

## Using iron (II) sulphate (iron vitriol) to colour lime render

**Background** I have recently carried out some research on the use of iron vitriol to get a lime wash that has a particular shade of orange, similar to that used on some of the houses in Nybboder, Copenhagen. This is a summary of what I found out.

The use of iron vitriol to colour limewash is a Swedish innovation from 1743 by Johan Julius Sandberg. Because of its effectiveness and low cost, it was the only method allowed for painting facades in Sweden in the 18<sup>th</sup> and early 19<sup>th</sup> centuries. Over the subsequent years its use spread across the world until replaced by modern facade paints and treatments. These days it is possible to buy iron vitriol that is pre-mixed with lime milk (kalkmjölk). In Sweden Målarkalk (malarkalk.se) has the product "Kalkmjölk PK608", while in Denmark Kalk A/S (kalk.dk) has the product "BL13A Jernvitriol". The Danish product is recommended for Nyboder houses. In my test set-up these products give slightly different shades of orange when applied to fresh lime render. The colour of PK608 tended to orange-yellow while BL13A had a redder tinge. As neither of these products gave the shade of ochre orange that I was looking for, I decided to look up the different recipes that have been used over the years and to change their composition to achieve my target colour.

**Recipes:** One of the challenges I faced is that historical recipes for iron vitriol mixtures are often ambiguous about exact quantities and sometimes about the materials. In terms of chemistry, the orange colour comes from the reaction of iron (II) sulphate (iron vitriol) with calcium hydroxide (lime) to form a hydrated iron (II) hydroxide, which is dark green. This oxidizes to iron (III) hydroxide (orange) and eventually forms a hydrated iron oxide. Thus, when the ingredients are blended the resulting mixture has a dark green-grey colour. With time, this changes to orange and deepens in intensity. Here are some examples of historical recipes:

<i>iron vitriol</i>	<i>water</i>	<i>lime</i>
850 g	4 L	Mix lime with water to form a putty. Mix the iron vitriol solution with the putty until the solution is thin enough to use as paint
142 g	4.5 L	Mix enough lime to give the required colour
1 part	5 parts at 50-60 °C	A 1:1 mix of iron vitriol solution with lime milk (made from 1 part lime putty and 5 parts water) is mixed with 1 L of water.
<i>Historical recipes for iron vitriol and lime mixtures.</i>		

In my tests I used iron (II) sulphate heptahydrate as the iron vitriol. This can be purchased from chemical suppliers or builders' merchants (e.g. as Nitor Järnvitriol). The iron sulphate

should be a crystalline solid with a pale apple-green colour. A yellow-brown coloured iron sulphate is indicative of a partially oxidized material, so is less effective in giving a predictable colour. I used lime milk (Hyllingegårdens Kulekalkmjölk) and lime water (kalkvatten) from Målarkalk.

For my colour tests I coated a piece of plywood with a 1 cm thick layer of lime render (Hydraulisk kalkbruk NHL3.5) and painted on it small squares with the different iron sulphate mixtures. In parallel, I covered an outside brick wall with the same render and painted on it squares from the mixtures. (figure below). To try and match colours – which have different hues depending on the light – I also compared my indoor sample board with the wall of one of the Nyboder houses in Copenhagen.



*(top left) colour samples (indoor), (right) colour samples on outdoor wall, (above left) indoor colour samples against wall of house from Nyboder, Copenhagen.*

The main variables I changed in my experiments were: amount of iron sulphate, of water and of lime. I used lime milk, lime water and hydraulic lime render (hydraulisk kalkbruk) as the sources of lime, as well as pure calcium hydroxide. All react with the iron sulphate to initially give a dark green mixture, which after application changes to a shade of orange. I also did a small study to see whether the presence of chloride, nitrate or carbonate ions affected the final colour.

**Rules of thumb:** There are two useful rules-of-thumb that emerged from my studies. The first, and obvious, one is that irrespective of the lime (putty/milk/water/render) used, the higher the amount of iron sulphate, the more intense the colour that is achieved. The

resulting orange. The amount of water used is only of importance to control the viscosity of the mixture. Chloride, nitrate and carbonate in the mixes had little, if any effect on the final colour.

*Maximum amount of iron sulphate:* The maximum amount of iron sulphate that can be included in a mixture is limited by its solubility. As this increases with temperature, warm or hot water should be used when dissolving the iron sulphate. In this way the maximum amount that can be dissolved is around 585 g/L.

*Amount of calcium hydroxide:* The amount of calcium hydroxide that is available to react with the iron sulphate depends on whether one uses lime milk, lime water or lime render. Lime milk typically contains around 100-110 g/L of calcium hydroxide, while limewater has 1.7 g/L. Lime render has the highest amount of calcium hydroxide per unit weight. However, unlike the other two, it may contain significant amounts of calcium carbonate (limestone) and sand, depending on how it is produced.

*Using Lime render (kalkbruk):* Mixing iron sulphate crystals with hydraulic lime render and then adding water, followed by thorough blending, gave a thick mixture that could be applied either as a render or as a wash that gave coatings with a uniform pale orange/orange-yellow colour throughout their thickness. The dry surfaces were slightly dusty. A typical mixture is:

#Q	iron sulphate: 536 g	water: as needed	Hydraulisk kalkbruk NHL3.5: 1 kg
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*Using Lime milk (kalkmjölk):* Lime water is the source of lime used in the commercially available orange limewashes. A mixture that gives a strong orange colour is:

#SP8	iron sulphate: 375 g	water: 1 L	kalkmjölk: 570 mL (contains ~57-63 g calcium hydroxide)
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The iron sulphate is first dissolved the warm water, and the lime milk is added gradually with vigorous stirring. The mixture thickens but can be applied using a brush. I found that higher amounts of lime milk than used in #SP8 gave a paler and dustier orange. Mixtures should be prepared freshly and, in my experience, the best results are obtained if they are used within 2 hours of mixing. They should be stirred repeatedly during use.

*Using Lime water (kalkvatten):* Lime water is not often employed as the source of calcium hydroxide in iron vitriol limewashes and I could not find any recipes that used it. However, there are records that iron vitriol mixed with limewater, with no added lime, was used on the façade of the newly-built royal palace in Stockholm in the mid 18<sup>th</sup> century. It is reported that its reaction with fresh lime plaster produced an intense orange ochre colour that darkened with time. As for the case of #SP8, the iron sulphate is first dissolved in warm water. A recipe for this mixture is:

#F7	iron sulphate: 585 g	water: 1 L	kalkvatten: 1.5 L (contains ~2.5 g calcium hydroxide)
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The limewater is added slowly with constant stirring. Stirring is continued for some minutes after the addition is complete. The mixture has a viscosity that is similar to water but it can be applied using a wide brush. Mixture #F7 gave the most intense flaming orange ochre colour of all the mixtures I studied, (see figure below). Once dry the surface is dust free and the colour does not leach.

In use this mixture should be stirred frequently and should be applied carefully to avoid and drips run-offs. It needs to be prepared freshly before use and used up within 2-3 hours of preparing. I have observed that if this mixture is applied onto a layer of render that uses lime recovered from earlier use and blended with fresh lime, then the resulting colour will be uneven, giving a pleasing lively appearance to the wall. If a more uniform colour is required, then only fresh lime should be used for the top layer.

With this mix each wall needs between 5 and 8 coats, ideally finished with a final coat of limewater. However, mixture #F7 has very good coverage. I used a total of 8 kg iron sulphate and 17 L of kalkvatten to paint to completion ~76 m<sup>2</sup> of fresh render (equivalent to 400 mL/m<sup>2</sup>).



*Mixture #F7 applied to fresh lime render. Photographs were taken under different lighting conditions.*

**Overview:** The use of iron sulphate in limewash to colour lime render allows for a wide range of orange hues to be achieved. To achieve paler or yellower oranges, the amount of calcium hydroxide relative to the iron sulphate should be high, and is most easily achieved using either lime render or lime milk. Conversely, to achieve the strongest and most red hues requires the iron sulphate to be present in vastly higher amounts than the calcium hydroxide. This is most easily achieved in mixtures that use limewater.

## References and Links

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