This is a webbed copy of my 1996 TI article, in the form in which I emailed it to the TI editor.

Notes to editor: Kuhn (in the bib) and Durer (in the text) both need umlauts over the u in their names.

Working Title: Will the real Massicot please stand up!

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I will tell you the punchline first: yellow lead oxide (PbO), often called massicot and sometimes called giallorino, didn't exist in medieval and renaissance palettes of pigments. Massicot was actually a manufactured lead-tin oxide, Pb2SnO4 or Pb(Sn, Si)O3. The former was made by melting together lead oxides with the mineral cassiterite (SnO2). The latter was made by adding silica (SiO2) into this same melt. The first was more common in painting and the second was more common in glass and ceramics, though it too was sometimes used as a paint pigment. Prior to 1300 CE, lead-tin oxide didn't exist as a paint pigment, though the Romans used Pb(Sn,Si)O3 as a pottery glaize. Lead-tin massicot reached its peak during the fifteenth and sixteenth centuries. After approximately 1750 CE, lead-tin massicot disappeared.

The rediscovery of lead-tin yellow corresponds with the great explosion of spectroscopic methods in the 1930's and 40's. In 1941, Dr. R. Jacobi of Munich investigated yellows on old paintings spectroscopically. He found that most had high lead and tin contents. Very few hosted pure lead yellow (PbO), usually as an adulterant in the lead-tin pigment. At first, this was merely an odd but interesting result. Over the years, however, conservation scientists have found lead-tin yellow almost everywhere. Prior to mass spectroscopy, conservation scientists used microscopes and wet chemistry techniques to identify pigments. Prior to Jacobi's rediscovery, everyone identified massicot as lead yellow: everyone assumed they were the same. If the wet chemistry test showed a positive result for lead, then massicot it was. No one bothered with the wet chemistry tests for tin, so no one discovered its presence. This is a good example of a bad assumption.

The list of artists who used lead-tin yellow reads like a who's who of period art: Giotto, Gaddi, Fra Angelico, Durer, Vasari, Altdorfer, Cranach, Titian, Rubens, Rembrandt, van Dyck, Hieronymous Bosch. The existence of lead-tin yellow as massicot is now commonly accepted in art conservation science, a field overpopulated with chemistry nerds. The rest of the world has not yet caught up. Artists and art historians have not

yet realized that period massicot is not lead monoxide (PbO). Here's an example from Mayer's _Artist's Handbook_, a standard art reference:

"MASSICOT. An obsolete yellow oxide of lead, similar to litharge; usually deeper or more pinkish in hue. Never was considered permanent."

Litharge, by the way, is either yellow or red reagent-grade PbO, usually used in pyrometalurgy and chemistry. But let us continue. It is interesting to look at Mayer's definition of giallorino:

"GIALLORINO. Naples Yellow."

Back tracking in Mayer we find:

"NAPLES YELLOW. Lead Antimoniate made by calcining litharge with antimony trioxide. A heavy semiopaque yellow...made artificially since at least the fifteenth century. Cennini supposed it to be a native volcanic earth from Vesuvius."

Here we have an apparent contradiction. We stated earlier that massicot and giallorino were both lead-tin yellow. But now we have a definition from Mayer that giallorino is Naples yellow instead. This sort of confusion is very common when matching period pigment names to modern compositions. The yellows are fairly confused, actually, and so are the period reds; reds, however, will have to wait for another article.

The art conservation folks have not been idle since Dr. Jacobi rediscovered lead-tin yellow. Thus far, every period Italian painting investigated with modern techniques generally hosts yellow ochre (FeOOH.nH2O), orpiment (As2S3), and/or lead-tin yellow. The Italian palette in the fifteenth and sixteenth century contained three common yellows: yellow ochre, orpiment and "giallorino." It doesn't take a huge stretch of the intellect to conclude that Italian giallorino is the same as the northern European massicot. On the other hand, there are no documented examples of Naples yellow prior to the seventeenth century. In fact, many paintings previously thought to host Naples yellow are now known to host lead-tin yellow instead.

Last, there's the confusion which Cennini (15th century) introduced to the world with his remark about giallorino and volcanoes. The historical mis-identification of giallorino as lead-antimony yellow is one of the symptoms of this confusion. The mineral form of lead antimoniate is bindheimite, which is indeed found in areas of active volcanism. Also found at volcanoes are the yellow minerals of native sulfur and the aforementioned orpiment. Sulfur makes a lousy pigment but orpiment is as good a candidate for giallorino as bindheimite. To confuse the issue further, near Naples there is a yellow volcanic tuff (a glassy silica-rich volcanic rock) historically used as a building stone. It too has been proposed as Cennini's giallorino. Even stranger things than these have been labeled giallorino and/or Naples yellow. Go figure.

Suggested Reading: _Artists' Pigments_, volumes 1 & 2, copyright 1986 and 1993 respectively by the National Gallery of Art, Washington, DC. These two volumes summarize the current state of the art in conservation science as applied to pigments.

Selected Bibliography:

Kuhn, H., 1993, "Lead-Tin Yellow" in: _Artists' Pigments_, vol. 2, A. Roy, ed., National Gallery of Art, Washington, DC, pp. 83-112.

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