



# Physical Chemistry of Pigments in Paper Coating

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## Preface

Pigmented coatings are applied to paper and paperboard in order to form a uniform, smooth, and receptive surface on which to print. This coating may also improve the general appearance of the sheet or provide for some special function. The bulk of the coating is made up of pigment particles which cannot pack together perfectly and, consequently, a pigment coating is a porous layer which forms the new surface.

The coating consists primarily of the pigments. However, a binder is required not only to hold the pigment particles together and to the base sheet but also to exert some control over the manner in which the coating layer accepts the printing inks. Certain additives are required, in addition to the basic pigment/binder combination, to meet specific operational requirements. The materials are all suspended in a liquid for convenience, usually water; and the suspension is referred to in the trade as a coating color. This is then applied to the surface of the paper and a drying step follows in which the fluid medium, water, is removed. The properties of the final coating are highly dependent, therefore, on the many interactions which always exist between materials, processes, and conditions.

The coating of paper has been traditionally one of considerable art; and the science, which helps one to understand the process and is a prerequisite for further progress, has generally followed behind. The TAPPI Pigments Committee attempted to assemble the important technical and scientific information together with fundamental principles concerning the coating pigments, which are widespread in journals, books, references, etc. of many kinds, into one text and to apply this to the paper coating system. Since this book is concerned with fundamentals, many standard references have been cited to both recent and older literature. The chapters were written over a period of several years, completed at different times and then updated as necessary. The basic concepts are emphasized and little attempt was made to cover that literature which is related to processing and is continually being revised.

## PREFACE

This monograph is intended as a scholarly work which should speak to the problem of paper coating and to help workers in the area to become more effective. The needs for this undertaking fell into four areas of basic interest: I. Pigment Properties; II. Solid-Liquid Interfaces; III. Rheology and Flow; and IV. Properties of Coatings Controlled by Pigments.

The authors of the various chapters were chosen as authorities in their respective fields to discuss the physical-chemical fundamentals. Therefore, real basic principles can be brought to bear on the coating of paper. The reader is thus called upon to use this fundamental information to relate to his own problems.

C. L. Garey  
Editor

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# Section I

## Coating Pigment Properties

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Assoc. Ed.

### INTRODUCTION

In discussing the physical chemistry of pigments in paper coatings, it is desirable to begin with a description of the basic properties of the pigments themselves. Some of these properties were described in previous monographs (No. 20 and No. 30) which emphasized technology. The information in Section I of the present monograph is considerably more comprehensive and fundamental.

Chapter 1 explains modern concepts of the structure of crystals and gives details of the structure of the seven pigments most commonly used in paper coatings. Chapter 2 discusses the nature of the bonding between atomic constituents in pigment crystals and how it relates to properties such as hardness, density and optical behavior, all of which are important in the utilization of the pigment. Chapter 3 describes methods for measuring particle size and points out the precautions that must be taken in interpreting these measurements.

# Crystallography and Physical-Chemical Properties of Paper-Coating Pigments

J. H. FANG

A number of inorganic pigments, in various combinations, are applied as a coating to paper and paperboard in order to form a new surface which is smooth, opaque, and usually white as well as bright. The new surface makes it possible to produce high quality printed images because there is not only a significant increase in smoothness but also a reduction in porosity from that of the base sheet which is both rough and highly porous due to its fibrous nature.

The important coating pigments are similar in both composition and physical structure to materials found as minerals in nature and, therefore, can be described on the basis of their mineralogy. Thus, all the pigments have definite chemical and physical properties. Certain of the natural pigment forms can be made useful directly by industrial beneficiating processes, such as in the case of kaolinite clay, which is the most widely used pigment for paper applications. However, many must be reformed or synthesized in order to have appropriate properties. Coating pigments are characterized, for the most part, as being stable, insoluble, chemically inert, and relatively pure materials. Special organic pigments, used in small amounts, and those materials used as colorants in paper applications, are excluded from this discussion.

The purpose of this chapter is therefore two-fold: to introduce crystallography at its most elementary level and to give pertinent data on important pigments used in paper coating. Due to space limitation, crystallography is not discussed in any great detail, but rather the chapter is concerned only with the definitions of vocabulary, so that the last section of this chapter—descriptions of some mineral pigments—can be understood. We shall start considering external symmetry which is manifested in the crystal morphology, and how symmetry requirements result in the existence of a limited variety of crystal classes. Miller indices and directions are then in-

troduced because it is often necessary to describe a particular crystallographic plane or a particular direction within a real three-dimensional crystal. A brief discussion of crystal habit is also included. The chapter continues with a look at the internal symmetry of a crystal—crystal structure. This leads naturally to a discussion of the unit cell, the fourteen Bravais lattices and space groups (*vs.* point groups of external symmetry). Next, the chapter considers physical-chemical properties of minerals and ends with a descriptive list of important mineral pigments. Under each pigment, a brief description is given, then pertinent crystallographic data—space group, unit-cell dimension, a drawing of the crystal structure, and x-ray powder diffraction lines—are listed. Under physical properties, specific gravity, hardness, cleavage, habit, color, etc. are given. Lastly, natural occurrence of the mineral is cited, for the benefit and interest of chemists. If a mineral occurs in more than one type of structure (polymorphism), the different structures are also mentioned.

## BASIC CRYSTALLOGRAPHY

### External Symmetry: Crystal Morphology

**The Symmetry Elements.** Mineralogists were first able to catalog crystals by recognizing them as a special kind of solid, bounded by plane faces. Certain simple crystals were found in which each type of plane occurred as parallel pairs on opposite sides: such a crystal has a center of symmetry. Even if it is not so symmetrically bounded, a crystal can still be divided into two parts in such a way that one part is the mirror image of the other part; such a crystal has a plane of symmetry. If a crystal can be rotated about an axis in such a way that it repeats itself two or more times during a  $360^\circ$  rotation, it is said to have an  $n$ -fold axis of symmetry ( $n = 360^\circ/X$ ;  $X$  is the repeat angle). Observations showed that  $X$  can assume only the values  $360^\circ$ ,  $180^\circ$ ,  $120^\circ$ ,  $90^\circ$  and  $60^\circ$ ; that is, in addition to identity axis ( $n = 1$ ), there appear only diad ( $n = 2$ ), triad ( $n = 3$ ), tetrad ( $n = 4$ ), and hexad ( $n = 6$ ) axes in the crystal world. Knowing the allowed symmetry elements (center, planes, and axes), space geometry can be used to derive the number of crystal classes made possible by various combinations of such elements. For example, a cube contains the largest number of symmetry elements: one center, nine mirror planes, and thirteen axes (3 tetrads, 4 triads, 6 diads). Fig. 1.1 (1) illustrates these symmetry elements.



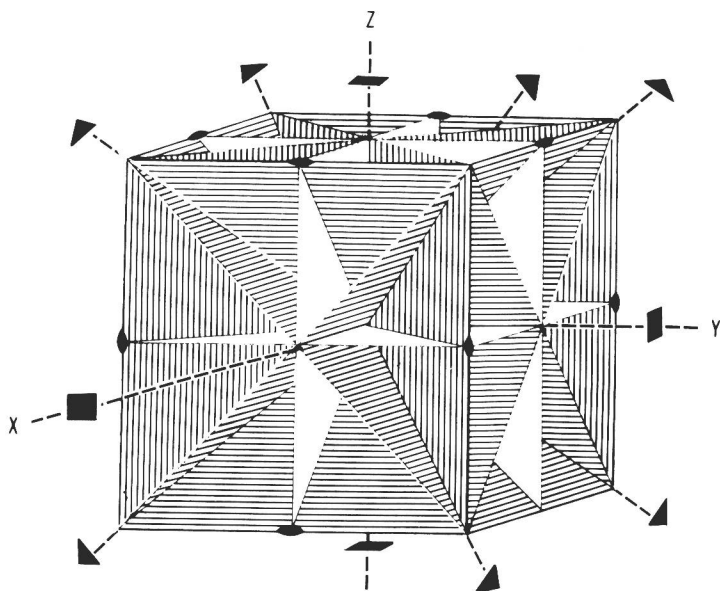


Fig. 1.1. Symmetry elements in a cube: a symmetry center; nine mirror planes; three 4-fold, four 3-fold, and six 2-fold axes (*I*).

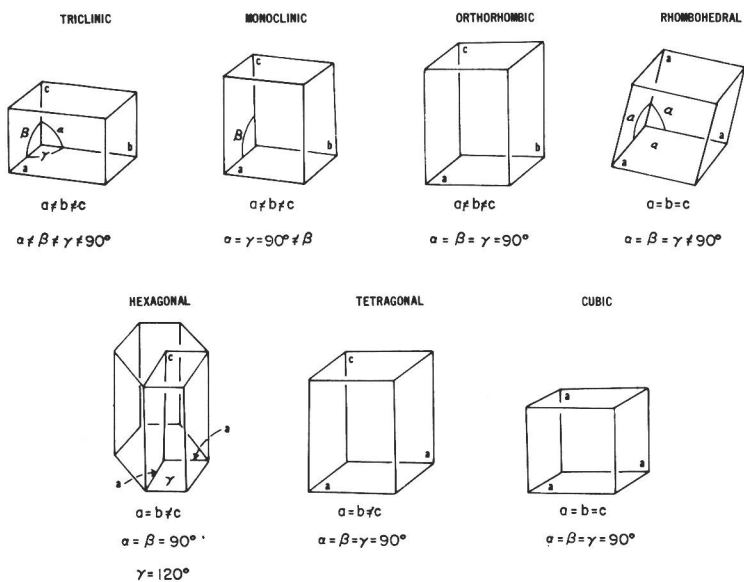


Fig. 1.2. The seven crystal systems.