INTERNATIONAL MOLYBDENUM ASSOCIATION
THE VOICE OF THE MOLYBDENUM INDUSTRY

Coloring the world

Molybdenum compounds have been used in commercial pigments for over a hundred years. They continue to play an important role in today's sustainable and environmentally safe colorings.

Color comes to us as visible waves directly from a light source and from light reflected off objects. An object might have a natural color or it might take its color from a pigment. Pigments are particles of a coloring substance, added to give color to paints and solid materials like plastics. Molybdates began to play an important part in the pigment world about one hundred years ago and continue to do so today.

A colorful history

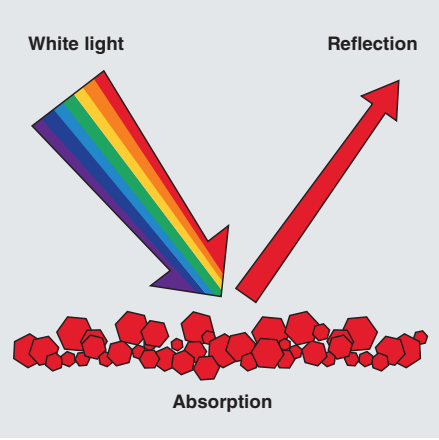
Pigments were vital to the earliest human art. In the Lascaux caves in Southwestern France, prehistoric artists mixed burnt wood, clays, and oxides of iron and manganese with water and animal fat to produce colored drawings depicting wildlife and hunting scenes. From early historic times, people also used inorganic oxide pigments to color bowls and other useful objects. These simple pigments were used later to color religious manuscripts. In the 15th century, "natural earth pigments" (oxides of iron colored by impurities) appeared in architectural decoration.

Innovative 19th century artists like Turner and Delacroix used new synthetic pigments to incorporate color into paintings. Common pigments of the time included Chinese White (zinc oxide), Chrome Yellow (lead chromate) and Cadmium Yellow (cadmium sulfide). In 1863, H. Schultze first identified molybdate as a possible pigment constituent in his studies of lead, chromium and molybdenum compounds. The resulting early 20th century pigments are now known as molybdate pigments.

Throughout the 20th century, chemists developed many oxide-based inorganic pigments and a wide array of organic pigments with bright, pure colors. Today, pigments are loosely categorized as commodity/high-performance and inorganic/ organic. Molybdenum compounds are found in commodity and high-performance inorganic and organic pigments.

Function and performance

A pigment absorbs light of certain wavelengths from the light striking its surface and reflects wavelengths that produce its color. For example, a red pigment absorbs the violet, blue, green and orange wavelengths, reflecting red. Scientists can manipulate pigment compounds to control which wavelengths are reflected and which are absorbed.



A simplified example of the function of pigments. Only the red part of the white light, which contains the spectrum of colors, is reflected from a red pigment surface, the rest is absorbed.

Depending on the application and the manufacturing process, different pigment properties are important. Some of them are:

- Lightfastness, the ability of a pigment to resist discoloration over time by light
- Heat stability, the ability of a pigment to resist elevated temperatures
- Tinting strength, the ability of a pigment to alter the color of the paint or plastic
- Hiding power/opacity, the ability of a pigment to obscure the background of a contrasting color
- Resistance to chemicals such as acids or solvents

More recently, toxicity and environmental impact have come to the fore in pigment science, generating a push to replace older, sometimes toxic, pigments. New compounds can also help improve sustainability. In buildings, for example, metal roof coatings now can employ a pigment specially designed to absorb infrared radiation if passive heating is required, or to reflect solar energy if cooling is desired. In each case, the pigment lowers energy costs.

Molybdenum pigments today

Molybdate orange is a mixed-phase crystal containing varying proportions of lead chromate, lead sulfate and lead molybdate[1]. In experiments with molybdenum, H. Schultze noticed that the yellow mineral Wulfenite (lead molybdate, $PbMoO_4$) was colored strongly red when it occurred with Crocoite (lead chromate, $PbCrO_4$). Modifying lead chromate with molybdate allows the resulting molybdate orange pigment to ›

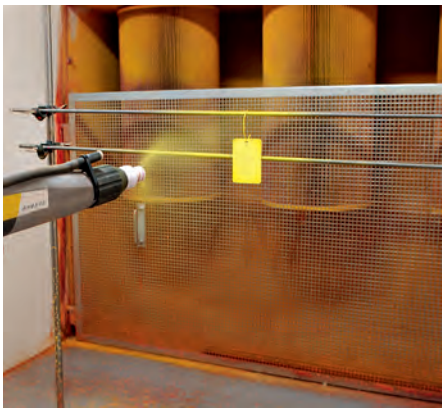
1 Typically the contents range from 75–90% lead chromate, 3–15% lead sulfate and 10–15% lead molybdate.

take hues from bright red-orange to red-yellow. Due to its brightness, it rapidly became a popular pigment in the 1930's. Today, the pigment is known as Pigment Red 104. It is generally described as having good opacity, durability, and heat stability and is especially noted for its solvent resistance. Usage is around 12,000 tons per year, primarily for industrial coatings and coloring plastics. In recent years, toxicity concerns[2] limited its use in consumer products such as children's toys. Its toxicity derives from the lead and chromate components of the pigment, not from the molybdate. The EU has scheduled it to be phased out by 2015.

Bismuth vanadate yellow, known as Pigment Yellow 184, typically incorporates 1–5% molybdenum in the $(BiVMo)O_4$ mixed-metal oxide, when it is produced by aqueous precipitation. It comes in bright greenish-yellow to reddish-yellow colors and has high opacity and excellent solvent and heat resistance. Molybdate stabilizes the color and confers corrosion protection very similar to that obtainable with lead chromate[3].

This pigment was first synthesized in 1924 and commercialized around 1985. It produces yellows equivalent to those of the toxic chromium or cadmium-containing pigments and can also be used to mix colors such as beige, orange and green. Between 2,000 and 5,000 tons are used annually for high-quality automotive and industrial paints, coil coating, indoor and outdoor architectural paints and plastics coloring. It is an excellent replacement for pigments containing lead or cadmium where weather resistance is important. It also enhances the color stability of organic pigments. Free of lead and very stable, these pigments pose low environmental and health risk and appear frequently in food packaging.

Rare Earth – molybdenum oxide pigments is an emerging group of what might become the next class of high-performance pigments, combining molybdenum with rare earth metals like cerium, lanthanum, and samarium to make new colored oxides. These green-yellow pigments are stable and environmentally benign. Molybdenum will play an important role here in replacing traditional lead, cadmium, and chromium pigments.



Powder coating with bismuth vanadate.
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Complex inorganic color pigments are a new class of high-performance pigments created from oxides containing two or more metals, boasting outstanding resistance to dissolution by chemical agents. These complex oxides use the transition metals V, Cr, Mn, Fe, Co, Ni, and Cu to form their basic oxide structure and color. Adding molybdenum modifies their color. As a class, they are the most stable and durable type of colorants commercially available.

Bismuth vanadate pigments are used in the yellow paint of ski mobiles.
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The molybdenum corner of the pigment world

The worldwide annual market for all kinds of pigments is about 8 million tons with a value of nearly $20 billion. Molybdenum-containing pigments account for a small part of the six-million-ton inorganic pigment market. However, increasingly they play an important role in meeting the need for environmentally friendly pigments, and can be expected to occupy a greater percentage of the market in years to come. Molybdenum helps make our world greener in more ways than one! (Curtis Kovach)

2 Lead chromate molybdate sulfate red (C.I. Pigment Red 104) is described as "a substance of very high concern because of its CMR properties" by the European Chemicals Agency (27 November 2009). [CMR: the abbreviation for Carcinogenic, Mutagenic and toxic to Reproduction]
3 US Patent 4,455,174. Arthur A. Tracton, Coatings Technology Handbook, Third Edition 2005