Stabilizing Dichromatic Annatto Colorant

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Abstract

Annatto is a beautiful colorant varying from bright yellow to orange and dark red due to optical dichromatism. Although it is notoriously fugitive, a proteinaceous medium such as casein can protect annatto from destructive light and oxygen. Thus, annatto can serve as a multicolored wood stain as a ground for varnish.

INTRODUCTION

Annatto (*Bixa Orellana*), also known as achiote or urucum, was introduced to Europe in the 16th century by Spain in its conquest of Central and South America. The plant seeds yield an orange-side red colorant that became a popular additive to some cheeses needed to match the yellow-orange color of quality cream [1]. Nowadays, it also serves as a natural colorant in various foods and cosmetics. Nevertheless, annatto can be fugitive.[1] Fabric dyers and paint artists know all too well that as a dye, or even as a pigment made into a lake, annatto's varying colors are challenging to control and will fade in daylight [2].

Luthiers admire its seemingly magical color variations extending from yellow, orange, to dark red depending upon the viewing angle and layer thickness. Harnessing this property would produce beautiful instruments. Using annatto's color properties for violin making has a historical basis among early Parisian violinmakers, but controlling and stabilizing this colorant can be challenging [3].

The color variation serves as an excellent example for studying an essential optical effect. This color property is not unique to annatto; other colorants such as "Indian Yellow" artist paints share this color effect.[2] While paint artists may refer to this phenomenon as "dual-tone," physicists define this as "dichromatism." Some luthiers have dubbed this color variation "dichroism." The words are similar, but their technical meanings are light years apart. More importantly, such incorrect terminology can lead to unproductive experiments.

Typically, colorants in varnishes or stains change strength (value) but not color (hue) as the layer concentration or viewing angle changes.[3] They become darker in color to the point of appearing black. These are called monochromatic.

Figure 1 shows a sample of a monochromatic pigment, Perylene Maroon (PR 179), that is similar to madder [4]. Two microscope slides touch at the right end, and a thin spacer on the left end separates them. The pigment fills the void such that the thickness of the film wedge ranges from 0 to ~80 microns. As the colorant thickness increases to the left, the brightness diminishes because more light is absorbed. The color (hue) of the monochromatic sample remains fixed, or nearly so, while its strength (value) increases and becomes darker.[4]

Dichromatic materials, however, do change color according to how they are viewed or deposited on a surface. Their thin films appear yellow or green but become orange or red with increasing thickness or concentration. A simple explanation is that blue light is absorbed the most, followed by yellow, then by red and that the color absorption changes considerably near the peak of eye sensitivity in green light. Figure 2 shows a wedge sample of potassium norbixinate made from annatto. The color variation is due to dichromatism.

The color variations exhibited by annatto's colorants have nothing to do with light wave interference, namely dichroism. For dichroism, the thickness of a transparent film must be near the wavelength of light, namely $\lesssim$1 micron. The classic example is oil floating on water, where overhead light produces bright colored reflections.

Figure 1. A film wedge of monochromatic PR 179 has a uniform color (hue).

Figure 2. A film wedge of dichromatic potassium norbixinate changes color (hue).

The question is whether varnish or wood figure can reproduce dichroic interference like the example of oil on water. Thin films that show light interference range from only 0.5 to ~3 microns. The colors merge at the top surface in thick films to form a bright (white) reflection.

Varnish films are 20 microns or more. Thus, not only are varnish coatings too thick for light interference, but they are also not uniformly flat on wood surfaces. (A wood surface cannot replicate the ultra-flatness of water.) The same issue holds for colored stain infused within the wood structure where chatoyance (reflective grain surfaces) occurs. The cellular surface structures of wood lack the nano-sized flatness and uniformity needed for light interference from a violin surface. The fact is that wood does not have a uniform crystalline lattice like some dichroic minerals. It is a terrible medium or substrate for light interference, which is observed only in laboratory-controlled experiments on microscopic levels. Thus, "dichroism" or "dichroic" are misnomers for varnishes or grounds.

Annatto seeds have a shell of bixin, an orange-side red apocarotenoid [5]. The red coating of annatto seeds yields two colorants, bixin and norbixin, with dichromatic properties. Both are fugitive. Dissolving bixin in an alkaline solution stabilizes it. The bixin methyl ester converts into a carboxylic acid known as norbixin which, in turn, can be transformed into a salt called a norbixinate. Of the common salts, potassium norbixinate has high solubility and clarity. Moreover, food chemists know that norbixin and its salts have a strong affinity for proteins that protect from light and oxygen degradation [6].

As it turns out, aqueous norbixin can be stabilized apparently to the same degree as other natural organic colorants used in lutherie. A successful method is to make potassium norbixinate in an alkaline solution and add this to a protective protein made with casein. The procedure starts with immersing annatto seeds in water with potassium hydroxide. When the solution becomes red with potassium norbixinate, filtering removes particulates. Then, the alkaline red dye and potassium caseinate (casein dissolved in potassium hydroxide) are combined. The solution is filtered further if needed and diluted with water. Details are given later and in the Appendices.

Potassium norbixinate spread on wood and left in sunlight fades rapidly. The norbixinate reacts with atmospheric oxygen and sunlight (UV). So, the stain color disappears except in intense flames, deep in the wood structure where it is protected somewhat from air and light. Still, the flames fade to chestnut brown, presumably the reflective color of degraded norbixin.

Protecting norbixin from air and light degradation takes a page from artist colorant preparation that learned the importance of proteinaceous mediums centuries ago. Casein protects norbixin which harkens to their historical link to cheese. Repeated tests show that combining them before applying them to the wood surface maximizes the protection.

Figure 3 is an unprocessed photograph of a test rib infused with the caseinate-norbixin stain as discussed. A thin layer of colorless, particulate-free, lean (4:1) varnish overcoats the stained wood. A Mini Maglite AA LED (~6,000 K color temperature) is the only light source directed at the photo center from the right inclined ~30° to the surface 40 cm away. The camera is a Lumix DMC-ZS100 operating in the macro mode 20 cm

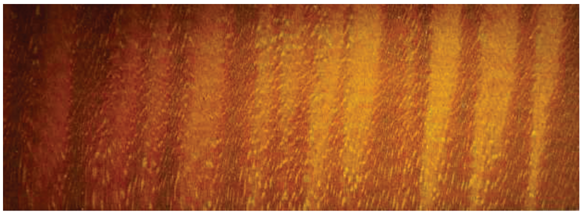

Figure 3. Maple rib infused with caseinate-norbixinate stain and overcoated with one layer of colorless lean (4:1) varnish.

above the stained strip. Notice how the dichromatic effect is redder to the left, where the light path passes through more stain.

Converting bixin to a water-based norbixinate with superior stability is an important property. Aqueous dyes readily penetrate the wood pores by capillary action to the point where the dye can bleed through violin ribs. More importantly, the straw-like cellular structure of curly maple has a wave-like pattern that tilts the top layers in and out of the line of sight, producing a beautiful optical illusion of varying depth [7]. The flames infused with a dichromatic stain change color for different viewing angles or incidences of shining light. A colored varnish can enhance the flame colors, but the infused stain creates the dichromatic effect.

Figure 4 shows another maple sample where the pores fill with the norbixinate. The red dashes and dots are open pores cut at different angles, obliquely and perpendicularly, respectively. Their red color is due to the dichromatic effect of concentrated norbixinate.

Combining potassium norbixinate and potassium caseinate produces a stain that is essentially an artist's distemper [8]. However, its all-important stability depends on the procedure used for its production. Adding the norbixinate to caseinate at a very high pH ~13.5 with potassium hydroxide produces good stability. (See the Appendices for details.) This solution is applied diluted and allowed to dry between successive coats. The alkalinity loses strength as it reacts to darken the wood.

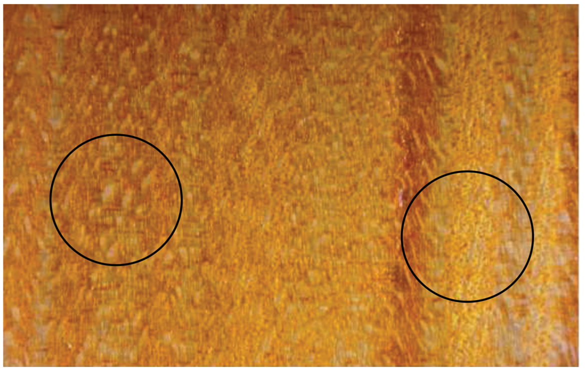

Figure 4. Magnified section showing red-side orange pore filling stain: dashes right, dots left.

An alternative method used in the food and cosmetic industries explains the chemical details behind the above procedure. The key to stabilizing the norbixinate involves making an *adduct*, a binder at the molecular level [9]. Caseinate molecules (proteins) wrap around norbixinate molecules as the pH decreases with the addition of a weak acid. This *adduction* stabilizes norbixinate to light and oxidation. Thus, this explains the role of protein in stabilizing norbixinate.

Finally, the luthier's issue is how the casein-norbixin wood stain is applied. Brushing the wood stain in excess produces something akin to a coat of paint obscuring the wood figure. The violin will then appear very orange. The strength of the wood stain is controllable by dilution and by applying multiple coats to enhance the dichromatic effect of an annatto wood stain. See Appendix 3.

CONCLUSION

This work shows how dichromatic effects appear in varnishes and grounds. Moreover, annatto's water-soluble extracts, norbixin or norbixinate, produce a stable dichromatic wood stain. The particular results are dependent on the preparation and application procedures.

APPENDICES

Appendix 1: Potassium Norbixinate Dye

Add distilled water to fill a large screw-top jar 25%. Carefully add potassium hydroxide to get a 5% w/w (~1M) solution. For example, add ~20 g of KOH to 400 ml distilled water. After the KOH is fully dissolved, add ~100 g of annatto seeds. Seal and set aside for about a week in a cool, dark place with occasional mild shaking. If the solution is swirled around in the jar, dichromatism is apparent. Tiny thin droplets look yellow while large thick orange drops run down the sides to a magenta solution.

The objective is to form a transparent aqueous alkaline dye. After a few days, a nylon #100 mesh filter removes the seeds and debris. The pH should be >13 [10]. It is permissible to store the alkaline dye for many months in a cool dark cabinet, allowing sedimentation of any particulates.

Casein can neutralize excess KOH and any unreacted casein removed with paper coffee filters.

Appendix 2: Potassium Caseinate Medium

Using wine-maker's potassium caseinate (clearing agent) in a 3-4% w/w distilled water solution gives consistent and fast results. This medium is a stand-alone size, but it should be made fresh like hide glue. However, its primary function is to transport and protect the norbixinate colorant.

Potassium caseinate can also be applied as a light size, not as a strong sealant, for additional protection from blotching of spruce. The size will seal absorbent end grain on maple scrolls.

Appendix 3: Colored Stain

Pour 200 ml of potassium caseinate medium (Appendix 1) in a ~400 ml sealable jar. Warm to ~35C. Slowly add 175 ml of the potassium norbixinate (Appendix 2) while stirring. The solution should appear magenta. If the stain makes the wood orange, it is too strong and should be diluted 1:1 with distilled water. Several thinned stain applications build the color according to personal preferences. Absorbent paper towels can control the stain's strength.

NOTES

1. See remark in Michael Darnton's unpublished book, p. 4. http://www.darntonviolins.com/violinmagazine/book/1varnishing.pdf. See this Maestronet.com thread: https://maestronet.com/forum/index.php?/topic/113037-saffron-colored-violins/&tab=comments - elControls_113041_menu.
2. Dichromatic colorant Indian Yellow (NY20) is a complex composite of euxanthic acid and its derivatives. There are many modern substitutes under the rubric, "Indian Yellow," such as Nickel Dioxine Yellow PY153. Sometimes paint artists refer to dichromatism as "dual-toned." See: http://realcolorwheel.com/indianyellowtobrownPY153.htm.
3. Paint artists often use the terminology of the Munsell Color System. Hue is color (red, green, etc.), the angular position of the colorant on the standard color wheel. Chroma is the purity or vividness of a color, namely the radial distance from the center to the edge of the color wheel. Value, a third dimension normal to the color wheel plane, differentiates a light color from a dark one. MacEvoy, Bruce (2005). http://www.handprint.com/HP/WCL/color7.html#MUNSELL.
4. When used in thin coats as a glaze, some monochromatic pigments show a slight color shift.

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[3] Dipper, Andrew, "A Look at Parisian Violin Makers' Approach to Varnish," Strings, Oct. 7, 2016. Dipper explains that Lupot used annatto as part of a varnish *system*, namely that he used it in the ground with saffron.

[4] The Color of Art Pigment Database, http://www.artiscreation.com/red.html#PR179.

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[7] M.R. Molnar, "Optical effects in Lutherie: Reflected Glories," The Strad, Vol. 124, No. 1480, August 2013, pp. 48–53.

[8] Mayer, Ralph. "The artist's handbook of materials and techniques." United Kingdom: Penguin Publishing Group, 1991. p. 643. Mayer demands strict definitions for distemper but confused dichroism with dichromatism on the same page.

[9] J. Todd, Paul H. "Norbixin Adducts with Water-Soluble or Water-Dispersible Proteins or Branched-Chain or Cyclic Polysaccharides, US Patent 5,053,240, Oct. 1, 1991, (expired).

[10] Hanna Instruments HI98103 Checker pH Tester, https://www.hannainst.com/hi98103-checker-ph-tester.html.