Chemical Stains

by Bruce D Wedlock

Introduction

As my cherry bed construction progressed, I began thinking about how to achieve the patina of aged cherry without waiting 10 or 15 years. Current finishing articles suggest the use of aniline dyes to establish the desired color, but give little specific indication as to precisely what dye and concentration might be a good starting point. After trying several aniline dye offerings for cherry, I was no where close to the shade of the cherry Shaker table I'd built 16 years previously. Further research led me to explore chemical stains which were employed particularly on mahogany before aniline dyes became available.

Rather than dying the fibers (as with aniline dyes) or putting fine pigment particles on the surface (as with conventional "stains") a *chemical stain* reacts with the natural tannin in the wood to produce a brown to reddish brown. The depth of the color that can be achieved is stunning.

The final color of aniline-dyed woods can lighten through+ subsequent fading or can further darken through the wood's tannin oxidation. One advantage of a chemical stains is that the tannin is directly converted to produce the aged color, and therefore will not continue to darken with time.

How It Works

Woods like cherry (heartwood), mahogany, oak and walnut contain significant amounts of tannins or phenolics which in their electron-rich reduced state tend to be colorless to very slightly yellow. However, rearrangements in electronic structure that occur with oxidation (loss of electrons) cause the compounds to become a more highly colored brown to reddish brown. Some tannins are photosensitive and will oxidize in light with the atmospheric oxygen acting as the oxidizing agent. The reaction tends to be fairly slow, and is the process by which cherry and mahogany darken over time.

Placing wood in direct sunlight will speed up this process[1]. Sunlight on cherry causes the color to change much faster as the light acts as a catalyst to speed the oxidizing reaction. A week in the bright sun will darken your wood. But for a large project that may be impractical.

The oxidation process can be accelerate by the application of chemicals that are oxidizing agents. Potassium dichromate ($K_2Cr_2O_7$) is one of the most important chemicals historically used in woodworking. It is a potent oxidizing agent which is nearly colorless. Available as granules it can be mixed in varying strengths with distilled water to produce a range of oxidizing concentrations. An aqueous solution will convert wood tannins to their final color in a few minutes with the exact shade controlled by the concentration of oxidant. This is *not* a dye approximation to the final color; rather it chemically produces the color the wood would ultimately achieve after years of atmospheric oxidation.

The appearance of the brown color is the same process that occurs on a fresh slice of apple. Cooks know that application of acidic lemon juice will retard this browning. Conversely, placing tannins in a basic pH environment will also accelerate their oxidation. Application of a sodium hydroxide (NaOH) solution (or a solution of household lye) can also accomplish this color change.

Another method of providing a basic environment is to place the wood in an air-tight chamber with full-strength (*not* household) ammonia (NH_4OH). White oak Mission furniture achieved its distinctive brown color through ammonia fuming. This was particularly attractive for production since the furniture was simply placed in the ammonia chamber and left for a day or two. No liquid applications and every nook and cranny was uniformly dyed.

Safety

Woodworking is inherently dangerous, but few eschew a table saw for the far safer hand saw. Rather, one takes steps to reduce the table saw's danger by using push sticks and unplugging before changing the blade. The increased danger is accepted as the cost for improved performance. So it also is with chemical stains. One needs to understand the potential danger and take steps to reduce them to a tolerable level.

Potassium dichromate and sodium hydroxide are highly toxic. They are supplied as granular materials, so be careful handling them. The Material Safety Data Sheet for $K_2Cr_2O_7$ is located at http://www.jtbaker.com/msds/englishhtml/p5719.htm. The MSDS for NaOH is at http://www.sciencelab.com/xMSDS-Sodium_Hydroxide_50_-9924999. A significant deficiency of these sheets is quantitative description of toxicity for levels used in chemical staining. I have asked several chemists about this, but they have not been able to determine what the danger level is for a concentration on the order of one teaspoon in one cup of water. But it clearly is less than the dry powder. So once diluted to the concentrations suggested, it is not likely to be as dangerous as the MSDS would imply. One should avoid direct contact with the skin, eyes and face, so wear kitchen gloves, a dust mask and face shield protection when working with the powder. The diluted solutions will not emit any toxic fumes, so are less of a hazard than the powder. A solvent resistant disposable apron is also a good idea. Store waste quantities in a heavy plastic jug and take it to a hazardous waste disposal center.

Fuming with full strength ammonium hydroxide can be extremely dangerous. A whiff of the high strength ammonia can be fatal. This technique should be left to those with experience handling this chemical.

Stock Preparation

Surfaces to be stained should have their final sanding completed as sanding after staining will remove dyed wood altering the color. Since the chemicals are in water, any need for grain raising with water should be done before staining.

With cherry, a 1 lb. wash coat of dewaxed shellac (Zissner Sealcoat 50/50 with denatured alcohol) is recommended to seal the blotching areas. It makes an observable difference in the uniformity of the stain shading. While the wash coat won't eliminate blotching, it evens out the color substantially.

Flood the surface with the shellac watching for areas of absorption which should be keep wet. After 3-4 minutes, wipe the shellac off with a paper towel. The objective here is to fill end grain and minimize any surface film buildup. Let it dry for a day or two to be sure it's cured, and then hand sand somewhat aggressively with P180. The objective here is to expose the wood fibers to the staining solution. The areas of blotching will remain sealed if you only remove a thin surface layer.

If an area of insufficient sanding shows up as a lighter stained shade, let it dry and resand that area. Then reapply the stain. The shade should match quite closely as the final color depends primarily on the stain concentration. A before and after example of this is shown below. The photo on the left was not sanded sufficiently, resulting in some lighter areas when stained. These lighter areas were resanded and the stain reapplied. The right photo shows the light areas are now the same shade, and the original darker areas match the repaired sample.

Insufficiently Sanded Wash Coat

Resanded and Restained

Stain Preparation

Prepare a stock solution of the stain by dissolving one level teaspoon (t) of the chemical in one cup (c) of distilled water (1 t/c). Use distilled water, available in the supermarket, to eliminate and effects of chemicals in the water, particularly iron. Store the stains in glass or heavy plastic jars and label them as to contents and concentrations. The stock solution can then be diluted to achieve weaker concentrations. Equal parts of distilled water and stain solution will reduce the concentration by a factor of two. Use a small plastic container to do progressive dilutions. For example, one measure of 1 t/c stock solution plus an equal measure of distilled water will produce a 1/2 t/c concentration. One measure of 1/2 t/c concentration plus one measure of distilled water will produce a 1/4 t/c concentration, and so on. Store the diluted stains in labeled jars. You will not require much stain to do a normal size project, so keep the quantities down.

Below are photographs of various concentrations of stains on cherry , mahogany and oak to give you an idea of what concentration to use. I found that 1/4 t/c of $K_2Cr_2O_7$ gave me the desired color with cherry, but you should experiment with your actual wood samples to determine what concentration gives your desired result.

Stain Application

Prepare your work area with plenty of newspapers to absorb any drips, and position the piece to be stained in a horizontal position if possible. Apply the chemical stain with a small (1" x 1") sponge wearing kitchen gloves for hand protection. Rub it on, keeping the surface wet, for three to four minutes, then wipe dry with a paper towel. You don't want to have excess chemical drying and leaving crystals on the surface. You should see some immediate darkening, but it will continue to darken for several hours.

Finishing

When the stain has dried, apply whatever finish you want, shellac, oil or varnish. I've had excellent results with three coats of Minwax WipeOn Poly, clear or satin, which I apply with a brush. Brushing builds a film faster than wiping if you have horizontal surfaces. This finish dries quickly, avoiding dust pickup, and you can easily do two coats in a day. Two coats will seal the stain so you can then sand the finish smooth prior to the final coat. For comparison of finishes, the cherry sample shown below was stained with 1/4 t/c of $K_2Cr_2O_7$ and finished as follows. Left panel: boiled linseed oil (BLO) and mineral spirits followed by three coats of blonde shellac. Center panel: three coats of tung oil. Right panel: three coats of Minwax satin WipeOn Poly. All panels were rubbed out with 0000 steel wool and finished with amber paste wax.

BLO & Shellac **Tung Oil** **WipeOn Poly**

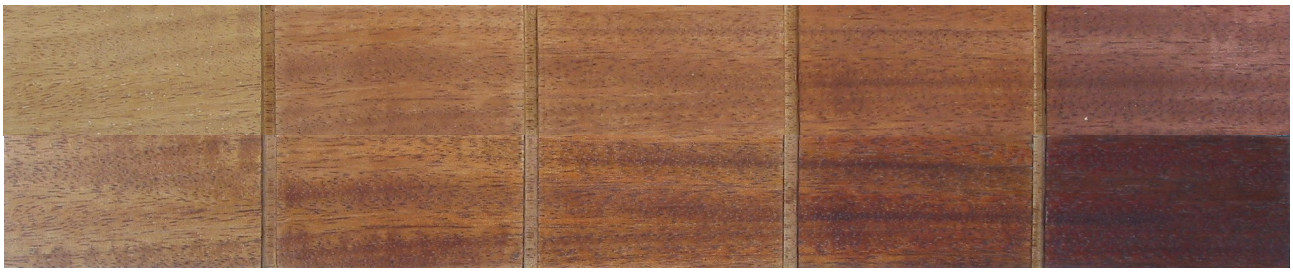
Stain Examples

A series of sample pairs were produced from cherry and mahogany. Each was freshly milled and sanded prior to application of the chemical stain. Upper sample in each pair is shown with just the stain applied, while the lower shows the panel finished with three coats of Minwax satin WipeOn Poly. In each case, the panels are stained with increasing stain concentrations of 1/8, 1/4. 1/2 and 1 t/c, left to right. Careful attention was paid to the lighting and camera settings to achieve accurate color reproductions.

Cherry Stained with 0, 1/8, 1/4. 1/2 and 1 t/c $K_2Cr_2O_7$

Cherry Stained with 0, 1/8, 1/4. 1/2 and 1 t/c NaOH

Mahogany Stained with 0, 1/8, 1/4. 1/2 and 1 t/c $K_2Cr_2O_7$



Mahogany Stained with 0, 1/8, 1/4. 1/2 and 1 t/c NaOH

The cherry samples pictured above are all heartwood. Cherry sapwood, the whiter part that grows at the outer diameter of the tree, contains no tannin, so it will not darken with the chemical stains. I am exploring the coating of sapwood with tannic acid to see if this will improve the match.

The white oak samples below are stained with the indicated concentrations and finished with three coats of Minwax satin WipeOn Poly. Note the greater range of stain concentration. White oak demonstrated a greater sensitivity to the stain, so the concentrations were changed to achieve a range of coloring. In addition for comparison, samples of white oak were fumed for 17 hours with full-strength (28%) ammonium hydroxide (NH_3OH) in a 60º F ambient. The left sample is unfinished; the right finished with three coats of Minwax satin WipeOn Poly.

White Oak Stained with 0, 1/16, 1/4. and 1 t/c $K_2Cr_2O_7$

White Oak Stained with 0, 1/16, 1/4 and 1 t/c NaOH

White Oak Fumed for 17 Hours in NH_3OH

Subsequent Color Change

It is generally accepted that wood treated with aniline dyes will continue to darken over time as the tannin oxidizes. It has been alleged that this will happen with chemical stains as well[2], but that is not the case. First, the color change using chemical stains to oxidize the wood's tannin leaves little or no tannin to subsequently darken, unlike the case with aniline dyes whose color is independent of the tannin. So the final color is achieved right away with chemical stains. Of course, if you apply a very weak concentration, there can be additional darkening, but in the case of cherry, a 1/4 t/c is sufficient to oxidize the tannin to the point that sunlight will not darken the color further. To prove this, a cherry sample was prepared with left to right stain concentrations of 0, 1/8, 1/4. 1/2 and 1 t/c. The upper half received 33 hours of direct sunlight while the lower half had the sun blocked, all prior to finishing with three coats of Minwax satin WipeOn Poly. The sunlight oxidation darkened the lighter concentrations to match the 1/4 t/c color which did not change from the shade of same concentration with the sunlight blocked. In addition, the sunlight appears to have slightly

bleached out the higher concentrations. In summary, a concentration of 1/4 t/c of $K_2Cr_2O_7$ will stain cherry to a shade that does not change with time. Note also the tannin-free sapwood stripe at the bottom is not darkened like the heartwood.

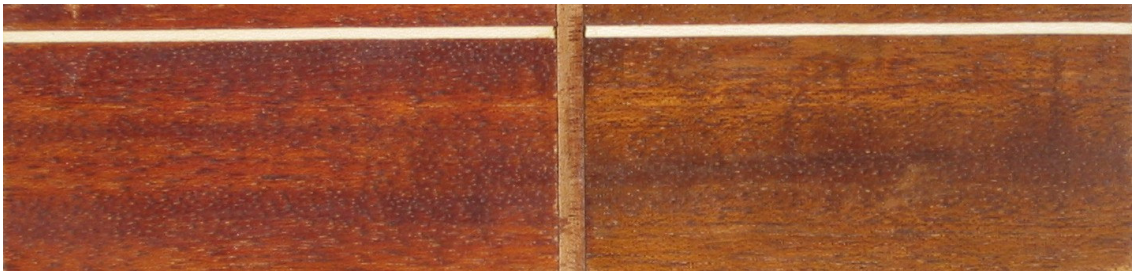
Stained Cherry with Upper Row Exposed to 33 Hours of Sunlight

Inlay

Federal period furniture is frequently decorated with inlaid white holly stringing in mahogany. Using a chemical stain can quickly improve the contrast by darkening the mahogany while leaving the tannin-free holly nearly unchanged. It turns out that NaOH bleeds substantial color from the mahogany while $K_2Cr_2O_7$ imparts a slight orange shade to the holly. Below are samples of chemically stained mahogany. In the upper sample the holly was inlaid and then the stain applied. In the lower sample the inlay was fitted but not glued. The stain was then applied without the inlay, and the inlay was glued in the dado after the stain dried, retaining the pure white color.

$K_2Cr_2O_7$ Stain **NaOH Stain**

Holly Inlaid in Mahogany



NaOH Stain **$K_2Cr_2O_7$ Stain**

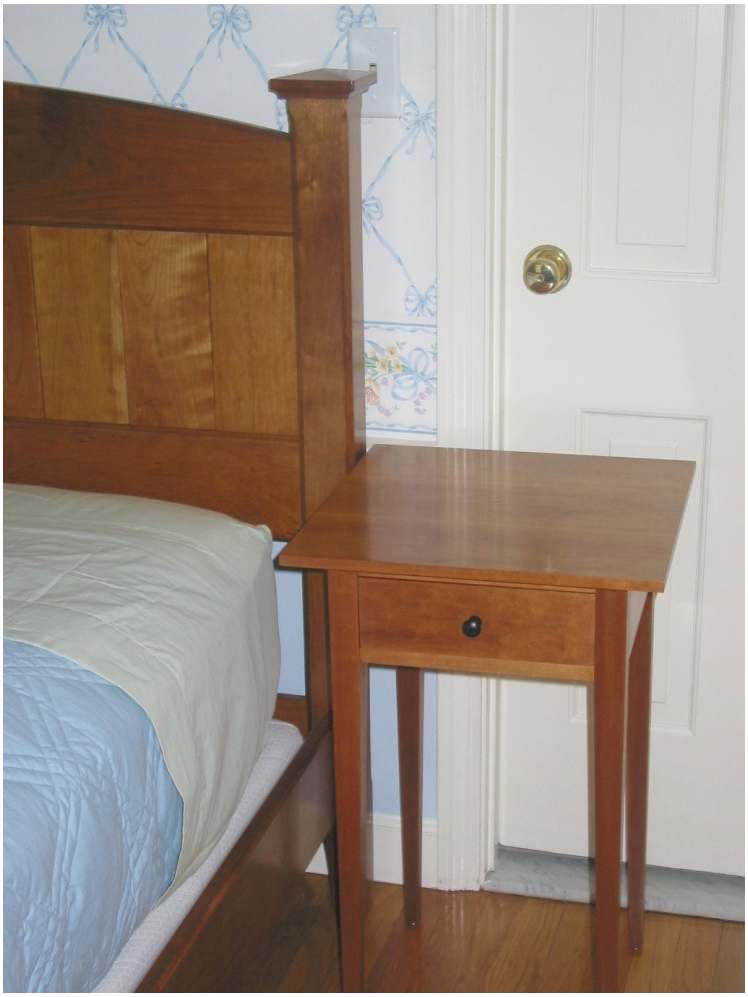
Holly Inlaid in Mahogany

Conclusions

Chemical stains provide a powerful tool to rapidly achieve the coloring certain woods develop after years of aging. While toxic materials, with reasonable precautions chemical stains can be safely used in the shop. Potassium dichromate at a concentration of 1/4 teaspoon per cup of distilled water gives a pleasing result with cherry. Sodium hydroxide at similar concentration works as well, but adds a slightly reddish tone which may be preferred with mahogany. White oak responds equally to either chemical, producing a result very close to that achieved by fuming with concentrated ammonia.

The chemicals for staining can be obtained from WoodFinishing Enterprises, 1729 N 68th Street, Wauwatosa, WI 53213. Phone/fax 414-774-1724, http://www.woodfinishingenterprises.com. Their web site has substantial information on a variety of chemical stains and their applications. The seem to be a small company and are not swift in filling orders.

My original problem was to achieve a patina in fresh cherry that matched that of my 16 year old table which was finished with just two coats of tung oil. The photograph below shows the two pieces for comparison.



Revised, February 26, 2010

[1] Keller, David E., *A Study of the Photo-Oxidation of Wood Using UV Light*, American Period Furniture, **8**, pp 4-8, 2008

[2] Fitzpatrick, Megan, *Adding Age to Cherry*, Woodworking Magazine, pp 30-31, Spring 2006.