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## CONTENTS

Introduction . . . . .	1
<u>Part 1 - Light, Color, and Color Perception</u>	
I. Light and Color. . . . .	3
II. Color Perception . . . . .	11
<u>Part 2 - Pigments: General Considerations</u>	
I. Pigments - Definition and History. . . . .	21
II. Pigments - Chemical Properties. . . . .	23
III. Pigments in a Paint Film - Physical Properties . . . . .	25
IV. Pigments - Manufacturing. . . . .	38
<u>Part 3 - The History, Properties, and Synthesis of Selected Pigments</u>	
I. Introduction. . . . .	42
II. Organic Pigments . . . . .	42
A. Alizarin Red . . . . .	43
B. Copper Phthalocyanine Blue. . . . .	59
C. Acetoacetarylide Yellow (Hansa Yellow). . . . .	84
III. Inorganic Pigments. . . . .	109
A. Cadmium Pigments	
Cadmium Yellow and Yellow Lithopone . . . . .	110
B. Cadmium Pigments	
Cadmium Red and Red Lithopone . . . . .	121
C. Chromium Oxide Green. . . . .	126
D. Hydrated Chromium Oxide Green. . . . .	130
E. Ultramarine Blue . . . . .	134
F. Cobaltous Aluminate Blue . . . . .	158
G. Titanium Dioxide White . . . . .	164
H. Bone or Ivory Black . . . . .	181
<u>Part 4 - Appendices</u>	
I. Appendix A: Alternate preparations for Selected Pigments .	186

II. Appendix B: The Testing and Evaluation of Pigments . . .	.195
III. Appendix C: Preparation of Paints and Paintings . . .	.215
Part 5 - <u>References: List of works consulted with brief annotation</u> . . .	.221

Please note: All temperatures given in this paper are in Centigrade.

## Introduction

A painter's control over the choice of the colors he uses is not as absolute as is generally assumed. Obviously, his decision is limited to those pigments commercially available to him and these, in turn, are determined by criteria not normally considered by the artist. While this may seem to be a trivial point, it is, in fact, of the utmost importance since it affects absolutely the qualities of the colors an artist uses.

A painter wishing to use a blue would have several choices, e.g., ultramarine, copper phthalocyanine, cobaltous aluminate, and cerulean blues. Each of these blues has its particular and unique color, saturation series, and opacity characteristics based on its inherent chemical structure and physical properties. The light absorbed and reflected by copper phthalocyanine blue differs enough from that absorbed and reflected by ultramarine blue for the actual blue color of these two pigments to differ appreciably. Likewise, their refractive indices differ, directly affecting their relative abilities to tint a white or cover a ground. The cumulative effect of these and other physical and optical properties is that no two blues are the same. It follows that other blue pigments, not commercially available, possess yet other color characteristics. The point here is that while the artist makes choices based on available pigments, these decisions follow selections previously made by commercial paint manufacturers. The manufacturers, in turn, supply paints containing those pigments which have been proven reliable after detailed evaluation for their color and fastness characteristics.

We felt that artists could benefit from an understanding of the

process of the selection of a compound as a pigment, the manufacture of pigments, and the production of the paints he uses. In other words, he would gain the broadest possible understanding of the interdisciplinary concepts involved in color and pigments.

To expedite this process, a project was designed in which the following five areas were investigated: (1) general aspects of light, color, and color perception, (2) pigments, their general properties, and manufacturing, (3) the history, chemical and physical properties, synthesis, and use of specific organic and inorganic pigments, (4) the testing and evaluation of pigments, and (5) the preparation of paint and paintings using the pigments synthesized. This paper gives specific details of the project.

## Part 1. Light, Color, and Color Perception

### I. Light and Color

#### A. Light

Hue or color can probably be considered the single most important property of pigments. In this section, an overview of the physical basis of light and color as related to pigments will be considered.

While light may be regarded as having a dual nature, that part which is particularly relevant to this discussion is its wave form. Many different forms of electromagnetic radiation, all traveling through space at a constant speed (186,000 miles per second), may be considered simply as waves of energy. These different forms may be characterized by differences in wavelength or frequency. The wavelength is related to the frequency as follows:

$$\text{wavelength} \times \text{frequency} = \text{a constant } (\lambda\nu=c).$$

Since the velocity of light is constant, frequency and wavelength are not independent but are inversely proportional to each other. Therefore, either frequency or wavelength can be used as a basis for discussion and for the purposes of this paper it will generally be convenient to refer to the latter. Figure 1 gives an indication of the range of electromagnetic radiation and the names given different regions based on the physical phenomena which distinguish them from one another.

Our major source of energy is obviously the sun, from which a vast spectrum of radiant energy is emitted. That part of the spectrum which is seen by the human eye as light is relatively very small. This visible light covers approximately the region from 380-720 nm. All other sources of visible light are artificial, e.g., tungsten, sodium, and mercury lamps or carbon arcs and fluorescent discharge tubes. These

differ from each other and from sunlight in terms of the relative amounts of energy each source contains at any given wavelength within the visible spectrum.

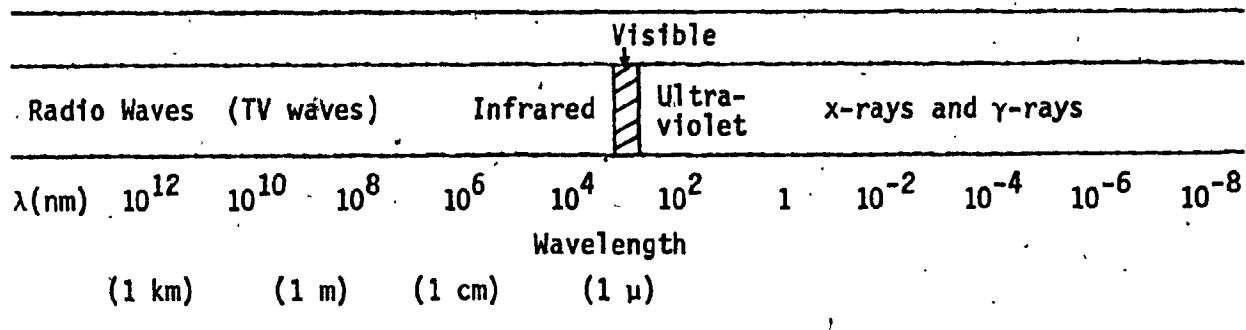


Figure 1. The Electromagnetic Spectrum

These differences in energy distribution can be measured either objectively by an instrument or subjectively by the eye. If the light falls on an object, the light reflected can again be measured. When this light is measured by the human eye, its measurement is obtained by registering a mental sensation which is called 'color'. Color, therefore, refers to an individual's mental conception of the sensations which result when a certain combination of visible electromagnetic radiation enters the eye. This sensation is modified by a combination of (a) the type of light falling on the object, (b) the change of the spectral distribution of the light by the selective absorption of different wavelengths by the object, and (c) the sensitivity of the observer's eye to various wavelengths within the visible spectrum. The first two of these factors will be discussed below while the relationship between the eye and color will be discussed in the section on color perception (vide infra, p. 11).

## B. Color

Sunlight, or white light, covers the complete visible spectrum as can be seen from the dispersion of this light through a triangular glass prism. The result is a continuous spectrum extending from the short wavelength (about 400 nm), which is violet, to the long, red wavelength (about 720 nm), with all the intermediate wavelengths producing their own color sensation.

When white light falls on an object such as a paint film, the object changes the character of the incoming, continuous spectrum light - called an incident ray - by absorption and scattering. The absorption of the light is due to electronic, vibrational, and rotational energy transition within the molecules of the colored object. Depending on the chemical bonds and types of atoms composing the molecule in the ground state, specific wavelengths of visible light will excite the molecule so that one or more energy transitions will take place. In this process, energy is given up by the incident light and converted to heat so that part of the spectrum is absorbed or lost.

The color of an object, or body color, is determined by the distribution of the remaining unabsorbed energy, i.e., the wavelength of the light reflected to the eye. The approximate wavelength-color relationships are illustrated in Table 1.

When light of a given color is absorbed, the complementary color - or remaining part of the incident light - is reflected or transmitted away from the object. Thus, an object absorbing light within the blue range is seen as yellow because only the yellow light is reflected and consequently reaches our eyes. It should be noted that green light has no complementary spectral color so the color seen as purple or magenta



is the result of a mixture of red and blue-violet light from the extremities of the visible spectrum.

LIGHT ABSORBED		COMPLEMENTARY COLOR SEEN	
Wavelength (nm)	Color	Allen <sup>15</sup>	Kuppers <sup>259</sup>
400-435	violet	green-yellow	yellow
435-480	blue	yellow	
480-490	green-blue	orange	orange
490-500	blue-green	red	
500-560	green	purple	magenta
560-580	yellow-green	violet	violet
580-595	yellow	blue	
595-605	orange	green-blue	cyan
605-750	red	blue-green	

Table 1. The Relationship Between Wavelength, Color of the Light, and Complementary Color Seen.<sup>15,259</sup>

In a painting, color may be seen as the effect which the artist produces in the viewer's eye by what he adds to the white canvas or paper. For white he may add a pigment which reflects all wavelengths or he may add no paint at all, producing the same effect. For gray, black, and all other colors, he adds pigments which modify the light falling on them, reflecting back wavelengths corresponding to the color seen.

### C. Light Sources and Their Effect on Color

While sunlight is often called white light, this term has no precise physical meaning. In fact, there are many pairs of pure spectral colors which, when mixed together, result in stimuli corresponding to white light. Examples of these are shown in Table 2.

Wavelength (nm)	Color	Stimulus
656 492	red green-blue	white
608 490	orange blue	white
585 485	orange-yellow blue	white
567 464-5	yellow blue	white

Table 2. Some Examples of Wavelength Pairs Which Produce a White Stimulus.<sup>16</sup>

In actual practice, such closely defined light sources are found only in special research applications. The normal day to day ambient light encountered by most people covers irregularly most or all of the visible spectrum. The makeup of this illumination is important in the determination of body color. For example, if the light from a tungsten lamp is passed through a prism, it will be seen to be deficient in blue and violet and richer in red light. A fluorescent lamp, on the other-hand, is deficient in red as well as exhibiting a generally discontinuous spectrum. That is, the light from a fluorescent lamp is formed from a mixture of a few separate bands of distinct wavelengths.\*

That the color of an object may be modified by the type of ambient light falling on it is manifested by a shift to red in the colors of a scene illuminated by a tungsten filament bulb. In this case, yellow and red objects seem to be brighter at the expense of blue ones due to the fact that relatively little blue light is present in the original source.

\* Visually excellent emission curves of various light sources may be found in Kupperts<sup>259</sup>, pages 45 and 47.

An object whose color falls in one of the gaps between bands of a fluorescent lamp will appear darker and different in hue. Even the relatively continuous energy of sunlight can be changed by atmospheric interference (such as mist) which can produce, for example, the blue haze on a distant mountain.

#### D. Describing a Colored Surface - Hue, Saturation, and Brightness

The characteristics of a colored surface may be defined in terms of hue, saturation, and brightness. Hue is determined by the predominant wavelength or wavelengths of the reflected light, described as red, yellow, blue, etc. Within each band, the hue varies with wavelength as the latter moves towards the next band in either direction. Thus, a blue becomes greenish as the wavelength is increased or reddish as it decreases. It has been said that between  $150^{16}$  and  $300^{216}$  different hues can be distinguished within the spectrum. The number may even be as high as 500 hues under the best conditions.<sup>241</sup> Of these hues, only a pure red, yellow, green, and blue are unique. All other hues are mixtures of two or more of these basic four and together these can be represented by any of several systems of color solids<sup>222,263,335</sup> and two-dimensional systems such as the color wheel.<sup>222,217,262</sup> Of these, the color wheel is the simplest and most easily understood. On such a wheel, intermediate colors would lie in a circle between the four unique hues with combinations such as red and yellow giving orange, blue and red giving purple, and yellow and green giving olive or yellow-green. This type of mixing is called subtractive, e.g., a yellow pigment (absorbing all except the yellow and green components of white light) mixed with a blue pigment (absorbing all except green and blue) would appear green since this is the only component which is not absorbed by either constituent of the

mixture. In other words, all visible wavelengths except those corresponding to green would have been subtracted. Theoretically, every possible hue could be represented within the circle by subtractive mixing of the circle colors. This is, in fact, what happens both in transparent layers (e.g., color photography and transparent printing inks) and pigment mixtures in paint.

The mixing of colored light, on the otherhand, is called additive color mixing. In this process, one would theoretically start with black and add wavelengths of light to produce a given color. In practice this can be accomplished by mixing of colored light either simultaneously or in rapid succession on a white surface. The spacings on a color wheel can be arranged evenly so that complementary colored lights lie opposite each other. In this case, when the complementaries are combined as light (not colored-objects) they would produce white light.

Additive mixture of subtractive colors, or simultaneous additive and subtractive mixture, functions much like pure additive mixture. The difference here is that the color source, instead of being light, is premixed (subtractive) pigments. If the pigments are placed closely enough together, their colors should be combined in the eye as light since a physical separation would be impossible. At the end of the 19<sup>th</sup> century, the Neo-Impressionists tried to make use of this phenomenon by applying their colors as small dots of paint. They theorized that the close juxtaposition of yellow and blue, for example, would result in green if viewed from a distance which would preclude separation of the dots by the eye. A similar effect occurs when a colored surface is spun so that individual elements cannot be discerned such as, for example, a pinwheel in the wind.

Changes in hue can be described as shifts in wavelength or frequency. For example, hues are said to increase in depth as they move from yellow to green. Thus, blue is deeper than red, red than orange, and orange than yellow. A shift of the absorption band toward lower frequencies, corresponding to a deepening of the hue from yellow to green is a bathochromic effect. The opposite effect, representing a lightening of color as a movement towards yellow is a hypsochromic shift. Intensity changes may also occur. A hyperchromic shift is an increase in the intensity of absorption, and the opposite effect is hypochromic.

Saturation is the difference in the amount of hue seen between two colors, either of the same or different hues. Comparison with the chemical meaning of saturation is misleading because it implies that a maximum is possible while no well-defined upper limit exists for color saturation. A better analogy would be concentration, i.e., with the amount of hue per given area as units and white light acting as a diluent. Saturation, then is inversely proportional to the amount of white light reflected by a surface.<sup>217</sup> Figure 2 illustrates a range of color saturations. Saturation series such as these with a single hue are rare in nature but an approximation may be seen in a blue sky which fades to pale blue or even white at the horizon.

The third variable used in defining a color is brightness, which is dependent on the absence of reflected light other than that of the hue concerned. Theoretically, the brightness of a color can vary from being too dim to be seen to too bright to look at.

Figure 2. The Variation in Saturation of One Hue. The saturation increases from left to right.<sup>217\*</sup>

## II. Color Perception

### A. Physiology of Color Perception

Color perception is an extremely complex subject encompassing physical, chemical and electrical processes, as well as poorly understood neural mechanisms. In addition, 'cognitive theories'<sup>\*\*</sup> have proposed that color perception may include a subjective element. Although experiments

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\* In 1905 A. H. Munsell developed a system in which hues are arranged in a circle, with zero saturation - or no hue perception - at the center. Points around the zero value are positioned so that a scale is produced with spacings of both hue and saturation based on regular intervals as perceived by the eye. In this system, chroma is roughly equivalent to saturation.

\*\* The cognitive theories base the perception of surface color on cues given by the illumination of the surface as well as the attitude - or set - of the observer. Helmholtz suggested that color perception is related to the impression of illumination derived from the cues provided by the light reflected from a surface. He wrote: "What is constant in the colour of an object is not the brightness and colour of light which it reflects, but the relation between the intensity of the different coloured constituents of the light, on the one hand, and that of the corresponding constituents of the light which illuminates it on the other. This proportion alone is the expression of a constant property of the object in question."<sup>388</sup> He goes on to say that human perception of the illumination is learned. This takes place both quickly and regularly so that an individual is not aware of it as a learning process and further, is not conscious of judging the illumination.

in color constancy\* both within and between individuals<sup>44</sup> have largely disproven the cognitive theories, very little is actually known about what takes place in the visual centers of the brain. The overall process of color perception includes the reception by the eye of the light reflected from colored objects and the subsequent encoding and transmission of the information to the visual centers of the brain.

As light reflected from colored objects impinges on the eye, the cornea and lens transmit and bend the rays so as to focus them on the retina. Two different types of receptors are present in the retina which have the capability of responding to black-white (scotopic vision) and colored (photopic vision) light. Rods, the black-white receptors, contain the pigment rhodopsin or 'visual purple,' an albumin-bonded pigment combined with vitamin A. Rhodopsin absorbs a wide range of wavelengths, upon which the complex is transformed structurally and chemically into 'visual white' by way of 'visual orange' and 'visual yellow.' Physiological stimulation results from energy liberated by this process. Cessation of the light stimulus brings about a regeneration of the pigment to its original 'visual purple' form.<sup>260</sup>

The primary concern here, however, is for the dominant theory of color perception which holds that three different cone receptors exist in the retina, each containing its own type of photosensitive pigments.\*\*

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\* 'Color constancy' is defined by Beck<sup>45</sup> as "the approximate constancy in the perceived color of an object despite changing illumination that alters the intensity and spectral composition of the light stimulating the eyes; lightness constancy refers to the constancy of lightness changes with changes in the intensity of the illumination, and hue constancy refers to the constancy of hue with changes in the spectral composition of the illumination."

\*\* Another theory, presently not widely accepted, assumes a single type

Each of these is made up of a protein, called an opsin, and retinene, the aldehyde of vitamin A<sub>1</sub>. One cone pigment, iodopsin, has been isolated and is made up of retinene and photopsin. The other cone pigments also appear to contain retinene and the differences between them are probably due to differences in the structure of the opsins.

Each of the pigments has a characteristic absorption spectrum that covers approximately one-third of the visual spectrum. One pigment reacts to violet and blue light, one to green and yellow, and one, iodopsin, to orange and red. When light is absorbed by the pigments in the cone cells, their structure changes and some aspect of this change is responsible for the initiation of an action potential in a nerve fiber associated with the excited cone. Thus, the energy absorbed by a pigment is converted into a coded nerve impulse which is subsequently integrated with other coded impulses by neural connections in the retina. The pathway for the transmission of this message from retina to brain is by way of the optic nerve bundle which passes through the optic tract to the lateral geniculate nucleus and finally to the striate areas of the occipital lobes (visual cortex) of the brain. Here the sensation of color is experienced. The processes involved in the transfer of light energy from the retina to the brain are too complex to be discussed at any greater length in this paper.<sup>43,384,464</sup>

However, it is important to note the relationship between the presence of only three cone pigments and the wide spectrum of colors actually perceived. Current evidence does not support the idea that

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of cone which functions similarly to the rods, i.e., all cones are sensitive to differences in wavelength and intensity, the rods being sensitive to intensity differences only.<sup>261</sup>



there are separate pathways from each of the pigments to the brain. Instead, these divisions effectively overlap so that, for example, yellow light stimulates a proportion of both the green and red receptors. These stimuli are integrated in the retina and the joint message is sent to the brain where it is interpreted to mean yellow. If both red and green are stimulated, but the green more than the red, the color is interpreted as a greenish-yellow. Likewise, if both green and blue are stimulated, the color is interpreted as a bluish-green. If the intensity of the blue stimulation is more than the green, the color is interpreted as more blue than green. Therefore, it is thought that by combining the degree of stimulation of the different cone cell pigments, not only can the brain distinguish among the three primary colors but also among the colors having intermediate wavelengths.\*

The intensity of a color is determined by the number of nerve impulses transmitted to the brain by way of the cones. For example, if both the green and red cones are stimulated by a yellow color and the number of integrated impulses (i.e., from the combined stimulation) transmitted from the retina to the brain is only 10 per second, the intensity perceived will be relatively weak as compared to a stimulation resulting in, say 100 impulses per second. Thus, the brain interprets the ratio of stimulations (here, red and green) as the degree of intensity of the yellow seen but not the actual intensities of each cone stimulation.

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\* It is interesting to note that this theory of three different cone types is not out of line with what we know about the manifestations of color-blindness and other defective color visions. In general, these problems can be explained by either the partial or total failure of one or two cone types.

This description is somewhat general since equally intense visible electromagnetic vibrations are not always perceived by the eye as equally bright stimuli. Instead, the sensation of brightness decreases dramatically towards either end of the spectrum, ending logically at the limits of the visible spectrum where light of any wavelength would not excite the cones.

#### B. Some Factors Influencing the Appearance of the Color We See

Thus far this discussion of color and its perception has had underlying it the theory originating with Newton, that all possible hues can be produced by using only three colored lights. However, it is important to note that discussions of perceived color must include the discovery over one hundred years ago by Helmholtz and Maxwell, that two colors which match do not necessarily have the same spectral energy distribution. This may be partly explained by the low sensitivity or accuracy of the human visual system. More important, however, are those aspects of appearance not inherent in the color of an object. The manner in which color is affected to produce the multiplicity of visual stimulations we know will now be considered.

##### i. Intensity

The intensity of a color may be modified by several factors. The first obviously is the degree of saturation - the less saturated the color, the less intense the color will appear to the eye. While this is an inherent property of a color, other factors can affect the apparent intensity of the color of an object regardless of the saturation. For example, we cannot see an object unless it is illuminated by something. While the color of an object can be seen as independent from the illumination, the color we see will nonetheless be affected by the intensity

of the light source. As mentioned earlier, of the receptors in the eye, only the cones are color sensitive and they function at normal intensities. At low intensities (such as in starlight), however, vision is confined to the rods which perceive only in black, a white, and grays. Thus, in low intensity illumination the minimal or threshold level of stimulation for the cone pigments is not reached and we experience difficulty in discerning the color of an object which itself has not changed.

Similarly, if the direction of a light source is normal but diffused, the colors will appear desaturated and dull. An example of this is an overcast sky through which sunlight comes at all angles. Although the intensity of the light may be above the threshold for normal cone vision, a desaturation occurs. On the otherhand, if the light is direct, colors will appear at their brightest. It should be noted that in either case, the color of the object is constant and neither the apparent desaturation or brightness are properties of the object. Instead they are functions of the illumination or light source.

#### ii. Simultaneous Color Contrast

The color we see can also be modified by the contrast of the object with its surroundings. For example, if two patches of an identical color are surrounded respectively by a black and a white border, even when viewed simultaneously, the latter will appear darker and less saturated than the former.\* The same thing will happen if the borders are lighter and darker shades of the same hue. It is this type of phenomenon which

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\* Ralph Evens in Industrial Color Technology<sup>218</sup> reports that his studies of this phenomenon showed that it is "not possible to produce a color on black which exactly matches one on white." This is based on the difficulty of reproducing the visual relationships between brightness and gray content of a color on black with any color on white.

accounts for our perception of grays. In other words, gray is produced by the interaction in the viewer's eye and brain, of the relationship between the stimulus and its surroundings rather than by a simple physical property of the stimulus. Of course the stimulus itself will determine how much gray is seen but the gray is not a physical entity even though it may appear as such. That this is so may be seen by viewing an object which appears gray in a fully lit room. The same object will appear white when illuminated separately in a dark room. It should be noted that the three color variables of hue, saturation, and brightness do not in themselves allow for the definition of a gray, black, or color which is seen to contain gray. In order to obtain a gray, the color must not be isolated and at least one other color must be present. It follows that gray can only be seen as a related color, i.e., in order for a color to appear to contain gray or actually be gray, it must not only have a background, but usually be darker than the background.

### iii. Color Contrast

A similar effect is 'color contrast.' A color will always appear brighter when viewed against a background of its complementary color. Even when the subject and background are not complementary, the eye will see them as if they were. For example, a gray wall behind a very saturated green bush will appear as a pinkish-gray because the eye will tend to balance the color towards green so that the wall will become redder in comparison.

### iv. Adaptation

It should now be obvious that in addition to appearance characteristics of an object, color perception is modulated by the eye and brain according to changing light qualities. In other words, the sensitivity of the eye adapts to changes in what we see, what has just been seen,

what is beside what we are seeing, and the length of viewing time. In viewing a particular scene, sensitivity to brightness and color reaches a steady state set by the brightness and color of the surrounding light, the average reflections of the nearby objects, and the colors in the scene. In 'color adaptation' the eye averages the colors to a 'neutral' or reference point for all visual stimulations. This may be illustrated by a subject viewed against a red brick wall. Here the subject is illuminated by the reddish light reflected from the wall. As a result, a photograph would record the subject as much more red than it really is because of the increase in reflected red light. The eye, on the other hand, adapts to the new color of the light so that the reddish light will now appear white. Even if this adaptation does not take place completely, the brain will still interpret the sensation from the eye to fit what it knows from experience. Thus, the face of the subject will not be seen as red but as having a normal flesh color. The hues and saturation of perceived colors depends on the adaptation state of the eye. Klappauf<sup>243</sup> has shown that a color appears less saturated and of a different hue after adaptation, the only exception being a specific yellow, blue and green. According to Klappauf, "hues between red and green are displaced towards constant yellow, those between green and blue towards constant blue."

The eye may also adapt itself to different colors of the illumination itself. This can be seen when one goes from sunlight to an indoor tungsten light situation. Here the light initially appears yellow since the eye is adapted to the relatively blue daylight 'white.' Within seconds, however, the eye adapts to the new light and will accept it as white. The same phenomenon occurs in viewing slides in a dark room. The eye will adapt to the overall color balance of an image which in a fully

illuminated environment would have had an objectionable color.

It should be noted, however, that while the eye can adapt to minor variations in the spectral curve of an illumination source, the appearance of the object will ultimately depend on the composition of the ambient light. In other words, in a dark room lit by red light, only red light is available so that objects will be visible or colored only if they are red or at least reflect some red light. Only with light in which most visible wavelength regions are at least partially present will adaptation or compensation of intensity fluctuation occur.

#### v. Other Factors

Certain aspects of appearance, such as glossiness, metallic reflection, and texture serve dual roles - not only modifying the apparent color of an object, but in so doing, giving it a form which can be interpreted as a shape and as having three-dimensions. A glossy or metallic object with a uniform color such as a vase (of glass or metal) will appear to have an uneven color due to reflections of the objects surrounding the vase, such as the light source itself. In this case, the colors of reflections are unaltered since no light is absorbed by the surface. At the point of reflection the reflecting object will assume the color of the light source, which is usually white. A similar effect gives the highlight often observed on the eyes in portraits of people. The end result in both cases is a uniformly colored object which appears non-uniform. This, in turn, helps a viewer to perceive the three-dimensional shape of the object.

Similarly, texture modifies appearance as in the simple example of randomly folded material. Where the light illuminates the material directly, such as on the tops of ridges, the material will be lighter

than in the folds or crevices where the illumination is relatively poor. This contrast of light and dark areas permits the viewer to interpret what is seen.

As can be seen, many factors, other than the inherent color of an object, play a role in the visual perception we have of that object's particular color. What we see is based on the object's color as well as its environment and illumination and our preconditioning.

## Part 2. Pigments - General Considerations

### I. Definition and History

#### A. Definition

A pigment may be defined as a colored, solid material which, in the form of small discrete particles, is insoluble in the medium in which it is employed. The medium may be air as in the case of smoke, which consists of soot or carbon particles in a column of air. In a paint film the medium may be a drying oil or synthetic resin, while other surface coatings such as lacquers may have nitrocellulose and plasticizer as medium. In all these cases the pigment particles are insoluble in the medium used and this differentiates them from a dye. The latter is a colored substance that can be applied to a substrate to give it a colored appearance in solution or dispersion form. The substrate is usually a textile fabric but can be paper, leather, hair, fur, plastic, wax, cosmetic base, or foodstuff. In general, the material to be dyed has a natural affinity for the appropriate dye and readily absorbs them from solution or an aqueous dispersion under suitable conditions of concentration and temperature. Insolubility in water is commonly used to characterize pigments but this can be misleading since some organic coloring matters which are insoluble in water are soluble in oils, and when used in these media, act as dyestuffs. On the otherhand, some coloring matters used as textile dyestuffs are soluble in water but insoluble in some non-aqueous media. In the latter case they would function as pigments. Examples also exist of coloring matters which can be dissolved in a liquid in which is simultaneously dissolved a film-forming material. At this stage the coloring matter can be considered as a dye. When the liquid is removed



in the formation of the film, e.g., by evaporation, the coloring matter will be precipitated in the film-forming material and become a pigment in the resulting film. Therefore, it is necessary to relate use as a pigment to the final form in which it is present in the medium.

### B. History

All pigment hue groups contain some important inorganic members accompanied, except for the whites, by a larger number of organic members. The earliest pigments for which we have evidence of use by man were inorganic and natural (usually meaning mineral) in origin.<sup>166</sup> Examples of these are white lead (basic lead carbonate -  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ), red lead (lead tetraoxide,  $\text{Pb}_3\text{O}_4$ ), the iron oxides (both hydrous -  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  - and anhydrous -  $\text{Fe}_2\text{O}_3$  - ferric oxides), and cinnabar or vermillion (mercuric sulfide -  $\text{HgS}$ ).

The oldest synthetic pigment is Egyptian Blue, a crystalline compound made by heating a mixture containing silica, a copper compound (probably generally malachite), calcium carbonate, and natron (natural sodium sesquicarbonate.)<sup>166</sup> Egyptian Blue has been found in murals dating from 1000 BC, as well as in Pompeian and other Roman and Mesopotamian wall paintings.

Preparations for white lead from metallic lead and vinegar were described by Theophrastus, Pliny, and Vitruvius, and there are numerous medieval recipes for it. Red lead has been found on wall paintings of China and Central Asia and Pliny has described its use in Graeco-Roman times. It was also a favorite with the Byzantine and Persian illuminators.<sup>160</sup>

Both iron oxides and vermillion have been found in nature, the latter as the mineral cinnabar, which is the principle ore of mercury.

According to Pliny, the entire Roman supply of this ore came from Sisapo in Spain. Vermillion has been identified in wall paintings in Pompeii and other Roman ruins and has been known even longer, since prehistoric times in China, having been found in Chinese oracle bones dating from the Shang epoch in the second millenium BC.<sup>172</sup> Recipes for the recombination of mercury and sulfur to form vermillion are common in the Middle Ages. The writings of Cennino Cennini<sup>85</sup> indicate that this artificially produced vermillion was used by 15th. century Italian painters.

The origins of the organic pigments have been lost in antiquity but they are presumed<sup>11</sup> to have included the use of natural products such as fruit juice and vegetable coloring matters for decorating tools, weapons, or people. Most of these were especially fugitive, although there were exceptions such as colorants derived from the madder root and woad plant. Organic pigments known to have been used were the lakes of Brazilwood (a yellow-red coloring matter extracted from the wood of 'Caesalpinia braziliensis'), logwood (a red dye extracted from the wood of 'Haematoxylon campechianum'), and Persian Berries (a yellow compound extracted from the dried unripe berries of various members of the buckthorn family, 'Rhamnus'). Each of these were 'fixed' on fibers with crude inorganic pigments - which helped to increase intensity and fastness - and also incorporated into oily and resinous materials or vehicles for decorative purposes.

## II. Pigments - Chemical Properties

Currently, some paint producers offer a choice of over 300 colored pigments with inventories of more than 200 additional ones. At the same time it is generally agreed that most of today's colors could be made by combination of as few as 20 pigments.<sup>219</sup> The reason for the seemingly

large number of pigments on the market, however, is that consideration of factors other than color is necessary when selecting a paint colorant. These are properties such as alkali resistance, light fastness, heat stability, etc., all of which are important in the consideration of a pigment for a particular use. Since very few pigments are ideal, that is, completely stable under all circumstances, selection of a pigment must take into consideration the stability of the pigment under the conditions required. In general, artist's pigments are stable in the widest variety of conditions, but the cost of some of these makes their commercial use prohibitive. Specific fastness properties are discussed in relation to particular pigments in Part 3 and tests for these properties may be found in Appendix B.

In general, however, it is possible to classify pigments broadly as either inert or reactive. A reactive pigment is usually regarded as one that reacts chemically with the vehicle, either in the liquid paint or in the dried film where reactive auto-oxidation products have developed during the drying process. Reactivity may also be characterized by a change in the physical properties of the paint film. An example of this is the absorption by the pigment of particular components of the vehicle or driers which leads to a decrease in the drying rate. Reactive and inert pigments also show differences in terms of their effect on mechanical properties of the dried film, such as tensile strength, elasticity, flexibility, and hardness, but "the considerable volume of experimental data relating to these aspects cannot as yet be sufficiently integrated to reveal precise and unequivocal relationships between pigment properties and paint film performance."<sup>402</sup> Some general tendencies are, however, observed; pigments that tend to neutralize the acidity of

corrosive atmospheres are useful in anti-corrosive paints, pigments that can absorb destructive ultra-violet rays in sunlight prolong the life of the paint, and adhesion of paint coatings can be improved by attention to the pigment composition.

Commercially, prudent selection of pigments reactive under certain conditions may be necessary or even desirable due to their beneficial properties under another set of conditions, e.g., heat stability for ceramic glazes or light fastness for exterior paints. Artists' colors, on the otherhand, require as complete compatability and stability as possible since their ultimate use is variable and they are often freely intermixed or closely juxtaposed - much more than are house or other commercial paints.

### III. Pigments in a Paint Film - Physical Properties

A pigment used in a paint film contributes certain features such as hue and degree of opacity to the film. It also influences the degree of resistance to light, acids, alkalis, and solvents, all of which obviously are related to the life of the paint film. Just as the chemical constitution of a pigment has a direct influence on its behavior towards substances with which there may be a possibility of chemical reaction, so does it also influence other properties such as solubility, refractive index, color and specific gravity. These physical properties of colored materials affect their suitability for use as pigments. In general, color characteristics such as hue, saturation, and brightness will depend intimately on the color absorption, size, shape, texture, refractive index, etc., of pigment grains/particles. Some general physical properties will be discussed now.

### A. Pigment Particle Size and Size Distribution

Pigment particles may be of variable size and shape within relatively narrow limits. Since they must be capable of producing a paint which can be applied evenly and smoothly as a uniform film, they must have a fine and uniform size. In addition, as pigment particles vary in size, so do their shade, brilliance, hiding power, and color strength. If very fine particles are used, the result may be floatation of the particles in the applied film. This is very noticeable in the case of blends of pigments of different colors, such as in, for example, a green paint containing Prussian blue and chrome yellow. In this mixture, the very fine particles of blue can collect in brush marks, which are then seen to be bluer in color than the surrounding paint. Conversely, no particles should be greater than a certain size. If a paint film has a thickness of say, 20  $\mu$ , it is desirable that the largest pigment particle should not exceed 3-4  $\mu$  in size. A larger size for any individual pigment particle would cause a weakening of the film in its area. It follows that an overall increase in particle size above this maximum would weaken the film everywhere. Consequently, most colored pigments have grains ranging from 1.5 to 10  $\mu$  in diameter, the majority being on the lower end of this range.

In fact, the vast majority of particles are smaller than 3  $\mu$ . Merwin<sup>301</sup> calls pigments that are less than 0.8  $\mu$  very small; between 0.8 and 2  $\mu$  small; between 2-5  $\mu$  medium; 5-10  $\mu$  large; and over 10  $\mu$  is very large.

While there is evidence<sup>400</sup> that some mixture of particle sizes is desirable for increased durability, reduced absorption, and reduced permeability of the film, it has also been found that the more narrow the

range of sizes, the brighter the color.<sup>177</sup> Pigments produced today by modern mechanical methods for grinding are generally finer and more even than those used by earlier artists.\* Gettens and Stout<sup>168</sup> claim that "granular, crystalline pigments give a certain pleasing quality to paint films that cannot be had from fine, well-dispersed pigments such as are produced for the modern paint industry."

Particle size is also related to the specific gravity of a pigment. Together these affect both the rate of settlement in a liquid paint and the texture of a dried paint film.

#### B. Pigment Particle Shape

Pigment particle shapes are variable and obviously depend on their crystalline structure. For example, mineral pigments (e.g., cinnabar and vermilion) are simply broken crystal fragments. Their size and shape develops directly from the type of fracture they make and the amount of grinding required to reduce them to a suitable pigment size. Generally this is not very small, instead approaching the limits for pigment grains, i.e., 5 to 10  $\mu$ . Their final shape is necessarily angular, sharp and irregular, being determined by the cleavage properties of the parent mineral.<sup>168</sup>

The earth pigments (e.g., raw sienna, raw umber) are sedimentary in origin and come as small, discrete, but unevenly shaped particles. The smaller particles (2 to 5  $\mu$ ) most suitable for use as pigments, are obtained by levigation of raw earth. Larger particles settle out and the finer particles are held in suspension. Because this process is

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\* Apparently, large particle size and graininess are characteristic of the pigments used in both early Chinese paintings<sup>168</sup> and Dutch painters such as Vermeer (1632-1675) and de Hoogh (1629-1684?).<sup>265, 267</sup>

carried out serially (i.e., a suspension batch is moved from tank to tank and allowed to settle for progressively longer periods of time) each tank will produce successively finer deposits.

Pigments produced by precipitation (e.g., the cadmium sulfides) are generally crystalline in nature so that each particle is a tiny crystal. Pyrogenic pigments (e.g., ultramarine, chromium oxide) will vary greatly from batch to batch as exact conditions of formation vary. Often these syntheses depend on the interaction of several substances at high temperatures. Several pigments (e.g., lamp black) are fume and smoke products so their particle size is generally fine and uniform. Lake colors are variable, depending on the type of base onto which they are precipitated.

Particle shape can affect the integrity and other properties of a paint film. For example, plate-like particles which have the capability of forming overlapping laminar structures in a film confer greater resistance to water permeation to the film.

Particle size, size distribution, and shape are also important in other properties such as hiding power, consistency, oil absorption, and application properties such as flow and brushability. These effects are referred to in the discussion of these individual properties (vide infra, the next several pages).

#### C. Tinting Strength and Reducing Power

The comparative amounts of two colored pigments which need to be blended with the same amount of a white pigment (and in the same medium) to produce a tint of equal strength in each case is a measure of the tinting strength of the colored pigments.<sup>401</sup> If two pigments are identical, their tinting strengths will be an approximate measure of the

effect caused by a difference in particle size, size distribution, and concentration. Conversely, the relative amounts of two or more white pigments which are required to produce a tint of equal strength in the same colored pigment is a measure of their reducing power.<sup>401</sup> The more opaque a white pigment is, the less quantity will be required because it introduces more white light through scattering and reflection.

#### D. Refractive Index

When light rays pass from one transparent medium into another, they are bent or refracted. The rays reaching the surface of the second medium are incident rays and those bent by the second medium are refracted rays. The refractive index of the second medium relative to the first is the numerical value of the trigonometric ratio of the sine of the angle of incidence to the sine of the angle of refraction. The refractive index of a pigment is usually quoted relative to air or a vacuum as the medium carrying the incident light. While the refractive index of a crystalline material, such as a pigment is different along different directions of a crystal, the refractive index for pigments is usually given as the average refractive index, which assumes that the directions of corresponding axes in the many small crystals are random.<sup>400</sup>

#### E. Hiding Power

Many factors influence the hiding power of paint. Among these are the effective particle size, shape, distribution, concentration, degree of aggregation, and refractive index of the pigments together with the thickness of the applied film. Both hiding power and tinctorial strength increase with decreasing particle size down to a particle size equivalent to the wavelength of light. At this point, many of the ordinary laws of optics based on the rectilinear theory of light no longer hold.<sup>400</sup>



Changes in the energy distribution of light inside a paint film are brought about by a combination of absorption and scattering of the light by each individual pigment particle. The relationship of these two factors is governed by several complex and separate factors, the relative importance of which is not fully understood.<sup>404</sup> However, in some cases, these factors can be used to relate fundamental physical properties of pigments to their actual behavior.

An example of this relates the refractive index of white pigments to their ability to reflect light and therefore appear whiter. Since for white pigments there is little or no absorption of light, the hiding power of white paints depends entirely on scattering of the incident light. The higher the refractive index of the pigment relative to the medium and the nearer the particle size to the optimum, the greater the scattering. This is based on a fundamental concept of the electromagnetic theory of radiation which says<sup>404</sup> that when light passes through an interface, i.e., from one transparent medium to another, it can undergo a change in velocity. Further, the ratio of the velocity in air ( $v_a$ ) to the velocity in the medium ( $v_m$ ) is the refractive index of the medium in air, ( $n_m$ ) so that

$$\frac{v_a}{v_m} = n_m$$

A white pigment particle also has a refractive index in air ( $n_p$ ) defined in the same way:

$$\frac{v_a}{v_p} = n_p$$

If this pigment is now part of a paint film, then the refractive index ( $n$ ) of the pigment in the medium is defined by the ratio of

$$\frac{n_p}{n_m} \text{ derived from } n = \frac{v_m}{v_p} = \frac{v_m}{v_a} \times \frac{v_a}{v_p} = \frac{n_p}{n_m} .$$

Moreover, development of the laws of electromagnetic radiation shows that for light incident at right angles to a transparent medium, the fraction reflected at the interface is equal to

$$\frac{(n-1)^2}{(n+1)^2} .$$

First developed by Fresnel, this law simply means that the greater the refractive index differences between particle and medium, the greater the amount of light reflected by the surface and the more the pigment will appear opaque.<sup>276</sup> This can be seen in the case of white pigments such as titanium dioxide and barium sulfate. Of these, titanium dioxide has a refractive index (in linseed oil) more than twice that of barium sulfate but the fraction of light reflected differs by a factor of nearly 33 based on the above equation. This is readily observed by the much greater opacity of titanium dioxide in a paint film.

Another factor which contributes to the ability of white pigments to scatter light concerns that part of the light beam which enters the pigment particle. For transparent media, this beam is bent from its original path, or refracted, by an amount which is dependent on the refractive index (n). The greater the value of n, the greater the angle of deviation of the light beam and consequently the greater the degree of scattering. The result of this, in combination with the property discussed above, is a greater whiteness for pigments with a higher refractive index.

The hiding power of a paint containing a colored pigment is

dependent on the ability of the pigment to absorb light as well as to scatter it. In the case of black pigments, good hiding power is obtained by complete absorption of light and opacity as such contributes little to this effect. With colored pigments, on the otherhand, absorption takes place with an associated change in the refractive index. In phthalocyanine blue, for example, the blue part of the spectrum is not absorbed but the scattering is also low because the difference in refractive index is low. The pigment begins to absorb in the green and the refractive index becomes less than that of the medium; it then becomes highly absorbent and extremely opaque in the red. For this reason, phthalocyanine blue in a concentrated paint film can exhibit a reddish tint, i.e., because of front surface scatter of the red portion of the spectrum<sup>404</sup> as illustrated in Figure 3.

It should be noted here that the magnitude of scatter also depends on the quantity of pigment per unit area of surface covered, and this in turn is a function of the concentration of the pigment in the paint and the film thickness applied.

There is also a close relationship between refractive index and color. Merwin says:<sup>302</sup>

To be most effective as a pigment when used alone, a substance should have a high refractive index for the color which it most freely transmits. In general there are large variations of refractive index near and through a region of color absorption. Refractive index is higher on the long-wave side of such a region than on the short-wave side. For this reason red, orange, and yellow pigments usually have much higher refractive indices than blue and violet pigments. The refractive index of lakes is largely determined by the base, and is always comparatively low. Some pigments so nearly match vehicles in refractive index that they diffuse very little light. They become effective only when mixed with a pigment of high refractive index which will diffuse their color, or when painted in thin films over a surface covered with a strongly diffusing paint. For example, Prussian blue, verdigris, and alizarine lakes.

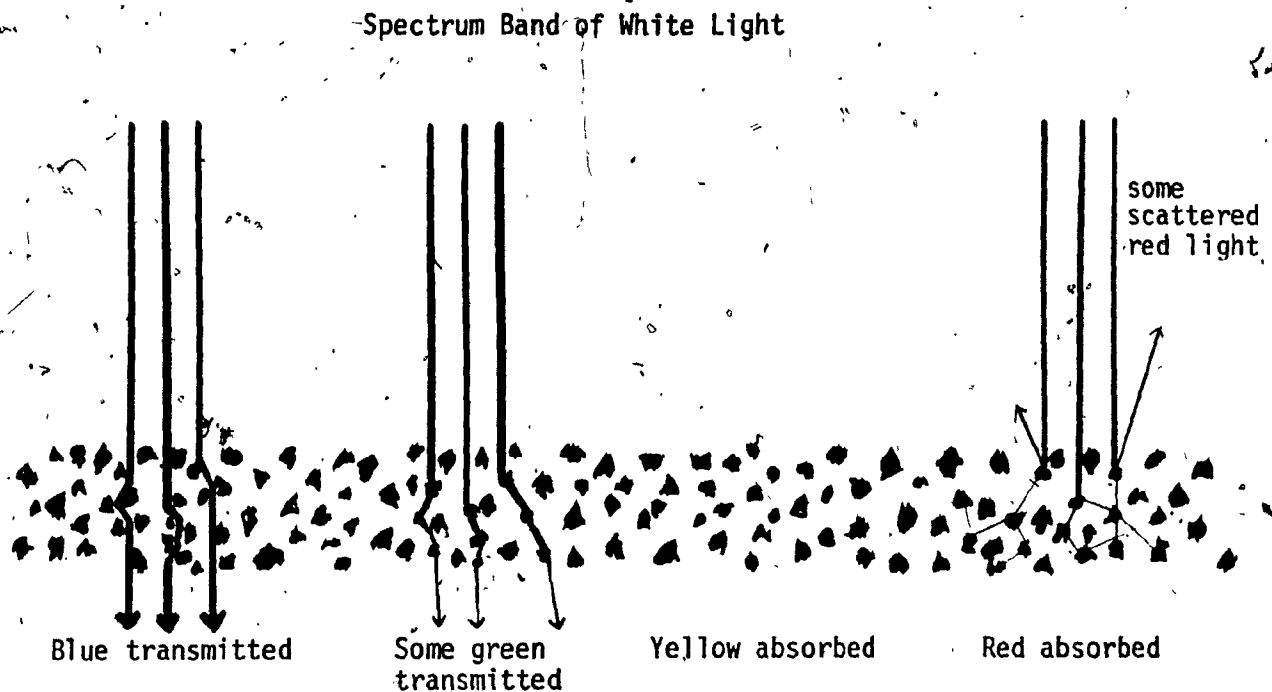


Figure 3. Representation of Light Transmission, Scattering and Absorption by Phthalocyanine Blue Pigment in a Paint Film.<sup>403</sup> Note that the transmitted light shown here would be reflected off of the background were the blue layer a paint film on a white ground.

The ability of a pigment to hide or obscure a surface when it is applied in a paint film is, therefore, dependent on the extent to which the pigment scatters and absorbs light throughout the spectrum. Opaque black pigments possess hiding power because they absorb light; colored pigments are affected by both properties. Inorganic pigments in general, have a greater hiding power than organic pigments of a similar shade because they have a higher refractive index in their non-absorbing regions.

#### F. Oil Absorption

The oil absorption of a pigment is the maximum amount of linseed oil which can be worked into a given weight of pigment so as to form a

coherent paste. Oil absorption varies from pigment to pigment and even with the same pigment unless testing procedures are identical. Thus, values cited in the literature are valid only when they have been determined under the same conditions and the end-point consistency closely reproduced for each test. In spite of the potential subjectivity of such a value, it is still a useful guide in formulating paints, enabling the manufacturer to predict accurately the consistency of a paint made from a given pigment in a known amount of oil medium.

#### G. Wetting or Dispersion

A vehicle permeates a mass of pigment in three ways; by distributing itself in the gaps between the particles, in the crevices of the individual particles, and as an especially close envelope over the surface of the particle. The oil in the gaps between the particles is considered to be in a 'free' state but on the surface of the pigment it is bound by absorptive or wetting forces.

These absorptive or wetting forces influence the ease with which a pigment is mixed in a vehicle. The optimum qualities of a paint are only produced when the pigment particles are evenly distributed throughout the paint medium. The mixing or dispersion of the pigment may be either easy or difficult depending on the facility with which each particle of pigment is coated. This process, called wetting, involves the displacement of air or moisture normally covering the surface of each pigment. There is a competition between the surface forces attracting the unwanted air or moisture and the forces attracting the desired vehicle (i.e., organophilic vs. hydrophilic properties). Wetting is facilitated by greater molecular attraction potentials between vehicle and pigment than air or moisture and the pigment. Dispersibility is also related to pigment

particle size, texture and agglomerate state. Some of these relationships will be discussed now.

#### H. The Effects of Oil Absorption, Wetting, and Dispersion on Flocculation

"Flocculation may be defined as the formation of clusters of particles which are disturbed and broken by relatively weak mechanical forces or by a change in the physical forces at the interface between the solid and suspending medium. The term flocculation derives from the Latin 'floccus' - implying a wooly, soft massing of fibres or particles."<sup>148</sup> Flocculation implies that the particles composing the flocculate (or discontinuous phase) were originally dispersed in the continuous phase of the medium. The flocculate or agglomeration of particles, is formed by movement of the particles in the medium towards each other and then adhesion due to surface tension effects at the point of contact. Accompanying this is a low value for a similar adhesion tension between the medium and the pigment. (See Figure 4). The freedom of particles to migrate is determined by (1) the chemical properties, polarity, and particle size of the solid, (2) the chemical properties, polarity, and viscosity of the liquid, and (3) the effect of other substances such as resins and surfactants on the system.

Pigment particles immersed in a liquid medium such as linseed oil would exist as undisturbed clumps (Figure 4a). Here the vehicle is only in contact with the exterior of the clumps while the interior contains air spaces. The finer the pigment particles, the greater the number of air spaces and the higher will be the oil absorption.

If the clumps are broken up by mechanical means, they will become completely dispersed as in (4b). Mechanical dispersion can be by a palette knife or other simple device. The air space has been eliminated and the

vehicle is presumably in contact with each particle.

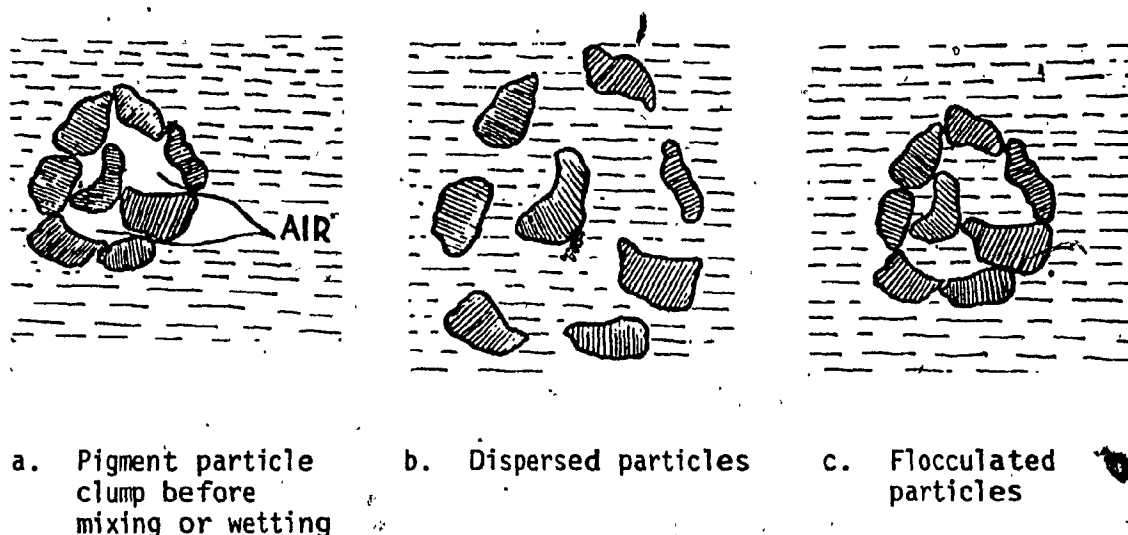


Figure 4. Wetting and Flocculation of Pigments.<sup>452</sup>

If the adhesive surface tensions of the pigments for the medium is low but relatively strong for each other, flocculates will tend to form (4c). The result of using such flocculated paint is that the applied film will have a reduction in hiding and tinting power, as illustrated in Figure 5.

As should be apparent, a larger proportion of incident light is reflected by a deflocculated system (Figure 5a) providing better hiding and coloring power than a flocculated system (Figure 5b). Flocculated paints can usually be redispersed by mechanical means. It should be noted here that certain pigments, such as some forms of copper phthalocyanine, exhibit the tendency to flocculate more than others.

One method of combatting agglomeration of organic pigments is the use of rosin soap. This was originally thought to coat the particles as they formed and so prevent their adhesion during drying. Today, however, the mechanism is not believed to be one of 'coating' but of a surface

active agent which interferes with the cohesive attraction between pigment particles and therefore prevents excessive agglomeration and growth.<sup>348</sup> Apparently, little is yet known about the exact mechanism or activities of surfactants.

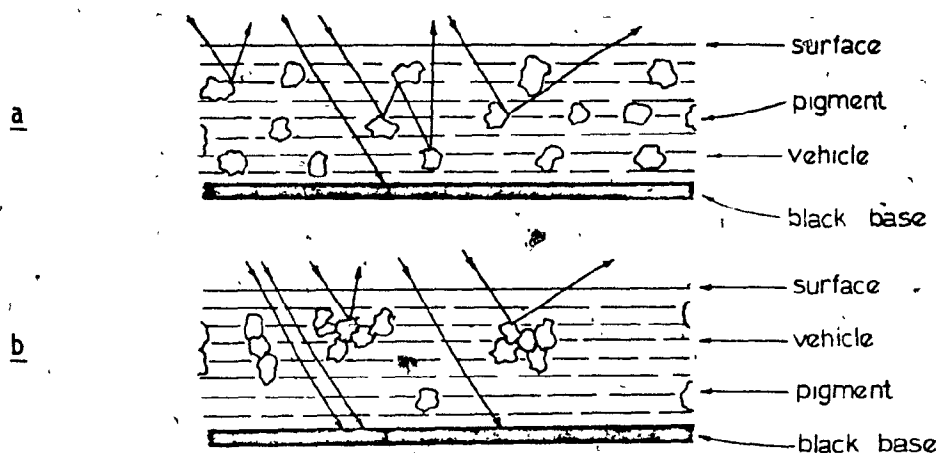


Figure 5. The Effect of Flocculation on Hiding and Tinting Power. (a) Dispersed particles reflect most of their characteristic wavelengths of light making the surface film appear the same color as the pigment particles. (b) Flocculated pigments allow a much greater proportion of the light through to, in this case, the black ground. The viewer sees the black as 'showing through' the paint film.<sup>177</sup>

### I. Polymorphism

The last general physical property of pigments to be discussed is polymorphism which is the general term applied to a substance which crystallizes with more than one crystal structure. As the crystalline system changes for chemically identical pigments, the crystalline form and degree of crystallinity influence other properties such as light fastness. In general, only one crystalline form is useful in terms of its shade and other properties. Titanium dioxide, for example, is known in three forms and the properties of these differ, especially in terms of whiteness and opacity. Many other pigments also exhibit polymorphism



because this property is present in all classes of organic pigments.<sup>276</sup>

One polymorphic form of a pigment can change into another if subjected to conditions which are more favorable to the formation of the alternate form. This is known as polymorphic transition and the process may be rapid or very slow, being brought about by changes in temperature or treatment with different solvents. The importance of polymorphism should become clear in the later discussion on copper phthalocyanine (vide infra, p. 65).

#### J. Conclusion

In summary, the useful properties of a substance which would make it suitable as a pigment are generally high or bright color strengths, chemical stability in the medium used, fastness to light, heat, weather, acid, or alkali, high hiding power (usually), facile dispersion in the medium used, and little tendency to agglomerate or flocculate. Furthermore, it is a minimum requirement that the pigment should be relatively easily ground into a suitable form. A paint incorporating this pigment should be capable of being stored for suitable lengths of time and being applied relatively easily as a film. If a pigment is to be incorporated into an aqueous medium, a water paste of the pigment is the best (more directly ready for use). If mixed in an oil medium, either a dry powder or an oil paste are the forms preferred.

#### IV. Pigments - Manufacturing

The manufacture of pigments requires quality controls in order that uniform shades and properties of the product result. Some of the concerns which must be considered are as follows:<sup>277</sup>

##### A. Purity of Intermediates

Pure reaction substrates are indispensable. In the preparation of

azo pigments, for example, minute amounts of other amines as impurity in the diazo component will give rise to a foreign pigment intimately mixed with the desired one. Inevitably, the shade and properties of the desired pigment will be altered. Or, the amine impurity could result in an insoluble and colorless by-product which would either alter the properties of the pigment or act as an extender by lowering its color strength. In many cases, the elimination of impurities after preparation is impossible, either because the process would be too costly or the treatment would alter the structure of the pigment.

#### B. Use of Surfactants

It is not uncommon that the synthesis of a pigment requires the use of surfactants. An example is the use of dispersing agents in the preparation of azo pigments. These agents, usually anionic or cationic compounds, make it possible to obtain a fine suspension of a coupling component which is insoluble under the reaction conditions. The essential part played by these surfactants is to ensure formation of the pigment as fine particles rather than agglomerates. However, it is not always possible to remove by washing or simple chemical extraction a dispersing agent which has been strongly absorbed on the paint. Unfortunately the presence of these agents in the final pigment product can negatively modify such properties as oil absorption, vehicle-pigment reactivity, and color shades, etc.

End-treatment surfactants are usually less problematic in that they are selected to be beneficial to the consumer's needs, while not affecting shade or other intrinsic pigment properties. In general, the pigment is left in a condition which is as similar to its potential vehicle as possible. For example, with drying oils or related vehicles, a fatty

acid coating or non-drying oil may aid the wetting of the pigment to shorten grinding time. For aqueous media, a hydrophilic protective coating would be used and for non-polar vehicles, a non-ionic or oil-soluble surfactant would be chosen.

#### C. The Effect of Varying Manufacturing Conditions on Pigment Shade

Different conditions such as, in the case of azo pigments, the relative proportions of reagents, temperature, pH and rate of coupling, and heating of the reaction mixture after coupling will yield pigments of remarkably varying shades. Other pigment classes are affected in diverse degrees by these factors and the result will be found in the crystalline form obtained, the size of the particles, the state of aggregation, etc. Consequently, the acceptable limits for manufacturing condition changes are both crucial and narrow.

#### D. Conditioning of Pigments Not Obtained in a Suitable Form

The principle treatments are acid pasting, salt-milling, grinding in an inorganic solvent, and treatment with hot organic liquids. If a pigment is polymorphic, these treatments can have a decisive effect on the product's crystalline form. It follows that manufacturing conditions must be arranged so that the desired crystalline form is produced.

#### E. Purification of Products

Most often, a manufactured pigment is 'finished' in an aqueous medium. The pigment in suspension in this medium has taken on the form it must retain as a powder or paste. It still must, however, be filtered, washed, dried and ground. Therefore, care must be taken in these steps so that the pigment is not altered; but at the same time, all soluble impurities, especially mineral salts which on drying would stick the pigment particles together, should be removed.

Drying is usually performed in a heated air circulation oven or under vacuum. Some pigments must be dried at precise temperatures in order to acquire the proper final shade. Occasionally drying is carried out by atomization in a spray drier. The pigment is then in the form of friable lumps which must be ground. After drying and grinding, the pigment has often lost some of its coloring power. In order to avoid this, pigments are sometimes sold as aqueous presscakes (concentrated aqueous pastes). The color loss is then avoided by transferring the pigment directly from the aqueous phase to the organic phase of the vehicle to be used. This is called the flushing process and is described later in the section on paints. The pigment manufacturer may also sell pigments already predispersed in a small quantity of the material to be colored or a vehicle miscible with it. Examples are flushed pigments or presscakes for printing inks or paints, nitrocellulose chips with the pigments dispersed in them for lacquers, and fluid pastes for paper or emulsion paints (this last form is the one we used). In each of these situations, the pigment is sold in the most advantageous form for a given use.

### Part 3. The History, Properties, and Synthesis of Selected Pigments

#### I. Introduction

Several pigments, which were subsequently synthesized, were chosen with the following criteria in mind: (a) color - at least one each of the primaries and other basic colors should be made, (b) chemical class - both organic and inorganic pigments should be represented, (c) reaction types - there should be differing types of reaction sequences involved, and (d) artists' colors - since the project was intended to generate an understanding of interdisciplinary concepts in terms of color and pigments, the pigments synthesized should be artists' colors which would then be mixed into paints and used in paintings.

#### II. Organic Pigments

In general, organic pigments are less durable and more transparent than inorganic ones but have superior tinting strength. The transparent tendency of the organics is more a function of their usage (concentration) than of a relationship by weight. In organic pigments, a sufficiently high molecular weight is necessary so that an acceptable degree of insolubility in the medium is obtained. Consequently, most organic pigments have a molecular weight between 300-1000 (some macromolecules are also colored<sup>273</sup>). Examples of this type of consideration are Benzidine yellows (mol. wt. > 600) which have better solvent resistance than the Hansa yellows (mol. wt. < 400). Organic molecules with a molecular weight less than 300 can be fast in solvents, etc., if substituents on the molecule allow hydrogen bonding and other stabilizing interactions between groups. Organic pigments can be broken down into three classes:

(a) lakes - these are formed by the precipitation of a soluble dye on an inorganic substrate. Here the substrate is an integral part of the product. It is also usually colorless (alumina hydrate, or barium sulphate are common) but nonetheless may play an essential role in the development of the final pigment color as will be seen in the example of a lake discussed in this paper (vide infra, alizarin red).

Lakes in paint media are generally translucent and brightly colored in relatively thin layers, but with successive application of paint can become progressively darker as less light is reflected off of a background.

(b) toners or full strength colors - these are insoluble dyes devoid of substrate and pigments which are in themselves insoluble.

Toners include both opaque and translucent pigments.

(c) extended toners - these are class (b) (above) pigments which have been reduced by an extender (not a lake substrate) which is incorporated with the pigment after the pigment is formed. Extenders are usually inorganic and not an integral part of the pigment. (Examples of extenders are hydrated alumina, barium sulfate, and calcium carbonate). Generally these extenders are added to reduce the cost of the pigment.

A. Alizarin Red (CI Pigment Red 83; CI 58000:1) \*

\* The designation 'CI Pigment Red 83' refers to the Color Index<sup>91</sup> standard number for alizarin. This reference book is the color chemist's standard encyclopedia, listing all coloring matter according to chemical class, color, and use. All references after a pigment name in this paper, e.g., CI Pigment Blue 31; CI 77437, refer to this Color Index standard number. The notation CI 77437 specifies the Color Index's structure and formula reference number for this pigment, CI Pigment Blue 31.

## 1. History

Alizarin is the principle coloring matter of the madder root (Rubia tinctorum) and was first isolated in 1826 by Colin and Robiquet.<sup>161,444</sup> Subsequent research established that alizarin is in fact 1,2-dihydroxy-anthraquinone (Figure 6). In its natural form, alizarin occurs in combination with two moles of glucose as the glucoside ruberythric acid. Alizarin was apparently used in ancient Egypt, Persia, and India, and an aluminum lake of madder has been identified among the artifacts recovered from the refuge in Corinth which are believed to predate the destruction of that city by the Romans in 146 B.C.<sup>21</sup> Artificial alizarin was first synthesized in Germany by Graebe and Lieberman in 1868 from dibromo-anthraquinone.<sup>444</sup> Their method was improved the following year by a reaction involving the fusion of an alkali with sulfonated anthraquinone. This procedure\* and minor improvements of it were patented successively by Caro, Graebe, and Lieberman.<sup>36,84,178-9,283-4,342-3</sup> Early commercial alizarin products typically contain a mixture of alizarin with small amounts of Flavopurin (1,2,6-trihydroxyanthraquinone) and Antrapurpurin (1,2,7-trihydroxyanthraquinone).<sup>444</sup> This event is of historical importance in organic chemistry as alizarin was the first natural dyestuff to be made synthetically. The discovery caused, or at least contributed to, the rapid decline of the French madder growing industry, although small quantities of natural alizarin were still being used as an artists' color up to 1930.<sup>196</sup> Today, these seem to have been replaced completely by the artificial product which in turn seems to be undergoing a decline, largely being replaced by  $\alpha$ -naphthol and arylamide red derivatives. In fact, the

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\* A variation of this procedure was followed for this project.

current production of alizarin in the United States, is about one-eighth of that twenty years ago and the number of companies producing it has decreased from ten to five.<sup>338</sup>

When alizarin was initially developed, it was used only as a dye for natural fibres. These were colored by applying the dye in conjunction with mordants consisting of various metal salts. Strongly colored insoluble metal complexes were formed which were precipitated within the fibres. By varying the metal salt it was possible to obtain several hues from the same dye and the resulting dyed product had excellent fastness properties.<sup>20</sup> For use as a pigment in paint, the metal complex of alizarin was precipitated in an aqueous solution and sold as a 20% paste.

Several other di- and polyhydroxyanthraquinones as well as sulfonic acid derivatives of these compounds have been used for making lakes, some of which are in use today. Most, however, seem to have been discontinued, presumably in favor of some less expensively produced or more permanent coloring matter.

#### ii Structure and Properties

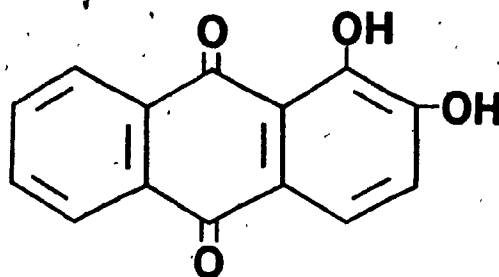


Figure 6. 1,2-Dihydroxyanthraquinone (Alizarin)  
(CI Pigment Red 83 - CI 58000).

Alizarin is a relatively simple anthraquinone derivative (Figure 6). Characteristically, it is soluble in alkali solution where it exhibits a



blue color. When formed into a lake by precipitation on a metal complex (discussed in more detail shortly), alizarin develops its pigment color, as well as its fastness properties, e.g., in organic solvents, water and paint media.

The artificial alizarin lake is more lightfast than the natural product which contains some purpurin as impurity. This latter is a fugitive color which dulls on exposure to light over a period of time, thus dulling the whole paint film in which it is mixed.

While alizarin lakes are soluble in acetone and boiling alcohol and slightly soluble in benzene and carbontetrachloride, the usefulness of this compound as a pigment is illustrated by its generally excellent fastness properties. It should be noted here that the normal properties of carbonyl groups are subdued in alizarin as might be expected from its structure.<sup>396</sup> A complete list of the properties of alizarin is given in Table 3.

Table 3. Physical Properties and Other Data for Alizarin Red (CI Pigment Red 83; CI 58000:1)

Chemical Class	Anthraquinone (Metal Compounds)	Reference
Hue	Yellowish Red - Bordeaux	93
Fastness Properties:		
1. Organic Solvents		
aliphatic petroleum	insol	
'cellosolve'	sol	
esters	V. gd	
ethanol	"	
ketones	"	
NC solvents	good	
xylene	insol	
acetone	sol	
alcohol (boiling)	sol	
alkali	sol	
benzene	sl. sol	
CCl <sub>4</sub>	sl. sol	
alcohol (cold)	insol	

Table 3. Physical Properties and Other Data for Alizarin Red (con't)

		Reference
2. Light	full strength: 7 ½ strength: 5	93
3. Heat	m.p. = 290° stability: 4 (120° for 30 min.) " : 3-4 (150° for " ) b.p. = 430° sublimes at 110° (2mm Hg)	391, 440 93 391, 446
4. Water	insol	93
5. Na <sub>2</sub> CO <sub>3</sub> 5%	fair to gd	
6. HCl 5%	" " "	
7. Linseed Oil	insol	
8. Oleic Acid	insol	
9. Plasticisers	V. gd	
10. Soap Gel Bleeding	slight	
Hiding Power	poor	
Density	1.59 g/cm <sup>3</sup>	161
Transparency	excellent	
Refractive Index	1.70	
Crystals	i. Orthorhombic, orange needles by sublim. or from absolute alcohol ii. solvated scales from dilute alcohol or by evaporation from ether	391, 446
Absorption Spectra		305
Parent Dye	CI Mordant Red 11 (an anthraquinone→Al) with Ca = bluish red Cr = dull bluish red Fe = dull purple	93
Color in Solvents	H <sub>2</sub> SO <sub>4</sub> conc.: yellowish red (on dilution - reddish yellow ppt) NaOH: violet	
Standard	none exist for alizarin due to impracticality of shade matching*	

\* An explanation of the scale values, used in this and other physical property tables in this paper is as follows:

### iii. Chromophore

The characteristic chromophore of anthraquinone and related coloring matters is the carbonyl group in association with the conjugated system.

The two hydroxyl groups acts as auxochromes.<sup>104</sup>

### iv. Experimental - Alizarin

The Color Index lists the following general types of reactions for the synthesis of alizarin:<sup>103</sup>

1. heat dibromoanthraquinone with KOH

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When a numerical value is indicated for fastness, the values in this paper will conform to the following scales:

- (a) Light fastness is scaled from 1 to 8 with 8 indicating most fast.
- (b) All other parameters are scaled 1 to 5 as:
 

excellent	very good	good	fair	poor
5	4	3	2	1

 so that in all cases the highest number indicates the optimum fastness.
- (c) Color changes are generally assessed by eye with reference to a standard.
- (d) Insolubility in a solvent indicates the highest grade. Solubility is considered a defect in that it can bring about crystallization and a subsequent change in color and other properties.
- (e) Bleeding is considered a serious defect for the obvious reason that dried paint film containing a pigment suffering from this problem would not necessarily have a constant or permanent relationship with its environment. In linseed oil or oleic acid, the 'highest' grade has no bleeding and a 'very good' rating indicates slight bleeding.
- (f) The usual test for alkali fastness is 5%  $\text{Na}_2\text{CO}_3$  solution at room temperature. The highest grade is unaffected, i.e., no bleeding or color alteration.
- (g) The usual test for acid fastness is 5% HCl solution at room temperature. The scale for acids is the same as for alkalis.

See Appendix B for specifics about the determination of these properties, as well as tests for particular pigments.

2. heat 2-anthraquinone sulfonic acid (Na) with NaOH in the presence or a nitrate of chlorate
3. heat anthraquinone with NaOH and sodium nitrate in the presence of sodium sulfite (GP 241806, 245987)
4. heat meso - nitro derivatives of anthracene with NaOH in the presence of oxidising agents, sodium sulfite, and lime (GP 292247)
5. treat 2-anthraquinone sulfonic acid in the presence of air with KOH moistened with alcohol (GP 287270)
6. alkali fuse 2-chloroanthraquinone in the presence of sodium chlorate (USP 1744815)
7. treat 2-methylantraquinone with caustic alkali in the presence of an oxidising agent (BP 293328)

Specifics of some of these as well as other methods may be found in Appendix A.

The synthetic method<sup>144</sup> chosen for this project is based on the general reaction number 2 listed above.\*

A mixture of sodium anthraquinone-2-sulfonate ('silver salt') (100 g), NaOH (260 g) and sodium chlorate (28 g) is dissolved in water (670 ml). This mixture is heated at 85° in a stainless steel bomb with continuous stirring for 48 hours, during which time the reaction develops a pressure of 6 to 7 atm. The reaction mixture is then cooled and a sample of the product tested to ensure that fusion is complete by taking 2 ml of the melt and precipitating with the necessary amount of concentrated HCl. The extract is then filtered twice with ether and the solution, now free from alizarin, is diluted to 15 ml and examined for fluorescence caused by unreacted monohydroxyanthraquinonesulfonic acid. If more than a very faint fluorescence is observed, the reaction is continued another 24 hours at 190°. At that point the melt is diluted with 2 $\frac{1}{2}$  of distilled water and heated to boiling. Alizarin is precipitated with 50% H<sub>2</sub>SO<sub>4</sub> (to pH 2)<sup>445</sup> giving a finely divided product which is filtered off at 50° and washed until free from salts. The expected yield is about 70 g pure alizarin from 100 g pure anthraquinone-2-sulfonate.

This procedure was essentially followed with the exceptions given below. The mixture, which required 12 hours for stabilization at 185°, and at one point reached 210° (and a pressure of almost 12 atmospheres), was heated for 67 hours. The test for unreacted silver salt showed no fluorescence so heating was not resumed. Precipitation of the alizarin by

\* A similar method may be found in Gatterman.<sup>157</sup>

$H_2SO_4$  was a vigorous reaction, overflowing a 4 l beaker. The finely divided precipitate was filtered off at  $50^\circ$  and washed repeatedly with water until the washings became clear. The desired product was obtained by evaporation to a muddy-brown suspension containing 26.2% (about 75 g) alizarin by weight. It is important that the product not be dried completely because the subsequent production of a lake becomes difficult.\*<sup>144</sup>

v. Notes on the Reaction

Shortly after alizarin was first produced synthetically, it was shown that the  $\beta$ -mono-sulfonic acid rather than the disulfonic acid derivative of anthraquinone was necessary as starting material because the latter resulted in trihydroxy products.<sup>443</sup> The formation of the 2-sulfonic-anthraquinone is generally from phthalic anhydride and benzene monochloride since anthraquinone is relatively unreactive and formation of the silver salt requires rather drastic conditions.<sup>395</sup> Hydroxylation of the 2-sulfonicanthraquinone may be performed directly by treatment with oleum but impure products (other di- and trihydroxy derivatives) result.<sup>397</sup> The procedure described above is a fusion of the sodium salt of the sulfonic acid with NaOH. Both dilute and concentrated hydroxide can be employed, depending on conditions. When using dilute NaOH (30-60%), it is necessary to work in an autoclave. The pressure makes no direct contribution to the reaction itself but is necessary in order to maintain the high reaction temperature, which is above the boiling point of the reactants.<sup>139</sup> The alkali fusion product of this reaction is the water-soluble disodium salt of 1,2-dihydroxyanthraquinone. Acidification by  $H_2SO_4$  yields the corresponding hydroxy compound. In this step, Alizarin is precipitated

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\* A method for regenerating dry alizarin is given by Fierz-David and Blangey:<sup>144</sup> Dissolve the alizarin in borax and reprecipitate with acetic or sulfuric acid.

from boiling solution because of the low solubility of the disodium precursor. In addition, it is said that only under such conditions can a "finely divided product be obtained."<sup>144</sup> The product crystals are brownish-yellow. The yield was found by Koch to be improved considerably by the addition of an oxidizing agent.<sup>20 444</sup>

It is generally agreed that the reaction takes place first, by replacement of the sulfonic acid group, followed by introduction of the second hydroxyl by oxidation (Figure 7).

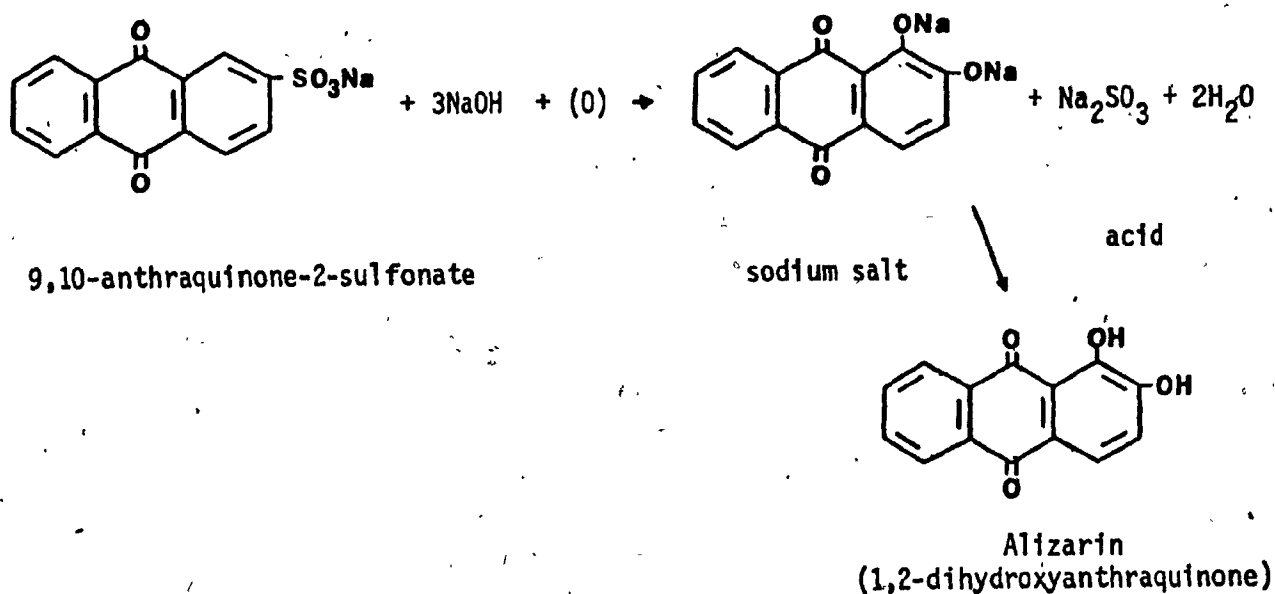


Figure 7. Alizarin Formation-Reaction Sequence<sup>445</sup>

#### vi. Lake Structure

The second stage in the production of alizarin into a suitable pigment form is its formation into a lake. A mordant or metal is complexed with the alizarin and is necessary to develop shade and fastness properties.<sup>82</sup> The color of the unmetallized dye is of no interest as can be imagined from the color of the alizarin product obtained above.

In lake production, the metal usually combines with some form of

base, such as alumina hydrate, which is used in two distinct ways for pigment manufacture: as ready made substrates or as simultaneously precipitated substances forming an integral part of the pigment product. The second type gives pigments of better covering power and a generally more homogeneous product because, unlike dyes, the coloring matter and substrate do not usually display any mutual affinity. Consequently they must be coprecipitated in order that they become an integral unit.

Alizarin lakes consist of both aluminum and calcium. The aluminum forms a chelate compound with the alizarin through the donation of oxygen electrons to the metal in a coordinate covalent bond.<sup>4</sup> According to Allen,<sup>12</sup> the joining of the aluminum to the oxygen is strong due to the formation of resonance structures associated with conjugation of the aromatic rings.

Fierz-David and Rutishauser<sup>28,146</sup> have regarded the lake as a well-defined compound containing alizarin, aluminum, and calcium (4:2:3). The structure they proposed contains five molecules of water (Figure 8). This structure is in accordance with the assumption that both salt-like and chelate bonds are formed. The calcium, which may be replaced by other metallic radicals including aluminum, is the cation and the chelate union of 2 molecules of alizarin with the 1 aluminum makes the complex anion.

Evidence supporting the chelate structure came from Geyer and Smith.<sup>174</sup> They prepared cobalt, copper, and other complexes of 1-hydroxyanthraquinone and have obtained analytical and spectral evidence to show that inner or chelate complexes of the type shown in Figure 9 are formed in the case of, e.g., 4 coordinate cobalt, nickel, and copper.\*

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\* A similar compound was obtained by Hoffman<sup>208</sup> by reacting alizarin with calcium oxide and aluminum acetylacetonate in aqueous pyridine. He proposed a macrocycle of 4 alizarin molecules, 2 pyridines, 2 aluminums,

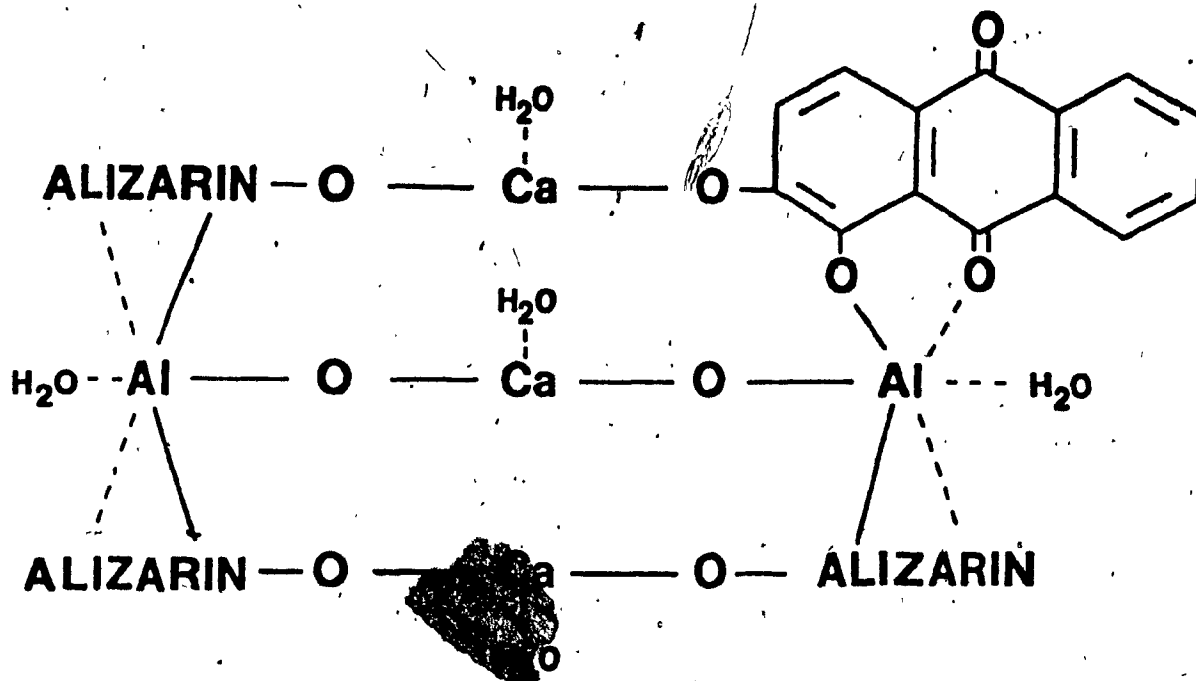


Figure 8. The Fierz-David and Rutishauser Alizarin Lake Complex Structure.<sup>146,447</sup>

Commercially, the amount of alumina used is usually much greater than either that employed by Fierz-David and Rutishauser in their experiments or the stoichiometric equivalent of the dye. The excess alumina hydrate is said to serve as a distending substratum which imparts desirable physical and optical properties to the finished pigment.\*

and 3 calcium atoms.

\* It is interesting to note that for many years alumina bases, including mixtures of aluminum hydrate, phosphate, and arsenite were considered to be one of those fillers used in cheaper paints. It is now recognized, however, that alumina, as a base, can confer such useful properties on a pigment as transparency and improved brilliancy. The addition of phosphates and arsenite as constituents of bases in cochineal and alizarin lakes gives bright shades (but also tends to reduce the lightfastness of the pigment). The alumina bases referred to here should not be confused with the cheaper form of alumina base used for wallpaper colors, high gloss printing inks, and rubber, etc.<sup>115</sup> This base is known as Alumina Blanc Fixe or aluminum alumina-barium



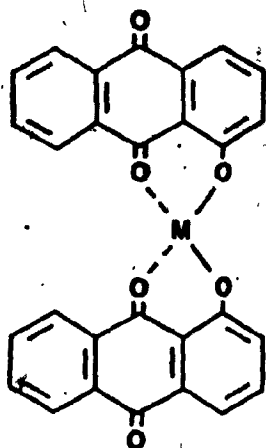


Figure 9. 1-Hydroxyanthraquinone - Metal Chelate Complex<sup>174</sup>

vii. Alizarin Lakes - The Effect of Mordant on Color.

Alizarin will yield a great variety of hues by merely altering the mordant. The mordant may be either a metal such as aluminum or a combination of metals. A list of mordants and their corresponding hues is given in Table 4.

Mordant	Alizarin Color Developed
aluminum	red
tin	pink
iron	brgwn
chromium	puce brown
copper	yellowish-brown
alum	Turkey Red

Table 4. Alizarin Mordants<sup>3</sup>

sulfate. These bases are used as filler meant to lower the cost of the paint. The barium sulfate, typically present as 75% of the Alumina Blanc Fixe,<sup>194</sup> gives some increased opacity but no other useful properties.

It should be noted that the presence of iron in the production of alizarin red pigments should be avoided since traces will give a lake with a blue undertone and brown overtones when the pigment is rubbed out in oil.<sup>198</sup>

#### viii. Experimental - Lake Production

Although many different methods of preparing alizarin lakes exist, combination is always brought about by boiling the alizarin with alumina hydrate in the presence of Turkey Red oil. Phosphates of aluminum or calcium are usually incorporated and these considerably improve the brightness of the resulting lake.

After precipitation, when the lake is first produced, it is very unstable and must be carefully boiled to ensure satisfactory results.<sup>365</sup> This may be done by either open steam or in an autoclave, with the best colors apparently obtained under pressure. The red color develops during heating and "considerable expert manipulation is necessary to make good alizarin lakes and only the most expert color makers can produce uniform products of good quality."<sup>432</sup> By varying the conditions of treatment, lakes of different overtones, undertone, texture and oil absorption can be obtained.<sup>446</sup> In fact, the conversion of alizarin into a lake was a closely guarded secret until the German processes were released by Allied intelligence agents as part of their investigation of all German industries following the war. Apparently such factors as source of water and chemicals affect the product shade so that even today alizarin pigments differ from one manufacturer to another.\* Several procedures for lake production do exist and the choice of method depends on the general shade

\* "Owing to the number of different lakes obtainable from one brand of dyestuff, the problem of matching an Alizarin lake is a very difficult one. The only method is to make small-scale experiments, carried out

and properties desired. It should be obvious from the above discussion that these shade and property differences would fall within fairly wide limits.

The method of lake formation chosen for this paper is given by Harrison and is said to give lakes "bright in appearance, and soft in texture."<sup>198</sup> Other methods may be found in Appendix A.

1. Aluminum sulfate (18-19%  $Al_2O_3$ ): 33.5 g  $Al_2(SO_4)_3$  in 335 ml water. To this solution at a boil is added slowly
2. Soda ash ( $Na_2CO_3$ ): (17.1 g in 171 ml  $H_2O$ ). The solution is stirred continuously for an hour, filtered and washed, and then made up into 800 ml water and the following added in order:
  3. Sodium phosphate: 8.2 g in 82 ml water
  4. Calcium chloride: 14.5 g in 145 ml water
  5. Turkey Red oil (50%): 13.0 g in 130 ml water
  6. Alizarin paste (20%): 40-60 g in 224 ml water

The mixture is stirred continuously and slowly brought to a boil over 2-3 hours. Boiling is continued 5 hours and then the product cooled, filtered, and washed. To obtain strong lakes, up to 60 g of alizarin paste may be used.

This procedure was used with the following variations and comments:

All quantities were doubled. 100 g of the 26% alizarin paste obtained in the first part of this section was used. Our aluminum sulfate contained 18 waters so that the quantity used was adjusted to the equivalent of 18-19%  $Al_2O_3$  as required. The alumina we obtained was a fine, white paste which was washed by decantation. It should be noted that the only reasonable method for lumpless resuspension of the settled alumina is

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under the same conditions, and with water and chemicals from the same sources as those which will be used in the actual works process. Alizarin is so sensitive to the slightest variation in the conditions of manufacture that a recipe cannot be passed from one works to another with any certainty of the exact lake being obtained."<sup>199</sup>

addition of an aliquot of water at a time. The lumps are then relatively easily broken with a glass rod. When the resuspending water is all added at one time, adequate lump breakup is impossible.

The remaining substrates (steps 3-6) were added slowly and the temperature raised slowly over 3 hours to boiling, which was continued for 5 hours. During this last period, hot distilled water was occasionally added to replace water boiled off from the open reaction vessel. The red color developed slowly over the first 3 hours of boiling, after which there was no perceptible change. The mixture was allowed to cool overnight with slow stirring as recommended by Zerr and Rubencamp.<sup>365</sup> The filtered alizarin lake pigment yield was approximately 170 g. Its hue was judged to lie between that of the alizarin produced by the color manufacturers, Grumbacher and Selectone. That it did not match either was to be expected given the wide hue variation normally found between different manufacturers and methods.

#### ix. Notes on the Lake Reaction

According to Curtis,<sup>112</sup> the first part of the reaction (steps 1 and 2 above) produces alumina hydrate by the following sequence of reactions:

1.  $\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2(\text{SO}_4)_2(\text{OH})_2 + \text{Na}_2\text{SO}_4 + \text{CO}_2$
2.  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2(\text{SO}_4)(\text{OH})_4 + \text{Na}_2\text{SO}_4 + \text{CO}_2$
3.  $\text{Al}_2(\text{SO}_4)(\text{OH})_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2(\text{OH})_6 + \text{Na}_2\text{SO}_4 + \text{CO}_2$

The formation of the basic sulfates is favored by cold and dilution in large quantities of water. Therefore, the reaction is carried out at a high temperature so that the basic sulfates are destroyed and a more crystalline product is obtained.<sup>112</sup> In order to obtain a uniformly fine product as well, the aluminum sulfate should be stirred rapidly and the sodium carbonate added slowly, the latter due to the rather vigorous

evolution of carbon dioxide. Since parameters such as temperature, concentration, and rate of precipitation all affect the form and general qualities of the alumina, commercial color houses will produce successive batches under carefully controlled, identical conditions in either rubber-lined or wooden vats.<sup>194</sup>

After the required reaction time, the hydrate must be washed until completely free from sulfates in order to obtain lakes free from milkiness. When the subsequent precipitation involves calcium (as in the procedure used here) or barium salts, alumina pastes containing sulfates will produce traces of calcium or barium sulfates which will impair the transparency and brilliance of the product lakes.<sup>194</sup> The filtered and washed alumina paste should be thinned slowly with stirring to prevent lumps from remaining during the subsequent lake formation. This process of diluting the alumina may take a good deal of time as the lumps are broken up only with great difficulty. Other, more rapid methods for the production of alumina exist. However, these usually involve the use of salts which may not be completely removed and consequently will affect the properties of the product lake. (See Appendix A, p.189 for an example of this type of method).

The presence of phosphate aids in the production of more brilliant pigments through some as yet unknown mechanism. The role of calcium has been discussed previously in terms of its structural and hue-conferring functions. Lastly, Turkey Red oil, an emulsion produced when sulfonated castor oil is treated with ammonia or sodium hydroxide, appears to perform an essential role in the development of the red product. While it is not indicated in the Fiertz-David and Rutishauser structure for the alizarin-alumina-calcium-complex, some sources<sup>197</sup> indicate that the

Turkey Red oil probably enters into some kind of chemical combination with the alizarin pigment matrix.\*

x. Commercial Uses of Alizarin

Because of its general solvent stability and high light fastness, alizarin pigment is used in many applications in addition to artists' colors. These are alkyd resin enamels, printing inks, lacquers, textile printing, wallpaper, rubber, plastics, and cosmetics. According to the Merck Index, alizarin is employed as a stain for both nervous tissue and live protazoa. It is also used occasionally as an acid base indicator.<sup>392</sup>

B. Copper Phthalocyanine Blue (CI Pigment Blue 15: CI 74160)

i. History

In 1928, workers at the Scottish Dyes Ltd. plant noticed a blue impurity on the walls of a vat used for the preparation of phthalimide from phthalic anhydride and ammonia.<sup>104</sup> This impurity, which was later shown to be iron phthalocyanine with the iron coming from the walls of the vat, was retained for investigation into its possible use as a colorant. While this was not the first synthesis of a phthalocyanine complex (metal-free phthalocyanine had been produced as a side reaction in the synthesis of o-cyanobenzamide in 1907 by Braun and Tcherniac<sup>75</sup> and copper phthalocyanine had been prepared by de Diesbach and VanderWeid in an attempt to make nitriles of benzene in 1927<sup>124</sup>), it was the first time that the pigment potential of this compound was recognized.

Three Scottish dye chemists, Dandridge, Drescher, and Thomas, under-

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\* Turkey Red oil is a widely used surfactant in pigment chemistry. It is often preferred to rosin soaps (another common surfactant) because it is effective at relatively low concentrations and can usually be removed during washing, although the latter does not seem to happen during alizarin preparation.<sup>348</sup>

took commercial development of the new color. Towards this end, R.P. Linstead and coworkers at the Royal College of Science were commissioned in 1929 to investigate phthalocyanine and in 1934 published the first of a series of papers in which they elucidated the structure of this series of compounds.<sup>33,71,83,125-6,285-8</sup>

In 1935, the first form of copper phthalocyanine pigment, Monastral Blue,\* appeared on the market.<sup>167</sup> Since then, because of their relatively cheap production, general stability, and good tinctorial powers, the phthalocyanine pigments have been subjected to a great deal of research which has led to a large production of phthalocyanines as both dyes and pigments. By 1966, for example, copper phthalocyanine blue and green production in the United States accounted for 12 million pounds of a total pigment production of 51 million pounds.<sup>353</sup>

#### ii. Structure

The structure of phthalocyanine as elucidated by Linstead and coworkers is now well known. It is derived from four isoindole units connected by four nitrogen atoms to form a strain-free, sixteen-membered ring known as a tetrabenzoporphyrine or tetrabenzotetrazaporphin nucleus. The two  $\beta$ -carbon atoms of each pyrrole unit are part of the adjoining benzene rings (Figure 10).

Londale<sup>290</sup> has shown that the tetrabenzoporphyrine nucleus exhibits a strong aromatic character and so is extremely thermodynamically stable due to electronic delocalization throughout the ring. In fact, this delocalization was seen to be 15 times as large as that of benzene.

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\* First notice of the commercial availability of a copper phthalocyanine pigment in the United States came in 1936 in Industrial and Engineering Chemistry, News Edition (Jan.10, 1936).

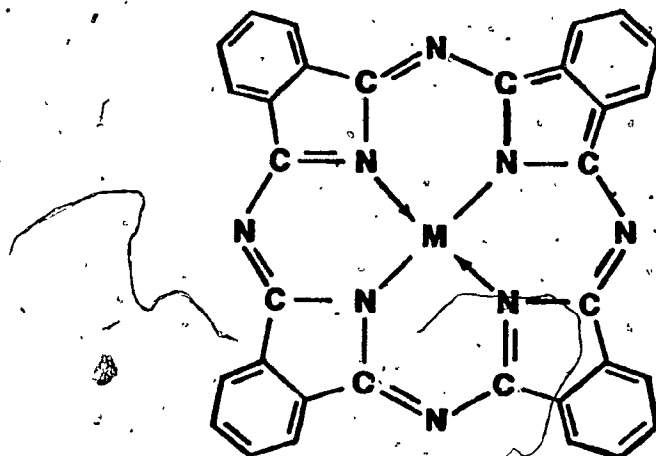


Figure 10. Tetrabenzoporphyrazine Nucleus. (m - metal ion)

The relationship between the tetrabenzoporphyrazine nucleus and the biologically important porphyrin skeleton of heme and chlorophyll-a is readily apparent (Figures 11 and 12). The difference between these two types of ring structures lies in the absence of benzene rings on the pyrrole units and replacement of nitrogen by methine groups between the pyrroles in the porphyrin.

Heme in combination with a protein called globin is hemoglobin, the coloring matter of mammalian red blood corpuscles which carries oxygen from the lungs to body tissue. Like the phthalocyanines, a central metal atom (iron) is complexed to the four pyrrole nitrogens.

Chlorophyll-a is the fundamental green coloring matter in plants and plays an important role in photosynthesis. It, too, is a porphyrin derivative, in which the four pyrrole nitrogens are complexed with magnesium.\*

\* In addition to their structural similarities, there is a close connection between the phthalocyanines and porphyrins in terms of physical properties. Both are stable to alkalis, less so to acids, they form complex metal compounds, can be degraded by oxidation to the imides of



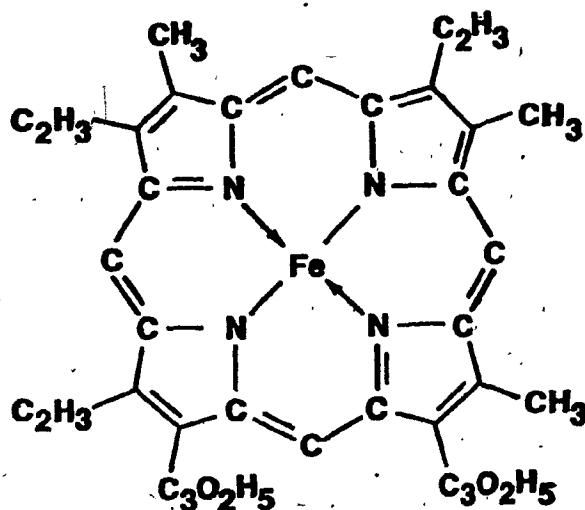


Figure 11. Heme.

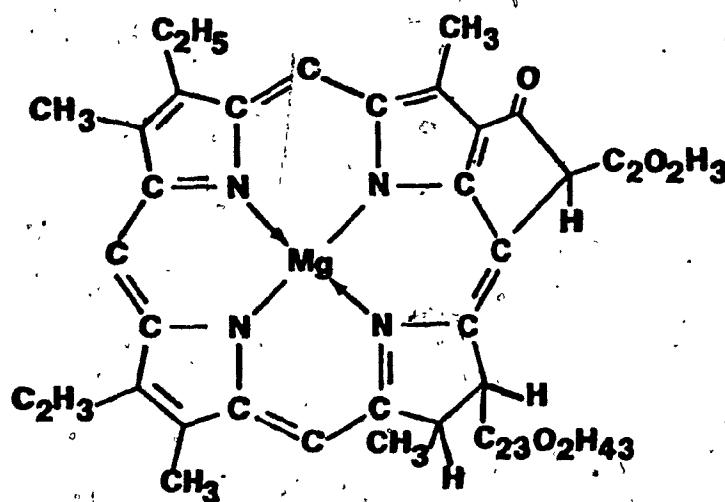


Figure 12. Chlorophyll-a.

The central position of the phthalocyanine, tetrabenzoporphazine mol-  
 dibasic acids, they have a similar order of stability within each series of metallic derivatives, and they both are highly colored.<sup>314</sup>

ecule may be occupied by either two hydrogen atoms or by any one of many metal atoms, the most commercially important of which is copper. Since the phthalocyanines may be considered as extremely weak dibasic acids, their metal derivatives are salts. These are of two types (a) covalent - copper, nickel, zinc, cobalt, aluminum and iron, etc. and (b) electrovalent alkali and alkaline earth metals - sodium, potassium, calcium, and cadmium.<sup>48</sup>

The central copper atom of copper phthalocyanine has a valence state of two (II) as determined by titration with 0.01 N dichromate, which disrupts the phthalocyanine ring.<sup>133</sup> Together, the copper and the tetra-benzoporphyrine nucleus form a polydentate chelate derivative. The copper atom supplies one electron to each of two of the isoindole nitrogen atoms and each of these nitrogens in turn supply an electron to the copper to form covalent bonds. The presence of these bonds is indicated by the stability of the copper in the nucleus to heat and chemical attack. Further bonds, this time two coordinate covalent bonds (indicated in Figures 13 and 14 by arrows), are formed by the unshared pairs of electrons in the remaining two isoindole nitrogens and the unfilled outer shells of the central copper atom. The molecule therefore contains four chelate six-member rings of the type shown in Figure 13.<sup>314</sup>

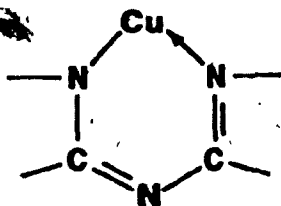


Figure 13. Copper Phthalocyanine Chelate Six-member Ring.<sup>314</sup>

X-Ray crystallography has shown that the phthalocyanine ring is approximately a square molecule with a center of symmetry around the central metal atom. In addition, the molecule is flat. With the exception of the two central imino-hydrogen atoms, the entire molecule - including the four isoindole units, their connecting nitrogen atoms, and the central copper atom - lies in one plane.<sup>314</sup>

Although the copper phthalocyanine molecule is extremely stable, it can undergo substitution of the four benzene rings relatively easily. For example, all sixteen of the available positions can be substituted by chlorine yielding hexadecachloro-copper phthalocyanine (CI Pigment Green 7). Commercially this pigment usually contains only 14 or 15 atoms of chlorine. In terms of production, it is the most important green in North America.

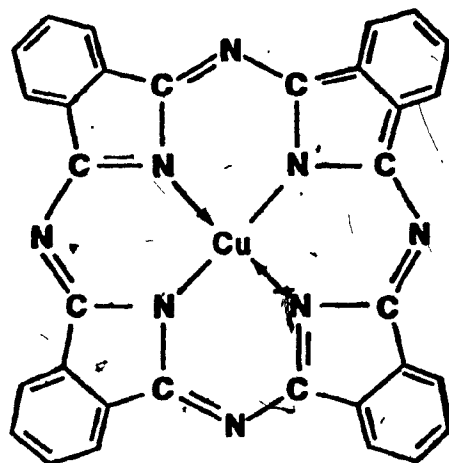


Figure 14. Copper Phthalocyanine (CI Pigment Blue 15 - CI 74160).

Much effort has been put into enlarging the range of phthalocyanine pigments. Examples of these are metal-free phthalocyanine (Figure 15), polychlorinated metal-free phthalocyanine, and sulfonated copper

phthalocyanine. Thus far, however, these have not proven especially successful and only the blue and green remain important.

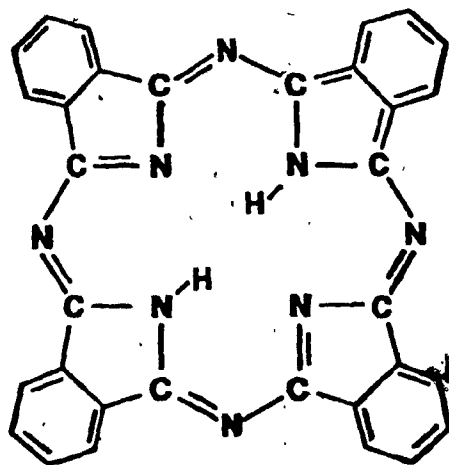


Figure 15. Metal-free Phthalocyanine.

### iii. Chromophore

Copper phthalocyanine contains no single chromophore as such. Instead, the color may be said to arise from a chromophoric system consisting of the whole tetrabenzoporphyrine nucleus and the complex it forms with the central copper atom.<sup>5</sup>

### iv. Polymorphic Forms of Copper Phthalocyanine.

Six forms of copper phthalocyanine are known to exist, two of which are well established and commercially important. These last two are the metastable, redder  $\alpha$ -form, which is obtained by reprecipitation of the crude pigment from concentrated sulfuric acid (acid-pasting) or by 'salt-milling' with an inorganic salt which is later removed by washing, and the stable, greener  $\beta$ -form, which is the initial product of most synthetic methods. The  $\beta$ -form can be obtained from the  $\alpha$ -form by heating the latter to 200°.

Booth<sup>59</sup> cites four other forms which have been patented recently and which are distinguished from the  $\alpha$ - and  $\beta$ -forms by x-ray diffraction spectra. Of these four, a  $\gamma$ -form was obtained by slurring crude phthalocyanine prepared in a solvent medium with 60% aqueous sulfuric acid.<sup>128</sup> A second type, claimed to be redder and more stable than the  $\alpha$ -form, was prepared by a fusion of phthalonitrile, urea, and cupric chloride under shear conditions and designated the R-form.<sup>349</sup> The last two have been both called  $\delta$ -forms. A suggested differentiation has been to call the pigment prepared by treating the  $\alpha$ -form with benzene in aqueous sulfuric acid the  $\delta$ B-form<sup>72</sup> and the pigment produced from milling crude copper phthalocyanine in the presence of sodium chloride, sulfuric acid, and urea, the  $\delta$ K-form.<sup>236</sup>

#### v. Properties

Two defects are common in copper phthalocyanine pigments when left for any length of time. The first of these, recrystallization, is especially relevant to the  $\alpha$ -form. In the presence of aromatic hydrocarbons and other solvents, the  $\alpha$ -form pigments will tend to grow and slowly be converted to the larger  $\beta$ -form crystals. The result, in a can of paint containing such solvents, is that the color will become slowly, but progressively greener. As the particles become larger, the paint will lose as much as 90% of its coloring strength.<sup>322</sup> It should be noted that neither shade nor strength will be detrimentally affected as long as the particles resulting from the crystal changes remain in the optimum pigimentary size range for copper phthalocyanine - 0.01-0.2 $\mu$ .<sup>50</sup> Crystal growth may be inhibited by the addition of stabilizing agents.

A second defect which affects both crystalline types, although the  $\beta$ -form is susceptible to a lesser extent, is the agglomeration of pig-

ment particles within a liquid vehicle. In a flocculated system, it will be recalled, the particles adhere to each other due to surface forces which cause the formation of clusters of particles. In a paint, flocculation can reduce the hiding power of the final paint film. Generally, however, the agglomerated particles can be separated by relatively weak mechanical forces or by a change in the forces at the interfaces between the particle and the suspending medium. Shur<sup>386</sup> has studied the effect of variation in the composition of organic dispersing media on the flocculation of copper phthalocyanine and found that while the polarity of the dispersing phase is not the sole factor affecting flocculation, the medium does have a great influence on the tendency to flocculate, especially in the absence of surfactants on the pigment particles. Of the media solvents tested, alkyl acetate esters have the best deflocculating properties.

In spite of the above mentioned defects, copper phthalocyanine remains one of the most permanent and consequently widely used blue pigments. The properties which reflect this permanence (listed in Table 5) can be summarized as an excellent fastness to almost all agents which normally act to degrade a pigment in a paint film. Lenoir<sup>274</sup> reasonably attributes this quality to the structure of the porphyrine macrocycle rather than to the pigment's nature as a metallic complex. This conclusion is based on the fact that the metal-free phthalocyanine possesses the same fastness properties as the copper derivative. It should be noted, however, that copper phthalocyanine, rather than its non-metallic parent compound, is universally used because it has the additional property of being the only blue colorant known which reflects an almost pure blue light (vide supra, Figure 3). For this reason, copper phthalocyanine is also used in

photographic color emulsions and in three-color printing where it is known as 'cyan'.<sup>167</sup>

As mentioned at the beginning of this section, a great deal of research has been carried out on the phthalocyanines, and the obvious result is an abundance of literature dealing with their chemical and physical properties. Table 5 summarizes those properties which are relevant to the usefulness of copper phthalocyanine as a pigment. For an excellent review of other properties, a very complete survey of the literature may be found in Moser and Thomas.<sup>314</sup>

As mentioned previously, copper phthalocyanine exists in two crystalline forms. While the  $\alpha$ -form is generally preferred due to its size (the crystals fall within the optimum particle size range) and consequent color and covering power, the  $\beta$ -form has recently been used advantageously in some pigment applications. In addition, several standard commercial treatments exist for both crystalline types which minimize their inherent defects of recrystallization and flocculation. For this reason, the Color Index lists five distinct types of copper phthalocyanine (CI Pigment Blue 15). The properties and modifications, where applicable for the four types not specified in Table 5, are listed in Table 6.

Table. 5. Physical Properties and Other Data for Copper Phthalocyanine Blue (CI Pigment Blue 15; CI 74160).

		Reference
Chemical Class	Phthalocyanine: copper complex (pigment)	95
Hue	Bright Blue	
Formula and Composition	$C_{32}H_{16}N_8Cu$ (calculated mw = 575.5)	

Table 5. Physical Properties and Other Data for Copper Phthalocyanine (con't.)

Fastness Properties:		Reference
1. Organic Solvents		95
aliphatic petroleum	5	
'cellosolve'	4-5	
esters	5	
ethanol	5	
methanol	5	
ketones	5	
NC solvents	4-5	
xylene	5	
pyridine	v. sl. sol.	125
pyridine-ether	v. sl. sol.	
quinoline	v. sl. sol.	
2. Light	full strength: 7-8 1/3 strength: 7-8 (printing ink)	95
3. Heat	m.p. = - ; stability: 4-5 (150° for 30 min.)	
4. Water	5	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	5	
6. HCL 5%	5	
7. Nitric Acid	decomposes.	125
8. Dilute Acid Permanganate	decomposes	
9. Phosphoric Acid (conc.)	soluble	
10. H <sub>2</sub> SO <sub>4</sub> 96%	soluble in 12x its wt at 20 soluble in 5x its wt at 100 *	95
11. H <sub>2</sub> SO <sub>4</sub> 85%	soluble in 7x its wt at 100 *	
12. Linseed Oil	5	
13. Oleic Acid	5	
14. Plasticisers	5	
15. Soap Gel Bleeding	5	
Density	α 1.54 - 1.74 β 1.53 - 1.75	310
Specific Gravity	1.6	169
Refractive Index	Ave. = 1.38	169
Oil Absorption (1b/1001b)	α 30-58 β 42-65	310

\* Unsatisfactory pigments are apparently obtained from H<sub>2</sub>SO<sub>4</sub> solutions with temperatures greater than 100°.



Table 5. Physical Properties and Other Data for Copper Phthalocyanine (con't.)

Standard	ASTM D 963-65 (1970) BS 3599/6-15: 1964 (Copper Phthalocyanine)	95
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Table 6. Physical Properties for Modified Copper Phthalocyanine Blues.<sup>95</sup>

CI Pigment Blue 15:1 - An  $\alpha$ -form pigment rendered solvent stable by the addition of small amounts of chlorine into the molecule. Chemical class, hue, etc., are the same as Blue 15 except:

Ketone Fastness: 4-5

Xylene Fastness: 4-5

CI Pigment Blue 15:2 - An  $\alpha$ -form pigment treated to prevent flocculation and increase solvent stability (i.e., prevent separation from white pigments when used in paints and lacquers). Properties are the same as 15:1 except:

Linseed Oil Fastness: 4-5

Plasticiser Fastness: 4-5

CI Pigment Blue 15:3 - A  $\beta$ -form copper phthalocyanine which is unmodified but has the natural  $\beta$ -form property of increased stability and crystallization resistance. Fastness properties are the same as for 15 except:

Ketone Fastness: 4-5

This pigment is somewhat greener and brighter than Blue 15; 15:1, and 15:2.

CI Pigment Blue 15:4 - A  $\beta$ -form phthalocyanine treated to overcome any tendency toward flocculation. All properties are as for 15:3.

#### vi. Experimental

The Color Index lists the following two types of reactions for the synthesis of copper phthalocyanine:<sup>104</sup>

1. heat phthalonitrile with cuprous chloride at 180-200°.  
(Phthalonitrile process)
2. heat phthalic anhydride, phthalimide, or phthalamide with a copper salt and urea, cyanoguanidine, or p-toluenesulfonamide and cuprous (or cupric) chloride in the presence of ammonium molybdate or arsenic oxide in high boiling solvent such as nitrobenzene, kerosene, or trichlorobenzene.  
(Phthalic anhydride/urea process)

These general reactions are the only technically feasible ones although many modifications of both exist (see Appendix A). Of the two basic reaction types, variations of the phthalonitrile process are used most often industrially based on their generally higher yields and shorter reaction times. The process is, however, more expensive than the phthalic anhydride/urea process and consequently this latter method remains in common use.

The phthalic anhydride/urea process was the method chosen for this paper due to the availability of starting material, i.e., phthalic anhydride. Originally developed by Wyler<sup>465</sup> as a cheaper method for the synthesis of copper phthalocyanine than the phthalonitrile process, the phthalic anhydride reaction may be carried out as a dry or 'melt' process or in a high boiling organic liquid which serves as the reaction medium. Wyler's melt process combined 130 g urea and 5 g boric acid, which were heated to 150°. To this he added a mixture of 100 g phthalic anhydride and 20 g anhydrous cupric chloride. The reaction mass was then heated to 200° until the color developed completely.\* After purification, the product was acid pasted as described on page 78.

Riley<sup>367</sup> improved the Wyler method by replacing the boric acid with 0.2 g ammonium molybdate, the use of which was found to give an increased yield. Today, cuprous chloride has generally replaced cupric chloride for several reasons:<sup>313</sup> (1) it is less expensive especially in terms of

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\* A similar process involving ammonia rather than urea was developed by Dandridge, Drescher, and Thomas at the Scottish Dyes, Ltd. plant in their initial attempt to resynthesize the color they had observed:<sup>123</sup> They heated 100 g phthalic anhydride and 10 g cuprous chloride to 200-260°. 12 g ammonia was introduced with agitation. After 1 hour, 12 more grams of ammonia was added. The product was cooled, ground, extracted twice with 10 times its weight of 2% soda ash, and extracted twice with 3% HCl. Note: The product contained 10-27% copper.

its copper content, (2) it is easier to keep in the anhydrous form, (3) it has less tendency to produce chlorination of phthalocyanine benzenes, although in some cases partial chlorination may be desirable as we will see, and (4) its use results in a slightly higher yield.

Because of the difficulty of working with the hard cake product of the melt process, today the phthalic anhydride/urea process is usually carried out in a high boiling organic solvent. The overall method used is similar to Riley's except that trichlorobenzene is added as the reaction medium.\* A further advantage of this "solvent process" according to Moser and Thomas,<sup>319</sup> is that the reaction product contains a higher proportion of copper phthalocyanine (10-15% greater yield) than the melt process product.

A number of variations for both the melt and solvent phthalic anhydride/urea processes have been proposed. For example, the urea in the Wyler process may be substituted by biuret, aminosulfonic acid, or ammonium sulfamate. The copper chloride may be replaced by powdered copper and an oxidising agent or it may be added in the form of copper phthalate.<sup>318</sup> Many of the patents for the variations claim increased yields. Examples of this type of alternate method are the addition of equimolar amounts of a sulfate<sup>159</sup> or inclusion of 0.4-1.5 moles ammonium chloride per mole phthalic anhydride.<sup>149</sup> Other variations are specifically aimed at producing a pigment especially suitable for a particular use, such as ceramics.

The synthetic method chosen for this paper was essentially a 'standard' phthalic anhydride/urea process:<sup>145</sup>

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\* Many other solvents have been used with varying product yields. See references 58 and 319.

40 g urea, 37 g (0.25 moles) phthalic anhydride, 0.2 g ammonium molybdate, and 260 g 1,2,4-trichlorobenzene are stirred in a 500 ml 3-necked flask equipped with thermometer, condensing tube, and entry for the addition of powdered cuprous chloride. The mixture is stirred and heated to 195° over one hour (if an oil bath is used for heating, the internal temperature of the oil will be approximately 220°). The temperature is maintained as closely as possible for four hours with stirring, while 10 g cuprous chloride is added gradually in small portions. Because the condensing tube must not become closed off by sublimed phthalic anhydride during the heating, the accumulated sublimate should be melted down occasionally. After four hours, the mixture is cooled, the resulting viscous greenish-blue paste filtered on a sintered glass funnel, and washed successively with hot alcohol, hot 2N HCl, hot 2N NaOH, and hot H<sub>2</sub>O until each filtrate is colorless. The dried product should be a finely crystalline violet-blue powder weighing 27-28 g or 75-78% of the theoretical amount.

This procedure was essentially carried out as given, with the following variations and details. The reaction temperature was monitored by a thermometer placed in oil in a sealed tube which protruded into the reaction mixture. Heat was applied by means of a sand bath whose internal temperature reached approximately 242° for a reaction temperature of 195°. As the temperature was raised, definite changes took place in the reaction mixture. At 90°, the mixture turned clear. At 110°, a precipitate formed and the mixture began to bubble vigorously corresponding to the evolution of CO<sub>2</sub>. At 130°, the mixture foamed again as ammonia was released. It is recommended that the condensing tube be fitted with some sort of vacuum or that the reaction be carried out in a hood since the ammonia was released in irritating quantities. Sublimation of the phthalic anhydride began at 150°. From this point on, it was necessary to melt down the sublimate which collected in the condensing tube every half hour. Also, from this point the reaction mixture turned to a progressively darker green. After 1½ hours, the temperature had reached 165° and the addition of small amounts of cuprous chloride was begun. The reaction mixture immediately changed to a blue which became darker as more cuprous chloride was added.

Addition of the cuprous chloride took  $4\frac{1}{2}$  hours so that the total reaction time was six hours. The product was washed as directed (with several liters being required for each solvent), followed by acid pasting (see p.79). The washed pigment weighed 27.1 g based on a small dried portion. Its color was a dark blue with reddish overtones as would be expected from the nature of the absorption of light by copper phthalocyanine.

#### vii. Reaction Mechanism

The changes that were observed in the reaction mixture as the heat was increased indicate that the reaction passed through more than one intermediate stage. These steps are illustrated in Figures 16, 17, and 18. The by-products of this reaction are phthalimide, ammonia, carbon dioxide, ammonium carbonate, and water (from phthalic anhydride, urea, and cuprous chloride as starting materials). The origins of these by-products will be discussed now.

The chemistry of the formation of the phthalocyanine involves the union of four isoindole units around a central metal atom. The first step (Figure 16) is the conversion of phthalic anhydride to phthalimide. This is then converted to monoiminophthalimide. The source of nitrogen for this reaction is obviously the urea which supplies three atoms of nitrogen per molecule of phthalic anhydride, even though four molecules of urea per molecule of anhydride are used. The urea may not react in its original form because it both decomposes and polymerizes at the elevated temperatures at which the reaction takes place. Consequently, it is believed that the nitrogen comes from a combination of urea, urea decomposition products, and urea polymers.<sup>316</sup> The excess urea may serve to assist and stabilize the reaction<sup>58</sup> and some nitrogen is given off in the form of ammonia and ammonium carbonate.

It has been shown that neither urea nor its decomposition products supply carbon to either the phthalimide or the product macrocycle. When  $C^{14}$  labelled urea was used in the synthesis of copper phthalocyanine, no radioactivity was detected in the product phthalocyanine. It was also found that phthalic anhydride labelled in the C-7 position produced both copper phthalocyanine and phthalimide which were radioactive but the evolved  $CO_2$  was not.<sup>78-9</sup>

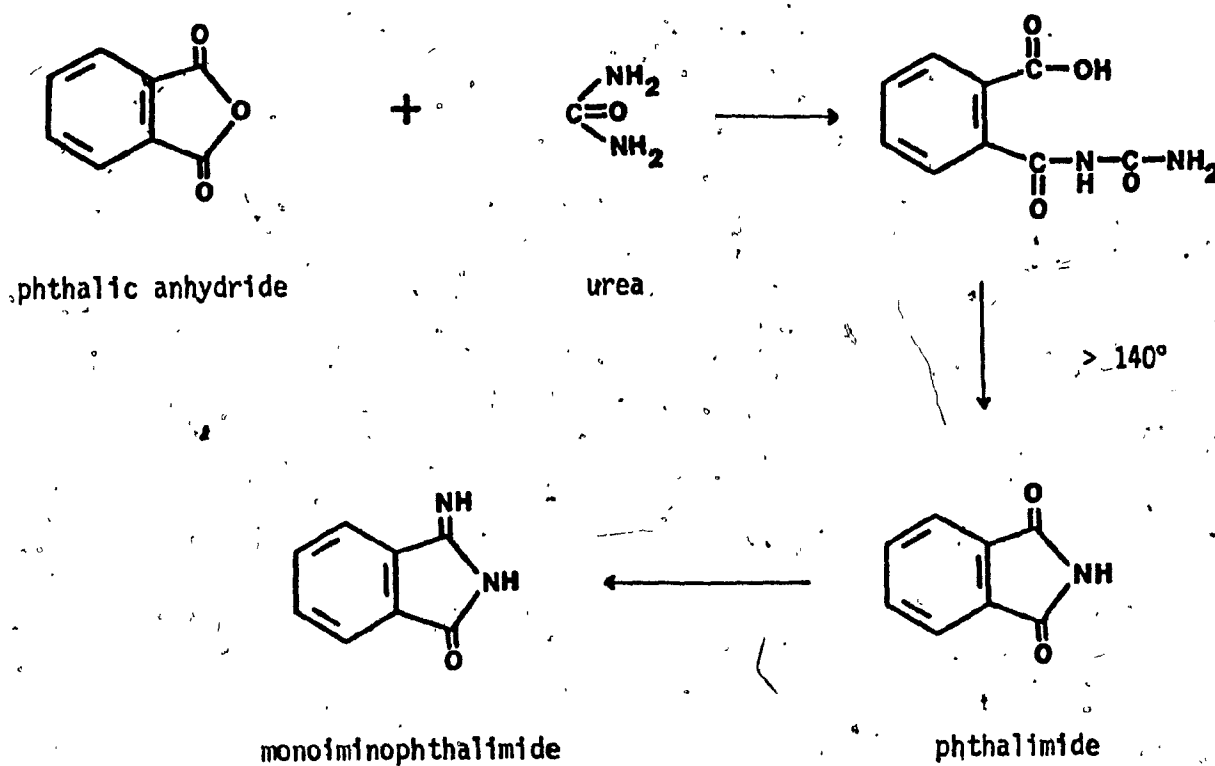


Figure 16. Copper Phthalocyanine Formation. Part 1: Formation of the Monobiminothalimide.<sup>459</sup>

According to Haddock,<sup>186</sup> but contrary to Sander,<sup>381</sup> iminothalimide is formed as an intermediate product because the interaction of phthalic anhydride and urea, in the presence of ammonium molybdate and the absence of a metal, gives a good yield of iminothalimide. Haddock was supported

by a series of patents in which phthalocyanines have been made from mixtures of phthalimide and urea, monoiminophthalimide, and diiminophthalimide.<sup>316</sup> In addition, phthalimide and monoiminophthalimide have been isolated from the reaction mixture in the formation of phthalocyanines.<sup>34</sup> Lastly, it is doubtful that phthalonitrile is formed in the reaction sequence even though phthalocyanines can be made from it.<sup>316</sup>

The next step in the reaction sequence is the formation of diiminophthalimide (Figure 17), which was isolated by Borodkin<sup>61</sup> when he was studying the formation of copper phthalocyanine from phthalic anhydride, urea, and cuprous chloride. At this point, the diimino molecule condenses either with itself, giving off ammonia, or with a monoiminophthalimide molecule. The resulting dimer, I (Figure 17), may then react with cuprous chloride to give II. I and II subsequently condense to yield the product copper phthalocyanine.<sup>58,316</sup>

An alternate sequence for the condensation of the dimers to copper phthalocyanine has the copper being added after condensation, followed by ring closure (Figure 18).<sup>459</sup> In either case, according to Bigelow and Perkins,<sup>49</sup> pigment formation begins at about 180°.

#### viii. Notes on the Reaction - The Catalyst

The role of ammonium molybdate in the preceding reaction is as a catalyst. In a study of various catalysts for the phthalic anhydride/urea process, Borodkin and Usacheva<sup>62</sup> found ammonium molybdate to be the most effective (Table 7).

In addition, they found that an optimum concentration of this catalyst could be reached, after which its effectiveness in the reaction diminished (Table 8).

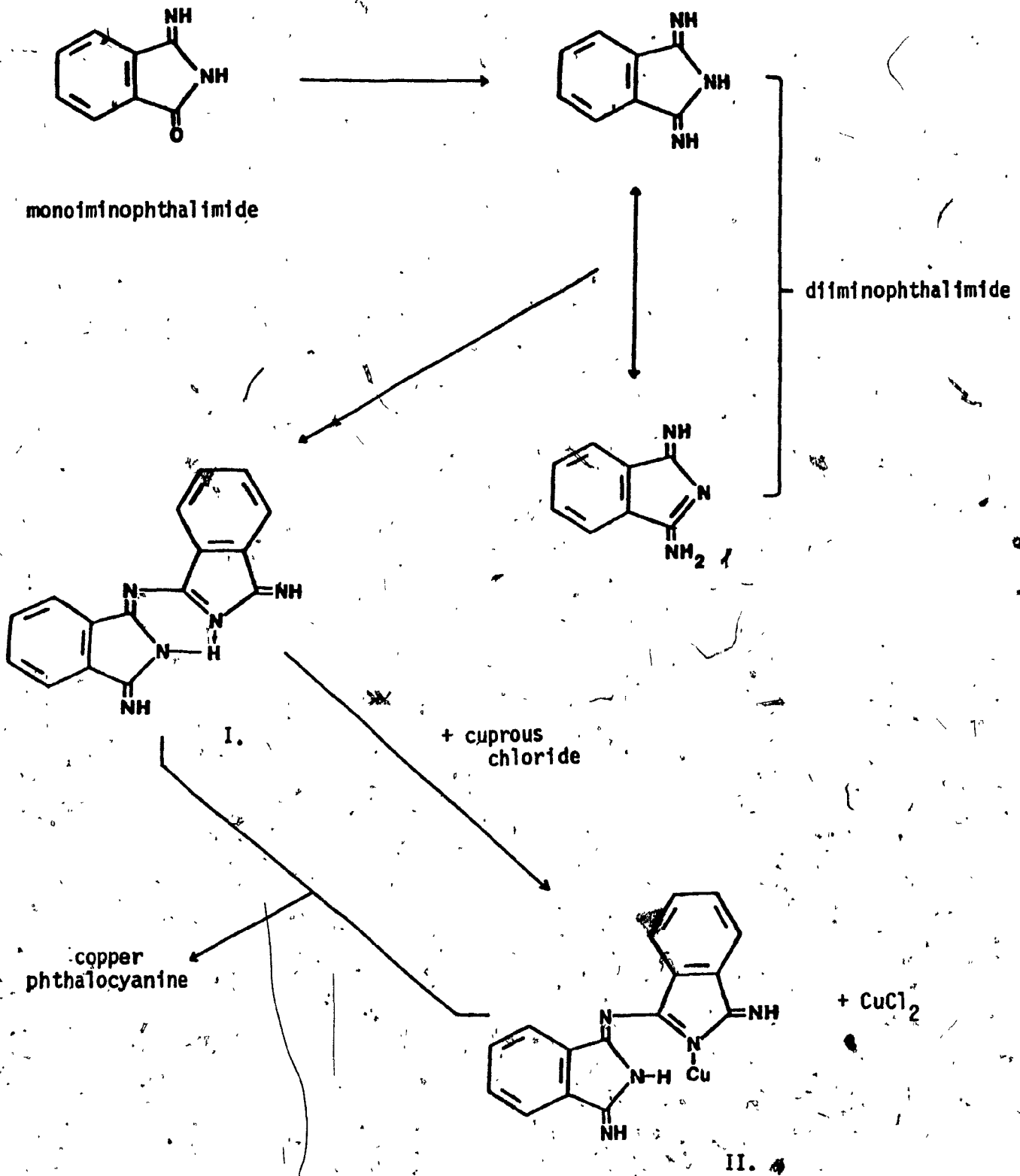


Figure 17. Copper Phthalocyanine Formation. Part 2: Formation of Dimiminophthalimide, dimer, and product.<sup>58, 59</sup>



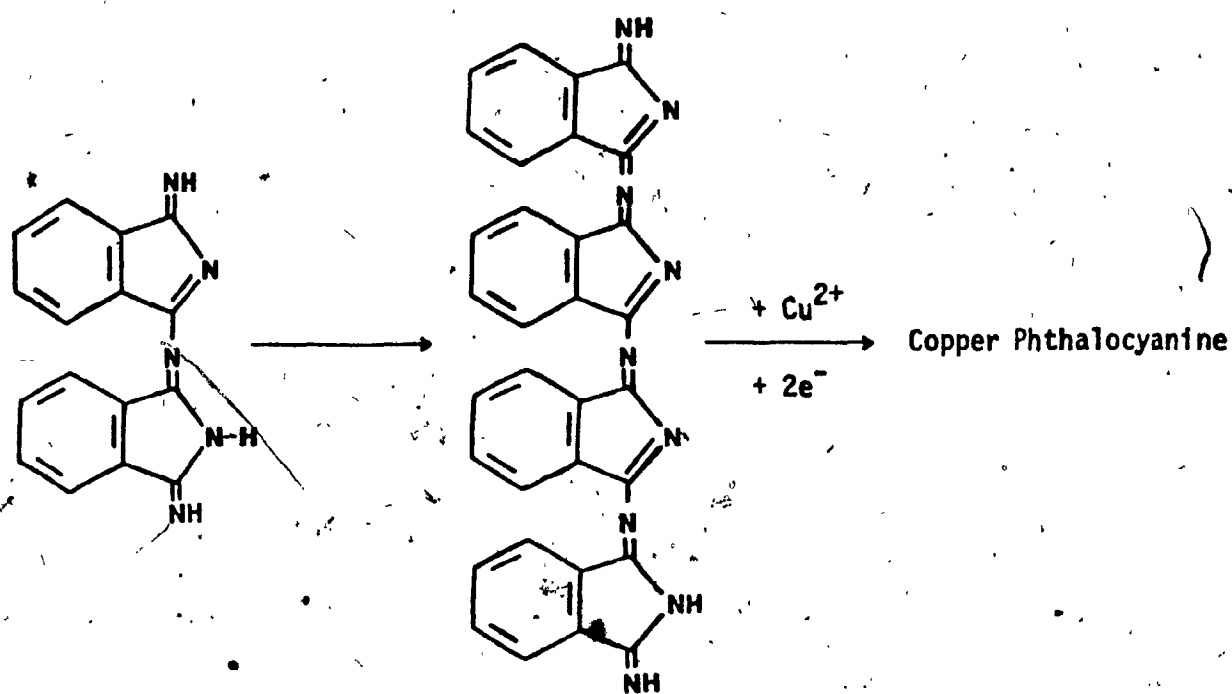


Figure 18. Copper Phthalocyanine Formation, Copper Added After Condensation and Before Ring Closure.<sup>459</sup>

Catalyst	% Yield
boric acid	26.3
ammonium chromate	27.3
chromic oxide	41.0
selenic acid	48.0
ammonium chloride	51.2
ferric chloride	60.0
potassium vanadate	40.0
vanadic acid	63.0
lead monoxide	65.0
lead dioxide	66.5
zinc oxide	51.2
arsenous oxide	65.0
arsenic oxide	66.5
antimony oxide	75.0
molybdic oxide	78.0
phosphomolybdic acid	92.0
molybdic acid	94.5
ammonium molybdate	96.0

Table 7. Effect of Catalyst on the Yield of Copper Phthalocyanine Listed in Increasing Effectiveness.<sup>133</sup>

% Ammonium molybdate based on phthalic anhydride	% Yield at Reaction Temperature	
	150°	170°
0.6	49.4	85.5
1.6	74.0	88.0
3.0	71.7	87.0

Table 8. Effect of Ammonium Molybdate on Yield of Copper Phthalocyanine.<sup>62</sup>

A great number of catalysts besides those studied by Borodkin and Usacheva have been used with varying degrees of effectiveness. These are listed in Moser and Thomas.<sup>319</sup>

ix. Notes on the Reaction - Finishing Procedures

Purification of the copper phthalocyanine to remove both soluble by-products and unreacted starting material is usually done with (a) dilute mineral acid, (b) dilute alkali, or (c) both. In the method used for this paper, both 2N HCl and 2N NaOH were used, along with alcohol (methanol and ethanol) and water. The product obtained was crude copper phthalocyanine. The use of the term 'crude' indicates that the product is not yet in suitable pigimentary form, i.e., the crude product is in the  $\beta$ -form crystal which has a hard texture and large particle size, both of which make it unsatisfactory for use as a pigment. It is therefore necessary for the product to undergo a pigimentary conditioning treatment which converts the  $\beta$ -form to the useful  $\alpha$ -form. The treatment, may be acid pasting, acid or permutoid swelling, or salt milling. While the two acid treatment methods give an  $\alpha$ -form product in a finely divided form, the salt milling procedure yields a useful  $\beta$ -form pigment.

The first treatment, acid pasting, is probably the most commonly used method because it is the most easily performed. The process generally involves dissolving the crude copper phthalocyanine in concentrated

$H_2SO_4$  followed by reprecipitation in  $H_2O$  or ice. Dilution of the copper phthalocyanine takes between eight and eleven parts concentrated sulfuric acid per part of phthalocyanine. Opinions differ as to whether the precipitating water should be cold<sup>200,334</sup> or hot<sup>23,246,448</sup> in order to obtain the best pigment. However, both apparently yield the desired  $\alpha$ -form. Variations also exist with respect to the addition of water to the dissolved pigment. For example, Bigelow and Perkins<sup>50</sup> state that the sulfuric acid-pigment solution should be drowned in water as fast as possible and that the more rapid the dilution, the finer the product. Other workers<sup>240,245</sup> suggest precipitating the sulfated copper phthalocyanine slowly first, with either 50%  $H_2SO_4$  or water, and then drowning the suspension. The relative merit of these two procedures remains in question, however, due to work by Borodkin, Usacheva, and Dormidontova.<sup>63</sup> They found that precipitating the pigment prior to drowning did not improve either the quality or purity of the product.

Acids other than sulfuric acid have been used or suggested for acid pasting in various patents. These include oleum, chlorosulfonic acid, and phosphoric acid.<sup>320</sup> In all cases, acid pasting is followed by thorough washing to remove acid.

Acid or permutoid swelling is an alternate pigmentary conditioning treatment which involves slurring the crude pigment in sulfuric acid of a concentration insufficient for dissolving the pigment but capable of converting the copper phthalocyanine to its sulfate. The  $H_2SO_4$  concentration is usually between 62 and 80%. The slurry is stirred for several hours until it becomes thick due to sulfate formation. When the pigment suspension is drowned with water, hydrolysis occurs and the pigment is freed in a finely divided  $\alpha$ -form. The advantages of this method over

the pasting process are claimed to be an improved shade, softer texture of the product, and the use of less acid.<sup>50,320</sup> Both processes, however, yield  $\alpha$ -form particles of  $0.01 - 0.5\mu$ ,<sup>50</sup> which is within the optimum particle size range for this pigment.

The last general process for the conditioning of copper phthalocyanine is salt milling which may be broken down into two categories, salt grinding and solvent grinding. The first involves grinding the crude product of the synthetic reaction with an inorganic, water-soluble salt or other solid, and the second, grinding the crude product with some soluble salt in the presence of an aromatic hydrocarbon or certain other solvents. If the salt grinding method is carried out in the presence of a small amount of formic or acetic acid, the  $\alpha$ -form pigment results.<sup>320</sup> To obtain a  $\beta$ -form pigment, the solvent grinding method is used with aromatic hydrocarbon as solvent.<sup>280</sup> In either case, care must be taken not to over grind the pigment to prevent loss of tinctorial strength.<sup>50</sup>

One problem with all of these methods for conditioning copper phthalocyanine is that the conversion to the  $\alpha$ -form is not necessarily permanent since, as mentioned previously, this form is metastable. The consequence in a paint is that recrystallization can occur on standing and so the paint will lose its ability to both tint and cover a surface. In an attempt to solve this problem, much research has been carried out in an effort to produce a non-crystallizing and non-flocculating phthalocyanine blue. The thrust of this work has been towards stabilizing the pigment once it has been converted into the useful  $\alpha$ -form. Two relatively successful solutions have involved chemical alterations of the copper phthalocyanine by chlorination and sulfonation.

Partial chlorination of the molecule reduces its tendency to crystal-

lize and flocculate in solvents. Shigemitsu<sup>385</sup> studied copper phthalocyanine derivatives containing varying amounts of chlorine (4, 8, and 16 atoms per molecule). By means of x-ray diffraction patterns, he found that the degree of polymorphism involved is related to the chlorine content. As the amount of chlorine increases, there is a related increase in the inhibition of crystal growth.

In order to take advantage of this  $\alpha$ -form stabilization, many patents have been granted giving various methods for the partial chlorination of the pigment.<sup>60,280</sup> These methods yield anywhere from one to sixteen atoms of chlorine per molecule of phthalocyanine and range from chlorination of the product copper phthalocyanine (for example, chlorination of the pigment at 200° in a vertical bed fluidized with nitrogen)<sup>32</sup> to building the chlorine into the molecule through the addition to the reaction medium of the appropriate amount of 4-chlorophthalic anhydride.<sup>223</sup> It should be noted that even without these treatments, some chlorination of the molecule takes place. In the phthalic anhydride/urea process, if copper is added in the form of cuprous chloride, the product will contain about 2% chlorine and, if added as cupric chloride, it will contain up to 6% chlorine.<sup>323</sup> Chlorination as a stabilizer is not universally used, however, because the introduction of chlorine not only reduces crystallization but it also progressively changes the color of the copper phthalocyanine from blue to green.

Another major type of alteration of phthalocyanine is that which claims to reduce flocculation. Primary among these is sulfonation brought about by stirring crude phthalocyanine with a sufficient amount of fairly strong sulfuric acid in an inert organic liquid, especially nitrobenzene. The produce is said to be a good non-flocculating pigment.<sup>269</sup> Other

methods for producing pigments with diminished tendencies toward flocculation and crystallization are mixing the copper phthalocyanine with a few percent of another metal (mainly tin) phthalocyanine,\* introducing other chemical groups into the phthalocyanine molecule besides chlorine and sulfate,\*\* and treatment with organic liquids after acid pasting.<sup>324</sup>

Once the pigment is purified and in the desired crystal form, it is generally prepared for its final use by being dried into either a diluted or undiluted powder, made into dispersed or undispersed paste or press-cake, or made into a water-dispersible powder. The form chosen depends on the pigment's intended use.<sup>50</sup>

Conversion of copper phthalocyanine into an undiluted powder form is not straightforward because the acid pasted pigment tends to agglomerate irreversibly on drying. The result is a hard and gritty powder of low tinctorial strength. This is generally avoided by mixing the wet paste with a surface-active agent such as an inert organic liquid or a fatty acid. Salt milled pigments, on the otherhand, can be dried with little loss of tinctorial strength so no pre-treatment of the wet paste is necessary.<sup>50</sup>

The problem of drying the acid pasted pigment may be avoided by leaving the pigment as an aqueous paste. This was done for the copper phthalocyanine made for this project since the pigment was to be mixed directly into a water-soluble acrylic medium. When the medium to be used is organic, the pigment can also be left as an undispersed aqueous

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\* Other metal phthalocyanines used are Al, Mg, Mn, Fe, Co, Ti, and V phthalocyanines. Patents for these may be found in Lepoir.<sup>280</sup>

\*\* Examples are  $-\text{CH}_2\text{NMe}$  or  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{NMe}_2$ , etc.<sup>280</sup> These moieties must not only confer anticrystallization and anti-flocculation properties but must have a minimal affect on the pigment's shade.

presscake. This can be easily mixed into the paint medium by a process known as flushing (the pigment is directly transferred from the aqueous phase to an organic vehicle). Dispersed presscakes of copper phthalocyanine are made by heating a water slurry of the pigment to a temperature between 100° and 300° under pressure.<sup>321</sup>

x. Commercial Uses of Copper Phthalocyanine

Copper phthalocyanine is the most widely used of all blue pigments because it can be used in almost all pigment applications due to its high fastness to most agents. These uses include paints, printing inks, lacquers, and distempers. Non-coating uses are as a colorant for rubber, plastics, leather, cloth, paper, wax, and cements.<sup>95</sup>

The modified copper phthalocyanines share these uses and are especially suitable for particular applications. CI Pigment 15:1, a partially chlorinated copper phthalocyanine, is used for paints, lacquers, and inks containing organic solvents. CI Pigment 15:2, an anti-flocculation treated copper phthalocyanine, is used for all types of paints as well as gravure inks.<sup>95</sup> The last two pigments, both  $\beta$ -form, are especially valuable as cyan blue process inks of maximum brightness. These are CI Pigment 15:3,  $\beta$ -form copper phthalocyanine with no modifications, and CI Pigment 15:4, which has been anti-flocculation treated.<sup>96</sup>

C. Hansa or Arylamide Yellow G and 10G (CI Pigment Yellow 1; CI 11680 and CI Pigment Yellow 3; CI 11710)

i. History

For many years Hansa Yellow has referred to a relatively large series of monoazo pigments. In Germany, where these pigments were first developed and patented, the name Hansa yellow even included colors of other chemical classes. Numerous efforts have been made to agree on more exact names for these different colorants and since 1970 the monoazo yellows

have been identified by the more specific title - acetoacetarylide yellow. Use of the words Hansa yellow has persisted, however, especially as a trade name for these pigments when used as artists' colors.

Yellows were not the first azo colors to be developed. Between 1870 and 1905 several successful red dyestuffs, such as  $\alpha$ -Naphthol Amine Maroon and Toluidine Red, became commercially available.<sup>449</sup> In the beginning of this century much work was done to develop yellow members of this class which might have a brightness and permanency similar to that of the reds. This research centered on condensation products of nitro-arylamines and formaldehyde and culminated in 1909 with the first yellow, a 4-chloro-2-nitroaniline derivative called Lithol Fast Yellow 66 (GP 257,488). The first of the yellows to become commercially available was patented the same year by Wagner (GP 257,488). This pigment, Hansa yellow G (CI Pigment Yellow 1: CI 11680), was the first - and still most important in terms of total usage - of a whole family of acetoacetarylide azo colors. The following year, several other yellows were patented, including the important Hansa (Acetoacetarylide) yellow 10G discovered by Desamari. This pigment became commercially available the following year.<sup>449</sup>

#### ii. The Azo Colors

The azo colors contain one or more azo (-N=N-) group which forms bridges between organic residues, at least one of which is usually an aromatic nucleus. It is interesting to note that the Color Index,<sup>91</sup> which is the most comprehensive compilation of coloring materials, lists nearly 3600 chemical constitutions of which more than 2250 are currently being marketed and more than half of these are chemically of the azo class. This group is also the largest class in terms of value and weight



manufactured.<sup>477</sup> These azo colors range from simple monoazo compounds to complex polyazo structures with a molecular weight of 1800 or more. Their colors and properties vary accordingly.<sup>17</sup>

Like most colored materials, the azo group can be divided into dyes and pigments, although the differentiation here is fairly subtle. That is, the pigments are actually one of two types of dyestuffs. The first is dyes which can be pigments in themselves, requiring no precipitation on a base to be classified or used in paint or other medium. These insoluble dyes can be synthesized 'in situ' on fibres or 'in substance' as pigments.<sup>435</sup> The second group of dyes has a particle size too small to be used in paint and consequently must be prepared as lakes by precipitation on a metallic base.

Common examples of azo color compounds used as pigments, besides the acetoacetarylides, are the monoazo  $\beta$ -naphthol derivatives such as Lithol and Toluidine Red, the  $\beta$ -oxynaphthoic arylamides such as Arylamide Red F2R and the diazo benzidines such as Benzidine Yellow. These pigments are all produced by a diazo coupling reaction between a diazotized primary aromatic amine and a second coupling component. Unlike the organic pigments already discussed, alizarin and copper phthalocyanine, the azo pigments have no analogs among natural coloring matters.<sup>435</sup>

The monoazo yellows are the most important organic yellows produced today in terms of both color and use. A significant part of this group is the acetoacetarylides whose consumption in the United States in 1970 was 1.5 million pounds.<sup>251</sup>

### iii. Structure

The acetoacetarylides have the general formula shown in Figure 19. It should be apparent that many acetoacetarylide yellows exist. These,

in turn, possess a variety of shade and fastness properties.

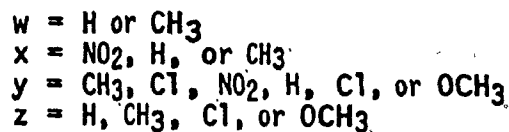
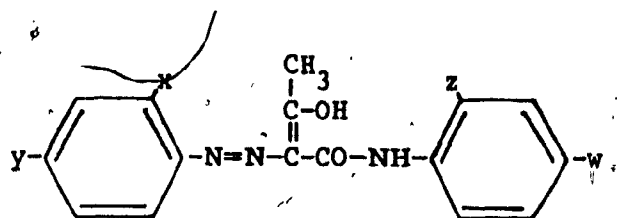


Figure 19. The General Formula (Enolic Form) of the Acetoacetyrides.<sup>278</sup>

The acetoacetyrides are produced by the coupling of a diazotized amine (usually diazotized o-nitroaniline) with the reactive methylene group of an acetoacetanilide derivative (Figure 20). This process, i.e., the coupling of two specific reactants, is indicated in the naming of these compounds. For example, the two yellows discussed in this section have the structures and names - and so derivations - shown in Figures 21 and 22.

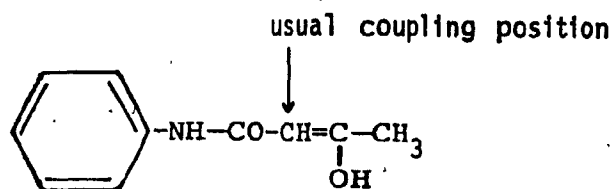


Figure 20. Acetoacetanilide With Reactive Methylene Group.

As is customary, both compounds are shown in their enolic forms. It should be noted that this is merely a convention and does not indicate

Electrophilic dinitrogen trioxide reacts with the amine - in a manner similar to that of an aryl chloride or anhydride - resulting in the attachment of a nitroso group to the amine nitrogen and the elimination of the  $\text{NO}_2^-$  anion (Figure 25).<sup>68,440</sup>

Since the aniline derivative is a primary amine, the N-nitrosoamine is unstable and isomerizes to a diazotic acid followed by decomposition to the diazonium ion.<sup>67\*</sup> In general, the diazonium ion (II) (Figure 26) is probably the main species because of its relative stability, although the diazonium ion (I) is probably the reactive form.<sup>400</sup>

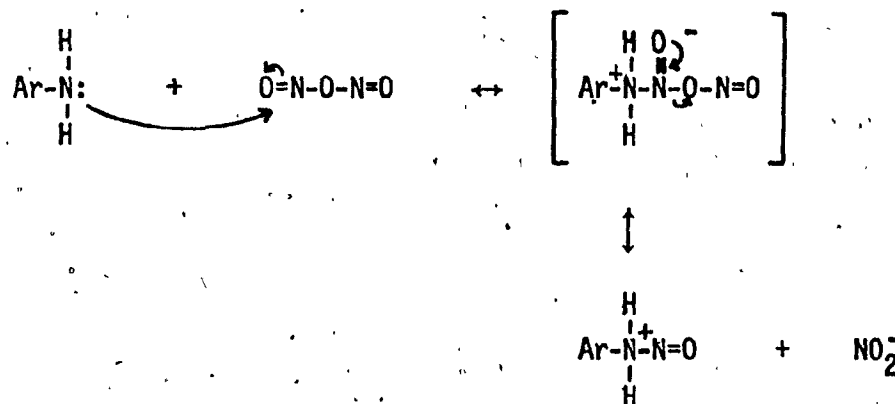
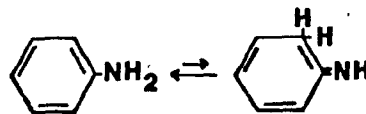


Figure 25. The Diazotization Reaction - Formation of the N-Nitroso Derivative.<sup>1</sup>

\* It is interesting to note that aliphatic diazonium salts are incapable of existence because the  $-\text{C}-\text{N}^+=$  bond is not stabilized by electron delocalization as are the aromatic derivatives. For example, aniline possesses a small degree of delocalization achieved by conversion to the less stable imine:<sup>391</sup>



While the imine structure is less stable than the amine because of the considerable stabilization of the benzene ring, the short existence of the diazonium ion is still assisted by this delocalization.

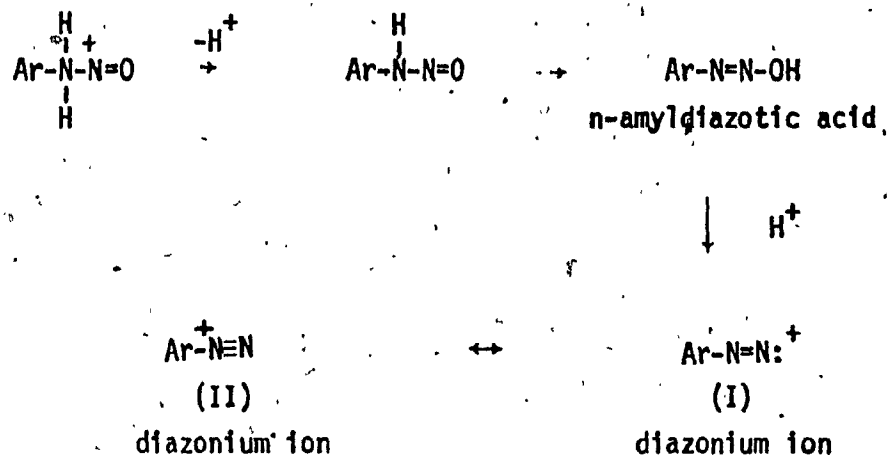


Figure 26. The Diazotization Reaction: Formation of Diazotic Acid and Diazonium Ion.<sup>1,68</sup>

It should be noted that at lower acidities, the concentration of the free amine is large enough to destroy the  $\text{N}_2\text{O}_3$  as rapidly as it is formed and so the formation of this becomes rate-determining. At higher acidities, however, the amine concentration is smaller so that the  $\text{N}_2\text{O}_3$  can approach its equilibrium concentration.<sup>68</sup> According to Zollinger,<sup>474</sup> at high pH, where dinitrogen trioxide formation is rate-determining, the diazotization becomes of zeroth order if a large excess of nitrous acid (relative to the amine) is present. The decomposition of  $\text{Ar}-\text{N}(\text{H})_2$  into  $\text{Ar}-\text{N}_2^+$  is considerably faster than formation of  $\text{N}_2\text{O}_3$  and the nitrosation of  $\text{Ar}-\text{N}(\text{H})_2$  since the rate no longer depends on the concentration of amine.

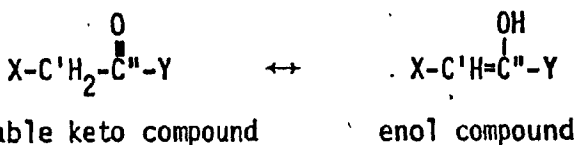
#### vii. Synthesis - The Coupling Reaction

One of the two types of reactions in which the aromatic diazotized amines take part is that in which the nitrogen is retained, as in diazo coupling with phenols, amines, or other compounds such as acetoacetylides which contain reactive methylene groups. Coupling of these compounds is always by attachment of the aryl diazo group to a carbon atom.<sup>438</sup> The coupling reaction basically results in the joining of each end of the azo group ( $-\text{N}=\text{N}-$ ) to the carbon atoms or organic residues to

give  $R-N=N-R'$ .<sup>475</sup>

The mechanism by which the coupling is achieved consists of an electrophilic substitution with the diazonium ion acting as the electrophilic species<sup>440</sup> which attacks that atom of the coupling component which has the greatest electron density or is the most nucleophilic. Because diazo compounds are relatively weak electrophiles, they are highly specific. As a result, the coupling component must possess a structure capable of building up a relatively high electron density at one or more carbons.<sup>475</sup>

The most common coupling reactions involve aromatic amines or phenols but the generation of a high electron density is possible in aliphatic compounds which contain enolizable keto groups represented by the formula:



where X = negative group (e.g.,  $-\text{CO}_2\text{R}$  or  $-\text{COR}$ )

Figure 27. General Formula of Enolizable Keto Compounds and Their Enolic Derivatives.<sup>476</sup>

This type of aliphatic compound is used in the production of the Hansa yellows. The high electron density is centered on the C' carbon (Figure 27). Acetoacetic ester (Figure 28) serves as an example of why this happens. Here the methylene group is activated not only by the carbonyl, but also by the ester substituent.<sup>476</sup>

While it was at one time thought<sup>279</sup> that the enol rather than the keto form was reactive, it now appears that, in fact, the "common anion" of both is the reactive species. Apparently, this is obtained more easily or rapidly from the enol than the keto form. Both carbonyls ad-

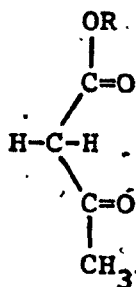


Figure 28. Acetoacetic Ester.<sup>476</sup>

adjacent to the methylene carbon act as acidifying groups, assisting the formation of the "active anion" (Figure 29).<sup>476</sup> Table 11 lists the varying abilities of the species illustrated in Figure 29 to couple.

Coupling activity is also affected by the electronic configuration of the diazonium ion. For example, while the presence of negative substituents (e.g., halogen and nitro groups) on the coupling component retards coupling, they accelerate the reaction when present in the diazo compound.<sup>475</sup> Thus, diazonium ions derived from nitro aniline or nitrochloraniline (as in the Hansa yellows) couple more rapidly due to the inductive and resonance effects of the nuclear substituents. This is especially true of ortho or para substituted nitroanilines. In either case, the diazonium cation has an increased 'coupling energy', i.e., it is more electrophilic, because of the positive polarization of the nitrogen atom brought about by the withdrawing of electrons from the ring and the resulting increased positive charge on the diazonium ion (Figure 30).<sup>2</sup> According to Venkataraman,<sup>441</sup> the diazo nitrogens are no longer just cationoid in character but are definite cations.

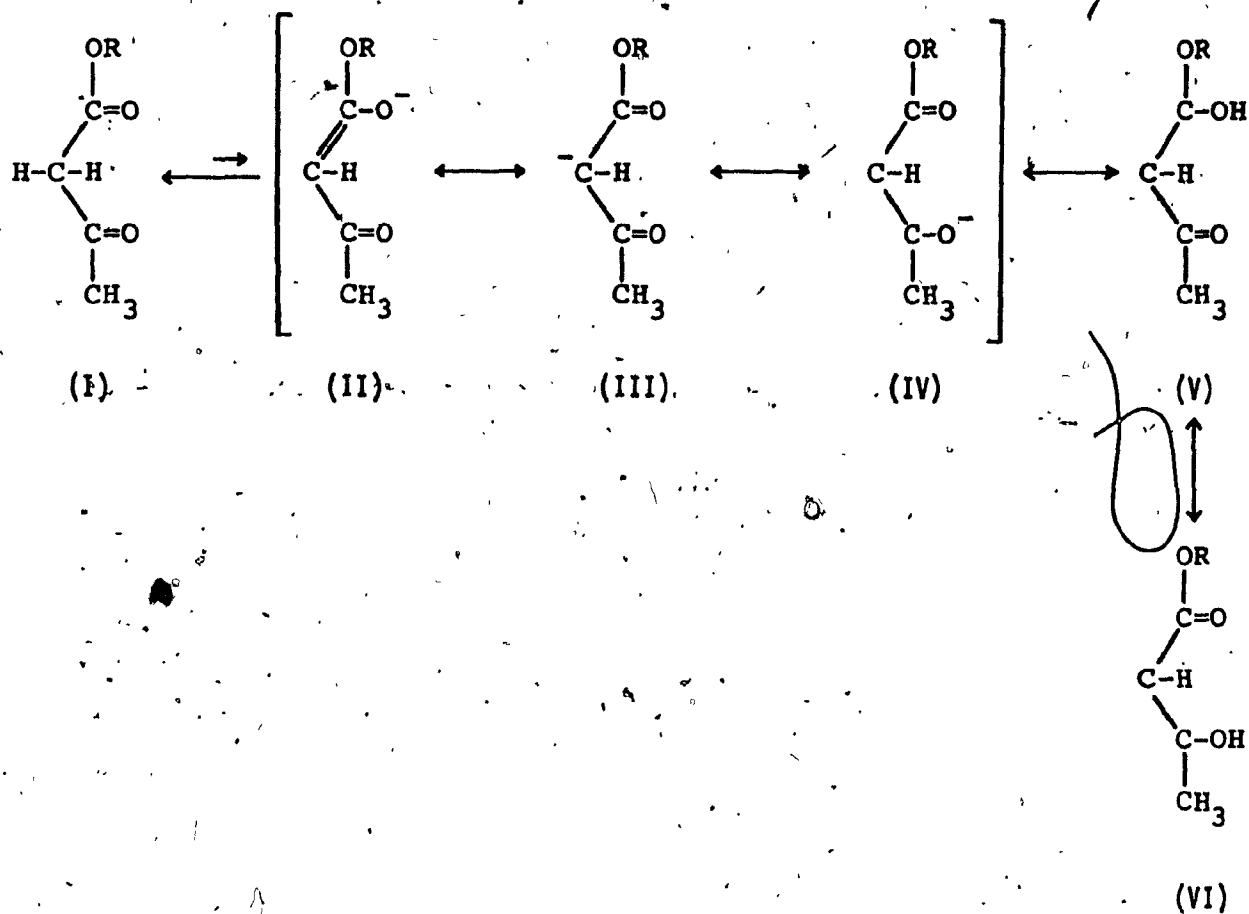


Figure 29. Acetoacetic Ester Interconversions Leading to 'Active Anion' Formation.<sup>676</sup> It should be noted that the activated forms do not represent a static electronic situation or configuration.

Species	Coupling Ability
(I)	none
(II)	great
(III)	great
(IV)	great
(V)	moderate
(VI)	moderate

Table 11. Coupling Abilities of the Various Species Illustrated in Figure 29.<sup>68, 676</sup>

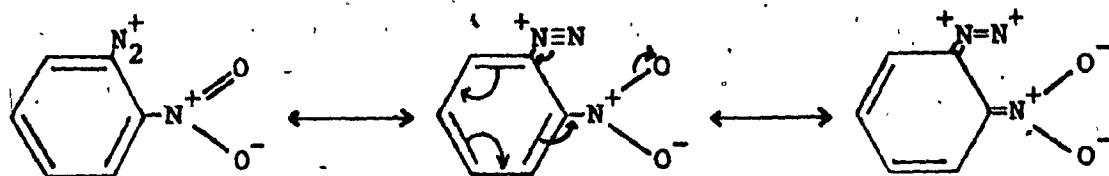


Figure 30. Polarization Effect of an Ortho Nitro Group on the Charge of the Diazo Nitrogen in Nitroaniline.<sup>2</sup>

The coupling reaction itself may be thought of as having  $S_E2$  connotations which could involve a transition state as in Figure 31.<sup>70</sup>

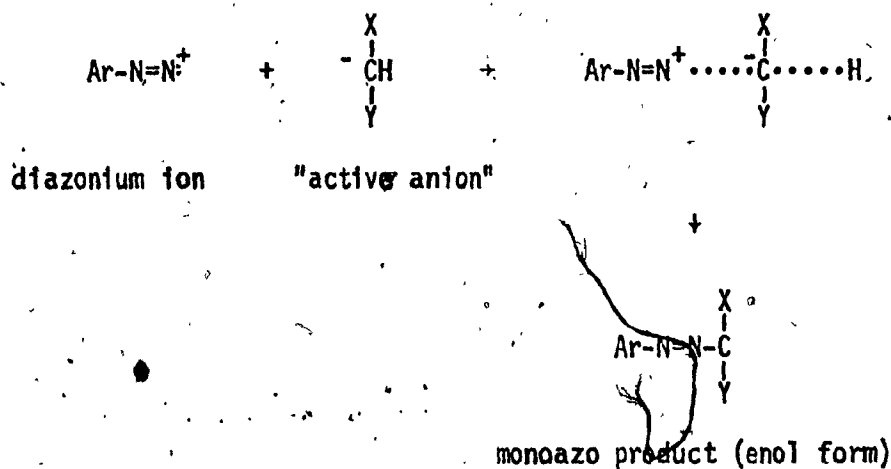


Figure 31. Possible Mechanism for the Formation of Monoazo Compounds from Diazonium Ion and Active Anion.<sup>70</sup>



viii, Experimental

A synthesis<sup>143</sup> for Hansa yellow 10G was chosen since this pigment is the arylamide yellow most often used as an artists' color.

(a) Diazotization: 4-chloro-2-nitroaniline is diazotized as follows:

To a well stirred mixture of 172.5 grams of a 10% paste of 4-chloro-2nitroaniline in a beaker are added 30 ml of concentrated HCl and 100 g of ice. (The latter precipitates anilinium chloride). Exactly 100 ml of 1N nitrite solution (standarized just before using) is added slowly. Stirring is continued and the mixture kept cold until only traces of nitrite remain in the mixture. This is determined by a strong blue coloration of Congo Red paper and an immediate but permanent weak blue when spotted on starch-iodide paper. If the mixture does not give the weak test for nitrite, more is added dropwise until the weak blue on the starch-iodide paper remains for several minutes. The diazo solution is then filtered to remove traces of undissolved material. The nitrochloroaniline paste may be prepared by dissolving the base in about 10 parts concentrated  $H_2SO_4$ , pouring the resulting solution (with stirring) onto ice, filtering off the precipitate, and washing with cold water until free from  $H_2SO_4$ . It should be noted that o-nitroaniline derivatives form a hydrochloride in concentrated HCl and are precipitated as the free base on the addition of water.

(b) Coupling:

0.1 mole of the diazotized amine solution is cooled with ice to 2-5° (the ice is added directly to the solution) and the solution neutralized with sodium acetate to the point where Congo Red paper is just turned violet (below pH 2).

A second solution is made by dissolving 0.1 mole of pure o-chloroacetanilide in 300 ml water (at 50°) containing the minimum amount of sodium hydroxide necessary to form a clear solution (usually about 12 ml 35% NaOH is required). This solution is stirred continuously while allowed to cool. Then 25 g of sodium acetate are added followed by dilute acetic acid which is added carefully until a faintly acid reaction to litmus paper is produced but no precipitation occurs.

The clear diazo solution is added dropwise with good stirring to the second solution. The stirring is continued for 12 hours by which time the dye is completely precipitated. It is then filtered, washed, thoroughly (the final time with hot distilled water), and ground in a mortar to a uniform paste,

preferably with the medium to be used if an opaque color is being prepared. The yield should be almost quantitative.

ix. Notes on the Reaction

According to Fiertz-David and Blangey,<sup>141</sup> it is essential that the laboratory preparation of monoazo pigments be carried out using pure starting materials. Freedom from isomers and closely related compounds is important because these too, can participate in the dye-forming reaction. Subsequent removal is particularly difficult since contaminant and pigment are very similar.

The amount of nitrite added is extremely crucial and should correspond exactly to the theoretical requirements. When the reaction is carried out in acid solution, as in the synthesis of Hansa yellow, diazotization is practically a quantitative reaction. An excess of nitrous acid would diazotize or nitrosate the coupler, altering the finished pigment.<sup>\*19,141</sup> For this reason, technical sodium nitrite, which is never 100%, should be titrated in order that only the required amount (e.g., 1 mole/l for this project) is used.<sup>141</sup> Completion of diazotization and a slight excess of nitrous acid are both tested with starch-iodide paper. For this test it is important to differentiate the blue obtained immediately, indicating an excess of nitrite, from coloration caused by nitro substituents of diazo compounds which appears after 1-2 seconds. The desired, very weak immediate reaction with starch-iodide paper corresponds to an excess of about  $10^{-4}$  mol/l. If a greater excess is present, Zollinger<sup>473</sup> indicates that it is possible to destroy the nitrite by converting it into nitrogen with sulfanic acid or urea. The probable

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\* In an alkaline reaction medium, an excess of nitrite is acceptable but too little leads to diazoamino compounds or coupling of the diazotized base with itself.

reaction follows a route via N-nitroso compounds (Figure 32).

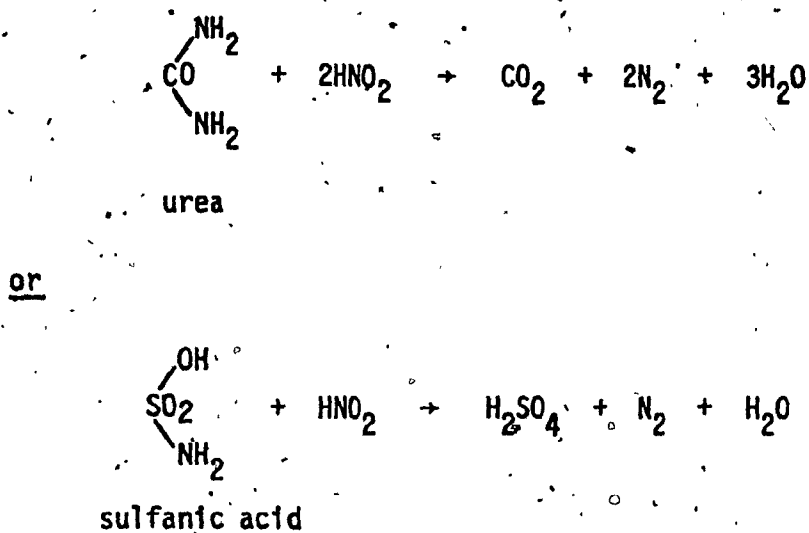


Figure 32. Overall Equation for the Elimination of Excess Nitrite Through Urea and Sulfanic Acid.<sup>473</sup>

The urea is generally preferred in strong acid solutions, however, because a possible side-reaction exists with the sulfanic acid under these conditions (Figure 33).

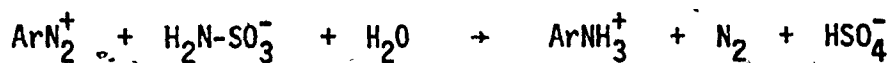
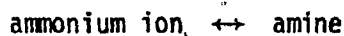


Figure 33. The Side-Reaction Between the Diazonium Ion and Sulfanic Acid in Strongly Acidic Medium.<sup>473</sup>

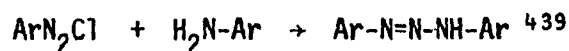
The purity of diazotizable amines is determined by titration with nitrite solution. Likewise, the coupling component's purity can be established by titrating with diazo compounds. In both cases, the purity is expressed in terms of their apparent molecular weights, i.e., the number of grams of material which contain one mole of the pure material.<sup>141</sup>

Unlike the amine and nitrite, the acid used in the diazotization reaction is present in excess. During and at the completion of diazo-

tization, the solution should react strongly acid to Congo Red, corresponding to a pH less than 2. This prevents the partial diazotization caused by a shift in equilibrium at higher pH's of the equation:



in favor of the free base.<sup>473</sup> At lower hydrogen ion concentration the diazo compounds formed would tend to react with the free base (unattacked amine) to form diazo amino compounds:



Excess acid also stabilizes the diazonium salt by inhibiting decomposition due to other secondary reactions.<sup>439</sup> A further side effect of an increase in pH is the conversion of the reactive form of diazotizing agents, namely dinitrogen trioxide, into ineffective ones, e.g., free nitrous acid ( $\text{HNO}_2$ ) and the nitrite ion,  $\text{NO}_2^-$ .<sup>473</sup>

While the overall equation for the diazotization of aromatic amines (Figure 26) shows that two equivalents of mineral acid are essential for a smooth reaction, in practice, an excess of at least half an equivalent of acid is added at the beginning. In those cases where the amine is weakly basic and the salts are readily hydrolyzed (e.g., chloro- and nitroanilines), the excess is increased up to three equivalents.<sup>439</sup> It should be noted that in some cases, such as for the nitrochloroanilines, even the excess acid is insufficient to dissolve the base. In this situation, as for the synthesis of Hansa yellow 10G, the diazotization is carried out as a suspension in which the base is in a finely divided state. In order to achieve this condition, the base is first prepared as a 'paste' from  $\text{H}_2\text{SO}_4$  (see Experimental, p.94)<sup>473</sup>

HCL is the acid usually employed in diazotizations because it generally gives the most soluble salts with aromatic amines. Concentrated

HCl reacts with nitrite to yield chlorine, however, which leads to side-reactions. Consequently, the diazotization mixture should never contain more than 20% free HCl.<sup>142</sup>

Hydrolysis of the anilinium chloride is prevented by the reaction temperature as well as the pH. Anilinium chloride is precipitated by the addition of ice before hydrolysis can occur.<sup>473</sup> In other words, although the solubility of the starting material is poor at 0° and the reaction rate is lowered, smooth diazotization occurs. Ice also assists the reaction by increasing the solubility of the free nitrous acid and so minimizes the escape of nitrous gasses.

Ice produced low temperature is also necessary for stabilization of the diazonium ion. Apparently, substituents ortho to the diazo group are susceptible to replacement by hydroxyl when the temperature and pH of the diazotization are increased.\* Substituents most sensitive to this type of side-reaction are nitro (as in the Hansa yellows), halogen, sulfo, and alkoxy groups.<sup>141</sup>

Decomposition is similarly accelerated by light and catalyzed by certain metals. The first sign of decomposition is usually the generation of nitrogen (and the concurrent conversion of diazonium ion to phenol). In general, the more basic the amine, the more unstable the diazo compound derived from it. The presence of negative substituents, such as nitro and halogen groups, on the otherhand, usually tends to stabilize the diazo compounds.<sup>141</sup> The nitrochloroaniline used in the synthesis of Hansa yellow may consequently be considered relatively stable.

Because of their instability, the diazonium ions or salts are

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\* This reaction is used technically for the preparation of o-hydroxy-diazo compounds.<sup>141</sup>

usually required only as intermediates and isolation of them is avoided.<sup>472</sup> Clarity of the reaction solution and the absence of foam are considered indicators of successful diazotization without decomposition.<sup>439</sup> The solution in which the diazo compound is formed should also be used for the coupling reaction, which should be carried out as soon as possible.<sup>439,472</sup>

Stability of the diazonium ion during coupling requires some consideration since the minimalization of side-reactions is essential to avoid impurities not readily removed from the water-insoluble pigment. Conditions are therefore necessarily chosen to favor coupling rather than diazo decomposition or side-reactions.<sup>19,22</sup> For example, although coupling is accelerated by warming the solution and increasing the pH, these conditions would simultaneously accelerate diazo decomposition.

Diazotized compounds are most stable in strongly acidic solutions.<sup>140</sup> In water, the diazonium ion reversibly forms aryldiazohydroxide and in alkaline solutions, diazotates are formed (Figure 34). It should be noted that the equilibria between (I), (II), and (III) will depend on the nature of the aryl group and the pH of the medium.

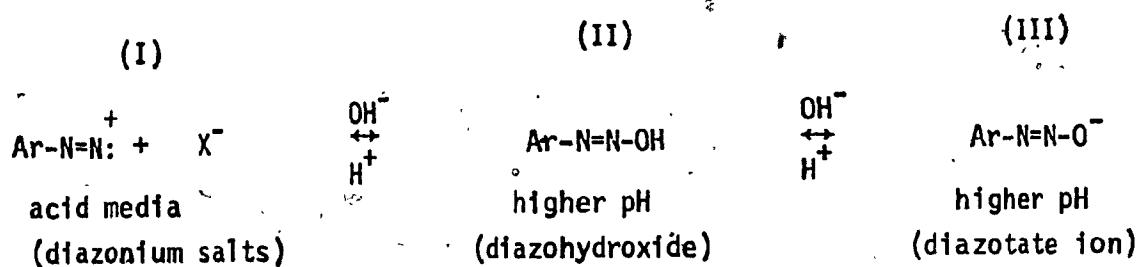


Figure 34. Diazo Forms at Different pH's.<sup>69</sup>

Of the species shown in Figure 34, compound (I) is the effective or reactive one, while neither the diazohydroxide nor the diazotate ion is expected to have much electrophilic character resulting in minimal

coupling activity.<sup>69</sup>

Reactive methylene compounds, on the otherhand, partake in the coupling reaction quite readily in alkaline media. In fact, as the pH rises, their ability to couple increases proportionately until a rate maximum is obtained. Above this pH, the rate decreases due to conversion of the diazo compound to non-coupling isodiazotate ions.<sup>207</sup>

To achieve a balance between these conflicting parameters, the coupling reaction is carried out at a low temperature in a weakly acid medium. The coupling component (reactive methylene compound) is insoluble under these conditions but if it is first reprecipitated from its sodium enolate form (in alkaline medium) by acidification with acetic acid in the presence of a surface active agent such as sodium acetate, the particle size is small enough to permit suspension - and so coupling - with a diazo compound.<sup>19</sup> In this system, the acetic acid-sodium acetate medium then serves as a buffer during coupling. While these conditions, in terms of the rate of reaction, are not optimal (in fact, the reaction may take a considerable amount of time as indicated in the Experimental), the monoazo color obtained is immediately usable as a pigment without further treatment.<sup>\*278</sup>

#### x. The Industrial Production of Azo Pigments

On an industrial scale, diazotizations have been carried out in wooden vats or, in more modern factories, in rubber-lined or glass pressure vessels. In both cases, the reaction mixture never comes into

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\* Curtis<sup>114</sup> suggests a method by which Hansa yellow may be extended for use in oil paints: 100 g BaSO<sub>4</sub> is suspended in water and thoroughly mixed with 15 g Hansa yellow paste. The product is filtered, dried, and ground. Artists' colors would not normally have extended Hansa yellows in them, however, since these pigments would have inferior tinctorial power and covering strength.

contact with metals which would have an adverse effect on the reactants and product.<sup>1</sup> Figure 35 illustrates by flow diagram the type of plant setup required for the manufacture of Hansa yellow G. Here the process includes the synthesis of 4-methyl-2-nitroaniline (m-nitro-p-toluidine) from toluene. The entry of mixed acids in the modern plant is controlled by a pneumatically-operated valve which is governed by a thermocouple probe in the reaction mixture. Entry of the acid is allowed between pre-determined temperature limits and the valve closes above the upper limit. Flow is also stopped if the stirring rod or agitator is stopped.<sup>6</sup>

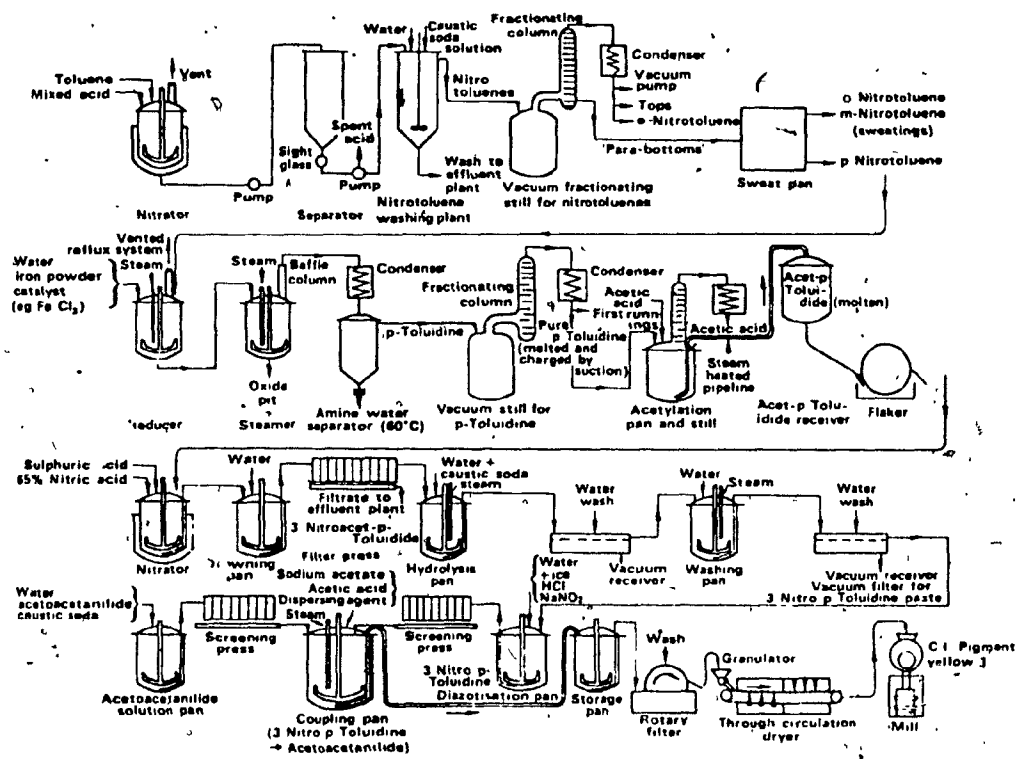


Figure 35. Plant Flow Sheet - The Manufacture of Monoazo Hansa Yellow G.<sup>6</sup>

Special care is needed in the manufacture of dyes and pigments to prevent the entry of any metal objects into the product since their



presence in the grinding mill can cause fire or explosions. Most manufacturing systems include magnetic traps to pick up "tramp" metal. Pigment production requires further special care to prevent the entry of dirt or other non-pigment matter because there is no opportunity in the production line to filter off insoluble matter from the product.<sup>6</sup>

xi. Uses of the Hansa Yellow G and 10G

As mentioned previously, the Hansa yellows have a poor resistance to migration or bleeding in nitrocellulose lacquers and stoving finishes. Consequently they are used mainly in decorative paints. Other uses are in printing inks, paper coating, wallpaper, textile printing, leather, and in plastics, although in the latter some migration occurs on heating.<sup>101</sup>

III. Inorganic Pigments

While organic pigments include a small number of natural products, such as vegetable dyes and earth minerals, the majority are derived from synthetic sources. They are also obviously characterized by a chemical composition which includes carbon as the basic part of the molecule. Inorganic pigments, on the otherhand, include many colors of natural origin, i.e., generally obtained from mineral sources. Almost all of these have a metal atom as a central or basic part of the molecule and many are complex mixtures of several types of metal and other atoms (e.g., ultramarine).

Because of the variety of inorganic pigments, they are not easily classified. Different systems are used based on such factors as (a) method of manufacture, e.g., fume process, fire process, precipitation, and natural mineral, (b) composition, e.g., grouped by the main metallic component or by the primary group such as chromate, ferrocyanide, etc.,

and (c) hue or color. The last is probably most widely used since all hue groups are represented by inorganic pigments and because color is usually the first consideration in the choice of a pigment. In fact, for this project, the inorganic pigments were chosen for both their range of colors (i.e., red, yellow, blue, green) and their variety of synthetic methods. Synthetic inorganic pigments are made by both wet and dry processes which include a variety of combinations of steps such as precipitation, fusion, calcination, etc. We will deal with many of these methods in this section.

It should be noted that, unlike that which exists for the organic pigments, no really comprehensive or satisfactory survey of the chemistry of the inorganic dyes and pigments has yet been written. In addition, authoritative information about many of them is difficult to obtain.<sup>105</sup>

A. Cadmium Pigments - Cadmium Yellow and Cadmium Yellow Lithopone (CI Pigment Yellow 37; CI 77199) and (CI Pigment Yellow 35; CI 77117)

The difficulty classifying inorganic pigments is particularly evident with the cadmium colors. This group of colorants includes pure cadmium sulfides, as well as blends of cadmium sulfide with cadmium selenide (CdSe), other metal sulfides (e.g., ZnS), and the inert extender pigment, barium sulfate (lithopone-type pigments).

The simplest approach would be to classify these pigments as a group based on their predominant metal, cadmium. However, their color range is from yellow - through orange - to red, deriving from the varying components associated with the cadmium. For example, pale shades of cadmium yellow are produced by addition of various amounts of BaSO<sub>4</sub> to the pure cadmium sulfide. The reds are blends of the sulfide and cadmium selenide. Since most physical properties of the cadmiums are similar and their chemical compositions form a continuous range of compounds rather than discrete

types, discussion of these colors is probably easiest when based on hue.

### i. History

The cadmium pigments are one of the most important of the inorganic artists' colors. Cadmium sulfide or pure cadmium yellow, occurs naturally in small quantities as the rare mineral, Greenockite. While this natural pigment was used 2000 years ago,<sup>116</sup> it is seldom used as a pigment today. The first synthetic cadmium yellow used was prepared in 1818<sup>158</sup> by Gay-Lussac who precipitated cadmium sulfide from a solution of cadmium salts with hydrogen sulfide. It was not until about 1846, however, that the new pigment became commercially available as such. Laurie<sup>268</sup> says that cadmium yellow was first shown at the Great Exhibition in the Crystal Palace in 1851.

By 1968, about six million pounds of cadmium sulfide were being produced in the United States per year. Of this approximately 10% was pure CdS and zinc modified CdS with the remainder being produced as the selenium derivative or as the extended (with 60% or more  $\text{BaSO}_4$ ) lithopone.<sup>340</sup> Both pure and coprecipitated (with  $\text{BaSO}_4$ ) cadmium sulfides are used as artists' colors.

### ii. Composition and Hue

Cadmium sulfide can exist as a range of hues from bright lemon-yellow to deep orange. Most manufacturers offer several shades of cadmium yellow which are sold as cadmium yellow 'light', 'medium', or 'dark', with the 'light' being the palest and the 'dark' being closest to orange. It should be noted that the terms 'light', 'medium', or 'dark' are only relative and one manufacturer's light may not necessarily match the so-called 'light' of another.

At one time, these shade differences were believed to be due to the

presence of impurities until it was found that the different shades contained identical impurities and pure forms of the compound had the same chemical composition, i.e., CdS.<sup>116,362</sup> While no clearcut composition for these compounds has yet been elucidated, some general agreement seems to exist that the various shades arise from differences in physical structure brought about during the synthetic process. Zaprometov and Prikhoho<sup>471</sup> found that the microstructure of both the CdS precipitate and the dispersion of CdS particles influence the color. They also postulated that shade was not affected by the orientation of the atoms or the crystal lattice structure but by secondary factors related to the structure of the colloidal aggregates. These, in turn, were determined by the valence of the so-called 'coagulating' anion. Their work supported the early  $\alpha$  and  $\beta$ -polymer theory of Buchner<sup>80</sup> who described two different forms of CdS. The first,  $\alpha$ -CdS, he described as a lemon-yellow color with a density of 3.9-4.2. The second,  $\beta$ -CdS, was said to be a vermillion color with a density of 4.47-4.51. Buchner found that the yellow form could easily be turned into the red by the action of acids and alkali. Consequently, he suggested that the latter was a 'polymer' of the former and that the variation in color was due to the admixture of these two forms in different proportions. Milligan<sup>303</sup> described the  $\alpha$ -form as being hexagonal and the  $\beta$ -form as cubic. However, Milligan claimed that either the cubic  $\beta$ -CdS or hexagonal  $\alpha$ -CdS may be yellow or red depending on the physical characteristic of the precipitate. 5

A manner in which this might be explained had been suggested previously by Allen and Crenshaw.<sup>14</sup> They had proposed that CdS crystallized in more than one form and that the different hues or shades were due to differences in the size of pigment particles which resulted, in turn, in variations of the amount of light transmitted and reflected by the powders.

The different forms of CdS can be produced during synthesis by varying the starting materials and reaction conditions. For example, the  $\beta$ -CdS tends to be precipitated from CdSO<sub>4</sub> solution and, under some conditions (heat or acid), from cadmium nitrite solution.  $\alpha$ -CdS, on the otherhand, tends to be precipitated from cadmium chloride, bromide, or iodide solutions, although these precipitates may contain some of the  $\beta$  modification.<sup>303</sup>

Yellow shades of CdS generally result from slow precipitation of weak cadmium solutions and pale shades from partial precipitation, i.e., retaining cadmium in excess.<sup>193</sup> Increasing temperatures, together with more complete precipitation, or using cadmium carbonate as starting material, produces dark shades.<sup>362</sup> Another common method for the production of pale cadmium yellows is the addition of BaSO<sub>4</sub>. This may be done either by mechanical mixture or by coprecipitation. The latter method produces a superior product in terms of shade, handling, and fastness properties. Commercially, most of these lithopones contain 60-65% BaSO<sub>4</sub> and the better coprecipitated grades are used in artists' paints.<sup>163,339</sup>

### iii. Properties

Since the production of pure cadmium yellows includes calcination, they display excellent heat resistance. In fact, they are unaffected by temperatures up to 500°. Similarly, they are not affected by hydrogen sulfide fumes, an important consideration in today's H<sub>2</sub>S-polluted cities. They are also resistant to most chemical attacks, are inert to organic acids and dilute solutions of some inorganic or mineral acids (50% HCl will dissolve CdS with concurrent loss of color), are sufficiently alkali fast to be used in most alkali environments (such as emulsion paints applied to plaster walls), and are particularly fast to light (although

fading can occur in titanium dioxide mixtures).<sup>117</sup> The water resistance of CdS pigments depends to some extent on the moisture resistance of the binder. Since cadmium metal and soluble cadmium salts are very poisonous, the cadmium yellows are potentially toxic. However, as long as the yellow is mixed in paint or plastics as CdS or one of its extended forms, it is relatively safe.<sup>119</sup>

Physically, the cadmium yellow pigment particles are finely divided and more or less uniformly of the same size. Their shape may be described as minutely rounded grains which appear as tiny globules at high magnifications.<sup>163</sup> Other physical properties of the pure cadmium yellow may be found in Table 12.

As a class, the cadmium yellow lithopones ( $\text{BaSO}_4$  extended pigments) have good hiding power but only poor to fair tinting strength. Other properties of the lithopones are essentially the same as for the pure cadmium sulfides. Like them, the lithopone pigment particles are finely divided, but are described as "fine composite grains."<sup>169</sup>

Since  $\text{BaSO}_4$  has a density of  $4.5 \text{ g/cm}^3$  (vs. 4.82 for CdS),<sup>119</sup> the densities of the extended pigments are essentially the same as for the pure pigment. The particle size distribution of the lithopones is also similar to that of the pure CdS.<sup>413</sup> The oil absorption level of  $\text{BaSO}_4$ , however, is less than for CdS alone, making the lithopones relatively easy to disperse effectively in oil. Other Cadmium yellow lithopone properties are listed in Table 13.

#### iv. Experimental - Preparation of Pure Cadmium Sulfide

The Color Index<sup>107</sup> lists the following general processes for the synthesis of pure cadmium sulfide:

1. Precipitate a neutral or faintly alkaline solution of a cadmium salt with a sulfide. Pale pigments are obtained from ammonium

Table 12. Physical Properties and Other Data for Cadmium Yellow (CI Pigment Yellow 37; CI 77199).

		Reference
Chemical Class	Inorganic	92
Hue	Bright Yellow - Reddish Yellow	
Fastness Properties		
1. Organic Solvents	insol in organic solvents	
2. Light	excellent	
3. Heat	1750° (turns dark violet-red on heating but original hue returns on cooling if pigment not oxidised)	107
4. Water	insol	92
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	poor (soluble) - dissolves with complete loss of color in mineral acids*	107
7. Linseed Oil	insol	92
8. Oleic Acid	insol	
9. Soap Gel Bleeding	none	
Density	4.6 g/cm <sup>3</sup> (pale yellow) 4.7 g/cm <sup>3</sup> (pale orange) 4.8 g/cm <sup>3</sup>	338 92
Specific Gravity	4.3 - 4.5	119
Particle Size**	< 5μ (95%) < 1μ (80%) none > 20μ	
Oil Absorption	32 - 35 (lb/100 lb.)	
Refractive Index	2.35 - 2.48 (isotropic)	169
Crystals	light yellow or orange-colored cubic or hexagonal crystals	92
Toxicity	Cd metal and soluble Cd salts are very poisonous but safe in paint and plastics as CdS	119
Standard	BS 2876:1957	107

\* Unaffected by H<sub>2</sub>S

\*\* Determined by modification of Anderson's sedimentation method.<sup>119</sup>

Table 13. Physical Properties and Other Data for Cadmium Yellow  
Lithopone (CI Pigment Yellow 35; CI-77117).

		Reference
Chemical Class	Inorganic	92
Fastness Properties	very similar to CI Pigment Yellow 37	
Specific Gravity	4.2 - 4.3	119
Oil Absorption	25-27	
Refractive Index	2.39 - 2.4	169
Others	as for CI Pigment Yellow 35	119
Standard	USA Fed. Spec. TT-C-83	92

monosulfide and cadmium oxalate and dark colors from sodium monosulfide and cadmium carbonate.

2. Fuse cadmium oxide or carbonate with sulfur.
3. Vaporize cadmium and sulfur in the absence of air.
4. Melt sodium thiosulfate in its own water of crystallization, add cadmium sulfate and zinc oxide and calcine at 400-500°.

The most common or simplest method for the precipitation of CdS involves cadmium chloride as the cadmium salt and hydrogen sulfide as the sulfide:

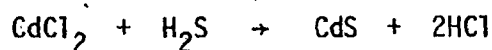


Figure 36. CdS Synthesis With Cadmium Chloride and Hydrogen Sulfide.

For this project, we dissolved 4 g of pure cadmium chloride in approximately 1 liter of distilled water. H<sub>2</sub>S was then bubbled into the solution with vigorous stirring. A yellow precipitate formed immediately. Precipitation terminated when no further CdS appeared to be produced (approximately 1/2 hour in this case). The 1.9 g of product were washed and dried.

Cadmium sulfate could also have been used to form the CdS:

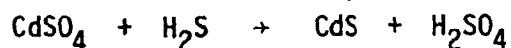


Figure 37. CdS Synthesis With Cadmium Sulfate and Hydrogen Sulfide.



#### v. Notes on the CdS Reaction

Historically, the hydrogen sulfide method is carried out in earthenware vessels (e.g., a Woulff's bottle).<sup>362</sup> Gas enters through perforations in a tube in the bottom of the vessel and excess gas is passed out through scrubbers into the plant's smoke stack.

A variation of this procedure, suggested by Harrison,<sup>193</sup> involves acidifying the  $\text{CdCl}_2$  solution with 20% of its weight of  $\text{H}_2\text{SO}_4$  before blowing in the gas. Toch<sup>428</sup> says that a slightly acid medium produces a yellow shade, while changing the proportions of acid and adding ammonium sulfide produces deeper shades up to the 'deepest orange.'

Variations also exist in terms of both the reaction medium and the sulfide. For example, Patton<sup>339</sup> recommends precipitation of CdS from a  $\text{CdCl}_2$  solution by the addition of a BaS solution added slowly over an hour or more. In this method, the reaction temperature is elevated to 71-90° using steam heat. The by-product,  $\text{BaCl}_2$ , is removed by washing and the filtrate calcined in a rotary kiln. A similar method may be used to produce cadmium yellow lithopone (vide infra).

Brauer<sup>73</sup> recommends precipitating pure CdS from a solution of  $\text{Cd}(\text{ClO}_4)_2$  in 0.1-0.3N perchloric acid with  $\text{H}_2\text{S}$ . Lower acid concentrations yield a product difficult to filter. At higher concentrations, the precipitation is incomplete.

A cadmium salt solution acidified by HCl may also be used:



Figure 38. CdS Synthesis with Cadmium Sulfate and Sodium Sulfide.

The  $\text{Na}_2\text{S}$  must be freshly made and the yellow precipitate washed free of  $\text{Na}_2\text{SO}_4$ .<sup>362</sup>

Fusion methods for the preparation of CdS also exist: A finely powdered mixture of cadmium carbonate and an excess of sulfur are heated in a Hessian crucible to red heat. At between 400° and 600°, complete conversion of the carbonate to the sulfide takes place. If the product is not bright or deep enough, more sulfur is added and the heating is repeated. When the mass is cooled, it is water ground in a ball mill in order to improve the texture and dried.<sup>362</sup> According to Curtis and Wright,<sup>117</sup> the CdS prepared by this method has a dark color and inferior hiding power to the precipitated product.

vi. Experimental - Preparation of Cadmium Sulfide Lithopone

Cadmium yellow lithopone may be prepared by either mechanical means or by coprecipitation. The only methods given here will be those involving coprecipitation since they give superior pigments, i.e., they won't separate into their components when suspended in a paint vehicle. Furthermore, coprecipitated pigments have better color, tinctorial strength, and fastness properties.<sup>118</sup>

The simplest preparation of coprecipitated cadmium sulfide lithopones is by mixture of equimolar solutions of CdSO<sub>4</sub> and BaS at 85°, the BaS solution being added slowly over an hour.



Figure 39. Coprecipitation of Cadmium Sulfide and Barium Sulfate (Cadmium Yellow Lithopone) From Cadmium Sulfate and Barium Sulfide.

The lithopone product contains 38.2% CdS and 61.8% BaSO<sub>4</sub>. A greener tone, giving lemon and primrose shades may be obtained by replacing some of the CdSO<sub>4</sub> by ZnSO<sub>4</sub><sup>118</sup> (see Appendix A).

A method similar to that above involves the use of CdCl<sub>2</sub> and BaS.

In this case  $\text{Na}_2\text{SO}_4$  is used to precipitate the  $\text{BaSO}_4$  (Appendix A).

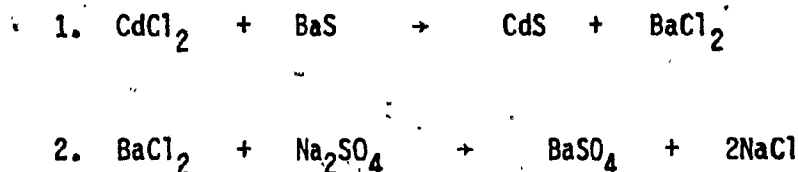


Figure 40. Cadmium Yellow Lithopone Production From Cadmium Chloride, Barium Sulfate, and Sodium Sulfate.<sup>339</sup>

A fusion method (G.P. 621,854; 1937) similar to that used for the pure cadmium sulfide involves calcining a thoroughly ground mixture of 100 g of cadmium carbonate, 37 g of sulfur, and 10 g alumina hydrate (A1OH) at 500° for 90 minutes.<sup>362</sup>

vii. Notes on the CdS Lithopone Reaction

Typical lithopones produced commercially contain between 30 and 38% CdS, 61 and 67%  $\text{BaSO}_4$ , and up to 5% zinc sulfide or oxide. Pure lithopones, i.e., containing no zinc, generally contain close to 38% CdS.<sup>116,362</sup>

In all of the synthetic reactions, for both pure and extended yellow, the precipitate is first filtered off and washed thoroughly to remove soluble salts. This is especially important for pigments which are used as artists' colors. In these cases, purity of the product is essential since often the pigment is mixed with other pigments before or during application of the paint to the canvas and there must be no possibility of chemical interaction. This is particularly true for free sulfur since sulfur can have a deleterious effect on paint media, especially synthetic resins.

The washed pigment is then carefully dried, calcined, wet-ground, dried, and finally dry-ground. Commercially, these steps are carried out

in rubber-lined vessels (wooden vats in the past<sup>53</sup>) and all steps are performed under carefully controlled conditions. In practice, a wide variety of products, in terms of quality and shade, are possible based largely on conditions of precipitation (e.g., concentration changes and addition of small amounts of zinc chloride<sup>193</sup>) and calcination. For example, in calcination the crystal structure of the precipitated pigment is altered to yield a pigment of improved color and brightness.<sup>116</sup> Calcination is carried out in an inert atmosphere in order to avoid oxidation of the pigment. Heating is begun at 200° and completed at 650°. Control of this stage is essential because overcalcination produces flat, green shades, undercalcination gives reddish shades, and uneven calcination results in color variation within a batch.<sup>138</sup> It should be noted here that, in general, the complete details of these and other reaction conditions in commercial manufacturing processes are not generally released and are protected by a large number of patents.

#### viii. Commercial Uses

Because of the tremendous cost of pure cadmium sulfide, it is primarily used only in high quality products. These include (besides the various shades sold as artists' colors) special paints, enamels, lacquers, ceramics, glass, and rubber. Occasionally pure CdS is also used in printing inks, plastics, and paper, but these products are necessarily expensive.

The lithopones, accounting for almost 90% of the cadmium yellows, are widely used in printing inks, wallpaper, and rubber. According to the Color Index,<sup>92</sup> cadmium yellow lithopone exhibits better dispersion in rubber than the pure cadmium yellow. High purity grades of the lithopones are also sometimes used in artists' colors. In general, both the

extended and the pure cadmium yellows are used where resistance to light, heat, alkali, and hydrogen sulfide, as well as freedom from bleeding in the vehicle, are desired.

B. Cadmium Pigments - Cadmium Red and Cadmium Red Lithopone (CI Pigment Red 108; CI 77202) and (CI Pigment Red 108 and CI Pigment White 22)

i. History

Although a red-orange cadmium pigment containing selenium was mentioned in a German patent (G.P. 63558) in 1892, the commercial production of cadmium reds did not begin until 1910, (this early preparation involved the fusion of CdS, S, and Se at  $600^{\circ}$ <sup>450</sup>) with the lithopone following in 1926.

ii. Composition and Hue

Originally prepared by the heating of cadmium sulfide, sulfur, and selenium at approximately  $600^{\circ}$ , cadmium red is essentially a solid solution of CdS and CdSe crystals rather than a unique compound. This has been shown through x-ray diffraction studies which have indicated almost identical patterns for CdS and CdS/Se. In the red pigment, however, the lattice expands, causing the pattern to close up and so indicate the presence of a solid solution.<sup>117</sup> Eroles and Friedberg<sup>134</sup> characterized the red pigments' structure as being a continuous solid solution of the substitutional type.

Physically, cadmium red pigment particles can be described as minute rounded grains. However, under the microscope they are seen as tiny red globules less than  $1 \mu$  in diameter, without any appearance of crystallinity.<sup>169</sup>

While a typical composition for these particles is  $3\text{CdS}\cdot 2\text{CdSe}$ , a wide variety of shades, from a yellowish red or orange to a dark maroon,

can be obtained by changing the proportion of selenium present. As can be seen in Table 14, the hue increases in redness and blueness with the proportion of selenium. Although pure cadmium selenide (CI 77202) exists, this compound is seldom used as a pigment.<sup>94</sup>

Pigment	Cd/Se	Color
A	100/12	orange
B	100/15	orange-red
C	100/20	light red
D	100/25	bright red
E	100/30	dark red
F	100/35	maroon
G	100/40	dark maroon

Table 14. The Relationship Between Selenium Content in Cadmium Red and its color.<sup>117</sup>

Like the cadmium sulfides, commercially available cadmium sulfo-selenides are marketed in artists' paints as cadmium red 'light', cadmium red 'medium', and cadmium red 'dark'. These classifications are arbitrary, i.e., differing in hue from brand to brand, although within one line, the reds are relatively light, medium, and dark. The 'light' red is generally the most orange and the 'dark', the closest to maroon.

It is interesting to note that together, cadmium red, cadmium yellow, and cadmium orange\* form a series of hues, from yellow, through orange and red, to bordeaux, composed of pigments of very similar chem-

\* Cadmium orange (CI Pigment Orange 20; CI 77199 and CI 77196) is the cadmium sulfo-selenide having a hue range from yellowish orange to reddish orange. The physical properties of cadmium orange, such as fastness and stability, are identical to both cadmium yellow and red. It is interesting to note that the cadmium red 'light' sold as an artists' color by at least one manufacturer (Permanent Pigments' Liquitex emulsion or acrylic paint) closely approaches orange in hue.

ical composition, fastness properties and use.

### iii. Properties

Like the cadmium sulfide yellows, the cadmium sulfo-selenides have generally good resistance to heat (they are calcined like the yellows) and chemical attack. Cadmium sulfo-selenide is not affected by hydrogen sulfide, the organic acids, dilute solutions of most inorganic acids, alkaline environments, and temperatures up to 500°. <sup>341</sup> In addition, the cadmium sulfo-selenides have good light fastness, opacity, and staining power. <sup>117</sup> They are also potentially toxic. Other physical properties and data for the cadmium reds are listed in Table 15.

Cadmium red is often marketed as the barium sulfate extended lithopone. While the cadmium red lithopones are generally sold as coprecipitated pigments containing 52% BaSO<sub>4</sub> and 48% CdS/Se, the shade of these extended colors may be varied from pale to dark red by varying the quantity of BaSO<sub>4</sub> added. The hue can be altered by changing the composition of CdS/Se during manufacture.

Cadmium red lithopones possess identical general physical properties to those of the cadmium yellow lithopones (vide supra) except that under the microscope (at high magnification), they also contain prismatic grains of barium sulfide. <sup>163</sup> As a class, they possess good hiding power but only fair to poor tinting strength.

### iv. Experimental

An early patent for the preparation of cadmium sulfo-selenide was granted to the Bayer Co. in 1917. This patent <sup>135</sup> covered the addition of a solution of alkaline sulfides and selenides to a cadmium salt solution. The precipitate was calcined to obtain a finished pigment. Variations of this method, based on the formation of alkali selenide (from

Table 15. Physical Properties and Other Data for the Cadmium Sulfo-Selenides (CI Pigment Red 108; CI 77202 and CI 77196).

		Reference
Chemical Class	Inorganic	94
Hue	Yellowish-Red → Bordeaux or Deep Maroon	
Fastness Properties:		
1. Organic solvents	insol	
2. Light	v. good	
3. Heat	m.p. = 1350° stability to 500°	391 94
4. Water	insol	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	poor (sol)	
7. Linseed Oil	insol	
8. Oleic Acid	insol	
Density	4.9 g/cm <sup>3</sup> 5.61 g/cm <sup>3</sup>	340 391
Specific Gravity	orange = 4.5 deep red = 5.3	119
Oil Absorption	20 lb/100 lb 22-28	340 119
Particle Size	75% between 2-3 μ over 90% between 2-5 μ v. few above 20μ and below 1 μ	
Refractive Index	2.64 (bright red) - 2.77. (deep red)	169
Crystals	white to brown cubic or hexagonal	391
Toxicity	as CdS (Table 12)	
Standard	CdSe - USA Fed. Spec. TT-C-80 CdSe x CdS - BS 2876:1957	

Table 16. Physical Properties and Other Properties for the Cadmium Red Lithopones (Mixed Pigments of CI Pigment Red 108 and White 22).

General properties similar to cadmium yellow lithopones (CI Pigment Yellow 35) - see Table 13. Exceptions are as follows:

		Reference
Oil Absorption	22-28	117
Specific Gravity	4.5 - 4.7	
Refractive Index	2.50 - 2.76	169



selenium metal dissolved in alkali sulfides before precipitation) are commonly used today. The Color Index<sup>107</sup> gives the following general preparation: "To a cadmium sulfate-soda ash solution (produces  $\text{CdCO}_3$ ) is added selenium metal dissolved in sodium sulfide ( $\text{Na}_2\text{S}$ ). The precipitate is filtered and calcined. The color varies from orange to maroon, becoming redder as the proportion of selenium increases. Maroon is obtained with equimolar quantities."

Numerous patents, claiming an improved pigment product, suggest such variations as the introduction of a reducing agent into the mixture before calcination and addition of aluminum phosphate. A pigment said to be free from hard aggregates and of a uniform color may be made by adding 1-4% barium carbonate or peroxide to a mixture of cadmium sulfide, cadmium oxide, and selenium before calcination.<sup>117-8</sup> Improved resistance is claimed to be obtained by the addition of clay to a mixture of cadmium sulfide and selenide prior to calcination. Lastly, Artamonov<sup>26</sup> recommends stirring the precipitate every four or five minutes for twenty minutes during calcination at  $580^\circ$ - $600^\circ$ .

Selenium metal powder may also be mixed with cadmium sulfide just before calcination rather than precipitated with it: mix 10-20 parts selenium metal powder with 80-90 parts  $\text{CdS}$  and heat in a muffle furnace to  $700^\circ$ . Without allowing the mixture to cool, place it on a cold plate or douse in cold water.<sup>455</sup>

An alternate procedure resulting in the production of  $\text{CdS/Se}$  with selenium in a highly dispersed form is given by Remington and Francis.<sup>362</sup> 1000 ml of a  $\text{CdSO}_4$  solution containing 188.5 g  $\text{CdSO}_4$  is mixed with 200 ml of a potash solution (70 g in 200 ml  $\text{H}_2\text{O}$ ). To this mixture is added 1380 ml of a sodium carbonate solution containing 138 g  $\text{NaCO}_3$ . To each 100 g of dried precipitate, 13 g sulfur and 8 g selenium metal powder are added. The mixture is calcined at  $500^\circ$  for 90 minutes in a muffle

furnace.

The cadmium red lithopones, which like the yellow lithopones display superior pigment properties when coprecipitated rather than when mixed commercially, are obtained by coprecipitation of cadmium sulfo-selenide with barium sulfate. They are made in the same general way as yellow lithopones except that alkali selenide is substituted for part of the alkali sulfide.

#### v. Commercial Uses

Commercial applications of the cadmium sulfo-selenide pigments are the same as for the cadmium yellows.<sup>94</sup>

#### C. Chromium Oxide Green (CI Pigment Green 17; CI 77288)

##### i. History

Chromium oxide green, a simple inorganic compound, is the most stable green pigment yet developed. Vanquelin, the discoverer of chromium (1797), suggested its use as a ceramic glaze in 1809,<sup>164</sup> but it did not appear as an artists' pigment until the 1860's.<sup>266</sup> Between the years 1957 and 1968, from 10-14 million pounds of chromium oxide were produced per year in the United States.<sup>373</sup>

##### ii. Composition

Chemically, chromium oxide green is almost pure anhydrous chrome oxide or chromium sesquioxide,  $\text{Cr}_2\text{O}_3$  (98.5% minimum)<sup>206</sup> composed of 68.4% chromium and 31.6% oxygen.\*<sup>372</sup>

##### iii. Properties

Chromium oxide green is the most permanent green pigment commercially available, being stable to heat up to 1000°. The pigment turns brown at

\* Chromium oxide can be used directly as a pigment, or a chromic oxide derivative, a pale green pigment known as 'leaf green', can be obtained by igniting a mixture of chromic oxide and pure aluminum hydroxide.<sup>41:</sup>

these temperatures, but reverts to green on cooling. It is extremely hard, having the ability to scratch quartz, topaz, and zircon.<sup>108</sup> Chromium oxide is extremely fast to light and highly resistant to acidic or alkaline attack. In addition, this green is relatively easy to disperse in paint media and mixes well with all other pigments. When applied as a paint coating, however, chromium oxide green has poor opacity, low tinting power, and a relatively dull shade.<sup>411</sup> It should be mentioned, however, that these last three properties are not necessarily undesirable, especially when used as artists' colors.

Physically, chromium oxide green pigment particles are fine, but irregular and fairly coarse crystal aggregates.<sup>169</sup> Other physical properties for chromium oxide green are listed in Table 17.

#### iv. Experimental

The Color Index<sup>108</sup> lists the following general methods for the synthesis of chromium oxide green:

1. Reduce potassium dichromate at high temperature.
2. Calcine ammonium or sodium dichromate, chromic chloride or mercurous chromate.
3. Precipitate chrome alum or chromium salts with an alkali, wash, and calcine.
4. Calcine, with caustic soda, the chromium hydrate obtained as a product in the oxidation of toluene to benzoic acid.<sup>52</sup>

Other general preparations are the reduction of sodium dichromate (identical to step #1, above) or reacting concentrated sulfuric acid with a solution of chromate or dichromate.<sup>391</sup>

In practice, either sodium or potassium dichromate and sulfur in excess (30-40% of equimolar quantities) are mixed mechanically and placed in a brick chamber fitted with a flue. On heating to 1100° in an inert atmosphere, the mixture turns brown (reverting to green only on cooling)

and excess sulfur is evolved as sulfur dioxide. After cooling, the mass is broken up and  $\text{Na}_2\text{SO}_4$  (or  $\text{K}_2\text{SO}_4$ ) removed by decantation. The washed pigment is filtered, dried and powdered in a ball mill.<sup>411</sup>

We essentially mimicked this industrial process. 29.6 g sodium dichromate was ground intimately with 4.4 g sulfur. This mixture was heated with a bunsen burner for approximately twenty minutes.\*

Table 17. Physical Properties and Other Data for Chromium Oxide Green (CI Pigment Green 17; CI 77288)

		Reference
Chemical Class	Inorganic	97
Hue	Yellowish-Green to Bluish-Green	
Chemical Composition	Cr = 68.4%    O = 31.6%	
Fastness Properties		
1. Organic Solvents	insol in all	
2. Light	excellent	
3. Heat	m.p. $\approx$ 2435° (stable to 900-1000°) b.p. $\approx$ 3000°	
4. Water	insol	
5. $\text{Na}_2\text{CO}_3$ 5%	unalt	
6. HCl 5%	unalt.	
7. Linseed Oil	insol	
8. Oleic Acid	insol	
Density	5.09 - 5.40	372
Specific Gravity	5.10	169
Refractive Index	$n_D^{25}$ 2.5	
Oil Absorption	12-14 g/cm <sup>3</sup>	372
Particle Size	ave. = .05% pass a 325 mesh screen	
Standard	BS 318:1952 USA: ASTM D263-46 (1970) D213-47 Fed. Spec. TT-C-235 (3) and TT-C-306 TT-C-347	97 108

\* Robinson<sup>374</sup> says the reaction should be carried out in a reducing atmosphere at temperatures up to 1100°.

The reaction for this synthesis may be written as in Figure 41.

Figure 41. The Synthetic Reaction for the Preparation of Chromium Oxide Green From Sodium Dichromate and Sulfur.

The mixture turned brown as expected and the appearance of a large number of bubbles indicated the evolution of  $\text{SO}_2$ . On cooling, the mixture became a mottled green-brown hard cake. Because it appeared as though the reaction had been incomplete, perhaps due to sublimation of sulfur during the reaction, the cake was crushed and ground with more sulfur. Reheating and cooling resulted in a more or less even green product, again in a hard cake form. The cake was broken up with a mortar and pestle and the resultant powder washed repeatedly by decantation to remove soluble salts. The entire process was repeated three times and the product ground into an acrylic emulsion paint base.

#### v. Commercial Uses

In addition to uses common to the rest of the pigments discussed previously, such as in printing inks, lacquers, paints, and plastics,<sup>97</sup> chromium oxide green is stable enough to be used in a variety of special applications. For example, because it can withstand severe conditions of exterior exposure, chromium oxide green is employed in the pigmentation of Portland cement, concrete, glazes for ceramic tiles, stucco paints, and roofing granules. Because it can tolerate any curing procedure, this pigment is widely used in the coloration of rubber. Since chromium oxide reflects infrared radiation, approaching, in fact, the reflectance properties of green chlorophyll, it is used extensively in the formulation of military camouflage paint.<sup>373-4</sup>

## D. Hydrated Chromium Oxide Green (CI Pigment Green 18: CI 77289)

### i. History

Hydrated chromium oxide green, also known as viridian, Guignet's green, or transparent oxide of chromium, was first made by Pannetier and Binet (color makers in Paris) about 1838.<sup>88</sup> Their manufacturing process was a secret until 1859 when Guignet patented a method based on the reduction of potassium bichromate with boric acid.<sup>108</sup> The new green was immediately successful, especially as a replacement for Schweinfurt or emerald green, an extremely toxic pigment which is blackened by sulfur both in the air and mixed with certain other pigments. Laurie<sup>266</sup> says that viridian, as the new green became known in England, was first introduced as an artists' color in the 1860's. Today, the production level of hydrated chromium oxide green is reduced from previous levels, the pigment having relatively minor commercial value.

### ii. Composition

Chemically, the pigment is hydrated chromium sesquioxide,  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  or mixtures of  $\text{Cr}_4\text{O}_3(\text{OH})_6$  and  $\text{Cr}_4\text{O}(\text{OH})_{10}$ , with 0.5-10%  $\text{Cr}_2\text{O}_3$  and boric acid. The formula is conventionally written as  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{Cr}_2\text{O}(\text{OH})_4$ , both of which have a molecular weight of 188.05 and a distribution of 55.4% chromium, 42.5% oxygen, and 2.1% hydrogen.<sup>375</sup>

### iii. Properties

Hydrated chromium oxide is a semi-transparent color whose blue-green shade varies slightly depending on minor variations in the manufacturing process.<sup>38</sup> When the blue-green shade is desired as an opaque color, the pigment is usually mixed with an opaque white or yellow to give it more hiding power. White hydrated chromium oxide green is more brilliant in color than the relatively dull chromium oxide green, the latter is some-

what more lightfast. Otherwise, the hydrated pigment is extremely permanent, being unaffected by acids, alkalies, and heat up to 250°. <sup>411</sup>

This maximum temperature stability is less for the hydrated chrome oxide than the non-hydrated variety (stable to 900-1000°) due to the water of hydration in the former. <sup>341</sup> However, hydrated chromium oxide green does not lose its green color within its stable range as does unhydrated  $\text{Cr}_2\text{O}_3$ .

Physically, this pigment has characteristically bright green, transparent particles when viewed under a microscope. They also appear as fairly large, irregularly spherulitic grains. According to Gettens and Stout <sup>173</sup> they are strongly birefracting in polarized light due to strain in the particles caused by cooling. Other physical properties and data are given in Table 18.

#### iv. Experimental

The following three general preparations for hydrated chromium oxide green are listed in the Color Index: <sup>108</sup>

1. Ignite potassium or sodium dichromate (1 part) with boric acid crystals (3 parts) at dull red heat in the absence of air, extract with water and steam, levigate, dry and grind. Insufficient boric acid results in a browner product.
2. Reduce sodium dichromate with molasses at 350-360° (300 atmospheres).
3. Heat chromium hydroxide,  $\text{Cr}(\text{OH})_3$ , with boric acid or silica gel.\*

Remington and Francis <sup>363</sup> give a more detailed procedure for method

(1) above:

"Grind together potassium bichromate and boric acid (1:3 by weight) until (they become) a uniform fine powder. Heat a muffle furnace to

\* A method given by Ruthruff <sup>379</sup> produces hydrated chromium oxide, from chromium oxide and ethanol, for use as a catalyst. However, the product  $\text{Cr}(\text{OH})_3$  has a higher oxidation number than the hydrated chrome oxide used as a pigment and, in fact, is brown in color.

a dull red heat (approximately 600°) and charge with the material (escaping boric acid is removed by pipes at the top of the furnace). Soon after, the mass of material collapses due to decomposition of the boric acid and escape of water. When the mixture begins to soften and form a spongy mass with bubbles (oxygen and steam) rising to the surface, watch carefully through sight-holes for the whole mass of material to turn red hot and take on a 'clinkery' appearance, the charge is withdrawn.

When the calcined product is cold, it should be spongy, free from brown spots; and be dark emerald green in color. Steam the product (the water is charged with potassium borate) until only traces of potassium borate remain. Test by taking samples and shaking with distilled water in a test tube. Filter and evaporate liquid in a porcelain dish. Only a very small trace of residue should remain. The color of the pigment at this point should be brighter and lighter than before.

Next run hot water over the pigment and filter. Finally either dry or use as a paste."

Table 18. Physical Properties and Other Data for Hydrated Chromium Oxide Green (CI Pigment Green 18; CI 77289).

		Reference
Chemical Class	Inorganic	97
Hue	Green to Bluish-Green	
Fastness Properties		
1. Organic Solvents	insol in organic solvents	
2. Light	excellent	
3. Heat	stable to 250°, then blackens	
4. Water	insol	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	unalt	
7. Linseed Oil	insol	
8. Oleic Acid	insol	
Density	2.9 - 3.7 g/cm <sup>3</sup>	341
Oil Absorption	80-110 lb./100 lb.	
Specific Gravity	3.32	169
Refractive Index	$\alpha/\beta_{\Sigma}$ 182, $\gamma_{\Sigma}$ 2:12	
Standard	BS 2876:1957 USA ASTM D12-47 and D213-47:1970 ASA K58.1, ASTM D126	97

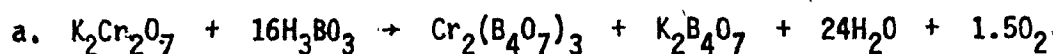


Bearn<sup>38</sup> suggests several variations to the Remington and Francis method given above. At the completion of heating, the charge is dumped into cold water. The mass is then levigated or decanted to remove all soluble salts such as potassium borate and excess boric acid. The washed produce is finally ground between flat stones, dried, and reground. In either method the production of hydrated chromium oxide green apparently "requires considerable processing skill."<sup>376</sup>

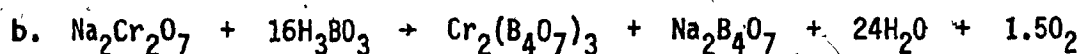
#### v. Notes on the Reaction

The synthesis of this pigment is a high temperature fusion reaction based on the equations given in Figure 42.

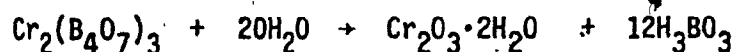
##### 1. Calcination:



or



##### 2. Hydrolysis:



or  $\text{Cr}_2\text{O}(\text{OH})_4$

Figure 42. The Reaction Equations for the Synthesis of Hydrated Chromium Oxide Green.<sup>376,431</sup>

Although the synthetic reaction equation shows one molecule of potassium (or sodium) dichromate decomposes by sixteen molecules of boric acid, in practice (as given in the synthetic methods above), larger quantities are required. The excess acid is apparently important in the

formation of chromium borate.<sup>363</sup> Although the excess boric acid does not appear to enter into the actual reaction (it sublimes during the calcining process), it is necessary for the production of a satisfactory, bright green pigment. Apparently, the excess acid acts in a mechanical way in regulating the mixture during calcining because, as the boric acid sublimes and the temperature rises, the mixture becomes more sensitive to color change. When sublimation of the acid is almost complete, the charge must be withdrawn to avoid discoloration (in the form of brownish-red spots) of the pigment product. Consequently, it is imperative that all stages of the heating be done with care.<sup>363</sup>

#### vi. Commercial Uses

Hydrated chromium oxide green pigment is employed in high grade paints, artists' colors, enamels, painting inks, ceramic painting, glass, rubber, plastics, and paper.<sup>97</sup>

#### E. Ultramarine Blue (CI Pigment Blue 29; CI 77007)

##### i. History

Ultramarine blue is one of the oldest blues in use today. The natural product, lapis lazuli, is a semi-precious stone which is extremely permanent under most conditions and so was used by the ancients in jewelry and in the decoration of sacred temples. Its earliest known use as a pigment took place in Afghanistan where it appeared in wall paintings of the 6th. and 7th. centuries.<sup>312</sup> During the Middle Ages, the natural product was brought into Europe from mines in Badakshan (now a province in north-east Afghanistan) which were visited by Marco Polo in 1271. The stone was known as "azzurro ultramarino" - the blue from beyond the sea.<sup>171</sup> The best lapis is now found in Tibet, China and Iran.<sup>171,210,366</sup> Ultramarine can be recognized in several 15th. century paintings and illus-

trated manuscripts where its original color is retained today.<sup>311</sup> The first use of ultramarine in oil paint is believed to have taken place about 1830.<sup>171</sup> Laurie<sup>266</sup> says that Turner used ultramarine.

By the Middle Ages, several recipes had been developed for the extraction of ultramarine blue from the other materials in lapis lazuli such as slate and minerals (e.g., iron pyrites). One method used by medieval artists in Europe was described in the 15th. century by Cennini<sup>86</sup> as consisting of kneading a paste composed of ground mineral, beeswax, resin, gum mastic, and linseed oil in a dilute alkaline solution. The paste was then stirred frequently over several days during which the by-products (calcite and iron pyrite particles) were retained by the dough and the fine blue particles passed into the alkaline solution from which they settled out as a fine deposit. A second, more straightforward method involved repeated grinding of the mineral in water to an extremely fine size and then washing through strainers.<sup>358</sup>

The first discovery of an artificial ultramarine blue occurred as an accidental by-product in a French plate glass works in 1814. A commercially feasible synthesis was not developed, however, until ten years later when the Société d'Encouragement de France offered a 6000 franc prize to anyone who could manufacture ultramarine artificially for under 300 francs per kilogram. A furnace method, with variations still in use today was proposed by Guimet and the prize was won when this process became commercial in 1828.<sup>358</sup>

Since Guimet's process produced artificial ultramarine which was identical to lapis lazuli, the use of the more expensive natural product soon declined. By the early 1950's, 17-18 million pounds of ultramarine were being produced per year in the United States, although present pro-

duction levels are lower due to the greater versatility and applicability of copper phthalocyanine. Ultramarine remains in use as an artists' color, however, in those cases where its hue cannot be replaced by another colorant and where cost is an essential factor - synthetic ultramarine is somewhat less expensive than copper phthalocyanine.<sup>310</sup>

ii. Composition and Structure

Chemically ultramarine blue may be regarded as a polysulfide of sodium aluminosilicate. Early theories<sup>54,209-11</sup> suggested that ultramarine was not one entity or molecular type, but two - a blue of high molecular weight and the basic silicates:  $\text{Si}_6\text{Al}_6\text{Na}_8\text{S}_4\text{O}_{24}$  and  $\text{Si}_6\text{Al}_6\text{Na}_6\text{O}_{24}$ . Today the artificial blue is thought to be an addition product of sodium aluminosilicate and sodium polysulfide having the general formula shown in Figure 43.

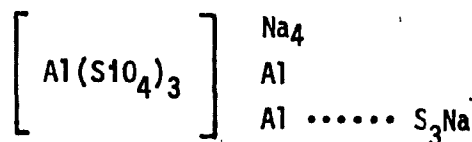


Figure 43. A General Formula for Ultramarine (halved for simplicity).<sup>228</sup>

This formula is not precise because ultramarine is really a kind of regular aggregation of atoms and ions having no constant composition corresponding to a single stoichiometrical formula. Different formulae exist for the products of different production processes. Even within any batch, the reaction produces a mixture of isomorphous and closely related ultramarines rather than one discrete type.<sup>226</sup> These different types of ultramarines, while having very similar colors and physical properties, vary in their aluminum, silica, sodium, and sulfur contents. Ultramarines with aluminum:silicon ratios as low as 1:1 are called 'sil-

'silica poor' and aluminum:silicon ratios approaching 1:1.6 'silica rich.'<sup>259, 358, 430</sup> The following table, based on three different production methods, illustrates three analogous products which differ in terms of their sulfur and sodium contents. All three types are commercially available.

Sulphate Process.	Sulphate-Soda-Process.	Soda-Process.
$\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ white	$\text{Na}_{12}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$ white	$\text{Na}_{14}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ (white) (unknown)
$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ green	$\text{Na}_9\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$ green	$\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ (green) (doubtful)
$\text{Na}_{7\frac{1}{2}}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ <u>blue</u>	$\text{Na}_{7\frac{1}{2}}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$ <u>blue</u>	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ <u>blue</u> (would correspond to the true blue pigment of lapis lazuli). It is also written as: $\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_6$ .
low sulfur	medium sulfur	high sulfur

Table 19. Three Ultramarine Types, all With 'Low' Silica Contents, With Varying Sulfur Content Based on Different Production Methods.<sup>226</sup>

It should be noted that these stoichiometrical formulæ are only approximate and do not actually have the exact, constant compositions indicated. Instead, the figures given are the average for an entire crystal.<sup>226</sup> A typical compositional analysis for artificial ultramarine is as follows:

Essential Components	Impurities
$\text{SiO}_2$ - 37.24	'free clay' - 1.46
$\text{Al}_2\text{O}_3$ - 27.78	'free sulfur' - 0.24
S - 13.54	$\text{Fe}_2\text{O}_3$ - 0.14
$\text{Na}_2\text{O}$ - 19.52	CaO - 0.06
	+ trace metals

Table 20. Typical Analysis of Artificial Ultramarine<sup>221</sup>

Although the exact constitution of ultramarine varies, a general structural model has evolved from various research undertaken over many years. For example, both natural and artificial ultramarines have been shown to be closely related to the natural minerals known as zeolites. Structural analysis and common properties of the zeolites has led to some understanding of the ultramarines.<sup>54</sup>

The zeolites are a mineral class characterized by hydrated alkali aluminosilicates made up of 3-dimensional networks of  $(\text{Si,Al})_n\text{O}_{2n}$  with balancing cations.<sup>412</sup> A similar matrix is found in lapis lazuli, indicating that it is essentially mineralized limestone. In thin sections under a microscope, lapis lazuli appears as a calcite structure in which are enclosed numerous blue and colorless granules. There are three different minerals: (a) haüyne (or nosean) - a colorless silicate of sodium and aluminum in combination with sodium sulfate ( $\text{Na}_4(\text{Na}_2\text{Ca})\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$ ), (b) sodalite - a colorless silicate of sodium and aluminum combined with sodium chloride ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ ), and (c) lazurite - a silicate of sodium and aluminum with sodium sulfides. The lazurite corresponds to ultramarine, although the composition and color of the natural pigment product is partially dependent on the relative amounts of all three minerals. Structurally, they are all addition compounds of a sodium aluminosilicate having the empirical formula:  $\text{NaAlSiO}_4$ .<sup>227</sup>

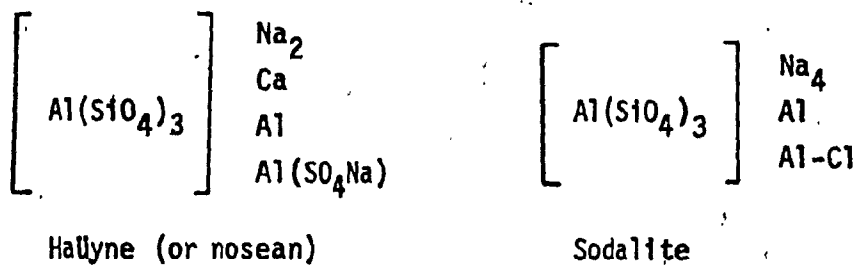


Figure 44.0 General Formuli for the Colorless Components of Lapis Lazuli.<sup>228</sup>

Like ultramarine, the composition of these minerals is never constant in nature. For example, the sodium in hauyne may be isomorphically replaced by calcium and vice versa.<sup>412</sup> Both ultramarine and the zeolites have been shown to have particles composed of molecules honeycombed with crevices and cavities. This open structure can loosely take up water, as well as gases and alcohols. Their alkali cations can be exchanged for other cations in solution.\* For example, the sodium cations in sodalite can be exchanged for  $\text{Ca}^+$  ions in solutions and then regenerated by passing a solution of sodium chloride through the mineral. The sodium in blue ultramarine can be replaced by silver through treatment with silver nitrate - yielding a yellow ultramarine. Ultramarines of other colors can be prepared by replacing the silver with other elements. Conversely, the blue can be reformed from the silver ultramarine by a sodium chloride treatment.<sup>412</sup>

The zeolites have the ability to take up from three to four sulfur atoms per molecule - probably in the form of polysulfides or  $\text{S}^{2-}$  and  $\text{SH}^-$  ions. In fact, the zeolites yield a blue product when treated with sodium sulfide solution at  $200^\circ$  under pressure. This product is very similar to ultramarine in terms of properties and x-ray diffraction patterns.<sup>419</sup>

The first x-ray diffraction studies of ultramarines were performed by Jaeger in the late 1920's.<sup>225,422</sup> He found that the powder spectra of all artificial ultramarines had identical patterns, irrespective of their color, shade, or chemical composition (e.g., high and low silica and sulfur contents). The blue ultramarines had patterns similar to

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\* This property makes them useful as a water softening agent.<sup>412</sup>

those of haüyne (or nosean) and the silver ultramarine.\* In the latter case, there was no significant change in the spacings of the lines, but slight differences were seen in their relative intensities. Insertion of smaller cations, such as lithium, in the ultramarine caused only a slight shrinking of the alumino-silicate structure.

Jaeger's x-ray diffraction studies led him to propose two possible structures for the ultramarine based on a simple or body-centered cubic lattice of uncertain symmetry (Figure 45).<sup>229,422</sup>

The unit cell in Jaeger's model contains 24 atoms of oxygen, six silicons, and six aluminum atoms ( $\text{Al}_6\text{Si}_6\text{O}_{24}$ )<sup>6-</sup>. The ionic radii of aluminum and silicon allow atom-for-atom replacement of silicon in the structure by aluminum and vice versa. Therefore, the number of silicon and aluminum atoms may vary from cell to cell so that the ratio of silicon to aluminum is actually a statistical average.<sup>228</sup>

Jaeger proposed two possible arrangements for the Si, Al, and O atoms within the cells. The first is a tetrahedron in which "each lateral face of the elementary cell (has) two aluminum and two silicon ions, each surrounded by four tetrahedrally placed oxygen ions."<sup>231</sup> The other model has two 6-fold positions in each cubic cell into which the silicon and aluminum are distributed with oxygen bonded to them around the cell. This model is more likely, according to Jaeger, since he determined that the tetrahedral model would necessarily require a closest-packed arrangement which he considered to be contrary to the low refractive index of the ultramarines. He also suggested that this type of structure might not allow space for the sodium ions.<sup>230</sup>

\* Sodalite exhibited a different pattern from both the ultramarines and the remainder of the zeolites studied.



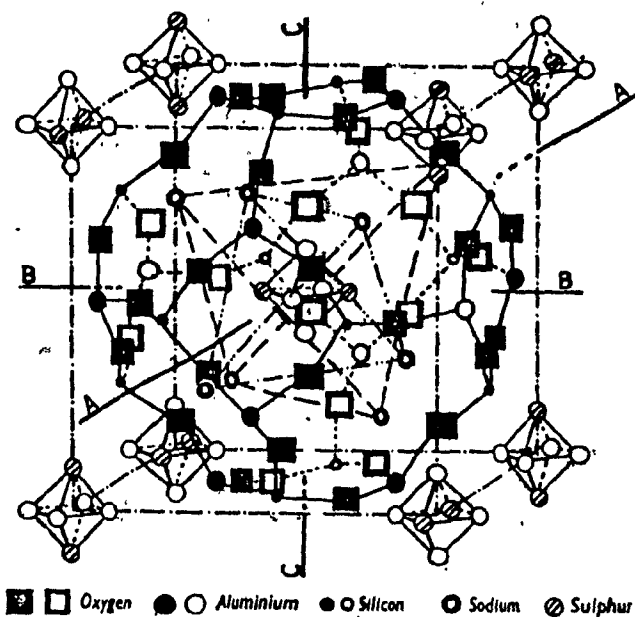


Figure 45. A Body-Centered Cubic Lattice for Ultramarine Based on Jaeger's Proposed Structure.<sup>422</sup>

A tetrahedral model was favored, on the otherhand, by Kumins.<sup>255</sup> As in Jaeger's model, the aluminum and silicon atoms occupy the center of each tetrahedron in a manner similar to carbon in methane. At the corners of the tetrahedral unit lie the oxygen atoms. Each of these is shared with the adjacent tetrahedron so that the equivalent of only two full oxygen atoms would be associated with each central element.

In either model, the metal atoms are considered to be ionized so that aluminum is present as  $Al^{3+}$  and silicon as  $Si^{4+}$ . Since each metal is associated with two oxygen atoms, it follows that a pair of joined tetrahedra involving one  $Al^{3+}$  and one  $Si^{4+}$  would have a charge of +7 while its four bonded oxygens would contribute a -8 charge leaving a net charge of -1 for the basic or minimal tetrahedral group. Presumably the balancing cation would be sodium. When the charge of the anion component is raised by the replacement of a silicon atom by aluminum, two sodium ions

would be needed to balance the tetrahedral unit while two silicons would require no sodium.<sup>255,422</sup>

Jaeger<sup>229</sup> could not locate the sodium ions through x-ray diffraction and consequently suggested that they could 'wander' through the lattice and so occupy random positions within the periodic alumino-silicate framework. While both Kumins<sup>255</sup> and Hoffman, Podschus, and Leschenski<sup>212</sup> agree that sodium is probably distributed randomly, neither group of workers assumes that it is necessary that these ions 'wander' in the lattice. Kumins<sup>255</sup> suggests that the sodiums are positioned so that they most effectively neutralize the whole molecule while Hoffman, et al, postulate standard locations for eight large cations in the lattice. Since ultramarines invariably contain less than eight atoms of sodium, it was suggested that these ions are statistically distributed among the eight available spaces.

The fact that the sodium ions seem to have no specific location within the crystal lattice may account for the ion exchange properties of the ultramarines. That is, the positions occupied by the charge-balancing sodium ions are likely the same as for ions or water taken up from solutions.<sup>232</sup>

Two types of polysulfides, differentiated by their location, appear to be present in the ultramarines. Clathrate compounds are probably formed with  $S_2$  polysulfides<sup>232</sup> since a bond between sulfur and the silicate framework does not seem probable. The polysulfide group is believed to be contained within the cavity or open structure formed by joining the tetrahedra at each corner.<sup>255,423</sup> The enclosed or sandwiched  $S_2$  is trapped within the alumino-silicate framework when it is formed and remains incapable of escaping as long as the crystal structure is intact.<sup>257</sup>

Support for this can be found in earlier work by Bock<sup>54</sup> who found that one-quarter of the sulfur in ultramarine blue was bound in some way to the aluminosilicate framework while three-quarters was free and could be precipitated. Other studies<sup>423</sup> indicate that ultramarine sulfur is completely nonvolatile and resistant to oxidation (for example, on fusion with sodium nitrate at 550°). Therefore, the polysulfide groups must be present in very firm combination (such as clathrates) with the molecule. In low sulfur ultramarines (see Table 19), this enclosed S<sub>2</sub> accounts for the majority of the sulfur. In ultramarines containing as many as four sulfur atoms per crystal unit (high sulfur ultramarines), the excess sulfur is probably present as S<sub>3</sub>, S<sub>4</sub>, etc. sodium polysulfides which occupy interstitial spaces.<sup>232</sup> Some sulfur may also be present as radicals since they have been found in both natural and artificial ultramarine by paramagnetic resonance experiments.<sup>155</sup>

In general, artificial ultramarines are not 'pure' in that they contain small amounts of free sulfur, silica, and alumina. The latter two are generally known as 'free clay' (after China clay or kaolin, one of the starting materials in ultramarine synthesis) which arises from material unreacted in the formation of the ultramarine. The free sulfur, which can be extracted as such with carbon bisulfide,<sup>95</sup> is invariably present as less than 1% of good quality ultramarine. According to Barry,<sup>35</sup> this small amount of excess sulfur does not appear to have any influence on the color or permanence of the pigment.

### iii. Color Effects in Ultramarine

The color component in the ultramarines may be small since small changes in the total molecule result in completely different colors. For instance, changes in either the sodium or sulfur content yield compounds

ranging from colorless to pink, violet, blue, and green. Replacement of the alkali by lithium gives a warmer violet than the blue sodium ultramarine.<sup>233</sup> Calcium and zinc ultramarines are nearly colorless and silver ultramarine is yellow.<sup>233</sup> Similarly, other ultramarines are prepared by heating the parent ultramarine with salt solutions of potassium, magnesium, barium, lead, and other metals. These changes are based on replacement of the sodium. A similar phenomenon is observed for the replacement of the sulfur. For example, the substitution of varying amounts of selenium for the sulfur gives a color range from pink, through blood-red, to brown.<sup>233</sup> Violet and red ultramarines are obtained by hydrating or acidifying ultramarine blue (see Appendix A).\*

Jaeger<sup>225</sup> found that the diffraction patterns of ultramarines of all colors were identical, indicating that the exchange reaction did not alter the basic crystal structure. In spite of this structural similarity, however, only the blue sodium ultramarine has any commercial importance, due mainly to the generally weak color of the other ultramarines. The green does find some use as an artists' color and the violet is occasionally used to eliminate the yellow tinge in certain types of clear plastics.

While it was originally believed that the color in ultramarine blue was due to colloidal sulfur, this was proven incorrect by x-ray data which showed no space available for colloidal particles in the unit cell, as well as by chemical tests which showed the sulfur to be completely nonvolatile.<sup>423</sup> Instead, the blue chromophore seems to be associated with the highly resonant alkali polysulfide groups and this may be modified or enhanced by some unknown interaction with the electronic structure of the crystal cavity or framework.<sup>233</sup>

\* The approximate formula for ultramarine violet is  $\text{Na}_5\text{HAl}_4\text{Si}_6\text{S}_4\text{O}_{24} + \text{H}_2\text{O}$ .

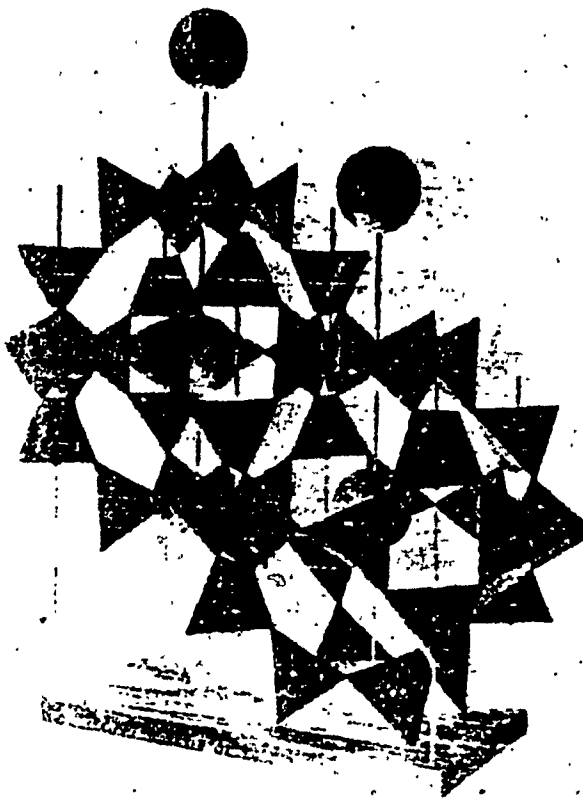
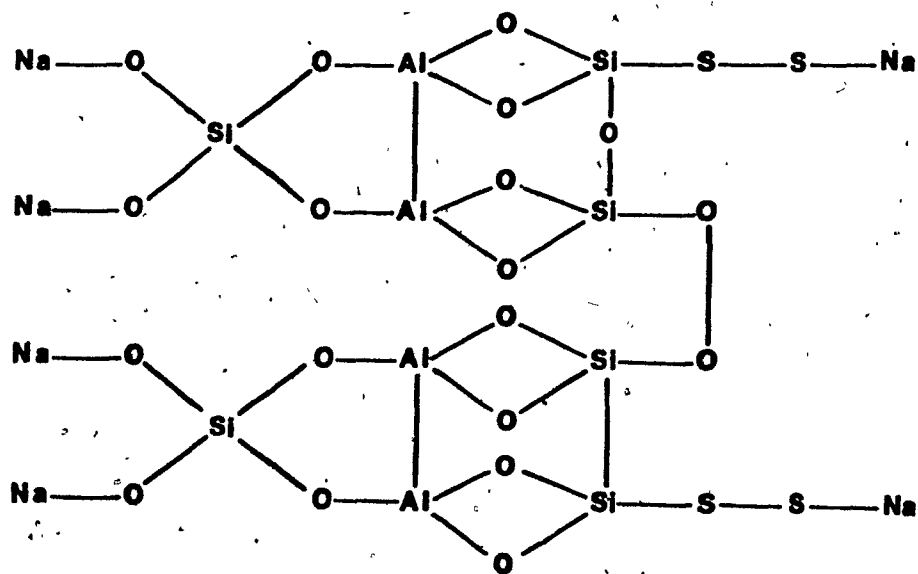


Figure 46. A Three-Dimensional Model of the Crystal Structure of Ultramarine Blue. The corners of the tetrahedra are occupied by oxygen atoms and the interior by either aluminum or silicon. Balls represent sulfur in the interstitial spaces.\* <sup>255</sup>

\* A structure with a bonding of four oxygens with each silicon atom but with a covalent (rather than ionic) bond between both sodium and oxygen and sodium and disulfide and a different arrangement around the aluminum was proposed by Hoffman (Liebig's Ann., 194(1878) 1): <sup>358</sup>



In general, the tinting strength of ultramarine blue is much less, by a factor of 15, than copper phthalocyanine blue, but this is variable. That is, the shade and depth of color depends on the amount of sulfur present, becoming more intense as the degree of sulfuration increases.<sup>256</sup> Table 21 gives an approximation of the type of changes which can occur with varying sulfur content.

<u>Approximate Chemical Formula</u>	<u>Shade</u>
$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$	light
$\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$	medium
$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$	dark

Table 21. Changes in Shade Based on Changes in Sulfur Content for Ultramarine Blue.

Large variations in sulfur are possible and a useful color can persist during chemical reactions which involve the loss of almost three-quarters of the sulfur.<sup>424</sup> The color does not actually disappear until either the sulfur is eliminated or the crystal lattice is destroyed. According to Kumins,<sup>256</sup> the best commercial colors contain as much as 15% sulfur. He also found that an ultramarine containing 2-4% sulfur improved its coloring power proportionately as the pigment was calcined in an  $\text{H}_2\text{S}$  atmosphere and as the sulfur content increased to 10%. Similarly, the intensity of blue is heightened by forcing a greater number and longer length of S-S chains into the crystal lattice.<sup>256</sup>

The shade of ultramarine blue may also be modified by the silica and related alumina contents. For example, the higher the silica:alumina ratio, the warmer and redder is the pigment. Conversely, the lower the ratio (or the less silica present), the greener and less warm the pigment color. Remarkably, changes in the silica and aluminum ratio do not

affect the covering power of the ultramarines as long as the silica content does not get too large. In other words, even though the structure of ultramarine blue is variable, i.e., aluminum may replace silicon and vice versa, their diffracting powers are almost identical.<sup>232</sup> According to Insley and Ewell,<sup>221</sup> this no longer holds when the silicon content becomes excessive. They found that a high silicon content inhibits crystallization causing a drop in tinctorial power.

The shade of ultramarine blue is also apparently sensitive to alterations in grinding time. In general, an average particle size of 3-4  $\mu$  diameter gives a pigment of dark, reddish shade and low tinting strength while smaller particles with an average diameter of 0.5-1.0  $\mu$  are paler, greener, and possess a higher tinting strength.<sup>412</sup>

#### iv. Properties

The ultramarines are extremely stable to alkali but are decomposed and decolorized by dilute acids with simultaneous liberation of some of the sulfur as  $H_2S$ .<sup>106,171,451</sup> For this reason, although the ultramarines are stable to light and most other degradative phenomena, they should not be used in either acid media or paint films exposed to acidic environments. Fading under these conditions is generally very fast, variations mainly being due to the composition of the medium. For example, fading is said to be slowed somewhat if the paint medium contains a high proportion of phenol-formaldehyde resins.<sup>412</sup>

It is interesting to note that while both the natural and synthetic ultramarines appear to be the same in terms of color and apparent structure as determined by x-ray diffraction, according to Toch,<sup>429</sup> the genuine ultramarine is not as quickly affected by acids. An acid resistant type of artificial ultramarine has been patented,<sup>381</sup> however, wherein

finished pigment particles are coated with a silica or silicic acid coating by treating with  $H_2SO_4$  and boiling off the  $H_2S$  evolved. The pigment is then mixed with sodium silicate in a water solution, followed by calcination at  $600^\circ$ . The acid resistant product is said to have a tinctorial strength one-half that of the original material.

Ultramarine blue acts as a negative colloid and displays extremely active Brownian movement when observed under the microscope.<sup>412</sup> Because of its negative colloid nature and ready dispersion in water, ultramarine has traditionally been used as a laundry blue where its high reflectivity for blue light tends to neutralize the yellow component in the light reflected from white fabrics.

Ultramarine blue also possesses definite hydrophilic properties. In the absence of special treatment, it migrates from the oil to the water phase of a dispersion in oil mixed with water.<sup>412</sup> Consequently, mixture of the pigment into an oil medium cannot be done by the flushing process useful for most pigments. Instead, ultramarine must be thoroughly dried before grinding into a non-aqueous paint medium.

Other properties of ultramarine blue are listed in Table 22. Although these pigments have identical x-ray spectra, because they are isomorphous mixtures of analogously constituted substances, they display varying physical constants. Unlike the other pigments discussed in this paper, many of the analytical values, such as specific gravity, vary from manufacturer to manufacturer and even batch to batch, so that the values are given in Table 22 as a normal range.

#### v. Experimental

Variations of Guimet's synthetic process for the preparation of ultramarine are still in common use today. These methods generally in-



volve a fusion of kaolin, sodium carbonate ("soda ash" in most old pigment chemistry literature),\* sodium sulfate ("Glauber's salts"), sulfur carbon (in a form such as rosin or pitch), and Kieselguhr (a diatomaceous earth)\*\* in the absence of air at red heat for, from 1 to 5 days.<sup>106</sup> Two alternate methods are possible. The 'direct process' produces the blue without further addition of substrates while the 'indirect process' produces a green ultramarine\*\*\* first. This is then converted to the blue by mixture with sulfur and reheating. In both cases, the blue product is cooled, wet ground, levigated, ground again, and then standardized by mixture of the various batches to make the finished pigment powder.

\* Kaolin (or China clay) is a hydrated alumino-silicate of the following composition:

Silica (SiO <sub>2</sub> )	45-47%
Alumina (Al <sub>2</sub> O <sub>3</sub> )	36-39%
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.4-2%
Lime (Ca)	0.4-1.2%
Magnesium Oxide (MgO)	0.1-0.2%
Alkalies (K <sub>2</sub> O)	0.2-0.8%
H <sub>2</sub> O	11-13% 359

Its principle use is as a raw material for the ceramics industry.

While kaolin is relatively inert, it is claimed to impart a soft and light color when added as a filler to certain colors such as the lead-eosine lakes.<sup>113</sup> Apparently kaolin has the property of forming "strong, continuous films" when used in water paints because its "particle shape (helps it) knit together in the film."<sup>195</sup>

Both kaolin and sodium carbonate should be well-calcined (usually at 800°) before use in the fusion reaction to remove chemically combined water.<sup>232</sup>

\*\* Kieselguhr is a loose or porous diatomate which is a friable siliceous material derived from diatom remains. Its main use is as a filtering material. Rosin is a resin that is obtained by chemical means from the oleo resin of dead pine wood and is used in the production of varnish paper, size, soldering flux, and as a surface conditioner on violin bows. Pitch is a residue from the distillation of tars and other organic materials.

\*\*\* Ultramarine green, a double silicate of aluminum and sodium containing oxygen and sulfur, is approximately Na<sub>5</sub>Al<sub>3</sub>Si<sub>3</sub>S<sub>2</sub>O<sub>12</sub> or Na<sub>8</sub>Al<sub>6</sub>Si<sub>6</sub>S<sub>2</sub>O<sub>24</sub>.<sup>106</sup> This pigment is sometimes used as an artists' color.

The hue varies from a pale greenish blue to violet depending on the silica-alumina ratio.

Table 22. Physical Properties and Other Data for Ultramarine Blue (CI Pigment Blue 29; CI 77007).

		Reference
Chemical Class	Inorganic	96
Hue	Bright Violet to Bright Bluish Green	
Chemical Composition	Al:15.8 - 17.6 Na:15.0 - 17.9 O: 37.5 - 42.0 S: 7.0 - 12.5 Si:16.3 - 18.4.	311
Fastness Properties		
1. Organic Solvents	insol	96
2. Light	excellent	
3. Heat	stable to 300°	
4. Water	insol	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	poor (decolorized)	
7. Linseed Oil	v. good	
8. Oleic Acid	insol	
9. Soap Gel Bleeding	none	
Density	2.20 - 2.70 g/cm <sup>3</sup>	311
Specific Gravity	2.34 2.50	311 + 169 42
Oil Absorption	25-39 lb/100 lb.	311
Tinting Strength	fair-poor	
Particles	uniformly small, rounded grains	169
Standard	BS 314:1968 USA Fed. Spec. TT-P-450(2) ASTM D 262-47(1969)	106

The direct process may be carried out in either a kiln or muffle furnace\* with the materials mixed or ground intimately in one of the proportions given in Table 23. Note that because ultramarine is not a single chemical compound, the proportions of starting materials can be varied within fairly wide limits.

The mixed starting material is placed in the kiln, which is then sealed to avoid the free access of air to the substrates. The kiln is then heated to approximately 800° over a period of ten hours and this temperature is maintained (usually for several days) until the following test is successful: A sample from the kiln is placed on a tile and half covered. If, after cooling a few minutes, the exposed area is blue and the covered portion green, the sealed kiln is cooled over a period of 6-8 days. Apparently faster cooling and exposure to air of the hot ultramarine would dull it. So the primary green ultramarine is oxidized slowly by air which diffuses through the door of the kiln. The final shade of the ultramarine is said to develop as the temperature approaches that of the surrounding atmosphere.<sup>360,420</sup> 'Raw' ultramarine obtained by this method contains 20-25% sodium sulfate.<sup>361</sup> This is leached out with water from the insoluble ultramarine which is then wet-ground between flat stones yielding particles ranging from 0.5  $\mu$  to 5  $\mu$  in diameter. These are separated by levigation and then remixed to obtain the desired shade.

The muffle process is similar to the kiln process, the difference being that the starting materials are placed in covered crucibles before heating so that loss of the surface scum which is necessary in the kiln

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\* Commercially, heating is done in large kilns or furnaces with the mixed ingredients in pots 9½" wide x 11" deep. An average kiln holds 440 of these pots.<sup>360</sup>

## A. Kiln Process:

	I	II	III	IV	V	VI	VII
Kaolin (China Clay)	80	70	70	764	76	75	78
Sulfur	85	85	70	826	78.5	73	79
Soda Ash	67	69	63	756	66	67	65
Silica (SiO <sub>2</sub> )	12	36	4	140	24	24	20
Rosin	12	12	4	108	14	--	--
Sulfide of Soda	--	--	--	--	5	--	--
Salt Cake	--	--	--	--	4	--	10
Pitch	--	--	--	--	--	11	12

## B. Muffle Process:

	I	II	III	IV	V	VI <sup>97</sup>
Kaolin (China Clay)	78	80	84	70	65	100
Sulfur	80	80	80	83	83	100
Soda Ash	60	58	60	62	62	150
Silica	10	9*	--	--	--	10-15
Rosin	12.5	12.5	13	12.5	13	30
Sodium Sulfide	--	--	--	3	--	--
Salt Cake	7	10	7	8	8	--
Kieselguhr	--	--	10	20	25	--

\* quartz silica

C. General or Typical Mixtures <sup>913</sup>

Color	Light	Medium	Dark
Kaolin (China Clay)	100	100	100
Sulfur	16	50	117
Soda Ash	8	100	103
Silica	--	--	16
Carbon	24	4	16
Sodium Sulfate	120	--	--

Table 23. Typical Mixtures for the Synthesis of Ultramarine Blue (reference 360 except as noted).

process (due to excess oxidation) is eliminated.<sup>37</sup>

The second general method, the indirect process, involves first the production of the green ultramarine in crucibles as before, followed by cycles of grinding with sulfur, reheating for 30 minutes to a temperature which ignites the sulfur,<sup>37</sup> and then regrinding with sulfur, etc., until the total weight of sulfur added is 7-9% of the original raw ultramarine. The sulfur content derived from this method is slightly higher than from the direct process.\*

We initially attempted a direct process carried out in a muffle furnace:

50 g calcined kaolin, 50 g calcined sulfur, 75 g sodium carbonate, 10 g silica, and 15 g of charcoal were mixed in a porcelain crucible and the crucible placed in a muffle furnace. This was heated to 750-800° over approximately 9 hours. After heating (3 days) and cooling (three more days), the mixture remained a dull, mottled gray. Two more test samples were mixed and this time the pots were sealed with ceramic clay. These were heated as before with similar results. Ignition of the gray product mixed with sulfur (as per the indirect process) resulted in no change.

That the process may be delicate in spite of the wide variation of possible starting materials was evident. A more controlled process will be outlined now.

#### vi. Notes on the Reaction

Certain built-in defects are inherent in the laboratory muffle furnace process. As outlined by Agte, et al.,<sup>7</sup> these are: (a) the process is too long, (b) the furnaces work intermittently to maintain only an approximate temperature, (c) the atmosphere regulation is irregular so

\* Different degrees of sulfuration may also be obtained by changes in the original mixture. Jaeger<sup>226</sup> calls these (a) a 'sulfate process' when only sodium sulfate and wood charcoal are mixed with the silicate mass, (b) a 'soda sodium sulfate process' when the silica is heated with a mixture of sodium sulfate, sodium carbonate, sulfur, and tar, and (c) a 'soda process' when the silica is mixed with soda ash, sulfur, and tar. The last, for example, may be used in the preparation of silica-rich ultramarines.

that a variety of products may be obtained, (d) it is impossible to take samples during ignition (in the kiln process, a special door allows this to be done), and (e) fireclay crucibles of uniform porosity are essential. In addition, the patent and other literature is lacking in terms of indicating precise conditions for the formation of ultramarine through calcination. Because conditions in the laboratory are not the same as in production, the quality of ultramarines obtained from the usual lab crucible and muffle furnace is poor. Since it is impossible to create the required atmosphere and other conditions during different periods of calcination with this equipment, a special setup is required. Some of the requirements of such an apparatus will now be discussed.

During the initial stages of the heating process, amorphous silica and alumina (produced by destruction of the kaolin crystal structure during calcination between  $550^{\circ}$  and  $950^{\circ}$ ) fuses with sodium carbonate to produce a zeolite structure. Simultaneously, the carbon, pitch, or rosin in the reaction mixture assists in the reduction of some of the sodium salts and sulfur to polysulfides and alkali metal sulfides. Excess sulfur is required to drive this reaction in the direction of, for example, sodium tetrasulfide and sodium pentasulfide. Due to the high reaction temperature and length of time necessary for the reduction of alkali metal salts, sodium carbonate, and sulfate, higher polysulfides may not form in large quantities due to a loss of sulfur through volatilization. Since it is believed that the color intensity, tinting strength, and hiding power of the pigment depend at least in part on the amount of sulfur carried into the crystal lattice by the sodium, the formation of higher polysulfides is obviously extremely important. Not only is the presence of a reducing agent and excess sulfur essential, but there

should be a reducing atmosphere in the furnace and the mixture must be free from the action of atmospheric oxygen.<sup>256</sup>

The next stage involves trapping of the sodium polysulfides in the zeolite structure. While no conclusive evidence exists for placing this event either before or after final formation of the zeolite crystal lattice, some clues do exist. It is known, for example, that at the high temperatures of the reaction, the zeolite lattice contracts and so becomes less susceptible to the entrance of the relatively large polysulfides. It has also been shown that maximum inclusion of sulfur (15-16%) can be obtained by producing high sodium polysulfides at low temperatures (below the boiling point of sulfur) and forming the zeolite structure around it at higher temperatures. Thus, while it may be apparent that the polysulfide is formed before the crystal lattice, it should be noted that as yet, no evidence exists that the alumino-silicate structure does, in fact, form completely around the polysulfide.<sup>256</sup>

During cooling, ultramarine is slowly oxidized by the oxygen of the air to obtain the blue pigment. It is apparently essential that the access of air to the furnace should be carefully controlled. According to Kumins, "the oxidation art (of green to blue) is said to be one of the most jealously guarded secrets of the process," and all steps are "difficult to control."<sup>259</sup> In order to obtain this control, Agte, et al., suggest using the apparatus in Figure 47.

With the setup in Figure 47, the temperature in the furnace is maintained within  $\pm 7^\circ$  by a thermoregulator, the system is closed to free access by air, and the oxidation rate may be strictly controlled. In a series of experiments using this apparatus, these workers were able to deduce sets of parameters under which various types of ultramarine could

be obtained. First, it was determined that in a controlled reaction, the entire synthesis time could be greatly reduced (Table 24). During the first stage, the reaction tube is completely filled with starting material to eliminate or decrease the degree of volatilization of sulfur into the empty space of the tube. With this procedure, the best green ultramarine was obtained.<sup>10</sup>

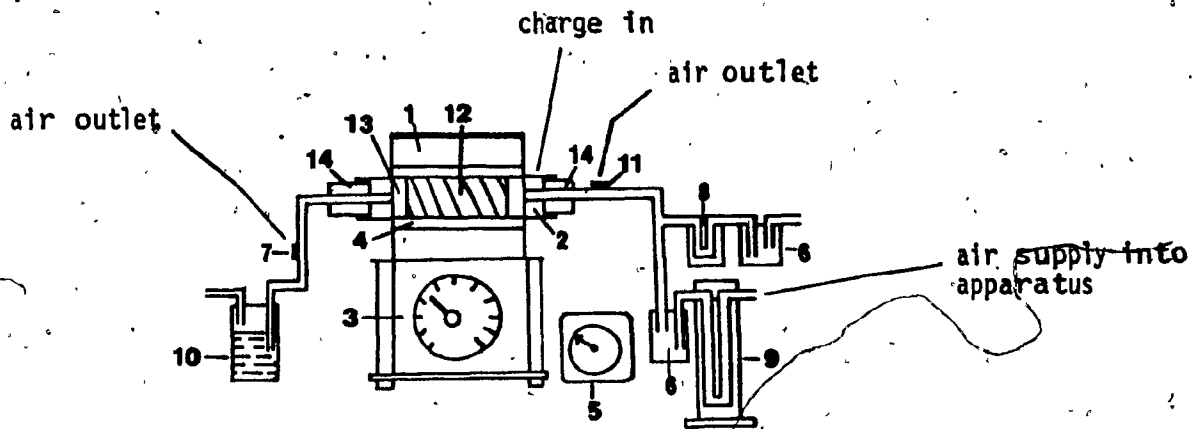


Figure 47. Suggested Setup for Producing Ultramarine in the Laboratory. 1) Tubular electrical furnace with thermoregulator; 2) porcelain tube (length 70 cm, internal 3 cm or, for another furnace 7 cm); 3) transformer; 4) thermocouple; 5) galvanometer; 6) catch pot; 7) clip; 8) manometer; 9) flowmeter; 10) liquid seal; 11) glass stopcock; 12) charge; 13) asbestos plug; 14) rubber bung.<sup>8</sup>

#### Running Conditions

	Temperature (in °C)	Time (hours)	
Rising	up to 300°	1.5	no airfeed
	from 300 to 450°	2.0	
	from 450 to 500°	0.5	
	from 500 to 730°	1.5	
Maintained at 730-750°		6.0-9.0*	with airfeed
Falling to temperature of oxidation		1.0	
Maintained at oxidation temperature		3.0-6.0	
	Total	16-22	

Table 24. Reaction Times for a Controlled Ultramarine Synthesis.  
\* Best ultramarine.



The second stage of the reaction, oxidation, was determined to be successful at a range of temperatures (Table 25), both high and low. It should be noted that while the best ultramarine is obtained at a low temperature because the process is more uniform, it is also slower. In addition, the time over which satisfactory oxidation products may be obtained at 400° is longer than at higher temperatures. At 630-650°, for example, the product is satisfactory after 3 hours but unsatisfactory if oxidized longer than that. Therefore, more control is obtained at 400°.

Temperature (°C)	Time of oxidation (in hours)	
	3	6
630-650	Satisfactory (product whitish)	Unsatisfactory (product whitish)
580-600	Satisfactory	--
530-550	Good	--
400-420	Satisfactory	Very good
330-350	Satisfactory (product greenish)	Good
260-280	--	Good
200-220	--	Unsatisfactory (product greenish)

Table 25. Oxidation Times and Temperatures for Ultramarine.<sup>9</sup>

Agte, et al., determined the optimum airflow rate (0.12-0.20 l/min.) and oxidizing agent (pure air). While the calcination reaction was best performed in a completely filled tube, the oxidation step was fastest and said to give the best product when the tube was less than 100% filled (see Table 26). As can be seen, the conditions of calcination and oxidation differ (in terms of the degree of filling of the tube) so that it is probably more convenient to carry them out in separate furnaces. However, if this is not possible or if identical degrees of filling are desired, this should not be less than 50%. With a lesser filling of the tube, low-sulfur, green ultramarine is obtained and consequently a poor quality blue

material derived from it.<sup>10</sup>

Degree of filling in % calcination	Time of oxidation (hours)	Stirring	Quality of products
100	100	Without stirring	Good
100	20	With stirring	
100	80	Without stirring	
100	80		Very good
75	75	With stirring	
50	50		Satisfactory
25	25		Unsatisfactory

Table 26. The Effect of the Degree of Filling of the Reaction Tube on Oxidation Time and the Quality of the Ultramarine Blue Product.<sup>10</sup>

#### vii. Commercial Uses

Ultramarine is especially useful as a pigment where fastness to lime or alkali (except calcium hydroxide which decomposes it) is required. It is generally unsuitable, on the otherhand, in acid media, although acid resistant brands have been claimed. Presently, ultramarine blue is used in paints, paper coloring and coating, wallpaper, rubber, plastics, soap, and artists' colors.<sup>96</sup> Although ultramarine generally has poor ink properties because of its relatively large particle size and hydrophilic character, specially finished brands are sometimes used in printing inks and cosmetics.<sup>412</sup>

#### F. Cobaltous Aluminate Blue (CI Pigment Blue 28; CI 77346)

##### i. History

A deep blue potassium silicate glass colored with oxides made from cobalt ores has been known since the mid-1500's. For use as a pigment, the glass was finely pulverized and sold as "smalt."<sup>185</sup>

Between 1802 and 1804, Thenard produced a number of cobalt compounds in his laboratory, including cobaltous aluminate. Because Thenard's co-

balt blue was cheaper to produce than natural ultramarine, it was a quick commercial success, becoming known as cobalt ultramarine even though it was a much deeper blue.<sup>202</sup> Today, because artificial ultramarine is even less expensive, it has replaced cobaltous aluminate as a pigment except for specialized uses such as artists' colors. It is interesting to note that this blue is not easily reproduced by color photography since no combination of the "cyan" (copper phthalocyanine blue) and other components of photographic emulsions can match its reflective properties.<sup>364</sup>

#### ii. Composition and Structure

Individual cobalt pigment particles are moderately fine, irregular but rounded grains.<sup>165</sup> Chemically, they are considered to be a cobalt/aluminum oxide having the formula  $\text{CoO} \cdot \text{Al}_2\text{O}_3$ . Hedvall,<sup>201</sup> Natta and Passerini,<sup>308</sup> and others, however, have shown that, in fact, this formula is only general, the relative amounts of  $\text{CoO}$  and  $\text{Al}_2\text{O}_3$  being variable. The theoretical composition for this blue is cobalt - 33%, aluminum - 30.5%, and oxygen 36.2% by weight. Commercially, these percentages deviate within fairly wide limits. For example, the amount of cobalt present may be between 15 and 28% with the theoretical 33% rarely found in practice.<sup>364</sup> It should be noted, however, that the intensity of the blue product depends on the percentage of cobalt present.

Cobaltous aluminate has been shown to be a solid solution of  $\text{CoO}$ , (in the form of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_6\text{O}_7$ )<sup>153</sup> and  $\text{CoO} \cdot \text{Al}_2\text{O}_3$  with an excess of  $\text{Al}_2\text{O}_3$ .<sup>203</sup> The  $\text{Al}_2\text{O}_3$  serves as a support for the blue cobalt oxide. Natta and Passerini<sup>326</sup> found that powder spectra of cobaltous aluminate blues possessing a variety of compositions exhibited similar patterns. Differences were seen only in the intensity of the lines.

### iii. The Family of Cobalt Colors

The tone and opacity of cobalt blue can be altered by the introduction of small quantities of other oxides, phosphates, and arsenites. For example, cobalt violets may be obtained by precipitating a cobalt salt with phosphates, drying, and igniting; by ignition of cobalt ammonium phosphate; and by precipitation with a pyrophosphate. A violet cobalt ammonium arsenate, as well as a cobalt pyroarsenate are commercially produced. The presence of the arsenates in these pigments is an obvious disadvantage and so they are not commonly used as artists' colors.<sup>150</sup>

A greenish-blue known as 'New Blue' is produced by mixing aluminum with the carbonates or hydroxides obtained from precipitating soluble chromium and cobalt salts. Presumably, the product is a cobalt-chromium aluminate.<sup>150</sup> Cerulean blue, the stannate analog of cobalt blue, is made by precipitating a cobalt salt with sodium stannate, drying and igniting the precipitate. This blue contains as little as 18-19% CoO. Cobalt oxide is also present in the pigment known as Rinmann's Green. Here, zinc oxide replaces the alumina of cobalt blue - mixtures of soluble cobalt and zinc salts (carbonate or phosphate) are precipitated and then ignited at carefully regulated temperatures. Rinmann's Green contains about 70% ZnO and from 11% or more of cobalt oxide.<sup>150</sup>

### iv. Physical Properties

Although cobaltous aluminate possesses a low tinctorial strength and low covering power, it is extremely permanent, being resistant to chemical attack by both the atmosphere and medium. Cobaltous aluminate is insoluble in strong acids and alkalies and is unaffected by heat, solvents, or sunlight.<sup>414</sup> In addition, it does not react with either media (including nitrocellulose lacquers) or other pigments. For these reasons, cobaltous

aluminate can be used in all painting techniques, including, for example, fresco painting where extreme alkali resistance is crucial. Similarly, its special heat resistance allows it to be used for the blue coloring of ceramic glazes. Other physical properties and data are given in Table 27.

#### v. Experimental

The Color Index<sup>96</sup> gives the following general methods for the synthesis of cobaltous aluminate:

1. Thenard's Blue - precipitate cobalt nitrate (free from iron or nickel) with sodium phosphate, wash well the violet precipitate of cobalt phosphate and mix with freshly precipitated alumina. Dry the mixture and calcine until the requisite blue is obtained. The reddish blue product is ground with water and dried. The hue is improved by addition of sodium phosphate or ammonium-magnesium phosphate.
2. Fuse alumina, zinc oxide, and  $\text{Co}_3\text{O}_4$  at  $1300^\circ$ .
3. Precipitate a cobalt salt with aluminum and sodium carbonate or phosphate and calcine.\*
4. Fuse aluminum sulfate, cobalt sulfate, and ammonium alum at  $1350-1700^\circ$ , wet grind, neutralize with ammonia if free  $\text{H}_2\text{SO}_4$  is present, dry and grind.

Another old method, given by Fox,<sup>150</sup> involves precipitating a cobalt salt with potassium phosphate, mixing the precipitate with about four times its volume of freshly precipitated aluminum hydroxide, drying and calcining. Cobaltous aluminate blue is also sometimes produced from calcination with a flux such as  $\text{KCl}$ ,<sup>203</sup> or with other oxides like magnesium. These products are claimed to be more satisfactory blues than the pure pigments.<sup>150</sup> For these and other alternate preparations, see Appendix A, p. 181.

For this project the preparation used was given by Harrison,<sup>196</sup> with

\* The arsenate derivative, Leithner blue, is prepared similarly using cobalt arsenate and alumina.

Table 27. Physical Properties and Other Data for Cobaltous Aluminate Blue (CI Pigment Blue 28; CI 77346).

		Reference
Chemical Class	Inorganic	96
Hue	Pure Blue with a slightly Violet shade in artificial light	
Theoretical Composition	Co - 33.3 Al - 30.5 O - 36.2	184
Fastness Properties		
1. Organic Solvents	insol in all	96
2. Light	excellent	
3. Heat	stable to 900-1000°	
4. Water	insol	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	unalt	
7. KHSO <sub>4</sub>	decomposes	204
Density	4.2 - 4.3 g/cm <sup>3</sup>	184
Specific Gravity	3.83	169
Refractive Index (max.)	1.74 <sub>blue</sub> (n + variable)	
Particle Size	0.5 - 1.0 μ	184
Oil Absorption	27.0 - 36.0 lb/100 lb	
Tinting Strength	poor	
Hiding Power	good to fair (gen. opaque)	
Dispersibility	excellent to good	
Toxicity	excellent to good	
Standard	BS 2876:1957	96

modifications by Remington and Francis:<sup>364</sup>

28 pounds of cobalt (in 100 gal. water<sup>364</sup>) and 240 pounds of potash alum (in 500 gal. water<sup>364</sup>) are dissolved separately and run into a mixing vat when both solutions are at 20°. To this mixed solution

sufficient 10% sodium carbonate solution is added very slowly, until precipitation is just complete. The product is filtered, washed, and dried to a hard cake which is then placed in a clean porcelain pot and heated in a muffle at a "dull red heat: (650-700°<sup>364</sup>) for 1/2 - 3/4 hour. The product is ground in a porcelain ball mill with white spirit containing approximately 0.5% linseed oil fatty acids. The brilliant blue is said<sup>364</sup> to develop during this grinding and the product should have a fine particle size and be very soft.

We prepared aqueous solutions containing 3.7 g cobalt acetate in 100 ml and 24 g potash alum in 500 ml and allowed them to come to room temperature. Addition of a 10% sodium carbonate solution immediately yielded a mauve suspension. Since this precipitate did not settle out, the reaction end point could not easily be determined. Consequently, a small, clear portion from the top of the solution was removed and an aliquot of 10% sodium carbonate added to this. When no precipitate was formed in this test, the reaction was terminated and the suspension filtered, washed, and dried to a cake which was calcined at 650-700° for 45 minutes. A jet black small grained product was obtained. Grinding in mineral oil did not bring about any significant color change.

The reason for the failure to produce a blue pigment was likely due to calcination at too low a temperature. Hackman<sup>184</sup> says that cobaltous aluminate blue is produced at temperatures between 593 and 1371°, the higher temperatures giving a more heat resistant product. According to Fox,<sup>150</sup> on the otherhand, calcination produces a black oxide at about 800° with the blue being formed at higher temperatures. Further evidence<sup>203</sup> has established that the calcination reaction is complete by 1100°. Heating to 1300-1400° converts the blue to a green having a composition somewhere between  $\text{CoO}\cdot\text{Al}_2\text{O}_3$  and  $4\text{CoO}\cdot 3\text{Al}_2\text{O}_3$ .<sup>205</sup> With this information in mind, we recalined our black product to approximately 1050° and a dark blue product was obtained.

#### vi. Commercial Uses

Commercial usage of cobaltous aluminate blue pigment for applications other than as an artists' color is limited because of its high cost (it is one of the most expensive blues available) and weak tinting strength.<sup>185</sup> However, due to its extreme stability, cobalt blue is sometimes employed in the manufacture of colored glass, bank note printing, special paints (e.g., heat resistant paints), lacquers, plastics (where it resists migration and bleeding), and rubber.<sup>96</sup>

#### G. Titanium Dioxide White (CI Pigment White 6; CI 77891)

##### i. History

Although titanium is the 9th, most abundant element - 100 times more common than zinc, lead, and copper<sup>213</sup> - it was not discovered until 1791 when an English minister, William Gregor, first noted the oxidated form, titanium dioxide ( $TiO_2$ ).<sup>356\*</sup> Titanium was considered a rare element for many years, although it is, in fact, widely dispersed in combination with oxygen, aluminum, and silicon. John Overton first recommended the use of the white titanium dioxide as a pigment in 1870, but purification and production problems hindered this development<sup>93</sup> until the beginning of this century. The first successful methods were an American process (Barton and Rossi) which involved fusion of powdered rutile  $TiO_2$  crystals with nitric acid and coke in an electric furnace, and a Norwegian process (Famp and Jobsen) which involved dissolving ilmenite ( $TiO_2$ ) ore in sulfuric acid, followed by reprecipitation of the  $TiO_2$ .<sup>27</sup> This proved to be a superior method and is the principle one used today.<sup>356</sup>

During the 1920's, the sulfuric acid process was improved to the

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\*The element was not named by Gregor but by the German chemist, Klaproth, in 1795.<sup>170</sup>



point at which titanium dioxide pigment production began to attain commercial and economic importance. This growth continued so that while one U.S. company produced titanium dioxide at a rate of 8 million pounds per year in the mid-20's, by 1971, eight companies were producing 1.6 billion pounds  $TiO_2$  per annum.<sup>241</sup>

ii. Composition

Titanium dioxide minerals are found in nature as ilmenite, rutile, and other common ores such as titanite. The most abundant ore, ilmenite, is composed of 53-60% titanium dioxide with the remainder being oxides of iron.<sup>293</sup> Ilmenite is black in color and found both as massive rocks and as sand on river bottoms and seashores. Major deposits are found in Norway (rocks), Quebec (rocks), and Florida (sand), among other locations.<sup>356</sup> Rutile ore contains 90-98% titanium dioxide and varies from a reddish brown to black in color. The remaining mineral forms, such as titanite (a calcium titanium silicate -  $CaTiSiO_5$ ), are not used as a source for titanium paint pigments but are employed in the production of pigments for the metallurgical and ceramics industries.<sup>293</sup>

Purified titanium dioxide exists in three crystal forms - anatase, rutile, and brookite. Of these, the orthorhombic brookite is relatively unstable and has little importance in the color industry. The pigment forms, anatase (or a-titania) and rutile (r-titania) are both tetragonal (Figures 48 and 49).<sup>241</sup>

Most chemical and physical tests are unable to distinguish between rutile and anatase. If a pure mixture of one or the other with a  $TiO_2$  content of at least 93% is available, differentiation is possible by a specific gravity determination and a tinting strength test in comparison with samples of known composition. It is generally agreed, however,

that the only certain method for differentiating between the two forms is by analysis of x-ray diffraction patterns (Figure 50). X-ray patterns also allow determination of the relative proportions of anatase and rutile in a mixture of both.<sup>409</sup>

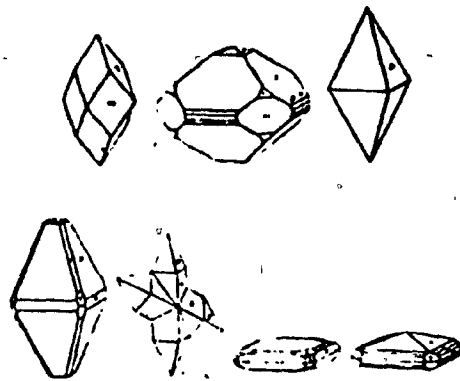
### iii. Physical Properties

Titanium dioxide possesses three properties which make it especially suitable for development as a pigment: (a) high refractive index, (b) good whiteness, and (c) great chemical inertness.

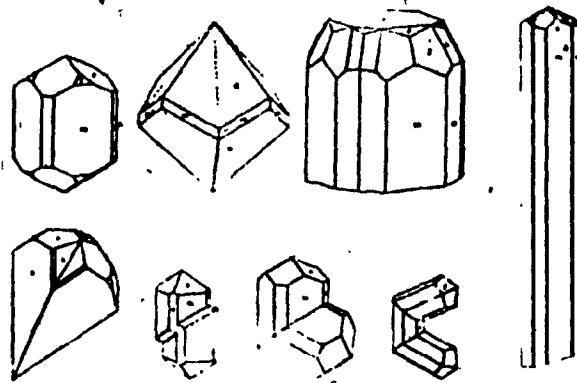
(a) Refractive Index - with refractive indices of 2.52 and 2.71,<sup>328</sup> for anatase and rutile respectively, titanium dioxide possesses an atomic and internal structure which gives it one of the highest refractive indices known among colorless substances. This accounts for its exceptional light-scattering ability in paint media.<sup>239</sup> In fact, titanium dioxide is the most opaque pigment available. For example, the light reflected back from a single pigment-oil interface by rutile is eight times stronger than zinc oxide, another common white pigment.<sup>407</sup>

Hiding or covering power (the number of square feet of a black surface which are completely hidden by a pound of pigment in linseed oil<sup>328</sup>) is a measure of the opacity of a pigment. The covering power of rutiles is 163 ft<sup>2</sup>/lb and for anatase is 115 ft<sup>2</sup>/lb as compared with the covering power of zinc oxide or lithopone (BaSO<sub>4</sub>) - 20 and 27 ft<sup>2</sup>/lb respectively.<sup>328</sup> Similarly, the tinting strength of rutile is 1600, for anatase, 1275, and for lithopone, 280 (Table 28).

Both covering power and tinting strength of a BaSO<sub>4</sub> or lithopone can be increased by mixture or coprecipitation with titanium dioxide. For example, a 30% titanium lithopone has a covering power of 46 ft<sup>2</sup>/lb and a tinting strength of 430,<sup>329</sup> almost doubling both values over the pure



ANATASE CRYSTAL TYPES  
Tetragonal System; Axis  $c = 1.7771$



RUTILE CRYSTAL TYPES  
Tetragonal System; Axis  $a = 0.64415$

Figure 48. Anatase and Rutile Crystal Forms. 329

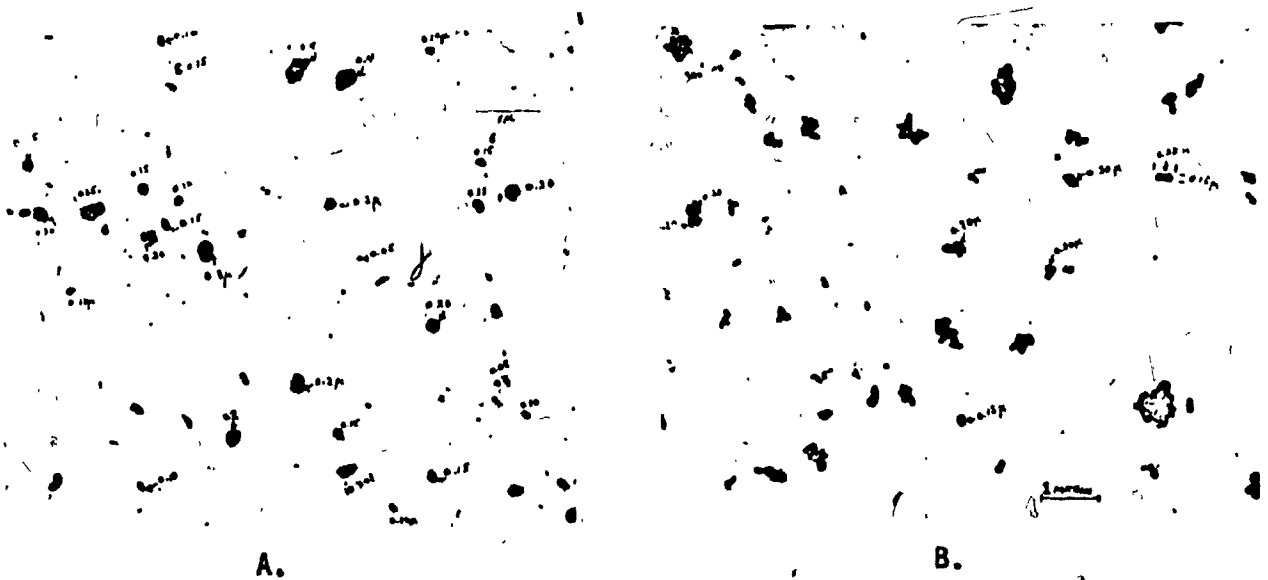
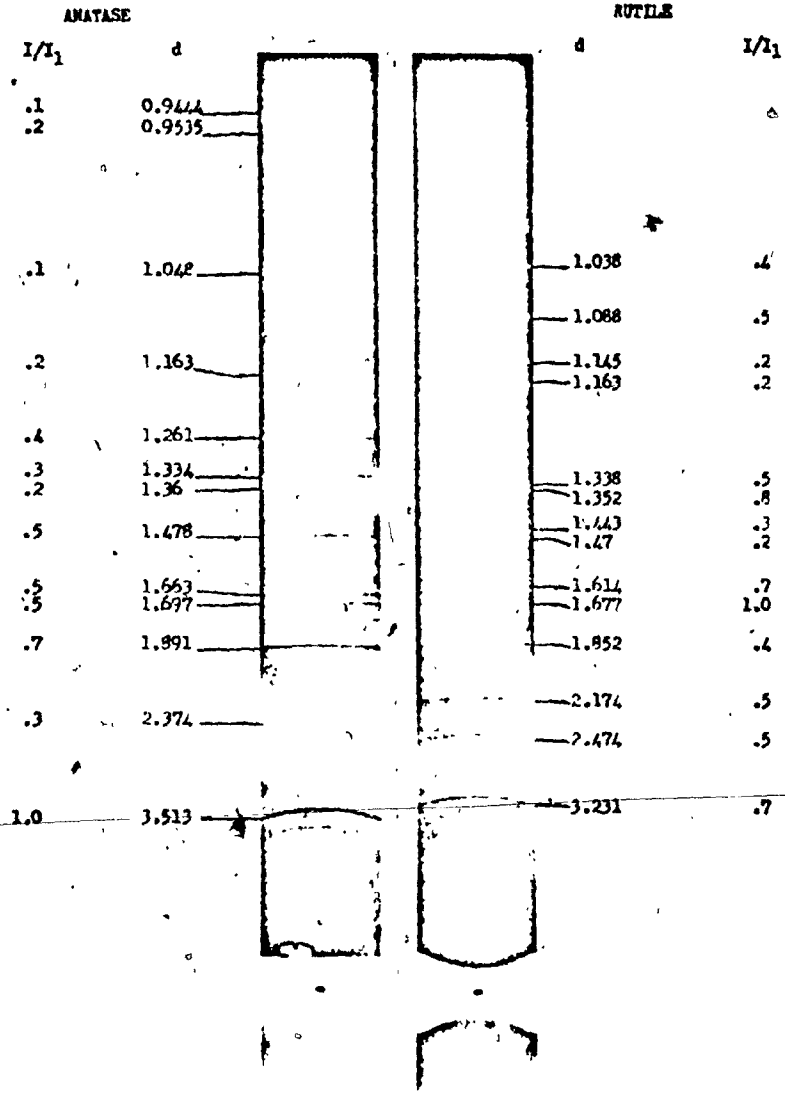


Figure 49. A. Photomicrograph of Anatase Titanium Dioxide Pigment - x25,000  
B. Photomicrograph of Rutile Titanium Dioxide Pigment - x20,000. 330



X-RAY DIFFRACTION PATTERNS OF ANATASE AND RUTILE

Figure 50. X-ray Diffraction Patterns of Anatase and Rutile.<sup>331</sup>

Pigment	Refractive Index	Tinting Strength (Reynolds)	Covering Power sq.ft./lb.	Oil Absorption (Gardner-Coleman)	Brightness %	Vehicle Reaction
TiO <sub>2</sub> (Anatase)	2.52	1275	115	30.0-SD 19.5-SD-LO 26.0-RG	98-99	Inert
TiO <sub>2</sub> (Rutile)	2.71	1600	163	Comparable or slightly lower than anatase	98-99	Inert
Zinc Sulfide	2.37	850	58	16.3	90	Inert
Lithopone (regular)	1.86*	280	27	15.0 Sunolith #96	88-90	Inert
Lithopone (titanated)	1.96*	430	44	13.5 Titanolith LO 16.0 Titanolith HO	90-92	Inert
Zinc Oxide	2.03	170	20	Low oil 12 High oil 18		Reactive
White Lead	2.09	140	15	Low oil 8 High oil 17	80-92	Reactive

(Hallet)  
(in linseed oil)

\* Approximately as calculated from % by wt.

Table 28. Some Relative Physical Properties of Various White Pigments.<sup>329</sup>

$BaSO_4$ . The relative importance of titanium dioxide as opposed to the other commonly used white pigments\* may be seen in Table 28.

From Table 28 it can be seen that rutile has a higher refractive index than anatase. According to Taylor and Marks<sup>407</sup> this may be attributed to the arrangement of titanium and oxygen atoms in the rutile being more compact than in the anatase crystal. As a result, the structure of rutile provides a greater hindrance to the passage of light (Figure 51).\*\*

For any pigment, the refractive index varies with the wavelength of light used for the measurement. For titanium dioxide, the refractive in-

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\* Of the non-titanium white pigments listed in Table 28, zinc oxide and white lead are used as artists' colors. White lead, or flake white, is the most important of the lead pigments and has the composition,  $2PbCO_3 \cdot Pb(OH)_2$ . This pigment has been known and used for centuries, being described by Theophrastus, Pliny, and Vitruvius. In addition, it was practically the only white used on easel paintings until the 19th. century. Its major drawback is its toxicity and for this reason has been increasingly displaced as an artists' color by titanium dioxide pigments.<sup>173</sup> In fact, titanium dioxide is the only white in the acrylic emulsion paint widely used today.

Zinc oxide or Chinese white, became commercially available about 1840 and was considered a color breakthrough because of its non-toxicity. Because zinc oxide is produced as a 'smoke', its particle size is very small and relatively large amounts of oil are required to form it into a workable paste. Consequently, zinc white paint films tend to dry brittle and crack. It is still used relatively commonly as an artists' pigment, however.<sup>329</sup>

Of the remaining white pigments in Table 28, zinc sulfide and regular lithopone (a coprecipitate of zinc sulfide and barium sulfate) are rarely used as artists' colors although they are found relatively commonly in less expensive interior paints, lacquers, and enamels.<sup>329</sup> Titanated lithopone (coprecipitated titanium dioxide and barium sulfate) is discussed further in this paper.

\*\* It is interesting to note that before the development of titanium dioxide pigment, a common formula used for exterior house paint was 60% white lead, 30% zinc oxide, and 10% extender. The hiding power of this paint mixture necessitated a minimum of three coats to cover any new surface. A later formulation for the same type of paint contained 15% titanium dioxide, 50% white lead, 25% zinc oxide, and 10% extender and was found to require only two coats to perform the same job. It follows that the hiding power of the new mixture was one-third greater than the old, and in fact, the covering power was  $300 \text{ ft}^2/\text{gal}$  for the new as opposed to the  $200 \text{ ft}^2/\text{gal}$  obtained for the old.<sup>294</sup>

dex is somewhat higher for shorter wavelengths and lower for longer wavelengths of the visible spectrum. Consequently, titanium dioxide paints tinted red or yellow, show a slight loss in covering power over titanium dioxide paints tinted with other colors.<sup>239</sup>

(b) Whiteness - the second important property of titanium dioxide is its whiteness. In general, whiteness in a pigment is achieved by reflecting all wavelengths of the visible spectrum more or less equally. Titanium dioxide reflects all the light from sources containing all wavelengths and so appears completely white. In fact, this pigment has an unusually high light reflectance, reflecting 99% more light than magnesium oxide. As a result, not only does titanium dioxide serve as an excellent white pigment, but tints obtained by mixture with other colored pigments are free from muddiness or undesirable undertones.<sup>294</sup>

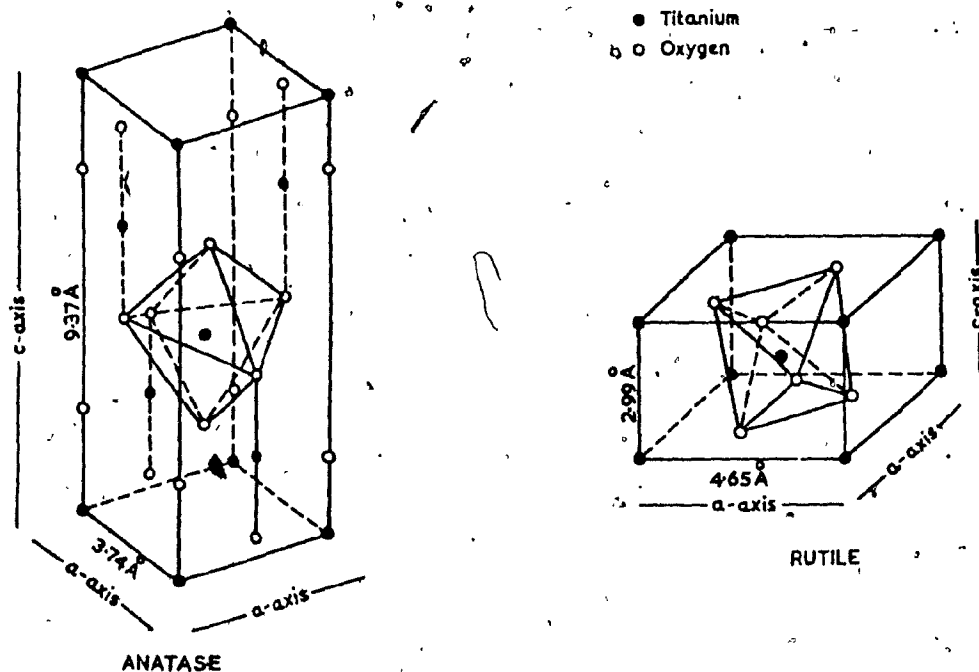


Figure 51. Crystal Unit Cells of Anatase and Rutile Titanium Dioxide.<sup>410</sup>

In a finely divided state, anatase crystals reflect and scatter all wavelengths of the visible spectrum equally. Therefore, the reflected and scattered light have the same compositions as the incident light and the dry pigment is a perfectly white powder. Rutile crystals, on the otherhand, absorb some of the visible light rays, less than 430 m $\mu$  (Figure 52) giving it a slightly cream tone compared to anatase. This absorption may be due to the greater ease with which rutile can accept impurities into its crystal lattice (Figure 51) and/or may be due to a special absorption band resulting from the configuration of the titanium and oxygen atoms in the rutile crystal.<sup>407</sup>

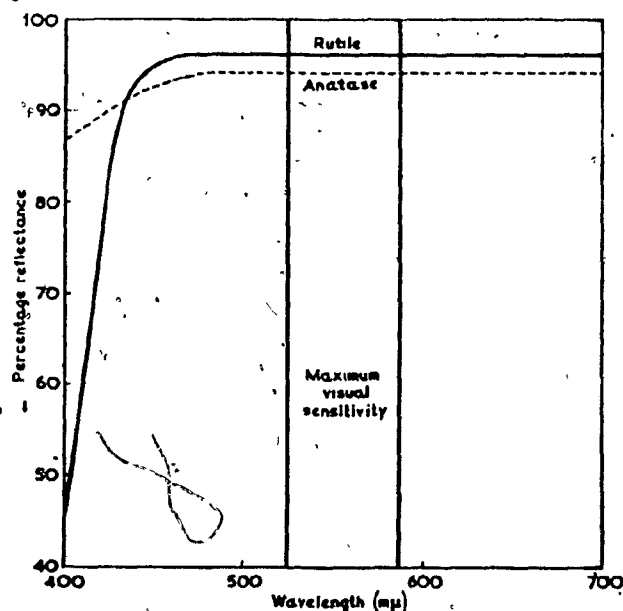


Figure 52. Reflectance Curves of Rutile and Anatase Titanium Dioxide.<sup>407</sup>

(c) Inertness - the third important property of titanium is its general chemical inertness. It is unaffected by most acids, acid fumes, chemical salts, or the common gasses or liquids with which it might come into contact both during manufacture and in an applied paint film.<sup>407</sup> An example of the latter is the ability of titanium dioxide to withstand darkening in sulfurous air or hydrogen sulfide.<sup>357</sup> Titanium dioxide is

insoluble in all liquids except concentrated sulfuric and hydrofluoric acids (which must be at extremely high temperature for sustained periods) and so may be used in all media.<sup>230</sup>

Titanium dioxide is also stable at high temperatures (over 1800°) due to a strong bond between the tetravalent titanium and bivalent oxygen ions. This can be conceived of as a screening of the titanium ions by the six oxygens in the crystal structure.<sup>238</sup> Under extreme conditions (700-950°) anatase crystals are transformed to the rutile form.

(d) Chaulking - weighed amounts of oxygen can be removed from  $TiO_2$  by reducing agents at temperatures of several hundred degrees centigrade. Small, unweighable amounts of oxygen can also be lost by radiant energy. These easily recombine by a reversible photochemical reaction if no oxidizable material is available. The study of this photoreaction, which can lead to chaulking, fading, and yellowing in exterior paint films containing  $TiO_2$ , has been the subject of a great deal of research. Jacobsen<sup>224</sup> attributes the chaulking to a cyclic oxidation-reduction reaction between titanium dioxide and the vehicle. The binding medium or vehicle is destructively oxidized and the products may be either gasses, liquids, or soluble compounds which are washed away by rain. The removal of the top layer of medium leaves the pigment exposed and loosely bound so that it is either easily rubbed off or ready to continue the cycle. Photochemically reduced titanium dioxide is readily reoxidized in the presence of air and absence of active sun rays. It is generally believed that only anatase type crystals of titanium dioxide are susceptible to this degradation process although Weyl and Forland<sup>458</sup> claim that rutile is also involved in some photochemical reaction in the presence of impurities.

Chaulking of either anatase or rutile can be minimized by a surface coating of small quantities (1%) of other inorganic oxides such as al-



umina.<sup>407</sup> A "slow chaulking" titanium dioxide mixture of anatase and small amounts of rutile is sold as "self-cleaning" paint. The drawback to this product is that tinted or colored paints in shady places have a slower rate of chaulking so that tone contrasts inevitable develop. A newer, non-chaulking pigment combination of rutile based lead titanate is said to minimize this problem. A common formula is 25% lead titanate, 20% zinc oxide, 30% white lead, and 25% extender.<sup>294</sup>

When used as an artists' pigment, the photochemical oxidation-reduction degradation of titanium dioxide is of little importance for works primarily intended for indoors, since they would be exposed to a negligible amount of direct sunlight. In any case, artists' colors generally employ non-chaulking rutile titanium dioxide. This pigment offers several important advantages over other available white artists' pigments. In addition to the opacity, whiteness, and inertness just discussed (vide supra), titanium dioxide has little tendency to crack or peel when used in thick layers<sup>409</sup> (such as an abstract expressionist layering, see Pollock and Borduas) and is completely non-toxic (a problem with the previously commonly used lead carbonate). Physical properties and other data for this pigment are summarized in Table 29.\*

Like the cadmium pigments, titanium dioxide is produced as a lithopone. In this case, the extending compound may be either  $\text{BaSO}_4$  or  $\text{BaCO}_3$  for anatase titanium dioxide and  $\text{CaSO}_4$  for the rutile form. Extended pigments are graded roughly as 'pure' - 97-99%  $\text{TiO}_2$ , 'good' - 50%  $\text{TiO}_2$  with 50% extender, and 'low' grade for a 25%  $\text{TiO}_2$  with 75% extender pigment. The lithopones are generally less opaque, have a lower refractive index,

\* Many review articles on the physical properties, etc., of titanium dioxide exist (ref. #'s 213, 355, 380, 425-6, 460)

Table 29. Physical Properties and Other Data for Titanium Dioxide (CI Pigment White 6; CI 77891).

			Reference
Chemical Class	Inorganic		99
Hue	-----		
Fastness Properties			
1. Organic Solvents	insol in all		
2. Light	excellent but liable to cause fading of organic dyes		
3. Heat	excellent stability		
4. Water	insol		
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt		
6. HCl 5%	unalt		
7. Linseed Oil	insol		
Density	Anatase 3.8-4.1 g/cm <sup>3</sup>	Rutile 3.9-4.2 g/cm <sup>3</sup>	238
Specific Gravity	3.9 (4.0-4.3 = average for both)	4.2	408, 169
Refractive Index	2.55 2.5	2.71 2.9	408 169
Particle Size	0.3 μ (average = less than 2μ with 2% up to 0.4 μ) (average = 0.3 μ)	0.2-0.3 μ	238 357 169
Oil Absorption	18-30 lb/100 lb 26-28% (pure pigment average) 22% (low absorption type average) 23-25% (average) 23%	16-48 lb/100 lb	238 357 169 41
Tinting Strength (Reynolds)	1200-1300 1200-1300	1650-1900 1450-1700	238 408
Resistance to Chaulking	poor-moderate	good to excel.	
Toxicity	non-poisonous		
Standards	BS 239...1851:1967 ASA K45 & 48, ASTM D476-82 & 45-1, Fed. Spec. TT-T-425 (2)		110

and a lower absorption value than the pure titanium dioxide. Otherwise they share the same general properties. Physical properties and data for titanium dioxide lithopones are given in Table 30.

#### iv. Experimental

The Color Index<sup>110</sup> gives the following general preparation for titanium dioxide:

The natural mineral, ilmenite, is digested with sulfuric acid, the solution hydrolyzed, and the precipitated titanium dioxide separated, calcined, and ground. The rutile is also purified through a chlorination process.

The manufacture of titanium dioxide pigment<sup>65,90,328,410</sup> from ilmenite requires a costly plant - a special location with access to large amounts of water, large steam facilities, and a large supply of sulfuric acid. In this process, purified ilmenite ore, dried to 0.5% water content is crushed to a 200-mesh powder and dissolved in concentrated sulfuric acid. The higher the iron content, the more concentrated the sulfuric acid must be.\*\*

The mixture is heated with steam to 110° to induce an exothermic reaction which gives soluble titanium sulfates (such as  $TiOSO_4 \cdot 2H_2O$ ) and iron sulfates (such as  $FeSO_4 \cdot 7H_2O$ ) from the original  $m(FeTiO_2) \cdot n(Fe_2O_3)$  ore. Because this reaction is both vigorous and exothermic, it is carried out in extremely heavy duty, acid-resistant tanks which can withstand the violence of the reaction.

When the reaction is complete (usually about ten minutes), the mass is diluted with water which reduces ferric iron to the ferrous state, the latter being a more stable and readily soluble salt. Dilution also allows

\* There are many general articles dealing with modern methods for the manufacture of titanium dioxide pigment. Most of these contain more or less the same information (e.g., ref # 65,90,328,410).

\*\* An alternate method to that most commonly used industrially is suggested by Czandera, A.A., A.F. Clifford, and J.M. Honig.<sup>120</sup> They recommend dissolving the titanium in an ammoniacal solution of 90%  $H_2O_2$  and claim a highly purified anatase product.

Table 30. Physical Properties of Titanium Dioxide Lithopone.

		Reference
A. 15% TiO <sub>2</sub> + 25% ZnS + 60% BaSO <sub>4</sub> :		357
Specific Gravity	4.19-4.25	
Oil Absorption	16-20%	
B. 25% TiO <sub>2</sub> + 75% BaSO <sub>4</sub> :		357
Specific Gravity	approx. 4.3	
Refractive Index	1.96	170
Oil Absorption	17.5% 17-18%	357
Covering Power	46 ft <sup>2</sup> /lb	

all the soluble components, such as the titanyl sulfate, to be taken into solution. The solution is then purified from unconverted residues and colloidal slimes. Scrap iron is added to completely reduce the ferric salts to the stable ferrous state and to ensure that a small amount of the titanium is in the trivalent (titanous sulfate) state. This is necessary to prevent oxidation of residual iron during later steps in the process. From the solution, ferrous sulfate crystallizes out and is removed by centrifugation and sold as "copperas."

Clarification is carried out by sedimentation and filtration, removing all suspended matter such as undecomposed ilmenite, colloidal silica, etc. The concentration of the solution is adjusted to 140-150 g TiO<sub>2</sub>/ℓ, 30 g Fe/ℓ, and 65-70 g free acid/ℓ and boiled with indirect steam which serves the important function of hydrolyzing the titanium sulfate and precipitating out titanium hydroxide (TiO(OH)) and metatitanic acid (HTiO<sub>2</sub>). Careful control over the conditions of this stage of the reaction are

essential to prevent the simultaneous precipitation of the remaining iron salts.

The precipitate is then washed repeatedly until completely free from iron in any form. Elimination of all iron from the titanium dioxide is crucial since oxidation of the iron would discolor (pink to red) the pigment. In fact, even minute traces of impurities alter the light absorption characteristics of a substance so that titanium dioxide pigment must be highly purified to retain its whiteness.

The small amounts of remaining  $H_2SO_4$  and basic sulfates are neutralized by the addition of barium carbonate. The precipitate is then calcined to convert it into  $TiO_2$ . It is this last step which converts the amorphous agglomerates to the crystalline form suitable for use as a pigment.<sup>65,90,328,417</sup> The particle size range for the products of a proper calcination is between 0.2 and 3.0  $\mu$ . If calcination is carried out for too long a period of time, the product is a gritty pigment which has a yellow tint. On the otherhand, too short a calcination yields particles too small to take advantage of the optimum covering power of titanium dioxide. For example, the maximum scattering efficiency of titanium dioxide for green light occurs with a pigment particle approximately 0.25  $\mu$  in diameter.<sup>237</sup> To function as a useful pigment, the particle size distribution must be optimized so as to contribute, along with its high refractive index, a maximum light scattering, which in turn contributes to a high reflectance and opacity. Consequently, particles under 0.1  $\mu$  must be excluded.

The process by which the amorphous agglomerate is converted to the crystalline form and the type of crystal obtained has been outlined by O'Brian<sup>333</sup> as follows: The original agglomerate, formed in the hydrolyza-

tion step, is made up of compounds containing two titanium hydroxide groups bonded loosely with a sulfate (he does not specify the type of bonding). The  $H_2SO_4$  content of this compound amounts to approximately 10%. In calcination, the crystal growth may go in one of two ways depending on the manner in which cleavage of the agglomerate particles occurs. With a rutile 'seed', the result is a simple molecule, e.g.,  $Ti_2O_4$ . The other type of cleavage yields an anatase crystal consisting of a more complex and less stable molecule of the general composition,  $Ti_4O_8$ . Different conditioning agents, such as potassium, sodium, zinc, and magnesium carbonate are used to promote specific types of cleavages. Finally, during the particle size change, the refractive index is increased from 1.8 to an average of 2.6.

Following calcination, the pigment is ground in water to remove aggregates (which would reduce its hiding power), dried, reground, and air floated. While wet-grinding is not essential, pigments refined by this method are generally easier to incorporate into paints.<sup>407</sup> The finished pigment may either be ground into a paint as it is or post-treated with small amounts of compounds such as oxides of alumina and silica to aid its dispersion in the media. Some post-treatments are used to prevent agglomeration. Figures 53 and 54 are flow diagrams of the commercial production of anatase titanium dioxide by the so-called "sulfate process" just described.\*

Rutile mineral, which occurs naturally as titanium dioxide (up to 98%) in the rutile crystalline form, is usually found contaminated with

\* The patent literature for the preparation of various types of  $TiO_2$  pigments is voluminous, but it does not seem to be generally known which of the many patents are significant. It is interesting, though, that one patent (USP 2,760,874 - 1956 to the National Lead Co.) claims a method for the preparation of synthetic rutile.

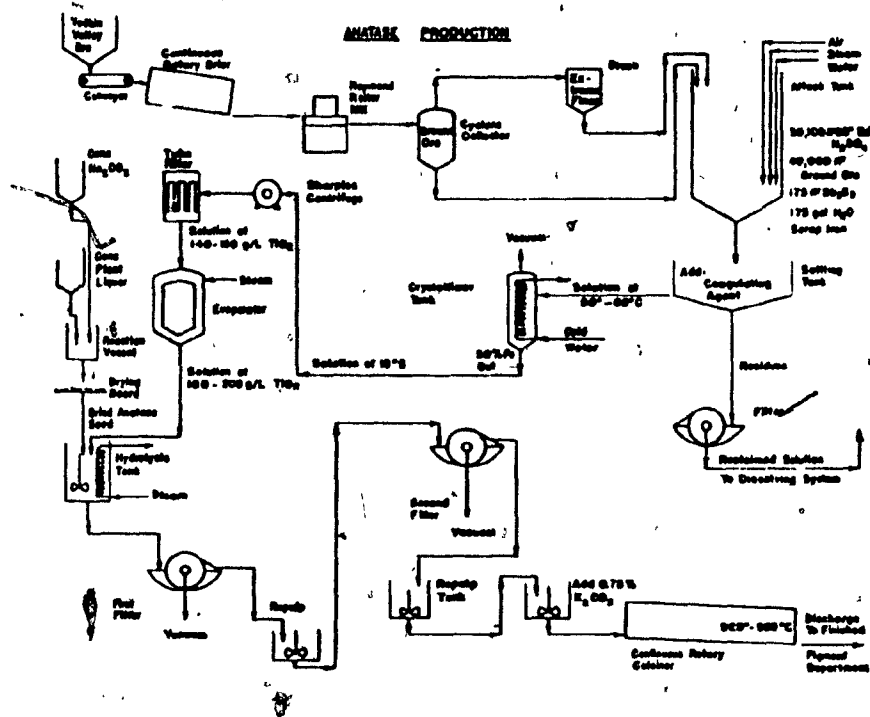


Figure 53. Flow Diagram of Anatase Titanium Dioxide Production to the Point of Milling.<sup>332</sup>

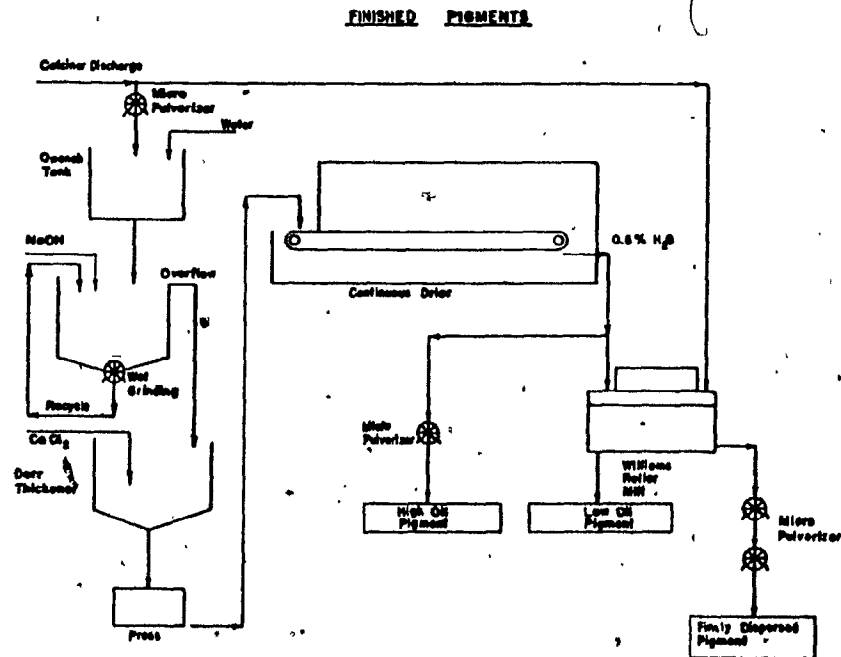


Figure 54. Flow Diagram of the Grinding, Drying, and Pulverizing of Anatase Titanium Dioxide.<sup>332</sup>

metallic compounds. The pure pigment may be derived by submitting finely crushed rutile ore to the "chloride process."<sup>407</sup> This involves conversion of the  $TiO_2$  content to titanium tetrachloride by heating in a special furnace in the presence of chlorine gas. The liquid tetrachloride is distilled to a high degree of purity and then burned in an oxidizing atmosphere to give titanium dioxide smoke with the liberation of chlorine:



Figure 55: "Chloride Process" Production of  $TiO_2$ .

The smoke precipitate is collected and the chlorine reused.

Particle size and crystal form are adjusted by selecting the conditions of oxidation. The pure titanium dioxide product, however, still requires subsequent modification to bring its durability and other properties up to the level of the sulfate process pigments. The quantity of pigment produced by this method is relatively small compared to the sulfate process.

Titanium dioxide lithopones are produced by a type of coprecipitation, co-calcination, or co-grinding<sup>409</sup> of the titanium with either barium sulfate, calcium sulfate, or magnesium silicate. Of these methods, the co-grinding or co-calcination alone are clearly inferior methods since the hiding power of a simple mixture of 70%  $BaSO_4$  and 30%  $TiO_2$  is much less than for the co-precipitated pigment with the same ratio of compounds. The co-precipitation method is much the same as the sulfate process, except that the titanium sulfate solution is mixed with the extender (usually  $BaSO_4$ ). The mixture is boiled by direct steam, precipitating titanium hydroxide on the base (extender). During this process, a mutual absorption takes place. It should be noted that the principle here is



not exactly the same as in the production of the co-precipitated pigments such as the cadmium lithopones in which there is a simultaneous double precipitation. Instead, the process resembles the organic lake production (like alizarin red, vide supra) in which the colors are fixed onto an extender. In fact, electron microscope studies<sup>240</sup> show that the extenders are an integral part of the pigment, with  $TiO_2$  particles precipitated onto the surface of the extender particles. The heat used in the precipitation causes a partial fusion of the two. Subsequent calcination converts the amorphous precipitate into the crystalline state, resulting in a complete coalescence.

#### v. Commercial Uses

Titanium dioxide pigments can be used in every kind of paint such as primers, undercoats, and finishes. Because the pigment is inert and therefore unreactive with paint media, it does not cause paint films to harden. Consequently, in good media, titanium dioxide pigments seldom fail by chalking or cracking.<sup>409</sup> Rutile  $TiO_2$  is especially good in exterior paint formulæ because of its high chalking resistance.

These pigments are also employed in acid resistant enamels, nitrocellulose lacquers, paper surfacing, plastic and vinyl products, rubber, ceramics, cosmetics, soap, and as a delustrant for artificial fibres.<sup>99</sup>

#### H. Bone or Ivory Black (CI Pigment, Black 9: CI 77267)

##### i. The Carbon Blacks

Although many blacks contain carbon as their essential constituent, they are classified as inorganic due to their generally high inorganic content and nature. Carbon can exist in three allotropic modifications: (a) a colorless type (diamond) is a highly refractive crystalline form with a specific gravity of 3.5, (b) a shiny, greyish-black amorphous

crystalline form (graphite) which exists as a lamellar, scaly, or flakey structure with a specific gravity of about 2.5, and (c) a non-crystalline or amorphous form of carbon which is obtained by the decomposition of a great variety of carbon compounds (such as the conversion of wood into charcoal). Type (c) is most commonly used for the carbon black pigments because it is generally very stable (unaffected by light, air, acids, and alkali). Only high temperatures can destroy it.<sup>39</sup>

While all carbon pigments are black, they vary considerably in shade and strength according to the amount of amorphous carbon they contain. Vegetable black (made by charring or carbonizing vine twigs, peach stones, cork, etc.), for example, has the best covering power and strength of the carbon blacks.<sup>39</sup>

They also vary in their commercial applications. Thermatonic black, produced by cracking or pyrolysis of natural gases under pressure, is a bluish-grey black used primarily in rubber. Graphite black, which is similar to diamond in composition but is extremely soft, is used as a pigment in conjunction with carbonaceous blacks to make graphite paints. These are used on metal surfaces, such as chimneys, where heat resistance is essential. Acetylene black, produced from waste calcium carbide, has occasionally been used as an artists' color. The most important and widely used carbon black used by artists, however, is bone black.

#### ii. History

Bone black has been known variously as animal black, drop black, and ivory black. All of these names were originated from either the source or mode of preparation from which the pigment was derived. Ivory black was originally made by charring the waste cuttings of ivory in closed vessels, then grinding, washing, and drying the resulting black residue.<sup>40</sup>

Drop black was charred animal bone moistened with a small amount of glue or gum and pressed through a perforated plate before drying. The product was a pellet which could be ground for use in paint. Today, however, both ivory and drop black are synonymous with bone black and the names are retained only to identify various grades.

At one time, South American sheep bones were the preferred source for bone black, but now the bone is obtained from the residue of glue manufacture. This residue contains bones which have been digested so as to remove the fat and glue from them.<sup>40</sup> The bone black pigment so produced is sold as a superior quality artists' color.

### iii. Composition

Chemically, bone black is a mixture of 7-22% carbon,<sup>415</sup> around 75% calcium phosphate tribasic ( $\text{Ca}_3(\text{PO}_4)_2$ ), which is also known as bone ash, approximately 8% calcium carbonate ( $\text{CaCO}_3$ ), and very small quantities of calcium sulfate, magnesium phosphate, calcium sulfide, and other soluble salts.<sup>108,391</sup> While the non-carbon constituents have no color value in themselves, they both serve as a residue on which the finely divided carbon is deposited and improve the working qualities of the pigment.<sup>40</sup>

### iv. Physical Properties

Bone black is the blackest of the black pigments but has a relatively low tinctorial strength because of its high ash content. Its tone is relatively pure but does range slightly from bluish to brownish undertones. Physically, bone black is extremely stable, being fast to light and unaltered by acids and alkali. In appearance, individual bone black pigment particles appear as irregular coarse grains.<sup>169</sup> Other physical properties and data are given in Table 31.

Table 31. Physical Properties and other Data for Bone Black (CI Pigment Black 9: CI 77267)

		Reference
Chemical Class	Inorganic	98
Hue	Black (Bluish overtone and Brownish undertone)	415
<b>Fastness Properties</b>		
1. Organic Solvents	insol.	98
2. Light	excellent	
3. Heat	stability v. gd.	
4. Water	insol	
5. Na <sub>2</sub> CO <sub>3</sub> 5%	unalt	
6. HCl 5%	unalt (cold) decomposed (boiling)	
7. Linseed Oil	good	
8. Oleic Acid	insol	
Specific Gravity	2.35 2.68 2.29	42 415 169
Refractive Index	approx. 1.65 - 1.70	162
Oil Absorption	30-65	415
Tinting Strength	low	
Standards	BS 285:1952 USA ASA K36.1; ASTM D20-47 (1969) Fed. Spec. TT-E-60	98

v. Experimental

The Color Index<sup>106</sup> indicates that carbonized bones, such as beef or lamb, as well as the "spent animal charcoal" used for decolorizing molasses may be used as bone black pigment. Industrially, the most common method is to crush hard bones to 2" diameter or less, extract with a solvent, such as benzene, to remove oily and fatty substances, and boil to remove any remaining soluble material. The bone is then placed in a

is sensitive to solvent, temperature, and source of copper.

(g) Many variations of the phthalonitrile process are listed in Moser and Thomas<sup>317</sup> and Booth<sup>57</sup>. Included are further references to both the literature and various patents.

(h) See Lecher, Lacey, and Orem<sup>270</sup> for a discussion on the mechanism of formation of copper phthalocyanine by the phthalonitrile-pyridine process.

(i) See Kujoshi<sup>254</sup> for a discussion of the reaction kinetics of the phthalonitrile process.

#### v. Metal-free Phthalocyanine

A preparation of this compound may be found in Gore.<sup>176</sup>

#### B. Inorganic Pigments

##### i. Cadmium Sulfide

Cadmium vapor methods for the synthesis of this pigment may be found in Czyzak, et al.,<sup>121</sup> and Grillot.<sup>181</sup>

##### ii. Cadmium Sulfide Lithopone

(a) A preparation using  $\text{CdSO}_4$  is given as: 185.5 g of  $\text{CdSO}_4$  is dissolved in 1  $\ell$  water. To this is added in order - 200 ml of a 30% potash alum solution, 207 g of blanc-fixe, and a solution of 138 g sodium carbonate in 1,380 ml  $\text{H}_2\text{O}$ . The precipitate is filtered, washed thoroughly, and dried. To every 100 g of dry precipitate, 37 g sulfur is added, mixed, and calcined for 90 minutes at  $500^\circ$ . A good cadmium yellow lithopone product is claimed.<sup>362</sup>

(b) "400  $\ell$  of purified  $\text{CdCl}_2$  solution are run into the precipitating tank. To this is added (over a period of 1 hour)  $\text{BaS}$  solution containing 200g  $\text{BaS}/\ell$  and heated to  $85^\circ$ , sufficient to precipitate all the  $\text{CdCl}_2$  as  $\text{CdS}$ . A calculated amount of the purified  $\text{Na}_2\text{SO}_4$  is then run

into the tank to precipitate completely all the  $\text{BaCl}_2$  as  $\text{BaSO}_4$ .<sup>138</sup>

iii. Cadmium Sulfo-Selenide

The preparation of cadmium sulfo-selenide by a direct heating method for use in preparing ceramic glazes was studied by Marley.<sup>295</sup> He gives optimum starting material ratios for various shades of red.

iv. Hydrated Chromium Oxide

A method given by Ruthruff<sup>379</sup> produces hydrated chromium oxide from chromium oxide and ethanol, for use as a catalyst. However, the product ( $\text{Cr}(\text{OH})_3$ ) has a higher oxidation number than the hydrated chromium oxide used as a pigment and, in fact, is brown in color.

v. Ultramarine Violet (CI Pigment Violet 15)

This pigment can be obtained by heating ultramarine with 5% ammonium chloride at 200-350° for four days or by heating with chlorine and hydrochloric acid. The violet product may be brightened by treating with indirect steam, and then washed and dried at a low temperature. The shade depends on the temperature used, concentration of gas, and the time period of treatment.<sup>424</sup>

vi. Ultramarine Red

Treat ultramarine violet with gaseous HCl at 70-200° (or at a higher temperature with nitric acid) for four hours.<sup>424</sup>

vii. Ultramarine Blue

An alternate method to the direct and indirect processes generally used in industry involves the use of  $\text{SiO}_2$  obtained from distilled silicon tetrachloride,  $\text{Al}_2\text{O}_3$  from sublimed aluminum chloride, sodium sulfate obtained by reduction with hydrogen of purified sodium sulfate, and sodium carbonate. An intimate mixture of these in the proportions of  $3\text{Na}_2\text{CO}_3 + 3\text{Al}_2\text{O}_3 + 6\text{SiO}_2 + \text{Na}_2\text{S}$  is heated in a nitrogen atmosphere for

15 hours at  $900^{\circ}$  resulting in a pale green product. This was heated in a steam of  $H_2S$  for 2 hours at  $900^{\circ}$ . On ignition in air, the yellow-green product is claimed to give a deep blue ultramarine. This method has not been used on a large scale.<sup>352</sup>

#### viii. Cobaltous Aluminate

(a) A more brilliant color is claimed when cobalt oxide and alumina are ignited in a KCl flux: A stoichiometric mixture of CoO (74.9 parts) +  $Al_2O_3$  (102.0 parts) is prepared to give  $CoAl_2O_4$  (176.9 parts). This is mixed with 1.5 times its weight of KCl. The mixture is heated to approximately  $1100^{\circ}$  in a porcelain crucible. The melt is cooled, pulverized, and extracted with boiling water until no further  $Cl^-$  is obtained. The residue is dried at  $60^{\circ}$  in a drying oven.<sup>74</sup>

(b) The addition of oxides such as that of magnesium is sometimes done. For this type of preparation, a sulfate such as  $ZnSO_4$  is added to CaO and  $Al_2O_3$  and the mixture calcined at  $1200^{\circ}$  (optimum). After ignition, the soluble sulfates are washed out.<sup>150</sup>

(c) Some manufacturers also add a phosphate. A solution of sodium phosphate is used to precipitate the cobalt as cobalt phosphate. In another vessel, potash alum is precipitated by sodium carbonate to form alumina. Both precipitates must be washed well and then slowly mixed together in the proportion of 8 parts alumina and 1 part cobalt phosphate. The filter cake from the mixture is heated in porcelain pots to a dull red heat for  $1/2 - 3/4$  hour. The product is ground in a porcelain ball mill with white spirit containing approximately 0.5% linseed oil fatty acid.<sup>364</sup>

## II. Appendix B. The Testing and Evaluation of Pigments

### A. Introduction

In the testing of a material for its potential for use as a pigment, the simplest and most accurate approach would obviously be to prepare a paint with the material, apply it to a surface, and observe its behavior to exposure over a long period of time. Since this method is generally impractical, laboratory tests are commonly used to accelerate this process. A known pigment of a given chemical composition will always exhibit the same chemical properties, such as durability or fastness to chemical attack. However, two or more different methods of preparation may result in many different physical forms of the pigment, not all of which are suitable for use in a paint. For example, the product of one type of preparation may be in the form of a coarse, hard powder which is difficult to disperse in a particular medium and has a low color or tinctorial strength while the same compound prepared differently may be free from these pigmentary defects. Consequently, laboratory tests have been designed to evaluate pigments for their color and physical properties, as well as chemical stability.

Some of these tests are absolute, such as specific gravity or fastness in solvents. But others can be subjective, such as tinctorial strength or color. The latter tests are therefore usually carried out through standardized methods set up by the American Society for Testing Materials (ASTM)\* and are carried out in comparison to another sample

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\* All tests in this appendix with references to ASTM numbers refer to standard methods or criterion as established by the American Society for Testing and Materials in their Annual Book of ASTM Standards.<sup>24</sup> The numbers indicate the following: e.g., for ASTM D192-53 (1969), the initial, 'D', indicates the ASTM committee responsible for the test. '192' denotes the test covered by the section. '53' specifies



or standard which serves as a control.

The ratings given a pigment for a particular property in the tables used throughout this paper are based on the following generally accepted convention:

i. Solvents

"insoluble" = the highest grade.

"solubility" = may bring about crystallization and a subsequent color change.

"bleeding" = a serious defect.

ii. Linseed Oil or Oleic Acid

"highest grade" or "insoluble" = no bleeding.

"very good" = slight bleeding.

iii. Water

"5" = excellent stability and insolubility.

"4" = very good stability.

to "1" = poor stability.

A slight degree of solubility is considered to show bleeding.

iv. Acids or Alkalies

"highest grade" = unaffected, i.e., no bleeding or alternation of color.

v. Light Fastness

"8 - 1" = most fast - least fast.

It should be mentioned here that pigments used in commercial protective coatings must comply with many requirements, such as weatherability and heat fastness, which are conditions not normally encountered by ar-

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the year the test, as written in the current edition of Standards, was established. A number in parenthesis, if present, gives the last year the test in question was evaluated and reapproved.

The standard in Britain for powder pigments for artists' use is BS 2876; 1957.

tists' colors. Conversely, many pigments classified as 'permanent' for commercial applications are only permanent for the lifetime of the coating which may be only several years. Artists' colors, on the otherhand, must be absolutely permanent for the lifetime of the work of art under conditions normally encountered.

#### B. Physical Properties

The following tests are those most commonly used for artists' colors.

##### i. Specific Gravity

Specific gravity, the ratio of the mass of a given volume of the substance to the mass of an equal volume of water at a given temperature, is useful in establishing a formulation for a suspension of the pigment in a vehicle or the ratio of pigment to vehicle. The test is also useful in determining particle size, specific surface, and compactness.

Specific gravity may be determined by vacuum or by packing in a centrifuge in order to remove the air trapped in the dry pigment particles. Both methods involve replacement of the air with an inert liquid in order to determine the actual volume of a known weight of pigment. The method is described in detail in ASTM D 153-54.

##### ii. Particle Size, Shape, and Distribution

The division of a pigment is important because it affects the shade, coloring strength, and hiding power of the pigment when mixed into a paint vehicle. Pigment particles are not generally of a uniform size so that a distribution of sizes is generally sufficient information. Several methods are used in this determination. The first, given by Bearn,<sup>42</sup> is a simple visual test: A small portion of pigment is spread on a white porcelain palette and rubbed (a) dry, (b) with oil, and (c) with turpentine. When the result is compared with similarly prepared standards, a general idea of the texture and degree of fineness may thus be obtained.

A more accurate test is by wet screening (dry screening gives results which are not easy to reproduce).<sup>405</sup> This process detects the presence and amounts of coarse particles. Standard ASTM D 185-72 is as follows. A 10 g sample of pigment is used in a 3" #325 sieve under a tap which delivers 300 to 500 ml/min. of water. The pigment is brushed lightly at all times, until the water comes through perfectly clear. The residue in the sieve is dried and weighed. In practice, no sieve size is fine enough to carry out a complete particle analysis because pigment particles commonly have diameters less than 10  $\mu$  and occasionally even less than 1  $\mu$ . Therefore a size distribution generally employs the following parameters (ASTM D 1366-65): (a) specific surface diameter (average particle size by surface average), (b) coarseness parameter (diameter below which 99.5% of the pigment falls, and (c) dispersion parameter (calculated from the distribution curve). The common method of determination is by electron microscopy, in which the counting is repeated on a number of slide fields of view of the same specimen in order to increase the sample size and so be more representative. This measurement may also be done by sedimentation centrifugation.

Problems inherent in both of these methods are that the medium may be different from that used in a paint (e.g., for E.M., nitrocellulose is employed since it is transparent to the electron beam) and the possibility exists that flocculation may arise due to the conditions of the test.

The determination of the crystalline form is generally dependent on the magnification supplied by the electron microscope, although the general form and color may be checked during manufacture by an optical microscope. X-ray diffraction patterns are useful in differentiating between polymorphous pigments (e.g., to estimate the proportion of  $\alpha$  and

$\beta$ -copper phthalocyanine blue or of rutile and anatase titanium dioxide).

### iii. Bulking Volume

This test is useful in determining formulation. In addition, a high bulking volume (e.g., 4 l/kg) is a good indication of the fineness and texture of a pigment. The measurement is carried out by filling a cylindrical container of known volume (e.g., 100 ml) with pigment but without tamping. The bulking value is calculated from the weight of the given volume of pigment.<sup>279</sup>

### iv. Oil Absorption

Oil absorption is the minimum amount of oil necessary to produce a stiff paste (with all pigment particles being 'wet') out of a given weight of dry pigment powder. This value, generally expressed as pounds of oil per 100 pounds of pigment (for ASTM D 281-31) or grams of oil required for 100 grams of pigment (BS 3483, 1962),<sup>279</sup> is important because it is related to the particle size and organophilic properties of the pigment. The oil absorption value can give some idea of the critical pigment volume concentration of a paint. If, for example, the oil uptake is high, the paint prepared from the pigment may be extremely viscous.

The method for oil absorption determination given by ASTM D 281-31 is as follows: 1 gram of dry pigment is placed on a glass plate, and raw linseed oil (with acid value 1 to 3) is run onto it, drop by drop, from a graduated burette. Each drop is incorporated into the pigment mass by rubbing with a spatula. The test is complete when enough oil has been added to produce a very stiff, putty-like paste. Oil absorption or the weight of linseed oil used in relation to the amount of pigment is calculated as the volume used (ml) times the specific gravity of the oil (0.93).

The problem with this test is that the transition from pigment powder to stiff paste is not always sharply defined and the end point is necessarily subjective. The value obtained is also affected by the amount and pressure used in rubbing in the oil. It should be noted here that since one of the factors involved in this process is the filling of interstitial spaces between pigment particles, it follows that the mixture of two or more pigments of different particle sizes may not necessarily give an oil absorption value which is the average of the individual pigments.

v. Water-Soluble Matter

Although almost all pigment preparations include thorough water washing at the end of the synthesis, some water-soluble material may remain, generally in the form of mineral salts, surfactants, or raw materials. These contaminants can alter the texture of pigments and other such properties. Soluble matter content can be determined (ASTM D 1208-65) by dissolving 10 g of pigment in 100 ml. water. Boil five minutes, dilute to 250 ml., and filter. 100 ml. of the filtrate is evaporated to dryness in an oven at 125°. Water-soluble matter is calculated from the weight of the residue.

vi. Water Content

A small amount of water can alter the behavior of a pigment in certain media in terms of dispersion and coloring power. Therefore, both the dryness of the pigment and the amount of water taken up when exposed to a humid environment must be checked if the pigment is to be used in these media.

Water content is measured (ASTM D 1208-65) by placing 50 g of pigment in 100 ml toluene and distilling. The condensate is collected in a graduated trap where the water separates from the toluene. Distillation

is continued until there is no further increase in the volume of water. From this volume, water content can easily be determined.

Hydrosopic water is measured (ASTM D 280-33) by the loss in weight of the pigment when kept for two hours at 105-110°.

#### vii. Dispersion Properties

Differing dispersion properties affect flow, gloss, and optical properties like tinctorial strength. During dispersion, air surrounding pigment particles is replaced by the binding medium and the average particle size is somewhat diminished by the breaking up of agglomerates. The fineness of the dispersion obtained depends on the size of the pigment particles, texture or softness of the aggregates, the hydrophilic or organophilic properties of the surface of the particles, the nature of the medium, and the time of grinding. Measurement of the time of grinding required to give a satisfactory product will take into account the other properties affecting dispersion. The first method for this determination involves monitoring the fineness of the dispersion in relation to the time of grinding.

At varying time intervals, the fineness is evaluated by a Hegman or North gauge (ASTM D 1210-64). This is a steel block which has a calibrated groove tapered from 0 to 100  $\mu$  deep. The paint is spread at one end of the groove and drawn down its length by a scraper. At some point along the groove, particles or agglomerates become visible and a reading may be taken at this point on the calibrated scale.

Another method, usually used for organic pigment dispersion tests, involves following the development of tinting strength after various grinding times. The tinting strength is compared to that of a completely ground and dispersed pigment which is given a value of 100. It should be

noted that graphs of tinting strength vs. time of grinding for different pigments indicate the relative so-called "ease of grinding" for a particular pigment.\*

### C. Chemical or Fastness Properties

#### i. Solvent Fastness

The fastness of a pigment to a particular solvent or medium merely indicates its ability to withstand exposure to that solvent. It should be noted, however, that this type of information is usually only essential for artists' colors when the binding medium would also deteriorate under similar conditions and thus expose the pigment to potentially deleterious conditions. In addition, since artists' paints are not made to withstand extreme conditions of exposure as would acid resistant paints, for example, the criteria need not be as demanding. Instead, as is commonly known, the chief source of danger to art paints in air pollution of various types.

The fastness of pigments to specific reagents is easily determined in the laboratory by suspending the pigment for one hour in a 1% solution of the reagent.

#### ii. Fastness to Acids and Alkalies

The concerns mentioned for solvents hold for acids and alkalies. Testing in this case is done in a 5% hydrochloric acid solution for acid fastness and a 1% sodium hydroxide or 5% sodium carbonate solution (the latter is less severe) for alkali fastness. ASTM D 970-65T calls for a two hour suspension at room temperature, followed by comparison of shade and bleeding changes with a suspension in distilled water.

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\* It is interesting to note that some methods exist for the identification of both organic and inorganic colors based mainly on their physical properties.<sup>30</sup>

### iii. Heat Fastness

These tests are largely unimportant for artists' colors since a painting is generally not exposed to temperatures higher than room temperature. In those cases in which a painting might be exposed to extreme heat, such as in a fire, the stability of the pigments is of relatively little importance since the supporting medium (e.g., canvas) is itself highly combustible.

### iv. Fastness to Light

While many commercial paint pigments are not intended to last for centuries, the opposite is obviously true for artists' colors. Of major concern to artists is the effect years of light has on the retention of the original color.

The resistance of a colored pigment to light is affected by the concentration, the medium used, and the nature and amount of white pigment present. Certain media, for example, provide a protective effect, while others accelerate changes in shade. In practice, however, the media used for artists' paints are chosen with protection as a major criterion so this problem is not of concern here.

Lightfastness also depends on the depth of shade. In other words, the greater the amount of reduction of the paint with a white, the faster will a color change occur.

It should be noted that some pigments become darker and stronger on exposure to daylight. Because this is a shift away from the original appearance of the color, it is considered to be as much of a defect as fading. Darkening rarely occurs with tints but happens fairly often with full tones.

Lightfastness is measured on a scale from 1 to 8 based on eight num-



bered patterns of wool cloth dyed with selected dyestuffs so as to fade in an approximately geometrical order (each standard takes about twice as long to fade a given amount as the one in sequence below it.)\* The measurement is made by covering a series of colored panels and standards with glass. The series is made up of varying combinations of different media and reductions: Half of each panel is covered with an opaque material and change in the test panels on extended exposure to sunlight can be compared to the standards.

If rapid information is required, exposure may be made with a carbon (ASTM D 625-70) or xenon-arc lamp (ASTM D 627-70) which gives a relatively good spectral energy distribution. While an acceleration of the fading process occurs, the results can be unreliable and may even differ from those obtained from daylight exposure (ASTM G 24-66).

#### v. Resistance to Bleeding

Although this category covers oil, solvent, water, plastics, and rubber bleeding, the types of most concern to artists' colors are oil, water and plastics. Bleeding in an oil medium is due either to solubility of the pigment itself in the oil or of some impurity present in the pigment. In oil painting bleeding occurs when the pigment in an under layer passes into an overlapping layer. This is especially serious when the upper layer is a lighter color, such as yellow, and the lower layer is dark, such as a maroon.

Oil bleed is tested (ASTM D 279-31) by rubbing the pigment and a small amount of linseed oil on a glass plate with a spatula until a thick paste is obtained. This is diluted with more oil until it is sufficiently

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\* For a complete description of this grading system, see Journal of the Colour Chemists Association 43(1960)586.

fluid. It is then spotted onto absorbent paper and the coloration of the oil halo is rated 1 to 5 when compared with a spot of oil alone. Extremely fine pigments may diffuse into the halo and make evaluation difficult. For paints made with other oils, such as poppy seed oil, these may be used in the test rather than linseed oil.

The relatively new acrylic-water plastic emulsion present the same type of potential bleeding problems. A test like that for oil may be performed or a small amount of the pigment may be placed with either water or the emulsion paint plasticizer into a test tube and shaken vigorously for five minutes. The tube is then allowed to rest until the pigment is completely settled out. If the pigment doesn't settle, or does so slowly, the mixture may be centrifuged or filtered until no pigment particles are in suspension. Fastness is rated as 1 (heavy bleeding) to 5 (no coloration). If a pigment is particularly hydrophilic either naturally (e.g., ultramarine) or from the presence of a surfactant, it may give the appearance of heavy bleeding.

Solvent bleeding determination is carried out by the same method as water bleeding. Examples of other tests used in commercial paints and which are of more or less importance depending on the type of paint are: Impact resistance, moisture vapor permeability, abrasion resistance, scrubability, washability, and weathering.

#### D. Optical Properties

##### i. Color

Since a dry pigment is a small colored particle in a gaseous medium (air), its appearance does not give any precise information as to the shade it will have in a liquid paint medium. Tests for color, therefore, necessarily involve prior incorporation into a medium. While it is pos-

sible to characterize a pigment by its colorimetric characteristics such as dominant wavelength, trichromatic coordinates of the color system divided by the International Commission on Illumination, or its hue, value (lightness), and chroma (saturation) of the Munsell System, etc., these precise determinations are not ordinarily done.\* In practice, simpler tests are regarded as sufficient:

ii. Masstone (or Overtone) or Full Color Tests (ASTM D 387-60)

These involve a simple dispersion of the pigment in the medium used: A weighed quantity of the pigment and enough vehicle to give a paste which "can just be thrown from the spatula by a gentle whipping motion of the hand" are rubbed intimately together on a glass slide with a palette knife or glass muller. After a set number of rubs in a precise fashion (an elliptical motion), the pigment is then heaped together again. This process may be carried out by an automatic muller consisting of two glass disks, one of which is fixed, rubbing over each other a fixed number of times. The "full-tone" paint prepared by the above method is applied onto a metal or glass panel or a sheet of bond paper with a spatula. This is compared with a standard pigment which is prepared in the same way and applied to the panel or paper in the same direction. It should be mentioned that inorganic and organic pigments differ in the amount of oil

\* When a test such as a spectrometric study of artists' pigments is desired it is carried out as follows:

- (a) hand grind the pigment with the minimum amount of medium necessary to make a paste.
- (b) apply the paint to a flat surface and let dry to a matt finish.
- (c) place the painted card in a photoelectric spectrophotometer designed to record light reflected at a single color (wavelength) as compared with a white standard.

This method was used by Barnes<sup>31</sup> who recorded:
 

- i. tristimulus values of forty pigments.
- ii. color purity of groups of pigments.

required for this preparation. For example, most inorganic pigments require from two to five times their oil absorption value, and organic pigments require from three to ten times their oil absorption value in order to give a consistency suitable for application to the panel or paper.<sup>406</sup> Both sample and standard should be applied in an opaque layer unless the pigment is normally transparent, e.g., alizarin red lake. Evaluation of the paint preparation is made either through the glass or on the surface in reflected light. Comparison gives data such as relative brilliance, possible bronzing, and degree of dispersion.

iii. Undertone

This is the color of a thin layer of pigment vehicle applied on a white background. It may also be determined by method ii. (above). In this case, comparison with the undertone of a standard may show slight differences not evident in the masstone. If there is a large difference between the color of the full strength paint film and the undertone, a great variation in color can be expected with varying film thicknesses.

iv. Tinting Strength (ASTM D 387-60 (1972) for Colored Pigments and ASTM D 332-64 (1940) for White Pigments).

Reduced color is produced by the mixture of a colored pigment with an opaque white. The mixture is prepared from separately mixed color and white paints, themselves made by the method in section (ii). The resulting mixture or reduced color is much lighter and much less saturated than the original color. In practice, the amount of white used may be from 5 to 200 times the amount of colored pigment, depending on the tincorial strength of the colored pigment and the type of white. Because it is a much stronger white, titanium dioxide is generally used in smaller quantities than zinc oxide. It is important in this test that the amount

of grinding of the pigment and the media and the mixture of colored and white paint be identical between standard and test sample in order to prevent visual discrepancies caused by a diminished development of color with either paint. Comparison of panels painted with standard and sample can give an indication of the tinting strength, hue, and cleanness of the sample. Results are usually reported as a ratio with the standard equaling 100. For example, a sample which has a greater tinctorial strength may be expressed as 'stronger 90:100' meaning that 90 weight units of sample are required to give the same tinctorial strength as the standard. Conversely, 'weaker 110:100' indicates a lower tinctorial strength and a need for 110 units of sample to produce the same results as 100 units of standard. Estimation of tinting strength can be exact only if there is no difference in hue between the sample pigment and the standard.

#### v. Hiding Power

The hiding power of a pigment is the degree to which it is capable of opacifying the medium in which it is dispersed. Hiding power of a pigment in a paint may be considerably variable depending on factors such as film thickness, pigment concentration and the degree of dispersion. For this reason, tests for measuring hiding power should be carried out in the same manner for each pigment in order that relative hiding power between, for example, various whites, be of value. The test may be carried out (ASTM D 344-30 (1970)) by applying fixed weights of sample and standard paints, having known concentrations of pigment, to identical paper charts. The latter usually have a checkered black and white pattern on them. After drying, the sample is visually evaluated to determine whether it reveals a contrast between covered white and dark squares relative to the standard. If there is a difference, i.e., equal to, inferior to, or

greater than the standard, the test is repeated with different weights of standard paint. The hiding power, or more specifically, relative dry hiding power, is then quantitatively expressed in terms of the proportional amount of paint required to produce the same contrast reduction (or uniform surface) obtained with the standard paint (sq. ft./gal.).

While a high degree of opacity is generally desired for commercial paints, this is not always true of artists' colors. It should be remembered that relatively transparent colors are as useful to the artist as opaque colors. The only criterion for artists' colors, in terms of hiding power, is that pigments that are accepted as opaque be sold in paints with a high enough concentration of the pigment to ensure that opacity. (See Arnold<sup>25</sup> for an optical evaluation of organic pigments).

#### E. Tests for Specific Pigments (Identification, Composition)

##### i. Alizarin Red

(a) Since this pigment can be so variable in shade depending on the manufacturing process, Harrison<sup>199</sup> suggests the following method for determining the brand: A small amount of alizarin lake pigment is decomposed by heating with pure concentrated hydrochloric acid and, after dilution, the yellow precipitate is filtered off, washed, and dissolved in an excess of potassium carbonate solution. The solution is compared with similar solutions made up of standard brands of alizarin. The variation shown by different brands is considerable and identification is therefore very easy.

(b) Alizarin pigment may be identified by its ability to turn a deep rose color in concentrated  $H_2SO_4$ . Dilution of the  $H_2SO_4$  solution yields a yellow precipitate.<sup>192</sup>

(c) Alizarin pigment may also be identified by the following spec-

ial. reaction. Boiled with 10% HCl and then made alkaline with NaOH, alizarin yields a magenta colored suspension.<sup>192</sup>

(d) The ash of burned alizarin contains Ca and Al.<sup>192</sup>

ii. Copper Phthalocyanine Blue

(a) Copper phthalocyanine blue may be identified by a flame test for copper.<sup>325</sup> A bright bluish-green colored flame indicates the presence of copper phthalocyanine. Since this is the only blue copper containing pigment used, the method may be considered specific to copper phthalocyanine. While phthalocyanine green also contains copper, the color of the flame is whitish due to the chlorine present.

(b) Copper phthalocyanine sublimes on burning to give a greenish vapor.<sup>192</sup>

(c) Dissolving copper phthalocyanine in concentrated  $H_2SO_4$  results in a yellow-brown solution.<sup>192</sup>

(d) Copper phthalocyanine is unaffected by hot 5% aqueous alcoholic KOH.<sup>192</sup>

(e) A test to determine the dispersion stability or resistance to flocculation of copper phthalocyanine blue is as follows (ASTM D 963-65): The blue pigment and titanium dioxide are dispersed separately in a vehicle based on alkyd resin and toluene. These are mixed and a portion of the resulting tint is sprayed onto a panel. When the film becomes tacky, a streak is rubbed gently on the panel with a finger. After thirty minutes, some of the tint is poured on a part of the panel. The panel is then dried for two hours at room temperature and baked for one hour at  $105^\circ$ . The strength differences between the sprayed, rubbed, and poured areas are compared with a standard. If the poured and rubbed areas are deeper in color than the sprayed portion, flocculation has occurred.

(f) The storage stability or the resistance of copper phthalocyanine

to crystallization and flocculation is measured as follows (ASTM 963-65): A tint, as in section (e) above, is prepared and sprayed onto a panel. Part of the dispersed blue color is stored for six weeks at 50-60° in a tightly closed container. After cooling to room temperature, a tint is prepared like that above and again sprayed. Comparison of the two panels will allow evaluation of the loss of tinting strength from crystallization or flocculation.

(g) A test for crystallization only of copper phthalocyanine is given as follows:<sup>64</sup> One g of pigment is added to 10 ml of xylene in a test tube. After thorough wetting of the pigment to produce a slurry, the tube is placed in a beaker of boiling water for 15 minutes. The slurry is examined under a microscope (x200) and compared with a control made from the original dry pigment mixed with xylene.

(h) Tests specifically for copper phthalocyanine pigment are given in ASTM D 963-65 (1970).

iii. Hansa Yellow G and 10G.

(a) The presence of an azo pigment is indicated by the complete burning (i.e., with no ash) of the sample on heating.<sup>190</sup>

(b) Azo pigments react with 5% aqueous alcoholic KOH in different ways depending on the position of the nitro group in the diazo component. If there is a diazo group in the p-position to the azo group, the color will change to the violet end of the spectrum. The Hansa yellows, therefore, exhibit no change in this reagent.<sup>191</sup>

(c) Beilstein's copper wire test is negative for Hansa yellow G and positive for Hansa yellow 10G.<sup>191</sup>

(d) The melting point for Hansa yellow G is 256° and for Hansa yellow 10G is 258°.



iv. Cadmium Sulfide Yellow<sup>118</sup>

(a) The amount of impurities or extenders in cadmium sulfide can be measured by dissolving 2 g of pigment completely in 10-15 ml HCl to give a clear solution of CdCl<sub>2</sub> and an evolution of H<sub>2</sub>S. The impurities can be filtered off and weighed.<sup>118</sup>

(b) Absence of soluble sulfate in cadmium sulfide can be shown by digesting 2 g of pigment in 2% hot HCl and filtering. The filtrate should remain clear on the addition of barium chloride solution.

(c) Absence of soluble chloride in cadmium sulfide can be shown by digesting 2 g of pigment in 2% nitric acid and filtering. The filtrate should remain clear on the addition of silver nitrate solution.

(d) Absence of free sulfur in cadmium sulfide can be shown by extracting 10 g of pigment with carbon disulfide for 1-2 hours. Evaporation of the extract should leave no residue of free sulfur. A blank should be carried out on the carbon disulfide.

(e) Absence of free acid in cadmium sulfide is shown by digesting 2 g of pigment with 10 ml of hot water and filtering. The filtrate should be neutral.

(f) The presence of cadmium carbonate is indicated by digesting 2 g of the pigment with 10 ml of glacial acetic acid and filtering. Any effervescence indicates the presence of carbonate.

(g) A quantitative test for cadmium in cadmium sulfide is as follows: 0.5 g of pigment is treated with dilute H<sub>2</sub>SO<sub>4</sub>, filtered if necessary, and the acidity adjusted to 2% H<sub>2</sub>SO<sub>4</sub> (by volume), H<sub>2</sub>S is then passed through the solution, the precipitate filtered off, washed, and redissolved in H<sub>2</sub>SO<sub>4</sub>. This solution is evaporated to dryness and ignited at not higher than 600°. The residue is weighed as cadmium sulfate.

(h) A quantitative test for the total sulfur content is as follows: dissolve the sulfide in 10 ml of a saturated solution of bromine in HCl to which a few drops of nitric acid have been added. The solution is evaporated to dryness on a steam bath, the residue dissolved in 10 ml HCl, filtered if necessary and diluted to approximately 100 ml. To this is added 5 ml of a 20% solution of ammonium chloride and an excess of barium chloride solution. The precipitate is removed by filtration, dried, ignited, and weighed as barium sulfate.

v. Cadmium Sulfo-Selenide Red

The quantitative tests for cadmium sulfide<sup>118</sup> (part iv., (g) and (h) above) may be used for cadmium red. For cadmium, the following must be done first:

(a) A quantitative test for cadmium in cadmium sulfo-selenide is as follows: 0.5 g of pigment are treated with a saturated solution of bromine in HCl and evaporated to dryness. This procedure is repeated several times to volatilize the selenium, and the estimation of cadmium is carried out as before. The following tests may also be performed.

(b) The total sulfur content of cadmium sulfo-selenide may be determined as follows: 0.5 g of pigment are treated with reversed aqua regia, and evaporated to dryness in a water bath. To the residue is added 1:1 HCl, and this is again evaporated to dryness. The residue is then treated with dilute HCl and BaSO<sub>4</sub> and other insolubles are removed by filtration. BaCl solution is then added to the filtrate, and the barium sulfate precipitate removed by filtration, dried, and weighed. From this can be calculated the total sulfur content of the pigment.

(c) The selenium content of cadmium sulfo-selenide can be determined as follows: 0.5 g of the pigment is treated with a saturated solution of

bromine in HCl and warmed until the insoluble residue is white. The latter is then removed by filtration, washed with 1:1 HCl, and discarded. The washings are retained with the filtrate and SO<sub>2</sub> is passed through them until precipitation of the selenium is complete (allow to settle overnight). The precipitate is removed by filtration on a porous crucible and weighed as elemental selenium.<sup>118</sup>

vi. Chromium Oxide Green

This pigment is extremely stable to heat, acids, and alkalis. One test for chromium oxide, given by Taylor and Marks,<sup>411</sup> is as follows: If the pigment is fused on a nickel crucible with sodium peroxide and extracted with water, it should give a solution of sodium chromate. Tests specific for chromium oxide green are given in ASTM D 263-46 (1970).

vii. Hydrated Chromium Oxide Green

This pigment is soluble in HCl, insoluble in alkalis, and, unlike anhydrous chromium oxide, retains its green shade on heating. Tests specific to hydrated chromium oxide are given in ASTM D 213-47 (1970).

viii. Ultramarine Blue

(a) An unknown blue sample is treated with potassium hydroxide to remove all blues except ultramarine and copper phthalocyanine. If the remaining blue is then treated with dilute HCl and the blue color disappears, the remaining sample is pure ultramarine. If the blue persists, copper phthalocyanine is present and ultramarine may or may not be present.

(b) The confirming test for ultramarine blue involves a reaction of the pigment with potassium or ammonium alum and the liberation of hydrogen sulfide. The latter is detected on filter paper moistened with lead acetate which darkens on contact with H<sub>2</sub>S vapors (lead sulfide being

formed).<sup>325</sup>

(c) Tests specifically for ultramarine are given in ASTM D 262-47 (1969).

ix. Titanium Dioxide White

(a) The presence of a titanium dioxide in a pigment is detected by boiling a sample of the pigment in a mixture of sulfuric acid and ammonium sulfate. To the diluted and filtered solution is added hydrogen peroxide. A clear yellow-orange color will be produced if titanium dioxide is present.<sup>409</sup>

(b) The presence of titanium dioxide in a paint is detected by the method above (a), except that the ash from the paint is boiled instead of the dry pigment.<sup>409</sup>

(c) If a titanium dioxide pigment is to be identified as either reduced or pure grade, two possibilities exist. If the sample is pure, the diluted sulfuric acid solution of test (a) will be clear. If the pigment is reduced with barium or calcium compounds, these will be precipitated from the sulfuric acid solution on dilution.

(d) Tests specific to titanium dioxide pigments are given in ASTM D 476-70.

x. Bone Black

Tests for this pigment are covered by ASTM D 210-47 (1967).

III. Appendix C. Preparation of Paints and Paintings

A. Preparation of Paints from Synthesized Pigments

The pigments were ground by hand (mortar and pestle) into acrylic artists' media (Liquitex acrylic polymer emulsion - gloss, matte and gel) until a small amount of the resulting paint when rubbed out onto a white porcelain palette had the consistency approximating that of the correspond-

ing commercial Liquitex paint, similarly rubbed out. In no case was grinding carried out for more than 4 hours.

#### B. Preparation of Paintings

For all the paintings, No. 10 canvas, glued with contact cement to a paper board support and coated twice with Liquitex acrylic polymer emulsion Gesso, served as the ground. The dimensions of the paintings in the first series varied from 18" x 18" to 24" x 36", while those in the second series were uniformly 25" x 28". Whenever one of the synthesized paints was used, a commercial Liquitex paint of the same pigment was used equally in terms of surface area, position, density of application, number of coats, etc. All the paints used were either full strength or mixed equally with Liquitex acrylic titanium dioxide white. No paint was mixed with any color other than white.

#### C. Discussion of Pigments and Paintings

A visual comparison of the raw synthesized pigments with commercial paints showed them to have a similar hue. In order to obtain a more realistic comparison, the pigments were ground into acrylic artists' media. This process, known as dispersion, involves replacement of the air surrounding the pigment particles with binding medium, as well as a slight lowering of the average pigment particle size by the breaking up of agglomerates. Industrially, dispersion is accomplished by automatic paint mullers in which the paints are ground for up to 24 hours, depending on the paint and pigment. Lacking automatic mullers, the paints were ground by hand using a mortar and pestle. Unfortunately, no data appeared to be publicly available for acrylic paints and so decisions about both the degree of grind and the pigment-to-media ratios had to be made by subjective visual comparisons with commercial paints.

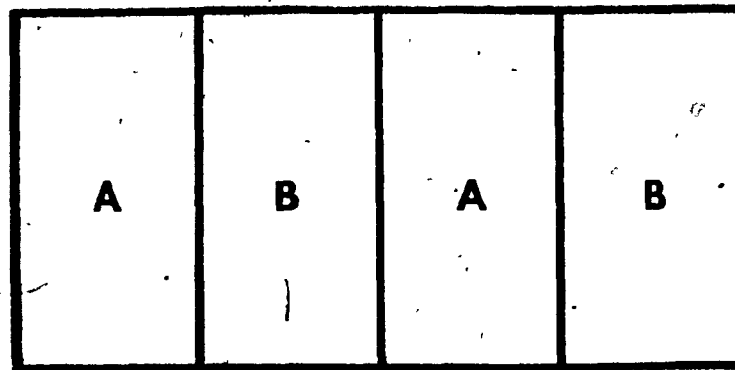
Theoretically, each pair of commercial and laboratory prepared paints should be identical. In practice, however, we expected some differences to arise owing to our lack of knowledge of the precise formulation of the media of the commercial paints and their pigment-to-media ratios. Also, the alizarin reds could actually be chemically different in the makeup of their lake substrates.

With these considerations in mind, we decided that the paintings should be as structurally straightforward as possible, i.e., color-field or hard-edge paintings, which can be defined as non-representational paintings in which the content is simply the relationship of the colors used. Two series of paintings were executed. The first series was relatively complex with several colors being used. This was based on the assumption that simultaneous comparison of several colors would be more interesting than a simple one-tone comparison. We discovered, however, that we were unable to make the desired comparisons owing to the interference of other painting problems, which could be traced directly to the most fundamental problem of painting on a two-dimensional surface, the figure-ground relationship.

Painting traditionally relies heavily on the use of illusionary devices for the creation of so-called "real" images. The illusion of space is achieved through various means, e.g., perspective, modulation of forms, horizontality, top-bottom relationships, overlap, etc., which all ultimately depend on successful manipulation of the figure-ground relationship. This factor is functionally and inextricably linked to the inequality of colors which arises from contributions made by a number of variables such as hue, saturation, brightness, shape, area, etc. The cumulative effect of these elements in traditional representational painting in the illu-

sionary buildup of three-dimensional forms on the two-dimensional surface. Implicit in this process is the effective obscuring of the separate contributions of the individual elements.

Our goal was the elucidation of the particular interrelationships between two colors. Isolating these from among the many figure-ground building elements we had introduced into our multi-colored paintings was impossible. Consequently, we designed a second set of paintings so that their structure was as limiting as possible. This was achieved by satisfying the following two requirements: (1) the paintings should be binary, i.e., only two paints A and B (A = our paint, B = commercial paint of the same pigment) should be used on each canvas; (2) A and B should be as equal as possible in terms of surface area, density of application, etc. Many variations are possible which meet these requirements, e.g., a checkerboard; we chose the following structure in which both A and B have



equal interfaces and identical borders. They are equally balanced left-to-right and there is no horizontal advantage for either. The only difference between A and B is that they are mirror images. With this arrangement, we found that the differences between A and B could readily be assessed.

This second set of paintings revealed the effect of such paint form-

ulation factors as the pigment-to-media ratio and the degree of gloss in the media. For example, the copper phthalocyanine paints, being transparent in paint films, were each mixed with an equal amount of opaque titanium white. While transparency is often a useful property of a pigment in a paint, it had to be avoided for our purposes. The reason for this is simply that the buildup of layers of transparent paint evenly is much harder to control than for an opaque paint, and evenness was crucial to our investigation. The mixed copper phthalocyanine blue paints were applied in three thin coats. The commercial paint proved to be both lighter and much less saturated than our paint, indicative of a lower pigment-to-media ratio which gave rise to the relatively low tinting strength.

Although we used the same brand of medium (Liquitex) as in the commercial paints, our medium had to be mixed from three different types (gloss, matte and gel). The standard colors, on the other hand, are available as semi-gloss, a media class not sold without pigments. That our medium mixture was different was illustrated by the chromium oxide green paintings. In this case, our paint was flat relative to the visual depth of the commercial green. This gloss-influenced difference is due to the fact that light reflected from the surface of a glossy paint appears to be reflected from a single, mirror-like plane. The paint seems to sit on the surface plane of the canvas. A matte surface, on the otherhand, has no single plane of reflection due to the apparent depth arising from light reflecting off multiple particles or layers created by the texture of the canvas ground.

Alizarin pigment, like copper phthalocyanine, has the property of forming transparent paints and so the alizarin paints were mixed equally



with opaque titanium white before application to the canvas. The resulting painting demonstrated another aspect of pigment and paint chemistry, viz., the striking difference possible for a pigment whose color development depends so much on reactants and reaction conditions. As mentioned earlier, commercial alizarins do vary from manufacturer to manufacturer and a similar difference was seen here. As mixed paints, the alizarins looked more or less similar. However, when painted in thin layers on the canvas, the two reds were remarkably different. Ours had a much lower grey content. In addition, our alizarin showed a much higher pigment-to-media ratio, being much more saturated and tending to go towards pink much less rapidly than the commercial alizarin (Selectone).

As far as could be determined, given the lack of information for the media, we found that our paints (with the obvious exception of the alizarin) and by inference, our original pigments, were extremely close in hue to those sold commercially as Liquitex paints. In the case of the cadmium sulfide yellows, there was no detectable difference between the commercial and laboratory prepared paints when applied to the canvas. Finally, over a year after the pigments were first synthesized (admittedly a short time for artists' colors), they show absolutely no signs of deterioration.

As a last observation, the general consensus of those who have seen the actual paintings is that they transcended their relatively objective origins to have a subjective appeal of their own!

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