WHY THE RED/GRAY CHIPS ARE NOT PRIMER PAINT

Niels Harrit, May 09

It has been suggested, that the red/grey chips discovered in the dust from the WTC collapse catastrophe[1] could originate from rust-inhibiting paint (primer paint) applied to the steel beams in the towers. This letter compares the elemental composition and the thermal stability of the two materials based on the description of the protective paint in the NIST report and observations on the red/grey chips.

CHEMICAL COMPOSITION OF THE PRIMER PAINT

The primer paint applied to the steel beams of WTC is described and characterized in NIST NCSTAR 1-3C appendix D.[2]

The primer paint is red/orange and was originally applied in order to protect the steel against corrosion.

Examples of typical beams are shown in Figure 1 and Figure 2.

Figure 1. M2-C2M (WTC 1, Col.130, Fl 98) from NCSTAR 1-3C appendix D[2].

Figure 2. Perimeter columns in WTC towers. From NIST.

The color is due to the pigments in the paint. Iron oxide is red and zinc chromate (”zinc yellow”) is – well - bright lemon yellow (Figure 3).

Table D–1. Composition of primer paint.

Pigment	Iron oxide	35.9 %
	Zinc yellow	20.3 %
	Tnemec pigment (proprietary composition)	33.7 %
	Diatomaceous silica	10.1 %
Vehicle	Soya alkyd resin solids	16.5 %
	Hard resin	2.8 %
	Raw linseed oil	35.1 %
	Bodied linseed oil	6.4 %
	Suspension agents	2.2 %
	Driers and anti-skin	4.8 %
	Thinners	32.3 %

Source: Sramek 1967.

Figure 3. Composition of primer paint from NCSTAR 1-3C appendix D[2].

Since the "vehicle" is obviously fluid, the values for the ingredients in it must refer to the paint before application in percentage by weight.

Even though the composition of the Tnemec pigment is proprietary, the content of this component can be obtained from the Material Safety Data Sheet, from which the pertinent information is reproduced in Figure 4:

INGREDIENTS	CAS#	% By Wt.
ZINC COMPOUNDS**		2.98
ORGANIC COBALT COMPOUNDS (AS COBALT)**		.10
IRON OXIDE FUME	1309-37-1	1-5
IRON OXIDE FUME	1309-37-1	6-10
CRYSTALLINE SILICA (QUARTZ)	14808-60-7	4.36
TALC (RESPIRABLE DUST)	14807-96-6	21-30
CALCIUM SILICATES AND ALUMINATES		6-10
AMORPHOUS SILICA	7631-86-9	1-5
MINERAL SPIRITS, AS STODDARD SOLVENT	8052-41-3	22.71

Figure 4 Extract from Material Safety Data Sheet for Tnemec pigment.[3]

Talc is magnesium silicate hydroxide, $Mg_3Si_4O_{10}(OH)_2$.

The content of calcium silicates and aluminates is inexact and the relative contribution of aluminates is not specified.

Since the Tnemec pigment contributed 33.7 % to the wet primer paint, the content of these two ingredients and the solvent in the wet primer paint was:

Talc $Mg_3Si_4O_{10}(OH)_2$	7 – 10 %
Calcium silicates or aluminates	2 – 3.3 %
Mineral spirits:	7.6 %

After application, the paint was baked at 120 °C. In this process all volatile ingredients evaporate. Thinners (Figure 3) and mineral spirits (from the Tnemec pigment) amount to (32.3 + 7.6) $\approx$ 40 %. If we subtract these from the composition percentages given above, we get a rough estimate of the composition of the hardened paint.

That is, by dividing by 0.6 we get the following values for the pertinent ingredients of the hardened paint (dismissing the trivial elements iron, silicon, carbon and oxygen):

Component	Composition in wet paint	Composition in dry paint
Zinc chromate ($ZnCrO_4$)	20.3 %	34 %
Talc ($Mg_3Si_4O_{10}(OH)_2$)	7 – 10 %	12 – 17 %
Calcium silicates or aluminates	2 – 3.3 %	3.3 – 5.5 %

Table 1. Pertinent components of primer paint corrected for solvent evaporation.

COMPARISON WITH THE COMPOSITION OF THE RED/GRAY CHIPS

The elemental composition of the red/gray chips was obtained by means of X-ray Energy Dispersive Spectroscopy (XEDS) in the SEM mode.[1] Before measurement, the chips were broken (with one exception to be discussed below) in order to secure a fresh uncontaminated surface from which the SEM XEDS was obtained. NONE of these SEM XEDS spectra, taken from four independently collected samples, showed signals from either zinc, chromium or magnesium in intensities significantly above the baseline noise. See the right panel of Figure 5 below in which the intensity scale is expanded. Strong signals from these three elements could be expected from the primer paint according to Table 1.

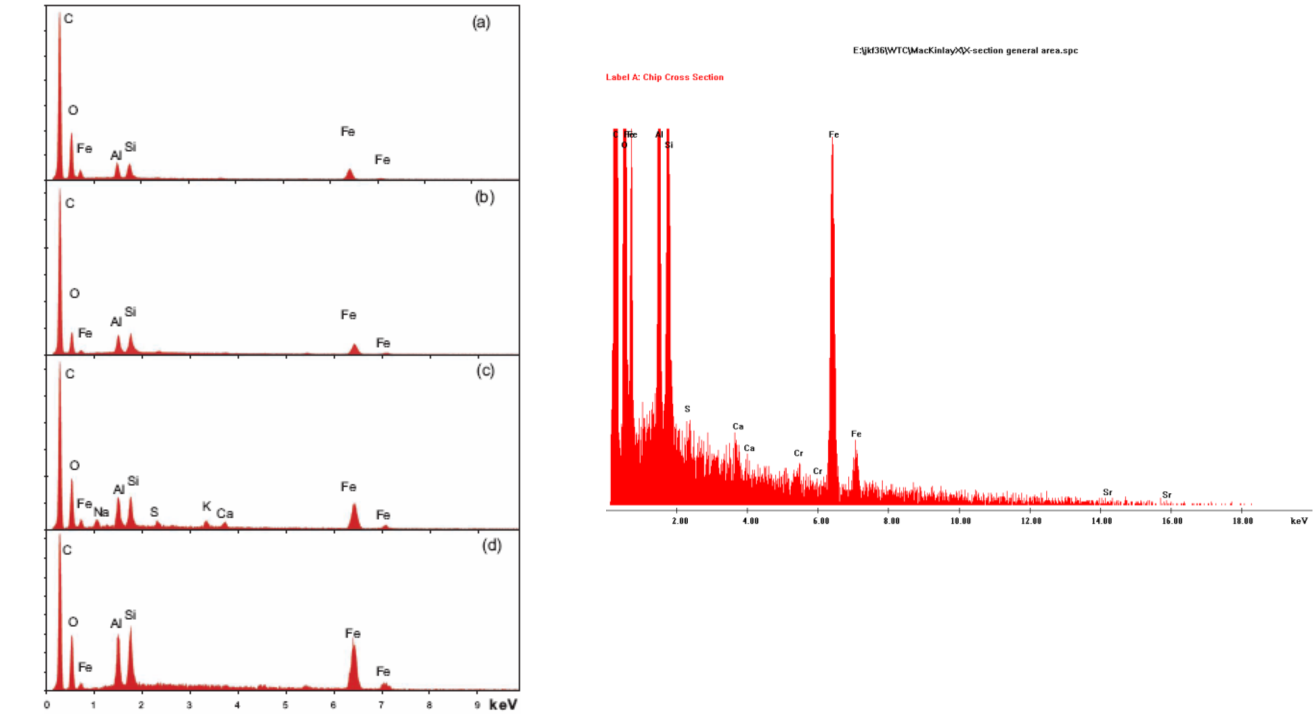


Fig. (7). XEDS spectra obtained from the red layers from each of the four WTC dust samples, with (a) corresponding to sample 1 and so on (b–d).

Figure 5. SEM XEDS (beam energy 20 keV) spectra from fresh surfaces of red phase of red/gray chips.
Left: Figure 7 in Harrit et al.[1], showing the four different samples investigated.
Right: The same spectrum as in frame (a) with intensity (vertical) and horizontal scales expanded. Minute signals in level with the noise are observed from sulfur, calcium, chromium and strontium.

In one experiment the chips were to be soaked in methyl ethyl ketone (MEK) and could not – for good reasons – be broken before. The resulting XEDS of this chip (Figure 6, below) displays tiny blips indicating the presence of chromium and zinc. They disappeared after the chips had been soaked/rinsed with the organic solvent. Therefore, they are believed to derive from surface contamination, which very well could have been from the primer paint(!).

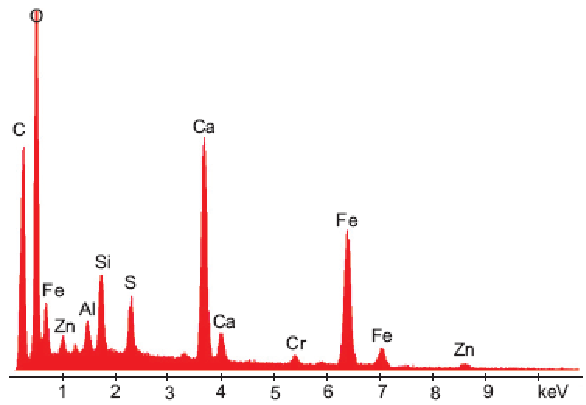


Figure 6. SEM XEDS (beam energy 20 keV) from unbroken chip before soaking in MEK. The calcium and sulfur are likely to originate from contamination with wallboard material (gypsum, calcium sulfate). The signals from zinc and chromium could be from a surface contamination with primer paint.

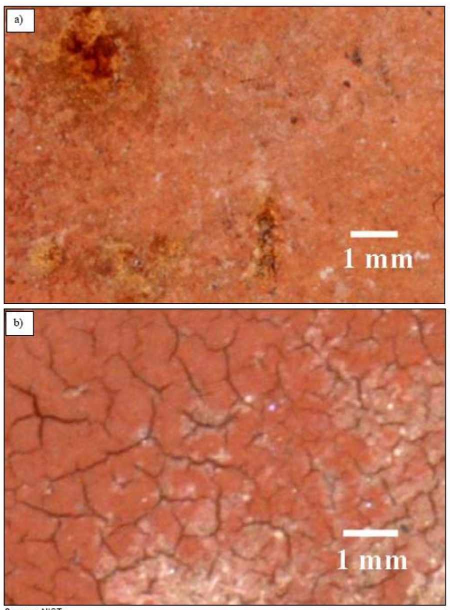
Magnesium was never observed, which is another element characteristic of the primer paint (Table 1).

It should also be noticed, that the only possible source of aluminum in the primer paint is the rather vague reference to ”calcium silicates or aluminates” in 3.3 – 5.5 % presence. Without attempting any quantitative estimates (not a trivial matter in XEDS), it is still very hard to accept this component as the source of the bright-and-clear signals for aluminum from the red phase of the red/gray chips.

THERMAL STABILITY OF PRIMER PAINT

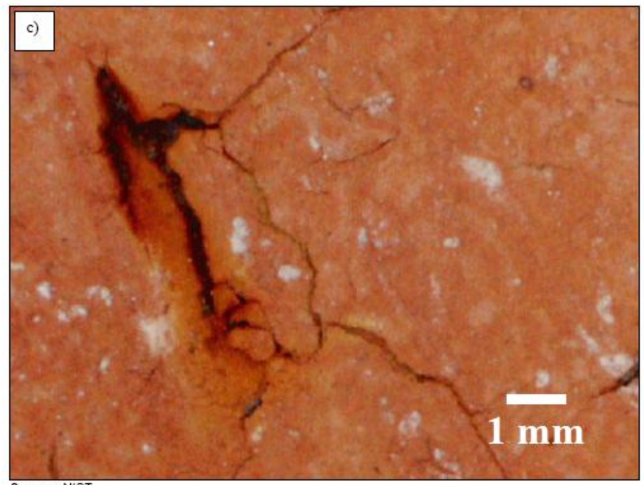
NIST was interested in the thermal response of the primer paint since examination of the condition on the recovered steel beams could be indicative of the temperatures they had been exposed to.

NIST carried out temperature studies on selected beams and made the following observations.[2] The paint is unaffected to temperatures up to 250 °C (Figure 7a). At higher temperatures the paint starts showing ”mud-cracks” as they can be seen in Figure 7b (left). This fracture is due to the different expansion coefficients of the steel and the paint. It gets worse at 650 °C (Figure 7, right) at which temperature black ”scales” (layers) begin to form between the paint and the steel (Figure 8). NIST took the samples beyond 800 °C at which temperature the scale formation and peeling off of the paint from the steel was prevailing. One may hypothesize that formation of the black scales is due to charring of the organic binder.



Source: NIST.

Figure D–1. Photographic images of the primer paint. a) paint in its original condition and b) mud cracking of paint after exposure at 250 °C for 1 h.



Source: NIST.

Figure D–2. Photographic images of the primer paint. c) mud cracking of paint after exposure at 650 °C for 1 h.

Figure 7. Left: Primer paint on exterior WTC column at temperatures below 250 °C (panel a) and beyond (panel b). Right: Exposure of primer paint on steel to 650 °C for 1 hr

Source: NIST.

Figure D–4. Formation of a black scale between paint and steel after exposure greater than 650 °C. Paint readily spalled.

Figure 8. From NCSTAR 1-3C appendix D[2] showing formation of a black layer under the primer paint at temperatures beyond 650 °C.

Notice, that the primer paint – being basically a ceramic material – is chemically stable at temperatures up to 800 °C.

COMPARISON WITH THERMAL STABILITY OF RED/GRAY CHIPS

In contrast to the primer paint, the red/gray chips react violently, igniting in the neighbourhood of 430 °C. The reaction must produce temperatures no less than ca. 1500 °C, since the residues from molten iron are clearly seen in the optical microscope (Figure 9).

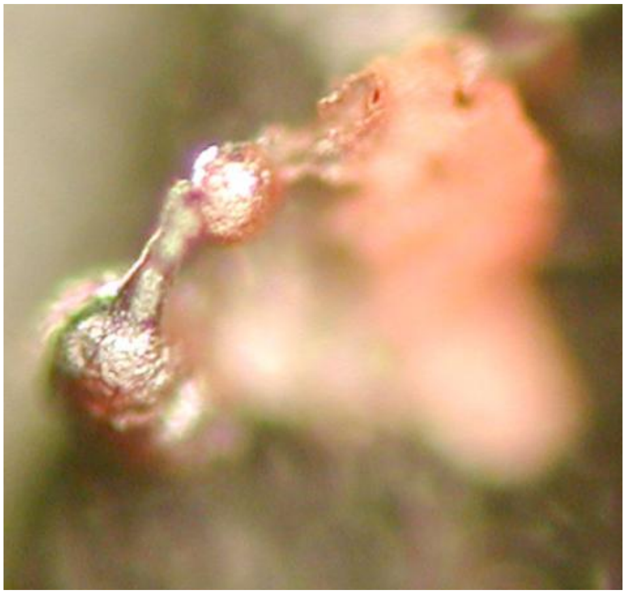


Figure 9. Optical microscope picture of red/gray chip after reaction in a DSC instrument.[1]

CONCLUSION

The properties of the primer paint and the red/gray chips are inconsistent.

The red/gray chips cannot be the primer paint as it is characterized by NIST.

REFERENCES

(1) Harrit, N.; Farrer, J.; Jones, S. E.; Ryan, K.; Legge, F.; Farnsworth, D.; Roberts, G.; Gourley, J.; Larsen, B. Active Thermitic Material Discovered in Dust From the 9/11 World Trade Center Catastrophe. *The Chemical Physics Open Journal* **2009,** *2,* 7-31.

(2) NIST. NIST NCSTAR 1-3C. 2005. http://wtc.nist.gov/NCSTAR1/PDF/NCSTAR%201-3C%20Appxs.pdf

(3) http://www.tnemec.com/resources/product/msds/m10v.pdf