerance can be reduced if the part interrupts the flow of heat from the flask wall.

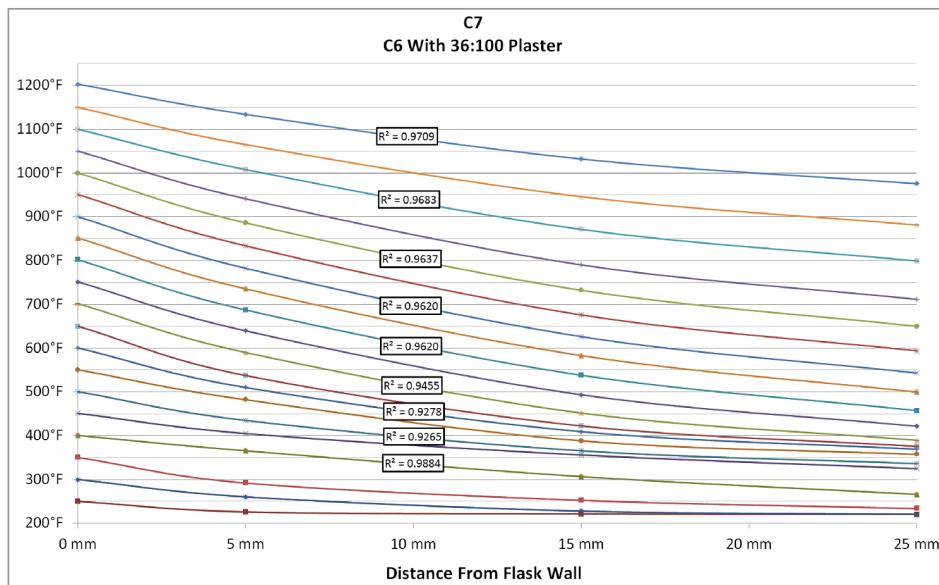


**Figure 30** Cold air requires a hotter, slightly carbonizing hold prior to ramping.

Consider a 30 mm disk pendant that is 2 mm thick. The thermal conductivity of plastic is considerably less than that of the mold. If the disk is oriented to face the flask wall directly, heat must travel around the entire part. This delays water removal and was found to produce ash consistently. When the pendant is sprued vertically facing the ceiling, the heat transfer from the wall is mostly unaffected.

The investment's strength, namely the w:p ratio, was shown to have no effect on a part's castability in the previous hypothesis. However, it was found to affect ash production. A decrease in water (increase in strength) significantly slowed the rate of water removal.

The only change from C6 to C7 was the w:p ratio. It was reduced from 40:100 to 36:100. While the 500°F (260°C) hold in C6 was able to drive off all the water, it remained until the flask wall reached 800°F (427°C) in C7 (Figure 31). This is counterintuitive for a few reasons. Lower w:p ratios contain less water by definition. More interestingly, lower w:p ratios increase the thermal conductance of the investment.



*Figure 31 Denser investment lessens convection and increases conduction*

With less water and more thermal conductance, the flask should dry faster, but it does not. Water influences the void space, or the porosity, in the mold. As water evaporates, it leaves a pocket of air in its place. The mold is stronger and more conductive with smaller pockets of insulating air.

However, decreased porosity also restricts the movement of water vapor and air through the investment. When water evaporates, the vapor molecules bounce aimlessly through the maze of gypsum and refractory materials. A denser maze requires more time to navigate.

C7 was also shown to be minimally impacted by convection. The flow of heated air was restricted from entering the mold. This could also lead to oxygen depletion during combustion. Combustion gasses and soot have a harder time escaping the mold, which draws in fresh air.

## DISCUSSION

Ash has proven incredibly durable and difficult to mitigate. The only successful strategy is to prevent carbonization. The first and most important step towards that goal is ensuring flasks become free of water during the first hold. Water arrests the flask temperature, and extinguishment from thermal inhibition creates severe ash deposits.

The point at which flasks are ready to ramp up to combustion temperatures is not apparent. Many factors, including the kiln load, w:p ratios, flask diameter, and airflow, influence the rate of water removal. Large production casters will likely opt for a more forgiving, slow burnout. The added time and heat holds parts under light pyrolysis but eliminates water efficiently and safeguards against extinguishment. This produces a consistent and acceptable amount of ash.

Small batch casters are better suited to a fast, ash-free ramp up to combustion temperatures. They can hone their settings and tailor burnouts to a given workload. The tests performed in this study show how a single 3"x 3" flask responds to specific variables. The demonstrated behavior is intended to increase understanding and enable craftsmen in discovering their optimal settings. Casters can verify their burnout with an inexpensive pyrometer by measuring the temperature of each flasks' sprue hole after the initial hold. Flasks are adequately prepared for a fast ramp rate once water ceases to arrest their core temperature (262°F/128°C).

The convective heating of gas-fired kilns is the most efficient method for water removal. Static air conducts heat poorly because its molecules are spaced far apart. It takes time for one energized air molecule to bump into another, which imparts some of its energy. A convective airflow increases the rate at which molecules contact and, therefore, the speed of energy transfer to the flasks. Convection overcomes the limitations of air without raising the temperature.

Water removal in electric kilns without a forced flow is much more difficult. Electrical heating elements glow, sending out waves of radiant energy. The waves pass through the air until they are absorbed by the kiln walls and steel flasks. These irradiating surfaces then warm the air. A small current is created as hot air rises, making the top of a kiln several hundred degrees hotter than the bottom. The elevation of the kiln's thermocouple can cause the actual temperatures of the flasks to be significantly different from the reported temperature of the kiln.

Consider what happens in an overloaded electric kiln during water removal. Flasks in the rear corners of the kiln face two heating elements and receive twice the radiant energy of those facing only one. More importantly, flasks packed into the center are in the shadow of other flasks and are shielded from radiant energy. This creates another difference of several hundred degrees between those flasks.

Static air cannot conduct heat fast enough to make up for this uneven distribution. It is possible for flasks exposed to two heating elements to be producing ash at 500°F (260°C), while the kiln reads 350°F (177°C) and flasks in the center remain below 250°F (121°C).

Adding convection will improve the energy distribution and efficiency of an electric kiln during water removal. Pumping cold air into the kiln will not. Cold air will fall to the kiln floor and displace hot air. This essentially vents energy out of the kiln rather than improving the energy distribution. Any added air must be channeled to move heat from the top of the kiln to the floor.

Resin parts should be cast with the higher recommended w:p ratios for an investment. This is contrary to a core tenant of resin casting. Lower w:p ratios are frequently employed to increase the investment strength. This is scarcely effective, and the perceived gains are at the real expense of ash production.

Finally, the spacing of parts and their orientation in a flask must be considered. Anything placed too close to the flask wall will combust early and extinguish, causing intense carbonization. Plastic is also an exceptional insulator. As heat travels from the flask wall, a large surface will shield the investment behind it. This requires heat to flow around the part to reach the investment in its shadow.

## **CONCLUSION**

For too long, the casting of additive manufactured parts has focused on curing and investment strength. This has been successful when casting most things but will never work for all things. They succeed in treating the symptoms but often fail due to their side effects.

The respective goals of eliminating investment reaction and breakout are neatly solved by addressing the causes. Boiling the parts in water dissolves the offending chemicals before they can leach into the investment. Annealing removes internal stress before it can be unleashed on the mold.

The prevention of ash cannot be solved as tidily. Eliminating ash is possible but remains an applied science. Plastic does not lend itself to burning cleanly, and the kilns and investment presently available today were not designed for such a challenging medium. Careful attention must be paid to part orientation and spacing, along with kiln load, mode of heating and burnout program.

In the future, kilns and investments will be designed for resin casting. Enough demand exists that, given an accurate definition of the problem, solutions will be developed. Convection can be added to electric kilns, along with a uniform distribution of radiation at lower temperatures. Additives can aid in the process by increasing the thermal conductance of investment to hasten water removal.

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