National Coil Coating Association
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Pigments for the Coil Coating Industry

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Introduction

The purpose of this document is to summarize for the members of the National Coil Coating Association (NCCA) matters relating to pigments in the coil coating industry. Much written information is currently available covering all the different aspects of pigments and working with pigments, so rather than write another summary which would be mostly rewriting what has already been written, the approach here is to outline the different topics pertaining to pigments and use the outline to organize a bibliography of the pigment literature. The goal is that a member of the NCCA, wanting to learn about a particular subject related to pigments, can use this bibliography to quickly identify references covering the subject of interest.

Pigments

Pigments are particulate matter added to other materials in order to change the properties of the other material. Usually, the properties that we think about changing are color and appearance properties, but pigments are also used to change physical properties of the system (e.g. rheology modifiers) or cost (e.g. low-cost fillers). Pigments differ from dyes in that they are not intended to dissolve in the host system. Upon incorporation into the system (i.e. the coating) they should retain the physical nature they had before incorporation and should not react chemically with the system components (i.e. they are intended to be inert). There are many types of pigments used in polymer coatings and they can be classified by the chemistry of the pigment, the color of the pigment, the function of the pigment, etc. The next section discusses ways of classifying pigments.

Classification of pigments

One common way of breaking the pigment world into smaller units is to split it into inorganic pigments and organic pigments. This division not only makes sense because of the different chemistry of the two types but also because the properties (color, strength, opacity, stability, etc.) of the pigments divide along the same line. Organic pigments are those made of carbon-containing molecules. Inorganic pigments are metal oxides, sulfides, or metal salts. (Some pigments, for example copper phthalocyanine, are complexes of a metal with an organic ligand. These are considered organic pigments.)

This Tool Kit is part of a series of educational aids developed by the members of the National Coil Coating Association. NCCA is a trade association of coil coaters and suppliers of raw materials and equipment used in the coil coating process. The association concentrates its efforts on providing educational resources and assisting its members in providing superior products and services to their customers. NCCA Tool Kits are information tools and should not be used as substitutes for instructions from individual manufacturers. Always consult with individual manufacturers for specific instructions regarding their products and equipment.

Another way to divide up the pigments is to classify them as colored or functional. Colored pigments are used to impart color, whereas functional pigments (usually white or colorless) are used to change the non-color properties of the system, for example fillers to lower overall cost, rheology modifying pigments, flatting agents, impact strength modifiers, etc. Most functional pigments are inorganic pigments.

The *Colour Index* [1], a product of The Society of Dyers and Colourists, is the most widely referenced classification system for pigments. It's useful when referring to a pigment because the *Colour Index* designation defines the chemical type of pigment. For example, C.I. (Colour Index) Pigment Red 101 is iron oxide red, and C.I. Pigment Blue 15 is phthalocyanine blue. The *Colour Index* also cross-references product trade names and manufacturers against the C.I. designation. The Color Pigment Manufacturers Association (CPMA) [41] publishes a useful guide classifying the subset of inorganic pigments called *Complex Inorganic Color Pigments* [2]. Organic pigments are commonly classified according to the chromophore that produces the color, for example azo pigments, quinacridones, etc. References [6], [7], and [8] all describe the classification according to chromophore.

For general information about a particular pigment I recommend the *Pigment Handbook* [3], and also the Kirk-Othmer articles [6] and [11] or the FSCT book [7]. In addition, pigment manufacturers are good sources of information and publications about their products.

Types of pigments

Though what follows is a list of types of pigments, the list is intended to cover most of the common types and may not include all pigment types. Good ways to determine suppliers of the different types of pigments are to consult the *Colour Index* [1], or one of the many Buyers' Guides (refs. [33], [34], and [35] and others) published by the coatings trade journals.

White Hiding Pigments

The main purpose of white hiding pigments is to provide the coating with bright white color and opacity. Several pigments are used, though titanium dioxide is by far the most common opacifying pigment.

<u>Titanium dioxide</u>

Titanium dioxide (C.I. Pigment White 6) is the most commonly used white opacifying pigment and is the largest single volume pigment used in coatings. Titanium dioxide is available in two crystalline forms, anatase and rutile. These two structures have different behavior with respect to both optics and durability. The application generally dictates the form needed, with rutile having better opacifying capability and durability. Many grades of titanium dioxide, especially the rutile grades, are surface treated with other oxides to improve their performance in one or more respects. Reference [3] (pp. 1-42) has a good discussion of titanium dioxide pigments, including the differences between the two crystalline forms, different grades available, typical physical properties, performance properties, durability, dispersibility, methods of manufacture, and manufacturers. The article dates from 1985, so some of the information may be out of date. Reference [12], pp. 43-70, has a more recent treatment (though not as detailed) of titanium dioxide. It covers grades, properties, manufacturing methods, producers, and applications.

ASTM D 476 (in volume 6.03) [40] is a standard classifying the several types of dry pigmentary titanium dioxide products and listing some typical properties. Suppliers of titanium dioxide can be found in the various buyers guides ([32], [33] and [34]) and in [12]. Understand that not all suppliers are always listed in a buyers' guide.

Photocatalysis

Photocatalytic degradation of polymer films is a consideration with titanium dioxide pigments. Exterior-grade titanium dioxide generally has one or more surface treatments to minimize the photocatalysis. References [36] and [37] give good discussions of photocatalysis by TiO_2. The subject is also included in [14].

Other white hiding pigments

Other opacifying pigments include zinc oxide, zinc sulfide, lithopone (a composite of zinc sulfide and barium sulfate), antimony oxide, zirconium dioxide and zircon. Reference [3] has information on each of these pigments. Also refer to buyers guides for suppliers.

Colored Pigments

Inorganic Pigments

Inorganic pigments include metal oxides, complex metal oxides, metal salts and others. The chemical makeup has a lot to do with the stability and other properties of the pigment.

Metal oxides

Iron oxide is a very widely used metal oxide pigment with many grades available. Some materials are naturally occurring [18] and some are synthetic, and the color range varies greatly from black to red, including the range of earth-tone colors. Many different particle sizes are available also, allowing not only a wide range of tint strengths and hues, but also a range of opacity/transparency. Hydrated iron oxide expands the color space into the yellow but the hydrated oxide is unstable to high temperatures where it will convert to red iron oxide. Reference [3], pp. 281-307, has good descriptions of both natural and synthetic iron oxide pigments, covering types of products, manufacturing methods, and properties.

Chromium oxide is a commonly used green pigment. As a very stable material, it has excellent fastness properties. See reference [3], pp. 311-313.

Complex metal oxides

Complex metal oxide pigments are similar to metal oxides in that they're crystalline materials with a metal oxide lattice. The complex metal oxides contain more than one metal. Some of the crystal forms achieved with complex metal oxides are the same as are found in metal oxides, while other crystal forms are specific to complex metal oxides. In general, metal oxides and complex metal oxides are inert chemically which gives them excellent performance in not only chemical stability, but also heat, light and weather stability. The mechanism of light absorption is different than in organic pigments though, so, in general, these pigments are not as strong and not as brightly colored as organic pigments. Of course, for specific performance comparisons more detailed references should be consulted. Reference [3] has chapters on many complex metal oxide pigments.

Blue

Cobalt aluminate (C.I. Pigment Blue 28) and cobalt chromium aluminate (C.I. Pigment Blue 36) are commonly used complex metal oxide blue pigments. Cobalt aluminate is a red-shade blue and cobalt chromium aluminate is a green-shade blue.

Green

Complex metal oxide greens include cobalt chromite (C.I. Pigment Blue 36, Green 26) blue greens, and cobalt titanate (C.I. Pigment Green 50) yellow greens.

Yellow

Complex metal oxide yellows include nickel antimony titanate (C.I. Pigment Yellow 53) green-shade yellow and chromium antimony titanate (C.I. Pigment Brown 24) red-shade yellow. Some suppliers manufacture antimony-free grades of these pigments by substituting niobium or tungsten for antimony in the crystal structure.

Brown

Many complex metal oxide brown pigments are available. Most incorporate iron to give the brown color. These include zinc ferrite (C.I. Pigment Yellow 119), iron titanate brown (C.I. Pigment Black 12) and several others. Manganese antimony titanate (C.I. Pigment Yellow 164) pigments are iron-free browns.

Orange, red, violet

As yet, complex metal oxides are not available in the orange, red and violet color spaces. This deficiency is well recognized but, despite continuing research, no one has yet developed a complex oxide in those color spaces. See below, however, for other inorganic pigments with these colors.

Black

Several black complex metal oxide pigments are commonly used in coil coatings. These include copper chromite black (C.I. Pigment Black 28), manganese ferrite black (C.I. Pigment Black 26), chrome iron nickel black (C.I. Pigment Black 30), and iron chromium oxide (C.I. Pigment Green 17, Brown 29, Brown 35,). The latter two pigments are attractive due to their high infrared reflectance relative to other black pigments.

Metal salts

Violet

Cobalt phosphate violet (C.I. Pigment Violet 14, Violet 17) and manganese pyrophosphate violet (C.I. Pigment Violet 16) are probably best classified as salts. As salts, their chemical and exterior stability is not as good as the metal oxides or complex metal oxides.

Blue

Iron blue (C.I. Pigment Blue 27) is iron ferrocyanide. Other names for this pigment include Milori Blue, Prussian Blue and Chinese Blue.

Green

You may see reference to “chrome green” (C.I. Pigment Green 15). This is a mixture of lead chromate yellow and iron blue.

Yellow

Several shades of bright yellow are available with lead chromate yellow (C.I. Pigment Yellow 34). These pigments are bright, strong, and inexpensive. They differ from the chromium-containing oxide and complex oxide pigments in that the chromium in the chromates is hexavalent chromium which, in the chromate anion, gives bright colors, but is subject to many hexavalent chromium regulations. The chromium contained in metal oxide and complex metal oxide pigments is trivalent chromium.

Yellow is also achievable with cadmium sulfides or sulfoselenide pigments (C.I. Pigment Yellow 35, Yellow 37, Orange 20, Red 108.) By varying the composition, the hue can be varied from yellow to orange to red to maroon. Cadmium sulfoselenides give bright colors.

Bright yellows can also be achieved with bismuth vanadate pigments (C.I. Pigment Yellow 184.) This green-shade yellow could be classified as a salt or a complex metal oxide.

Orange

Inorganic oranges include cadmium sulfoselenides referred to above (C.I. Pigment Orange 20) and lead molybdate orange (C.I. Pigment Red 104.) Molybdate orange is a solid solution of lead chromate and lead molybdate.

Red

Inorganic reds include cadmium sulfoselenide (C.I. Pigment Red 108) and the orange and red cerium sulfide pigments (C.I. Pigment Red 265, Red 275.)

Other inorganic pigments

Ultramarine blues and violets (C.I. Pigment Blue 29, Violet 15) are zeolite-like chemicals with red-shade blue or violet color.

Organic Pigments

Organic pigments are brightly colored, high tint strength pigments available in just about any color shade. They're often classified by chemical type, determined by the functional group that produces the color. Different types are selected based on the performance in many different respects, finding the optimum price and performance combination for the particular application. Rather than mention all the different classes here I'll suggest [3], [6], [7], [8], and [10] are excellent references on the different types and uses.

Carbon black

Carbon black, (C.I. Pigment Black 6, Black 7) whether considered an organic or inorganic pigment is ubiquitous where black is required. The low cost and superior strength make it attractive for a great many uses. Many different grades are available with properties tailored for many specific uses. References [9] and [3], pp. 743-758 provide information.

Effect Pigments

Several pigment types are available for special appearance effects. A metallic luster can be achieved in coatings by using metallic flake pigments. See [3], pp. 785-827.

A pearlescent appearance can be produced in a coating with pearlescent or nacreous pigments. These include the naturally occurring nacre, bismuth oxychloride plates, and the more common surface treated micas. See [19]; [10], pp. 77-101; or [3], pp. 829-858.

Similar in function to nacreous pigments are the interference or optically variable pigments which exhibit a different color depending on the viewing angle. Also called flop pigments. See [10], p. 96 for a description of how these function.

Functional Pigments

Filler Pigments

Filler pigments are inexpensive materials incorporated into the polymer coating with the purpose of lowering the cost of use. These include calcium carbonate, various grades of silica, clays and other silicates, and barium sulfate. They share the common properties of being uncolored and not good scattering pigment, because the goal is for them not to interfere with the color. See [3], pp. 77-280; and [14].

Rheology Modifying Pigments

Various grades of silica and silicates are also used to modify the rheological properties of coatings.

Flatting agents

These inorganic pigments are used to lower the gloss of polymer coatings.

Anticorrosive Pigments

Anticorrosive pigments are used in primer and other coatings to help retard corrosion of the metal substrate. Several chemical classes of pigment are used for this purpose and they function in different ways. One can classify the pigments according to their functional mechanism. These include inhibitive pigments, sacrificial pigments, and barrier pigments. The inhibitive pigments include chromate pigments, namely zinc chromate and strontium chromate, red lead (oxide), which has been used in years past, phosphates such as zinc phosphate, and silicates and molybdates. Sacrificial pigments are exemplified by zinc (metal). Barrier pigment are plate-shaped pigments such as mica and micaceous iron oxide that form barriers in the paint film. See [29] and [28].

Color (and other) Measurement

Color measurement is an important part of evaluating the performance of pigments. Pigments attributes commonly evaluated include color, hiding power or opacity, tinting strength, infrared reflectance, etc.

Though much critical evaluation is still visual comparison, color is usually measured by a spectrophotometer and reported using three color numbers. Quantifying color has the advantage of standardizing the evaluations, providing a scale of color differences and allowing for specification ranges. One can find many good references on color science and measurement. Brief discussions of color measurement can be found in the Gardner-Sward Handbook [27], and in Kirk Othmer [20]. Basic texts on the subject include Hunter [22], and Billmeyer [24]. A nice book that goes into more detail on many of the color topics is Judd and

Wyszecki [25]. The *Pigment Handbook* has some excellent (and theoretical) discussions about color theory [5], pp. 229-288, and pigment relationship to opacity and tinting strength [5], pp. 289-339. Those references in [5] discuss Kubelka Monk (K/M) theory and color matching using K/M theory. K/M theory is also treated in [25]. The science of color measurement continues to develop and recent work and advances are presented in [30]. Courses in color measurement are often put on by the instrument manufacturers.

Processing of pigments in paint

Dispersion

The major task with pigments and coatings is getting the pigment completely dispersed in the coating. The dispersibility of a pigment depends on several factors including the size and shape of the particles, the surface area, the surface chemistry, additives such as dispersing and stabilizing aids, and the nature of the solvent and resin. Dispersion is also greatly influenced by the equipment and means of dispersing the particles. Good references on this aspect of pigments are [15], [16], and [17]. Some chapters in [5] also treat this subject.

Regulations

Many regulations apply to pigments and coatings containing pigments, including manufacturing regulations, regulations for labeling, shipping and handling, regulations for use, and regulations for disposal. Regulations are increasingly a driver for pigment use and new pigment development. Recent regulations have greatly restricted the use of some elements and pigments containing them. Users of those pigments have been forced to adopt alternatives, sometimes with a lessening of performance. As a consequence, it's very important to stay up-to-date on regulations.

Given the dynamic nature of a regulatory situation and the vastness and complexity of the regulations themselves, it's very difficult to summarize the regulation of pigments. Two recent publications include some discussion of the topic. Endriss ([13], pp148-158) has a brief discussion of the meaning of the popular term "heavy metal". Smith [10] contains three chapters regarding regulations of high performance pigments. One covers regulatory activity in North America (pp. 363-379) including a breakdown by pigment. Another covers Europe (pp. 381-410) and the third (pp. 411-417) pertains to toxicology and hints at future trends. Reference [26] is particular to pigments for use in foods, drugs, and cosmetics. References [38] and [39] are websites that may help provide up-to-date regulatory information. For a specific labeling, use, or disposal question the pigment supplier is usually an excellent source of information.

Performance

The general pigment references hint at performance attributes for the array of pigments and will suggest typical uses. *The Pigment Handbook* [3] lists general performance data for each pigment type for lightfastness (Blue Wool Scale), weather resistance, bleed resistance, chemical resistance, heat stability, and optical properties. Some of the properties are based on standard scales and some are qualitative statements. Most information regarding pigment performance can be obtained from the pigment suppliers. To avoid recommending one type of pigment over another or one manufacturer over another here, we suggest one looking for a pigment to meet his needs contact the pigment suppliers and ask for recommendations for specific products. Pigment suppliers are very helpful at recommending specific products they think most suitable and are also willing to supply samples. The potential pigment user should then carry out his own testing to determine whether or not a pigment meets his performance needs.

Properties

For use in polymer coatings, the important properties of pigments to be aware of include specific gravity, specific surface area, oil absorption, particle size, sieve retain, moisture content, hardness, pH, loss on ignition, hiding power, and color numbers. One may also be interested in heat stability, weather stability, chemical stability, purity, presence of surface treatments, UV absorbance, IR absorbance (or reflectance), solubility, trace metal analysis, etc. Most of these properties are product specific, so this information must be obtained from the suppliers. Many of these properties (e.g. color properties, sieve retain, moisture content, etc.) can be certified to meet specifications when supply is established.

Testing

Much of the testing of the optical, physical, and chemical properties of pigments is standardized in ASTM methods [40].

References

Books

[1] *Colour Index International, Pigments and Solvent Dyes,* The Society of Dyers and Colourists, (P.O. Box 244, Perkin House, 82 Grattan Road, Bradford, West Yorkshire BD1 2JB, England) 1997. The Colour Index is a widely referenced classification system for pigments which assigns names to each pigment chemistry, be it organic or inorganic. The Colour Index lists, for each chemical type of pigment, what the chemical makeup is, and gives a list of commercial products of that type, the manufacturers, and the main applications for those products. The Color Index also cross-references other classification systems such as CAS number, and CPMA number. This edition includes an index which you can use to look up commercial product names to find the Colour Index classification.

[2] *Classification and Chemical Description of the Complex Inorganic Color Pigments,* 3rd ed., Color Pigments Manufacturers' Association, Inc., P.O. Box 20839, Alexandria, Virginia, 1991. A guide to classification of the Complex Inorganic Colored Pigments (Ceramic pigments, complex metal oxides, mixed-metal oxides, and complex inorganic pigments are other terms for the same class.)

[3] *Pigment Handbook, Volume I, Properties and Economics*, 2nd ed.; Peter A. Lewis, Ed.; John Wiley and Sons, New York, 1988. This volume of the Pigment Handbook series covers all the different types of pigments: one or more chapters on each class of pigment. This is an excellent (and expensive) reference book.

[4] *Pigment Handbook, Volume II, Applications and Markets;* Temple C. Patton, Ed.; John Wiley and Sons, New York, 1973. This volume of the Pigment Handbook series discusses pigment use organized by application. Chapter II-A-b-2, pp. 25-28, by Maurice Schaller, is called "Pigmentation of Metal Coil Coatings".

[5] *Pigment Handbook, Volume III, Characterization and Physical Relationships*; Temple C. Patton, Ed., John Wiley and Sons, 1973. This volume of the Pigment Handbook series covers characterization techniques, pigment behavior (i.e. color, opacity, etc.), and pigment dispersion and influence on rheology. Though it's 30 years old, the content is certainly still relevant.

[6] Edward E. Jaffe, "Organic Pigments" in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John-Wiley and Sons, New York, 1996; Vol. 19, pp. 41-78. General article summarizing organic pigments.

[7] Peter A. Lewis, *Organic Pigments*, 3rd ed., Federation of Societies for Coatings Technology, Blue Bell, PA, 2000. A review of organic pigments, types, manufacture, properties, and use. A good summary document to have.

[8] Willy Herbst and Klaus Hunger, *Industrial Organic Pigments: Production, Properties, Applications*, 2nd ed., John Wiley and Sons, New York, 1997. Comprehensive coverage of organic pigments.

[9] Eli M. Dannenberg, Lynn Paquin and Harry Gwinnell, "Carbon Black", in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., John-Wiley and Sons, New York, 1996, Vol. 4, pp. 1037-1074. A summary article on carbon black pigments describing the processes, chemistry, properties and types.

[10] *High Performance Pigments*; Hugh M. Smith, Ed.; Wiley-VCH, Weinheim, Germany, 2002. A recent book covering many aspects of "high-performance" pigments which is a term referencing pigments, both inorganic and organic, having superior performance attributes.

[11] Mirek Novotny, Z. Solc and M. Trojan, "Inorganic Pigments" in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John-Wiley and Sons, New York, 1996, Vol. 19, pp. 1-40. General article summarizing inorganic pigments.

[12] *Industrial Inorganic Pigments*, 2nd Completely Revised ed.; Gunter Buxbaum, Ed.; John Wiley and Sons, New York, 1998. Up-to-date summary of the commercially important inorganic pigments.

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[14] D.H. Soloman and D.G. Hawthorne, *Chemistry of Pigments and Fillers*, John Wiley and Sons, New York, 1983. Mostly about white pigments, including clays, zeolites, silica and silica/alumina, calcium carbonate, zinc oxide and titanium dioxide (including photoactivity). Also covers surface modification and surface catalysis of organic materials.

[15] Gerd Loebbert and Anand Sharangpani, "Pigment Dispersion" in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., John-Wiley and Sons, New York, 1996, Vol. 18, pp. 1059-1073. General article coving the topic of pigment dispersions.

[16] G.D. Parfitt, *Dispersion of Powders in Liquids*, 3rd ed., Elsevier Applied Science, London, 1981. A comprehensive treatment of dispersion of solid particles in liquids with focus on pigments.

[17] T.C. Patton, *Paint Flow and Pigment Dispersion*, 2nd ed., Wiley-Interscience, New York, 1979. Another reference on dispersing pigments in coatings.

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[27] *Paint and Coating Testing Manual: 14th ed. of the Gardner-Sward Handbook*, Joseph V. Koleske, Ed.; ASTM, Conshohocken, PA, 1995. A coatings handbook detailing testing of coatings and materials. Includes several chapters on different types of pigments.

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[30] *Color Research and Application*, John Wiley and Sons, New York. Bimonthly publication focusing on color measurement.

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[32] *Pigment and Resin Technology*, MCB University Press, Bradford, UK. Bimonthly technology journal.

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[34] *Coatings World*, *Annual Buyers' Guide*, Rodman Publications, Inc., Ramsey, NJ. An annual buyers' guide to materials (including pigments) for use in coatings.

[35] *Paint & Coatings Industry*, *Buyers' Guide Edition*, BNP Publishing, Troy, MI. *PCI* has an annual buyers' guide that has a section on pigments.

Articles

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[37] Simpson, L.A., *Polym. Paint Colour J.* **1986**, *176*, 408.

Websites

[38] *www.epa.gov*. The EPA's website provides a place to begin searching for regulations pertaining to pigments.

[39] *http://europa.eu.int/eur-lex/en/index.html* is the European Union's website to begin searching for regulatory information.

Test Methods

[40] ASTM International, West Conshohocken, PA., publishes standards and test methods relevant to paints and coatings, including methods for pigments. Volume 6.03 of the *Annual Book of ASTM Standards* is the one containing standards for pigments. Volume 6.01 contains standards for properties of coatings that are influenced by pigments, such as optical and appearance properties. Many of these standards of interest to the coil coating community are included in the special compilation, *ASTM Standards for the Coil Coating Industry*, published by ASTM for NCCA. Standards are revised and updated, so sometimes the standard in a book is not current. To insure that one has the current revision one can visit the ASTM web site, *www.astm.org*, and confirm that a possessed standard is current or obtain a new revision.

Organizations

[41] Color Pigments Manufacturers Association, Inc (CPMA), P.O. Box 20839, Alexandria, Virginia 22320-1839, (formerly Dry Color Manufacturers' Association (DCMA)) is a trade association representing color pigment companies in North America.