High Performance Pigments

Second, Completely Revised and Extended Edition

Edited by
Edwin B. Faulkner and Russell J. Schwartz

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Original artwork by Maria da Rocha, formerly manager of Analytical Services with the Colors Group on Sun Chemical, and chair person of CPMA's Analytical Committee. The work represents the expansive palette of colors now possible with today's organic and inorganic high performance pigments.

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Contents

Preface

High performance pigments are an important segment of the diverse and rich field of color and visual effect technology. The sub-category of pigments referred to as "high performance" generally denotes members of the larger body of pigments, both organic and inorganic, that exhibit enhanced durability. The most salient durability feature is generally regarded as resistance to visible and ultraviolet radiation (lightfastness), but heat stability and chemical resistance are also critical attributes.

The distinctions within the various pigment sub-classes are not always consistent with this definition and can cause some confusion to new participants in the field. For example, copper phthalocyanine pigments typically exhibit the excellent fastness characteristics associated with high performance pigments but are often relegated to the category of classical or commodity pigments due to their prolific use in lower cost applications (e. g. publication printing inks) where durability is of minimal consequence or value. The characterization of pigments as high performance or classical types by cost is unreliable and ill advised.

The situation is further complicated by the relatively broad range of durability within the high performance pigment class. Though many organic high performance pigments exhibit sufficient stability for long-term outdoor applications, they are still not as lightfast or heat stable as the most durable inorganic members of the field. Yet another complicating factor is that application systems can significantly influence the performance. For example, copper phthalocyanine pigment may exhibit extremely poor resistance to sodium hypochlorite in one paint system and excellent resistance in another, while a mixed metal oxide performs equally well in both. Pigment surface treatments can also confound the classification situation. Lead chromate and aluminum pigments can be rendered more stable by encapsulating them with a dense amorphous layer of silica. Without this surface treatment these pigments could hardly be considered high performance in many applications.

Though it is challenging to summarize trends in such a technically diverse industry there are a two worth mentioning because they may provide some relevance and context with regard to the ongoing technical evolution. The first is that as product stewardship has gained a more prominent role in the chemical industry it has influenced the technical efforts of companies and universities engaged in high performance pigment research and development. The Dyes & Pigments journal reported that over 60% of the research papers it receives pertain to environmental and product stewardship issues such as effluent treatment and toxicology. Most high performance pigments fall into the category of nano-particles which recently have been defined by the United States Environmental Protection Agency as particles having at least one dimension less than 100 nm. Nano-particle technology is receiving intensive scrutiny due to concerns over possible toxicological effects. The second trend is an increase in research directed toward elaborating high performance pigments for enhanced performance in emerging technologies such as digital printing, electronic displays, and solar cells, to name a few.

The chapters to follow are authored by some of the most knowledgeable innovators and practitioners in the field. Collectively, they have hundreds of patents and many have lectured throughout the world in their respective areas of expertise. Of equal importance to their technical depth is their knowledge of the commercial aspects which will influence the future of the technology and the industry. Their insights will hopefully prove to be valuable to the reader and their contributions to this collection are greatly appreciated.

Finally, thank you to Sun Chemical Corporation for its commitment and support of the project.

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Part I

1
Introduction to Inorganic High Performance Pigments

Gunter Buxbaum

1.1
Introduction

In 2005 the world production of inorganic pigments was approximately 6 million tonnes, representing a value of about $14 billions. For high performance pigment applications the market in paints and coatings is of special interest and was estimated at 2.4 million tonnes representing a value of about $5.6 billions. Some years ago the British Color Makers Association estimated the economic value of downstreamed colored industrial products using inorganic pigments at about the 80-fold of the pigment value.

In writing an introductory chapter to colored Inorganic High Performance Pigments, one is faced with a definitional dilemma, as the term "high performance pigment" is more usually met with in organic rather than inorganic literature. Cost alone is not the determining factor, otherwise the natural semiprecious stone lapis lazuli would have to be included, with its deep blue characteristics. One of the problems with high performance inorganic pigments is the limitation in available chemistry, so that very few really new compounds have been developed in recent decades.

Most inorganic pigment applications have thus been achieved by the well-known "workhorses" of conventional pigments, but the economic pressures of the last decade have dictated two main directions for product development: on the one hand an economization of existing pigment manufacture, in line with world price competition, and on the other hand, discovery and development of "new" and "improved" inorganic pigments with higher performing characteristics. Even in the more "commodity" or conventional inorganics such as chrome yellow, titanium dioxide, iron oxide, and carbon black, incrementally improved performance is required, e.g., in dust free preparations for the construction industry.

A third development started earlier. Driven by national laws and regulations in the ecological and toxicological area, "sustainable development" and substitution pressures have resulted in the replacement of formerly well known, and highly recommended inorganic pigments, such as red lead, lead molybdate, and chrome orange, by more "environmentally friendly" or less toxic substances, which can surely be considered as "high performance" pigments.

Finally, in the field of "functional pigments" such as corrosion inhibiting or optically variable types, the development of "high performance" types has been necessary.

1.2
Survey of Inorganic Pigments

When we consider a short survey of today's major inorganic pigments, we are faced with the realization that the three major pigment families: titanium dioxide, carbon black, and iron oxides, accounting for more than 90% of the worldwide tonnage, as shown in Table 1.1, are all outside of our subject matter. They are well known to everyone, and have already been discussed in depth in recent handbooks [1, 2].

Further inspection of Table 1.1, however, reveals a selection of "high performance" pigments classified according to their chemical composition. In particular, the families of complex (or mixed) metal oxides, and functional pigments show a wide variety in their chemical composition.

Table 1.1 Inorganic pigments, classified by composition.

Class	Pigment	High performance
Elements		
	Carbon black	+
	Al-flakes	+
	Oxide coated Al, Zn/Cu flakes	+
	Zn-dust	
	Nanoscale silicon	#
Oxides/hydroxides		
	Metal-oxide flakes	+
	TiO_2	
	Fe_2O_3	
	FeOOH	
	Fe_3O_4	
	Cr_3O_3	
	Pb_3O_4	
Mixed metal oxides		+
	$ZnFe_2O_4$	+
	$CoAl_2O_4$	
	$(Co,Ni,Zn)_2TiO_4$	+
	$Ti(Ni,Nb)O_2$	+
	$Ti(Cr,Nb)O_2$	+

Table 1.1 Continued

Class	Pigment	High performance
Sulfides		
	ZnS	
	$ZnS/BaSO_4$ (lithopone)	
	CdS	+
	Ce_2S_3	+
Oxide/nitride		
	$(Ca,La)Ta(O,N)_3$	#
Chromates		
	$Pb(Cr,S)O_4$	
	$Pb(Cr,Mo,S)O_4$	
Vanadates		
	$BiVO_3$	+
Silicates		
	$Na_3Al_6Si_6O_{24}S_3$ (ultramarine)	
	Mica, SiO_2 and glass-based effect pigments	+
Cyanides		
	$KFe[Fe(CN)_6]$	

Note: # not yet in industrial scale

In every pigment class illustrated, one will find at least one grade with a high performance characteristic, which may be the determining factor, or driver, for the end user to purchase this pigment in their application. It is self-evident, therefore, that degree of performance for a pigment depends on the demands imposed upon it for its intended application.

1.3 New Candidates on the Catwalk of Color

Bearing in mind the limitation in the color of inorganic pigments, one has to be surprised at the numbers of new compounds introduced with good pigment performance. More and more, specialized physical effects appear to dominate over variation in chemical composition. In Table 1.1, for example, we must point out that mica-based effect pigments, being still a "young" pigment class, have already become well established since their "breakthrough" introduction. Again, while bismuth vanadate yellow is in the early stages of its growth potential, cerium sulfides are in their industrial infancy, and are attempting to carve out a niche for themselves in applications where the well-established cadmium sulfide family is no longer the pigment of choice. On the more experimental side, "nanoscale silicon," with particle size below 5 nm, is now available as a laboratory curiosity in microgram quantities as the first in the series of "quantum effect pigments" predicted by theoretical physicists [3]. Nearer to introduction is another new family, the calcium, lanthanum, tantalum oxide-nitrides [4]. Reproducibility, however, must be proven first. Their published properties, viz., brilliance of color coupled with nontoxicity, appear ideal for inclusion in the high-performance category.

A study of the "old fashioned" and almost forgotten workhorse pigment ultramarine blue could also be significant in the light of its revival through recently introduced new manufacturing technology. And so it is possible that, in the future, development of new manufacturing processes for "old" pigments and enhancement of their properties might well revitalize these products to the point where they could also join the ranks of truly high performance pigments.

1.4 Challenges for the Future

This leads us to consider challenges for new high performance pigments, which can be designated as *Three Essential Es*:

Effectiveness	=	Technical performance
Economy	=	Benefits for the customer
Ecology	=	Environmental and toxicological safety

Better effectiveness could include higher tinting strength, greater ease of dispersion, better fineness of grind, higher saturation, and so on.

Better economy could include widening the fields of application for known high performance pigments by giving the customer enhanced value-in-use. And better ecology is today's task for industry as a whole, and is self-evident.

All three "E" will be optimized further on. New inventions will be made, hand-in-hand with steady process and product development. And as we can learn from a study of today's lowercost pigments, such as lead chromate, where the encapsulated specialties of yesteryear are now the norm for coatings application, the high performance pigments of today will become the conventional standards of tomorrow, with those of tomorrow having to be invented now. And so the development of high performance inorganic pigments is, in reality, a never-ending story.

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