The Chemistry of Thin Film Color

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Key Words: Thin film, Chemistry, Color, Decorative

ABSTRACT

Colored thin films are of great importance in the decorative coating industry but there is a limitation on the colors available in the current palette. Understanding the mechanism of color in compounds helps us recognize the possibilities for enlarging the color palette available in durable vacuum deposited coatings.

INTRODUCTION

Decorative coatings in any industry are important not only for the look they provide but also for the protection that they offer for the intended use of the product.

Color is one attribute that expands the usefulness of a decorative coating to many items and many markets. In the case of PVD coatings there is a limited color palette and this hinders the expansion of the decorative market for these coatings.

The purpose of this paper is to explain the nature of the color in these coating materials and to suggest that there are many opportunities to expand the color palette for PVD coatings.

First, we are talking about metal compounds (oxides, nitrides, carbides, and also these materials with carbon) which are transparent but with selective light absorption characteristics. These materials as thin films in the 500 to 1000 nanometer thickness range are semitransparent and may be weakly or stongly colored depending upon the absorption of light energy. In the case of weakly colored films it can be observed that the color becomes more intense as the film thickness increases. As the film becomes opaque light energy that is not absorbed is now reflected and scattered to give the color of the material in bulk.

If the absorption is (in the simplest case) strong in a wavelength region of the visible spectrum say from 4000 to 7000 nm, and then the film will appear black because only the energy in the wavelengths outside the visible range is passing through the film.

If the film absorbs energy at different wavelengths in the spectrum then the film can be a specific color because this light is transmitted through the film i.e.: light absorbed below 4250 nm and above 4250nm gives a transmitted blue color.

In a pigmented system of colorant the mechanism of "coloring" is accomplished by tiny particles in a carrier. These tiny particles act as light filters and if two different wavelength transmitters are mixed then the color will be a combination the same as if these two transparent colors were laid on top of each other. (See Figure 1.)

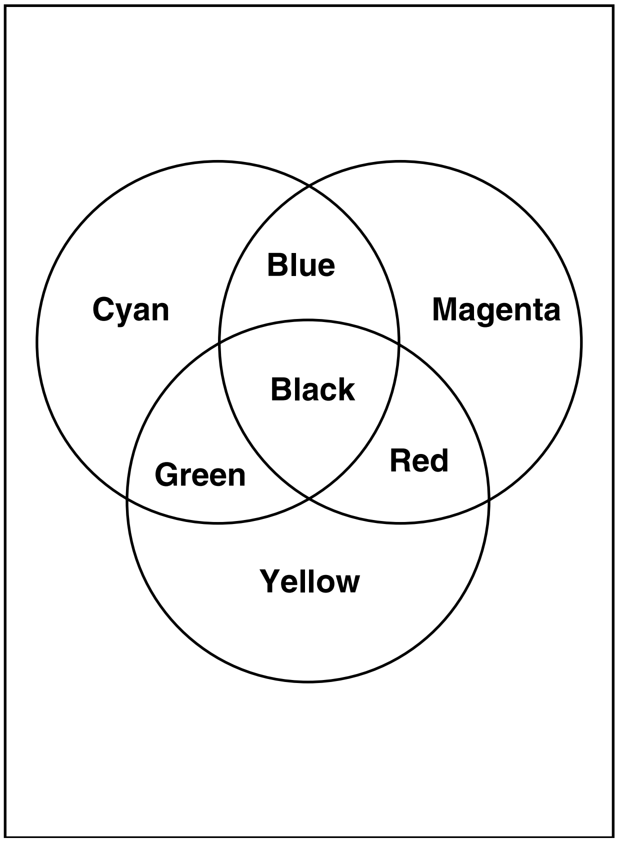

Figure 1.

For example: if blue and yellow colors are mixed then the resultant color is green.

43rd Annual Technical Conference Proceedings—Denver, April 15–20, 2000 ISSN 0737-5921

In a chemical compound that appears colored the mechanism is similar but it due to the interaction of light with the atoms in molecules. If there are different absorption frequencies in the compound the mixing of the transmitted or reflected light will make that compound appear a certain color because of the combination of the light that is transmitted and not absorbed.

Understanding how we can use this phenomenon of color mixing in thin films we can look for other compounds suitable for PVD that have the characteristics of wearability and color stability in order to broaden the PVD color palette.

Colored Compounds

If we take a material like titanium oxide and look in a chemical handbook we can find there are several different oxide colors. For example:

TiO	Black
Ti_2O_3	Blue
TiO_2	Colorless
TiO_3	Yellow

First lets examine TiO. Titanium is in the +2 oxidation state. So we have a pretty simple compound which appears black – but not a "true black", but a black with some grey tendency so if you look at it compared to a piece of anthracite coal you will see the difference. Which means that all visible light is not being absorbed in the film and there are other light frequencies that are being transmitted.

Why does this occur? In order to understand why light is absorbed or transmitted one has to look at the electronic structure of the material and what happens when light energy is absorbed.

If you map the electronic structure of titanium it has an argon nucleus with an additional 4 protons and 4 electrons.

The electron configuration can be represented as:

1s2 2s2 2p6 3s2 3p6 4s2 3d2
-or -
[Ar] 4s2 3d2

The key to color is in the unfilled "d" orbitals because when Titanium is oxidized to Ti+2 the electrons that are removed are the "s" electrons, so the electron structure of Ti+2 is:

[Ar] ___ ___ 3d1 3d2

Oxygen as O^{-2} has two electrons available to donate to the titanium ion so the combination that is formed fills the "s" electron energy level and the resultant compound retains the "d" electrons.

These "d" electrons are affected by light in the visible spectrum and the energy required to shift their energy level. The electronic influence of other ions such as the oxygen ion also affects the energy required to shift these electrons to another level.

Since the compound is black it means that most of the energy in the visible portion of the spectrum is absorbed which might mean that these "d" electrons are not tightly bound in the compound.

So what happens when we add more oxygen to a titanium compound to create Ti_2O_3 ?

First of all the oxidation state of titanium changes to Ti+3 with an electronic structure like this:

[Ar] ___ ___ ___ d1

combining with a bridging oxygen ion between two titanium ions each of which are bound to another oxygen ion. Again, the electrons from the oxygen ion fill the "s" electron level in both titanium ions and a "d" level in each. This leaves two "d" electrons that are available to absorb energy but there is a shift in absorption to the lower energy end of the spectrum (yellow, green, red) and the color of Ti_2O_3 is a very nice, rather pure blue.

We can produce some very nice mixtures of black and blue by varying the appropriate parameters in the deposition process and if you lose control of those parameters this results in the next compound, TiO_2 which is a colorless film.

This is the familiar TiO_2 which is used as a white pigment for paint but is clear in the thin film or mineral form. In this case titanium is in the +4 oxidation state as before but the empty "s" and "d" shells are filled with electrons from the O^{-2} . Since there are two oxygen ions both subshells are filled.

This configuration does not absorb any significant light energy at any wavelength in the visible region and this parallels it's stable electronic structure.

The final compound in the lineup is Ti O_3. This has been referred to as titanium peroxide.

In this case the chemistry becomes more complex because it is a peroxo compound with a structure $[\ Ti^{+4}\ O^{-2}\ ]^{+2}\ [\ O_2\ ]^{-2}$ with the electronic structure of the Ti^{+4}.

[Ar] ___ ___ ___ ___

with the empty "s" and "d" shells satisfied with electron contribution from an oxygen ion and a peroxo ion. The stability of this complex is high and absorbs some light in the visible region and gives a yellow color.

Conclusion

The inference of the above example of the varied colors of titanium oxide is that there are other metals unfilled "d" shells whose oxides, carbides and nitrides are colored and which may possess the characteristics of wearability and stability for application as decorative coatings.

Some of these metals, compounds and ions are shown in the table below:

Vanadium	4s2 3d3	
	V_2O_5	yellow
	$VO]^{+2}$	Blue
	$V_2\ [CO]_3$	green
Niobium	5s1 4d4	
	Nb_2O_3	Blue
Tantalum	6s2 5d3	
	Ta_3N_5	red
Chromium	2S1 3d5	
	Cr_2O_3	green
Manganese	4s2 3d5	
	$MnSiO_3$	red
Molybdenum	5s1 4d5	
	MoO_2	red

Hopefully this paper has shed some light, so to speak, on the task of enlarging the selection of colors available to users of PVD coatings.

By using the appropriate compounds and mixing the right colors it should be possible to achieve a wide variety of colors. With the right equipment and experimental technique all that is left to do is make them.

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