Cautionary Tale: Heat Treatment Oxide

During a recent training course given in China by the author on behalf of IST, a delegate asked many questions about the changing colour of 302 stainless steel spring wire during spring production at his factory. This prompted another delegate to ask about the colours arising during the manufacture of springs in music wire. They were not the first to ask these questions, but they were very interested to know the reasons for colour changes, and so I thought that would be a good subject for a cautionary tale. The first thing to point out is that the colour changes in both materials have the same root cause, and the colours are not real, but are merely a trick of light.

Whenever steel is exposed to temperatures above ambient the oxygen in air will react with the steel surface so that an oxide will grow. Steel will always have an oxide on its surface because this oxide will form naturally at ambient temperatures, but the oxide is much too thin (measured in nanometers) to be seen. Indeed, the existence of this oxide is seldom acknowledged for carbon steel in most texts, but please be assured that it is there. However, stainless steel is assumed to have a chromium oxide on its surface, and this explains why it does not go rusty. The surface of both carbon steel and stainless steel oxidises in air to form an oxide that confers corrosion resistance, and this brings the first cautionary aspect to this tale. Oxidation and corrosion are separate phenomena, but are frequently confused – a quick search on the internet for oxidation of steel brought up many articles on corrosion, a few articles on high temperature oxidation, but almost none on ambient temperature oxidation.

The main oxides of iron are said to be red (Fe_2O_3) or black (FeO) in colour. This is true when the oxide is micrometers thick, but the oxide forming on a bare steel surface in air is nanometers thick and is, to all intents and purposes, colourless and translucent. This very thin oxide confers corrosion resistance, and as springmakers know, steel springs do not generally go red rusty ($Fe_2(OH)_3$) in their factory despite having no protection from oil at various stages of manufacture – more about this later. The formula for rust contains H because rust occurs due to the reaction of oxygen <u>and</u> water with a spring surface.

This nanometer thick oxide is colourless and so cannot be seen on carbon or stainless steel. However, after coiling, carbon steel springs are heat treated in air at 200 – 350°C, and this will cause the oxide to grow thicker. At 225°C the oxide is thick enough to refract the yellow part of incoming white light and so they appear to turn yellow. Except that carbon steel spring wire often has a phosphate coating with some soap, and so the surface is quite black prior to heat treatment, and so this yellow colour is not usually observed unless the wire surface is particularly bright. At 275°C the oxide is thick enough to appear to be blue if the original black wire surface permits. The translucent oxide refracts incoming light, and this why it was stated earlier that the colours are a trick of light.

The colours are more readily seen after spring end grinding. A yellow colour indicates that the grinding did not heat up the ground end excessively, and the same can be said if the end coil goes light blue. However, the grinding may have been abusive if the temper colour was dark blue or black - indeed these colours can be used as a simple but effective quality control check for the grinding process. If carbon or SiCr spring steel is shot peened, then it is common practice to apply a low temperature heat treatment (or warm prestress) afterwards in order to recover the relaxation resistance, which is damaged during shot peening. The shot peening knocks off any oxide from previous processes and leaves the spring surface bright, but vulnerable to corrosion. The oxide will grow back at ambient temperature, but in conditions of 100% humidity, rust may form prior to the oxide. In tropical or monsoon affected countries springs can be seen to go red rusty soon after they emerge from the peener. Hence it is good practice to get freshly peened springs into an oven as soon as possible, and make that corrosion resistant oxide grow. Carbon or SiCr springs will go an agreeable yellow colour if the heat treatment is carried out at 225°C – a commonly used temperature for this process.

Up to now I have said the colours on carbon and low alloy steel have the same root cause. This is correct, but the temperature required that causes 302 stainless steel to go a light yellow colour is much higher than for carbon steel. The yellow colour is just visible if the heat treatment temperature after coiling is 350°C, and spring manufacturers often limit the stress relieving to this temperature so as to avoid the darker yellows that would appear at 400° or 450°C. Their customers frequently say don't like to receive yellow springs. This is despite the fact that heat treating compression springs at higher temperatures than 350°C will improve their relaxation and fatigue performance. If good performance is required and an absence of the yellow colour, then spring makers, after heat treatment, employ a pickle (to remove the yellow oxide) and passivate process, which puts in place a very thin and adherent oxide that is too thin to cause the yellow colour, and which has excellent corrosion resistance.

The second moral of this cautionary tale is that the thin oxide on spring steel is beneficial and the apparent colours formed can be used as a simple quality control tool in production.

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Readers are encouraged to contact him with comments about this cautionary tale, and with subjects that they would like to be addressed in future tales - e-mail m.hayes@springexpert.co.uk