

## Making Stable Glazes for Functional Stoneware and Porcelain

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Today, there must be thousands of glaze recipes in circulation. Potters trade recipes like sports fans trade baseball cards. Almost every issue of every pottery magazine includes a few glaze favorites, and there are entire books full of glaze recipes. However, it should not be presumed that published recipes are suitable for functional ware. Many were developed for color and surface texture, with little regard to functional attributes. Few of these glazes have been tested to determine how durable or stable they are in usage. In fact, unless you know a glaze has been tested, the safest assumption would be that it is not a durable glaze.

While many of the glazes used on studio pottery are extremely stable, there are also many that are thought to be food safe but are not durable at all! We know from testing that not only are they not durable in ordinary use, they can release (leach) materials into foods and beverages. Some of these glazes are so bad that they will change color in their first use, particularly when used for acidic foods, such as lemon slices or other citrus fruits.

In a regulatory, or legal, sense there is little wrong with the use of these glazes. Only the use of lead or cadmium is regulated in most countries; if they are not included in the ingredients, we can legally sell any glaze. Nevertheless, it is time to hold ourselves to a self-imposed, higher standard. Although there is not a single documented case of anyone having been harmed by materials leaching from a lead/cadmium free glaze, we owe it to our buying public to produce glazes that are as close to inert as possible.

No doubt the public would be shocked to learn that such materials as copper, manganese and cobalt leach from our glazes in significant quantities on exposure to weak acids. While some potters maintain these leachates are in such small quantities they represent no more than a modest food supplement, we believe we are not in the food-supplement business.

As a matter of good craftsmanship and/or assuring the safety of our glazes to the maximum extent possible, we should make all potential food- or beverage-contact glazes so stable that they are durable in use and leaching is minimal. We are risking our reputations and our future livelihood if we sell glazes that fail prematurely in use.

At this point you may ask yourself the question—so why hasn't this subject been covered before in the many texts devoted to studio pottery? The answers do not reflect well on the level of professionalism applied to pottery making in recent years or on the curricula of many academic ceramic programs. Somehow, the concern for durability of our glazes has been largely ignored, and there has been a general lack of interest in the technical side of pottery making. Most people interested in ceramic science have moved on from pottery and glazes to applications involving space, electronics and medicine.

## Approaching Glaze Formulation

How, then, should we approach glaze formulation? You may have heard that you can't have "interesting" and durable glazes; however, we have seen enough results from glaze-leaching studies to know that stable glazes can be made in a wide range of colors and surfaces. In fact, we maintain that if there are few interesting and stable glazes, it is only because nobody has been looking for them. Let's consider four possible approaches to assuring that studio pottery glazes are stable in use:

**1)** We could try to develop a comprehensive set of guidelines that would establish safe boundaries within which we could make only stable glazes. Some potters believe that current "limit formulas" define the parameters for glazes that will be durable in use. Unfortunately, a literature search has shown that these limits were derived primarily from visual examinations of recipes that gave "good glass." Leaching performance in the presence of acids or bases was not part of the criteria. Only rarely were any other criteria than "good glass" considered and then it was usually something like scratch resistance.

Virtually no research has been published on the subject of glaze stability except for a few articles on how to make lead-based glazes stable and one exploring the use of barium in glazes. This, then, is not a viable option.

**2)** We could limit the materials to those for which the toxicity concerns are minimal: ball clay, bentonite, dolomite, feldspar (sodium or potassium), flint (silica), borate, iron oxide, kaolin, magnesium carbonate, nepheline syenite, rutile, talc, tin oxide, titanium dioxide, whiting, wollastonite and zirconium. Suitable frits would be those that contain only sodium, potassium, calcium, magnesium, boron, aluminum and/or silicon. Among these would be Ferro frits 3110, 3124 and 3134; Hommel frits 14 and 90; and Pemco frits P-54 and P-311. There are undoubtedly some materials that could be added to this list (e.g. some people would add strontium carbonate and zinc oxide to give more choice of fluxes); however, the listed materials can provide sodium, potassium, calcium, magnesium, boron, alumina and silica for a base glaze, as well as zirconium, tin and titanium as opacifiers, and iron as a colorant.

Adhering to just this list will not, however, assure that the glazes developed will be durable in use. Although they may look good, they may degrade in the dishwasher or the surface may be etched by acidic foods. Of course, if they do degrade in these situations your customers may ingest some glaze ingredients, but they will be pretty innocuous materials. Still, this is not a very attractive alternative.

**3)** We could use the concept of a "liner glaze" for food surface glazes. For example, we could limit the materials to those for which toxicity concerns are minimal (as in the second approach) combined with staying within the limits for a balanced glaze (as in the first approach), then perform some easy-to-do studio tests.

Granted, we said above that limit formulas were derived by visually examining for "good glass"; however, our leaching data indicate we are much more likely to produce a stable glaze by staying within limits. Of course, there are unstable glazes within limits and stable glazes outside limits, but the odds are much higher for stability within limits.

When we couple using limits for a balanced glaze with some simple studio tests, we can be assured the glaze will be physically durable in use. Unfortunately, a glaze can be durable in use for years and still leach significant quantities of colorants into food under certain conditions; hence, the limited materials list.

Pursuing this third option assumes, of course, a couple more things. First, there has to be agreement on what the limits for a balanced glaze are—various authors have published various sets of limits. There is enough consensus on this, however, that we have listed a set of limits (below) that we believe will maximize the chances of making a durable-in-use glaze.

<b>Recommended Stable Glaze "Limits"</b>		
	<u>Cone 6</u>	<u>Cone 10</u>
(K + Na) <sub>2</sub> O	0.1-0.3	0.1-0.3
CaO	0.2-0.6	0.3-0.7
MgO	0.0-0.3	0.0-0.4
ZnO	0.0-0.2	
SrO	0.0-0.2	0.0-0.3
Al <sub>2</sub> O <sub>3</sub>	0.25-0.4	0.3-0.6
B <sub>2</sub> O <sub>3</sub>	0.15-0.35	0.0-0.3
SiO <sub>2</sub>	2.5-4.0	3.0-5.0

This set of limits is not a direct copy of any published set, but rather an amalgam of published sets and what we have learned from leaching studies. Others may have slightly different views on these recommended limits; however, we doubt anyone would argue that this is a "bad" set of limits.

For the most part, this approach is very safe, but it does in fact limit glaze colors to whites and tans and browns. We can, however, make a good range of glaze surfaces from semimatts to glosses and maybe even something approaching a matt (although matt glazes are not recommended as liner glazes for reasons other than stability to acids).

The bigger problem with the third approach is that the person developing the glaze must be able to calculate a glaze composition in standard molar ratio form (usually stated as "unity calculations"). Being able to do unity calculations is the "price of admission" for responsible formulation of glazes for functional ware.

There is no need to do these calculations manually, though. Computer programs can do this for us quite readily. In alphabetical order by author's last name (so as not to indicate a ranking or priority), three such programs are: HyperGlaze by Richard Burkett (more information can be found at <http://members.aol.com/hyperglaze/index.html>); Matrix by

Lawrence Ewing (<http://www.Matrix2000.co.nz>); and Insight by Tony Hansen (<http://www.digitalfire.com>).

4) The fourth approach is to freely experiment with any available glaze materials, but to have all glazes used on food or beverage surfaces tested for leaching. Of course, studio tests are done first and any glaze that fails is dropped without spending money on professional testing. While this approach clearly gives the best indication of glaze stability, it is not without complicating factors. The largest complication is what standards to use when assessing the test results.

It is important to point out that there has been no definitive research done to establish "food safe" limits for the standard acetic-acid-leaching test for materials other than lead and cadmium. In lieu of that, the most conservative approach is to use the primary and secondary standards for drinking water where they exist for materials of interest to potters. This is a very strict, difficult-to-achieve set of limits; however, it is achievable with some materials and, therefore, many colors outside the brown family would be available. We consider the water standards a useful reference, but want to be sure it is understood that there are no data indicating pottery glazes should be required to meet these standards in an acetic acid leaching test.

Note that the lead and cadmium standards, which must be followed if you use these materials, are from 7 to 200 times less strict than the above maximum contamination levels for drinking water, depending on the type of pottery vessel and whether it is subject to federal or California standards. Similar standards are in place in other countries.

<u>Primary Water Standards for Inorganic Materials of Interest to Potters</u>	
<u>Contaminant</u>	<u>MCL in mg/l *</u>
Barium	2.0
Cadmium	0.005
Chromium	0.1
Copper	1.3
Lead	0.015
Nickel	0.1

\*MCL is the maximum contaminant level permissible. Milligrams/liter or mg/l is one of the standard sets of units used to measure very small concentrations; it is numerically the same as parts per million or ppm.

### Relevant Secondary\*\* Water Standards

<u>Contaminant</u>	<u>Mg/l</u>
Aluminum	0.05-0.20
Copper	1.0
Iron	0.3
Manganese	0.05
Zinc	5.0

\*\*Secondary standards are nonenforceable guidelines for contaminants that may cause cosmetic or aesthetic effects.

Another problem with using drinking water standards as a reference is that there are no standards for several materials potters use, including cobalt and lithium. For boron, there is only a "health advisory" guideline of 0.6 mg/l.

Overall, regardless of what standard you decide to set for yourself, we have done enough research to feel confident that if any glaze leaches more than about 5 mg/l of any material the glaze could be made more stable. This probably can be done without limiting the color palette or glaze aesthetics in any meaningful way. If your glaze leaches more than 50 mg/l of any material, you have a very unstable glaze that is probably not suitable for any functional use. Today, for example, there are a number of copper-containing glazes in common use that will leach in the range of 5-50+ mg/l; we believe such glazes should never be used on food surfaces and it is a questionable practice to use them on other functional pottery.

### **Easy-to-Do Durability Tests**

We recommend four studio tests to determine glaze durability. The simplest is a three-day vinegar soak. If the glaze changes noticeably in either color or sheen, it is not durable enough for functional ware. A good way to do this test is by submerging half of a grease-free glaze sample in a cup of vinegar. When you rinse and dry the sample three days later, you can very easily see whether the vinegar has affected the glaze, especially if you examine it with low-level magnification. Stable glazes will not be affected in any visible way.

Resistance to basic dishwasher detergents is a very different matter than resistance to acids. Normally, glazes high in alumina resist exposure to bases better. The second test involves putting a glaze sample through 30 cycles in a dishwasher. Again, if color or surface sheen changes, the glaze is not durable. Here, since the entire sample will be in the dishwasher, it is necessary to have a second control sample set aside to use for comparison.

The third test is for knife-marking. If the edge of a table knife leaves visible marks on a glaze, the surface is too abrasive or matt for good performance. The marks are caused by metal abraded from the knife, and they are sometimes very difficult to remove.

Finally, there is the freezer/boiling water test for clay/glaze fit, which involves several cycles of placing a pot in a freezer for several hours, then removing it and immediately filling it with boiling water.

Do this test in a sink and be careful to avoid scalding yourself. The glaze is then examined under low-power magnification (10-100X) for signs of crazing and/or shivering. Low-power magnifying glasses are available from stamp and coin dealers for only a few dollars; Radio Shack also sells an inexpensive lighted 100X hand-held microscope.

## Laboratory Testing

Testing for leachates can be done by various laboratories throughout the country (for lists of accredited labs in North American and abroad, see the American Industrial Hygiene Association website at <http://www.aiha.org/lists.html>), but we are aware of only two labs that makes this service readily available for a modest fee:

Alfred Analytical Laboratory  
4964 Kenyon Road, Alfred  
Station, New York 14803  
Phone: (607) 478-8074

and

Brandywine Science Center, Inc.  
204 Line Road  
Kennett Square, PA 19348  
Phone: (610) 444-9850

While we work closely with both laboratories, we have no financial interest in either; they are simply the only places we know to have this kind of work done professionally and economically.

Having a glaze tested is very simple: Throw or handbuild a small cup. For consistency, many potters use 1 pound (450 grams) of clay and throw a cup with wet dimensions of 4 inches (10 centimeters) in diameter by 3 inches (7.5 centimeters) tall. Using the same size cup gives more comparable results. Be sure to identify each cup; scratching a number into the leather-hard clay or writing a number with iron oxide on bisqueware works well.

Coat the inside of the cup with the glaze to be tested and fire normally. Placing a cone pack near the cup will help document the firing conditions.

Leach-Tested Glaze Recipes			
<u>Charcoal Satin Matt Glaze (Cone 6)</u>			
Wollastonite	23.2	%	
Frit 3124 (Ferro)	31.0		
Edgar Plastic Kaolin (EPK)	31.7		
Flint	14.1		
	100.0	%	
Add:	Dark Rutile	6.0	%
	Mason Stain 6600	10.0	%
A semimatte derived from Tony Hansen's matte base but modified to increase silica content; must be cooled slowly or it will turn glossy. Note that Charcoal Satin is outside the recommended limits; however, it is still very stable. Leaching test results: chromium <0.01 mg/l; cobalt <0.05 mg/l; nickel 0.07 mg/l.			
<u>Xavier's Warm Jade Green Glaze (Cone 6)</u>			
Talc	9	%	
Whiting	16		
Custer Feldspar	40		
Frit 3124 (Ferro)	9		
Edgar Plastic Kaolin (EPK)	10		
Flint	16		
	100	%	
Add:	Copper Carbonate	3-5	%
	Rutile	6	%
A semimatte from Val Cushing's handbook, page 129. Leaching test results: Copper 0.68-3.07 mg/l			
Note: Both glazes also passed the studio tests when used on Standard Ceramics 306 clay. Firing was to large Cone 6, tip touching. The leach-test results are valid only under the conditions at Hesselberth's studio. Results may vary on different clay bodies fired in different ways.			

Send the cup to one of the laboratories along with instructions and payment. For details on their fees call the laboratories. Having one cup tested for one metal will cost \$18-20; having one cup tested for two metals will cost \$30-31. You can also find details on testing and on laboratory fees at:

<http://www.frogpondpottery.com/glazetest.html>

## Looking Forward

Even those of us who have been potting for many years are mesmerized by the possibility of creating the most beautiful glaze the world has ever seen. Formulating our own glazes is both fun and frustrating, but it continues to be something that many of us do without taking proper precautions. Although most of us are aware of the health benefits of handling glaze materials carefully (at least we hope that everyone uses a high-quality dust mask when mixing glazes and wears rubber gloves when dipping hands into glaze slurries), studio potters simply are making and selling too many pots with glazes of questionable durability.

In writing this article, our intent was both to give practical advice on making glazes more stable and durable in use, as well as raise awareness of this issue among our fellow potters. For our part, we are continuing to research glaze stability with the hope of some day being able to offer more definitive guidelines.

In addition to the examples of tested glazes shown here, an up-to-date list of tested recipes can be found at the website <http://www.frogpondpottery.com>. While these recipes will not relieve potters of the responsibility of testing a glaze under their own conditions, they do give everyone a place to start when developing functional glazes. To be certain a recipe will work well for you, it must be tested by using your ingredients, mixing in your usual way and, in particular, firing under your usual conditions in your kiln.

Meanwhile, should you do any testing of your own glazes, we would very much appreciate receiving a copy of the recipes, firing conditions and results to add to the database of tested glazes. Please mail to Post Office Box 88, Pocopson, Pennsylvania 19366-0088; or e-mail to [john@frogpondpottery.com](mailto:john@frogpondpottery.com).

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## About the Authors

John Hesselberth is a retired chemical engineer, who now makes pottery full time at his studio in Pocopson, Pennsylvania; Ron Roy is a studio potter in Scarborough, Ontario, a clay/glaze consultant for two suppliers, and a frequent contributor to the Ceramics Monthly Questions column.

When formulating recipes for functional pottery, Hesselberth uses professional leach testing combined with the studio tests to produce stable glazes, but he doesn't feel bound by the drinking water standards where they exist. He does believe, however, that the water standards serve as a useful reference. For example in regard to copper, one of the most difficult materials to retain in a glaze, he has decided to set a personal goal of 5 mg/l (the

drinking water standard for copper is 1.3 mg/l). Two leach-tested glazes that he uses are shown in the recipe sidebar.

Roy has been concerned about glaze durability for many years. When he started formulating recipes, professional leach testing was prohibitively expensive so he purposely limited his choice of materials to those with little or no safety concerns and stayed within traditional glaze limits. Now, when reformulating glazes (usually to eliminate faults or replace bad-acting or no-longer-available materials for other potters), he finds he can usually improve durability at the same time.