The Chemistry and Physics of

ORGANIC PIGMENTS

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By

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PREFACE

The immediate inspiration for this book grew out of my preparation of two chapters on organic pigments for Volume II of the series of books, *Protective and Decorative Coatings*, edited by Dr. Joseph Mattiello. Dr. Mattiello's keen interest in my book and his generous support are greatly appreciated.

A further reason for writing this book was my growing conviction, over a period of several years' contact with the commercial development of organic pigment colors, that the literature, with special application to the field of organic pigments, is so scattered as to offer little assistance to a student in building up an appreciation of the important factors involved in experimental investigation and industrial application. This book, therefore, was planned to include a rather broad background of history, theoretical considerations of the relation between color and chemical and physical structure, the raw materials for synthetic organic pigments and the chemistry involved in the formation of colored products, the typical chemistry of dyestuffs and organic pigments, systematic consideration of structural types, methods of testing known and unknown pigments, analytical procedures and identification, and uses to which the organic pigments are adapted.

In a special chapter, emphasis is placed on a new interpretation of the significance of physical structure as related to color, a factor not ordinarily recognized and undoubtedly of little importance in the field of dyestuffs, except for certain vat types, but of fundamental importance in the field of organic pigments.

Consideration of the variety of uses to which organic pigments are adapted reveals a surprising breadth of application, and each of these fields represents a group to whom the basic facts concerning organic pigments may be of interest. These fields include paint, varnish, lacquer, enamels, printing inks, carbon papers, typewriter ribbons, rubber, linoleum, natural and artificial leathers, paper, wax, plastics, synthetic and natural resins, surface coating of paper, wallpaper, textile printing and dyeing, cosmetics, military camouflage, visual signaling, ceramics, and cement, as well as those fields where these items are the raw materials.

Once it was customary for consumers to use pigments without knowledge of their individual characteristics, aside from tinctorial values. However, because of insistent demand for uniformity, changing raw materials, fluctuating formulations, and new techniques of application, it is essential that consumers become familiar with the chemical and physical properties of pigments. This book may aid in developing a fuller appreciation of these relations.

In assembling the material for this book, I have had the finest cooperation from a great number of individual scientists, industrial organizations, and publishers of scientific books and journals which I hereby acknowledge with grateful thanks.

Individuals whose contributions have been of very great help include E. R. Allen and A. F. Brown, who reviewed the original manuscript and offered valuable suggestions for form and content; R. Abbott, E. R. Allen, Charles D. Allen, A. F. Brown, D. G. Brubaker, M. B. Doty, William Howlett Gardner, Rutherford J. Gettens, V. L. King, Hsein Wu, Robert Moore, H. S. Reed, J. L. Saunderson, E. I. Stearns, Vincent Vesce, Andries Voet, H. E. Weisberg, F. J. Wick, and G. W. Wheland, who contributed text and photographic material; and W. R. Brode, Carleton Ellis, Henry A. Gardner, W. T. Hall, Paul Karrer, Joseph Mattiello, Harold Strain, and Herbert J. Wolfe, who kindly permitted quotation from their own books.

For permission to undertake this work I wish to thank the former United Color and Pigment Company (J. A. Allegaert, president), now a part of the Calco Chemical Division of The American Cyanamid Company; and for permission to publish it I am indebted to the Publicity Committee of the Calco Chemical Division.

I wish to take this occasion to acknowledge the invaluable assistance of my wife, Ethel Withee Pratt, who, in addition to her interest and encouragement, has performed all the exhaustive stenographic work in connection with preparation of the manuscript.

My final and most hearty expression of appreciation is to those young men who have shared with me during the past twenty years the studies directed toward development of products with new and improved characteristics, clarification of difficulties encountered in commercial operations, and establishment of techniques and procedures on more sound and rational bases. Through discussion and speculation they have contributed directly to the evolution of many ideas and conclusions which appear in the following pages.

L. S. PRATT

WESTFIELD, NEW JERSEY
January 19, 1947

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Chapter I

Introduction

The term pigment (44) is derived from the Latin noun *pigmentum*, from the root of *pingere*, meaning to paint. Today its meaning has been expanded to include materials which are incorporated in a great variety of vehicles and media. Pigments are to be distinguished from paints, inks, and other similar compositions which are prepared from them by the addition of a suitable vehicle or medium. Nor are pigments and dyes identical, although often the coloring matter which yields a dye or stain may also give rise to a pigment. A pigment is, in fact, a substance that is insoluble in the vehicle with which it is mixed to make a paint, varnish, lacquer, printing ink, or other coating composition. A dye is soluble.

In biology (28) a pigment is any substance whose presence in the tissues or cells of animals or plants colors them. This definition includes in the term pigment two of the most vital materials in the organic kingdom, hemoglobin, the red coloring matter and the oxygen carrier in the blood of nearly all vertebrate animals, and chlorophyll, the green coloring matter in the foliage and tissues of practically all vegetation. The annual production of these substances in nature is far beyond the realm of profitable estimation.

In addition to these two essential pigments, others of importance are found in nature in the hair, fur, feathers, eyes, skin, claws, and hoofs of animals, as well as in the petals of flowers, the bark, roots, and wood of plants, in the skin and pulp of various fruits, in the crustaceans of the seas, and in a variety of insects. In general these represent the natural sources of organic pigments, or coloring matters from which pigments can be made.

For the purpose of this book a pigment may be adequately defined as a substance, colored or colorless, possessing valuable properties because of color, opacity, or bulk. It is insoluble, or substantially so, in the medium in which it is to be dispersed. Until only comparatively recent times all organic pigments were of natural origin, for the reason that all organic coloring matters were obtained from such sources. At the present time, however, the natural products have been largely replaced by synthetic materials which possess many superior characteristics, such as variety, uniformity, resistance to light and other physical and chemical agents, and purity or brilliance.

Organic pigments have achieved a very broad general use in many of the surface coating as well as the body color industries, such as printing ink, paint, varnish, lacquer, enamel, linoleum, rubber, wax, and plastics industries, and they represent today a commercial development of very great value.

This book is to deal primarily with the chemistry and physics of organic pigments and the dyestuffs or colors from which they are derived. This branch of chemistry is of interest because of the diversity of molecular structure and the variety in type of chemical reaction involved, but more particularly because of the unusual importance of the physical state or condition of the material in relation to its characteristics as a pigment. It is in this phase of the subject that an opportunity appears to exist for a broad line of valuable and extremely interesting research in establishing relations between the chemical and physical factors which influence pigment properties, and in developing techniques for more satisfactory study and measurement of ultimate particle size and shape, aggregation, molecular space relationships, and surface conditions and activities. It is to be hoped that this book may inspire constructive work along these and other equally valuable lines and may eventually bring about a more complete understanding of this most interesting field of practical research. In the past, consideration of the relationship between color and structure has been largely restricted to the basis of chemical or molecular structure. In this field of organic pigments, however, it will be shown that a definite relationship exists between color and many of the physical and chemical properties, on the one hand, and physical structure on the other. A separate chapter will deal particularly with this important phase of the subject.

In general, the basic chemistry of the organic pigments, up to and including the formation of the color molecules, is similar to that of the synthetic dyestuffs, the differences beyond that point consisting in the various procedures by means of which the dyestuffs are converted to insoluble products. It is in connection with these final steps that the factors of physical condition involving size, shape, and aggregation of the ultimate particles represent principles which apply quite specifically to this field.

The insolubility of the final products, and the resulting ready recovery, may prove to be of value in the use of this branch of chemistry in college and university work. The fact that laboratory experiments in which yields are generally high, and in many instances practically quantitative, tend to create a well-founded confidence in the student is a factor which, perhaps, has received less than its justified emphasis in the past.

The fundamental plan of this book is to make available to those who may be interested in the factors underlying the formation and the characteristics of organic pigments, the known chemistry involved in their preparation, the physical principles which are of recognized importance, and the ideas held by present-day workers in the field. With them as a foundation, progress in the field of organic pigments should be appreciably accelerated.

Chapter II

History

From early until comparatively recent times all organic pigments were of natural origin. According to Gettens and Stout (54), it was logical for prehistoric man who desired to decorate his implements or his person, make records of his mode of life, or paint pictures of the world as he found it to use the materials with which he came in daily contact. They included earth colors, vegetable coloring matters found in flowers, seeds, berries, nuts, bark, wood, and roots, and more rarely colors of animal origin. In general the natural earth colors, including the yellow, red, and brown ochers and clays and carbon blacks in the form of soot or charcoal, were very permanent colors, whereas the vegetable colors were fugitive, with few exceptions, to the action of light. There were notable exceptions, however, like the materials obtained from madder root, the woad plant, or from the lac insect, which under conditions not too unfavorable sometimes lasted for centuries.

Somewhat less readily available than the earths and the vegetable coloring matters were the colored minerals of the heavy metals. Even so, such brightly colored minerals as cinnabar, orpiment, realgar, azurite, malachite, and lapis lazuli were known to the ancients and were used for pigments in very early historic times. Since these minerals were not widely distributed and were almost in the class of semiprecious stones, their earliest use was restricted to the particular regions in which they were found.

Long before the period of written records, however, such minerals became articles of commerce and were transported to regions far beyond their origin. There is archaeological evidence of the use of cinnabar as a pigment in China as early as the third millennium B.C., and azurite was used in Egypt fully that early.

Artificial pigments have been made from the beginning of historical time, as evidenced by archaeological as well as literary sources. For example, artificial vermilion was not known in the West so long ago, but it was mentioned in the Arabic alchemical writings of the eighth and ninth centuries. The archaeological remains of ancient Egypt are rich in information about pigments used for decorative and architectural purposes.

Materials employed for pigments remained much the same throughout the Dark Ages, and information about them came largely from direct observations on parchment illuminations.

During the centuries of the late Renaissance, many vegetable pigments continued to be used, particularly for book illumination. They included coloring materials from safflower, brazilwood, turnsole, and woad. Later sepia and bister came into use for water color work on paper.

The first years of the eighteenth century mark the beginning of modern synthetic pigments. It was in 1704 that Diesbach (32, 54) in Germany discovered how to make the pigment that is still manufactured in large quantities under the same name, Prussian blue. It is the first pigment about which there is fairly definite knowledge and written contemporary record of the circumstances surrounding the discovery. From then on, equally definite knowledge of the date of discovery of new pigments is available from published records in scientific journals. Conspicuous developments were the discovery of cadmium yellow by Stromeyer in 1817, of artificial ultramarine by Guimet in 1824, and of viridian in 1838.

A new epoch in the history of pigments, and particularly of the organic pigments, began in 1856 when William Perkin in England announced the preparation of the first synthetic dyestuff, mauve. It should, however, be clearly recognized that synthetic organic dyestuffs preceded this discovery. Woulfe (145) in 1771 prepared picric acid, which is still recognized as a useful wool dye, from indigo and nitric acid, and in 1834 Runge discovered rosolic acid or aurine (115).

The spectacular developments in the field of synthetic dyestuffs following Perkin's discoveries in 1856 were largely made possible by the researches of Hofmann and Mansfield (66) which resulted in the commercial production of benzene and the other aromatic hydrocarbons from coal tar. With these materials available at reasonable cost, it was possible for rapid advances to be made in this field of organic research. Commercial development followed with a speed that furnished a tremendous stimulus to further discoveries.

The development tree shown in Fig. 1 gives a picture of the extraordinary rate of discovery and industrial development during the early years of the dye industry. Even though more recent years have been less spectacular, it is still true that progress has been continuous and the end of the road is even yet hidden in the mists of the future.

Another measure of the rate of industrial progress is afforded by Fig. 2, which shows the number of commercial products discovered yearly as indicated by a survey of the Colour Index (32). It will be clear to the reader that this chart includes only those individual products which were successfully used commercially, and in most cases patented, and they represent no large percentage of the many dyestuffs discovered and worked upon during this period.

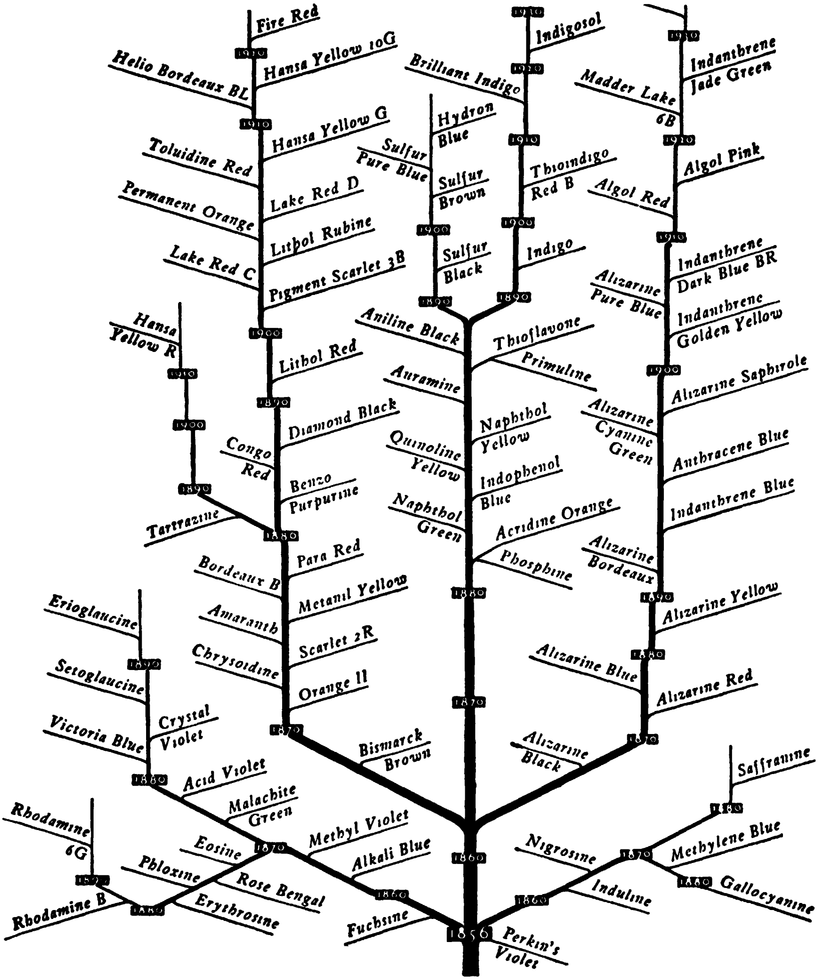


FIG. 1. Significant Developments in Organic Color Chemistry. (*Courtesy of Interchemical Corporation.*)

Dates are less readily established for the discovery of the individual organic pigments, with a few exceptions. It is quite generally true, however, that the possible pigment value of a given dyestuff was recognized early, and in many cases the dates may be regarded as identical with those accepted for discovery of the corresponding dyestuffs.

Ellis (42) says that the first manufacture of synthetic organic pigments in this country began about 1895 with para reds, hansa yellow, lithol red, Lake Red C, and toluidine red, the supplies before then having been obtained almost entirely from Germany.

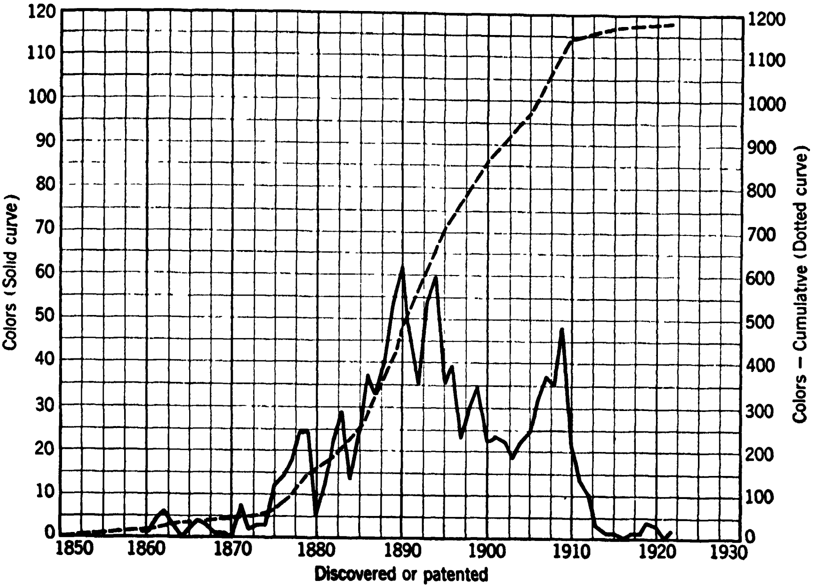


FIG. 2. Dyestuffs.

The history of the organic pigments has been featured by many changes in the requirements for quality. In ancient times these materials, derived as they were from a variety of natural sources, represented a curious mixture of desirable and undesirable characteristics. Included in the list were some of the most light-fast pigments known until very recent times, madder lake, for example, woad, and cochineal, as well as a large percentage of extremely fugitive and otherwise sensitive products. At that time such conditions were quite generally accepted as a matter of course, and no special effort was made to correct them.

With the introduction of the synthetic dyestuffs in the latter part of the last century many new and beautiful pigments were prepared. Some of them were derived from the so-called basic dyestuffs which were, and are, among the most brilliant colors known. It was found possible to convert these dyestuffs, which exist in all the colors of the rainbow, into pigments of extreme brilliance by treatment with, among other reagents, sodium arsenite. The arsenic products were employed in the manufacture of beautiful wallpapers and other surface coatings. It is quite understandable today that many instances of poisoning occurred, particularly among children playing about the house and rubbing their hands upon the walls. The danger of arsenic poisoning was recognized early in the present century, and from that time to the present the use of non-toxic pigments for surface coatings has been standard practice.

Just previous to and during the first world war, and encouraged particularly by the discovery and introduction of the phosphotungstic-basic color toners and lakes, the value of fastness to light became clearly recognized and it was made a feature of the pigment developments of that post-war period. Other pigments which also contributed to this change were the hansa yellows, the so-called rubines, and very recently the benzidine yellows and phthalocyanine blues and greens. These materials, in addition to the few excellent products previously available, have made it possible for the pigment user of today to select a list of very satisfactory colors for the usual commercial purposes.

Within recent years the most striking tendency in the field of pigment colors is toward improvement in cleanliness and strength and in what are generally referred to as "working properties." The stress on working properties is especially noticeable in the field of printing inks, in which so-called lithographic characteristics, including low consistency, flow, ease of grinding, and lack of bodying or livering tendencies are becoming more and more important.

The most interesting phase of organic pigment research and development probably lies in the immediate future and indicates the course to be taken in commercial and scientific investigations. The data on which these developments are to be based may be quite obvious, even though they are seldom interpreted in that way, and the real difficulties appear when the attempt is made to analyze the indications in some specific manner. Nevertheless, in a broad way it is clear that the near future will see more widespread use of new kinds of synthetic resins, new methods of printing, dyeing, and other types of color application, a great variety of new plastic materials which will appear in articles of everyday use, new varieties of artificial fibers, new appreciation of the possible practical uses of fluorescence and phosphorescence, and new principles in the art of aerial navigation, signaling, and communication resulting from solution of critical military and naval problems. All these developments will broaden the field of pigment colors and foster a continued search for new and valuable types to satisfy the new requirements.

A more distant look into the future is, as it should be, denied to us. Full realization of the goals to be reached at some remote period might so distort the viewpoint of today that the essential mechanism of growth could be disastrously altered or even interrupted. It is important, therefore, to build for the future on the concrete foundation of the present, and to employ every phase of scientific activity which may have something to contribute to maintenance of steady advancement.

Chapter III

Color and Chemical Structure

In a general way, dyestuffs and the synthetic organic pigments are similar. The distinguishing difference in most cases is the solubility of the dyestuffs and the insolubility of the pigments. This distinction, however, is not clear-cut as many of the recognized dyestuffs are insoluble, their use being dependent on special methods of application or development, whereas many of the pigments are soluble in non-aqueous solvents. Therefore, only from the chemical and structural point of view may they be regarded as similar.

The problem of the source of color in a dyestuff or pigment has occasioned a vast amount of work and speculation among both chemists and physicists. In the earlier periods attention was confined largely to what we now refer to as visible color, which, in principle, is similar to the broader field of wave absorption in the invisible ultraviolet and infrared regions of the spectrum. It was therefore natural that the earlier attempts to correlate color with structure should be concerned primarily with visual color, and a rather sharp distinction was often drawn between colored and colorless compounds.

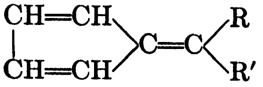
It was for a time believed that the position of absorption bands corresponded definitely with the presence of various groups in the molecule and the comparison of absorption spectra was used for the determination of molecular constitution. It is now recognized, however, that pure spectra cannot be obtained under the conditions then employed (in solution) owing to molecular collisions.

A correlation between unsaturation and color was first observed by Graebe and Liebermann (60). It was noticed that most of the colored compounds containing no aromatic groups possessed a conjugated chain of alternate double and single bonds. For example, glyoxal $O{=}CH{-}CH{=}O$ and biacetyl (diacetyl) $O{=}C(CH_3){-}(CH_3)C{=}O$ are yellow.

Among the following, the first two absorb only in the ultraviolet, whereas the third is colored intensely yellow:

1. $CH_3CH{=}CH{-}CH{=}CH\cdot COOH$ (sorbic acid)
2. $CH_3(CH{=}CH)_3{-}COOH$ (triethylenic acid)
3. $CH_3(CH{=}CH)_4{-}COOH$ (tetraethylenic acid)

The fulvenes are also excellent examples of colored conjugated hydrocarbons:



Orange to Deep Red

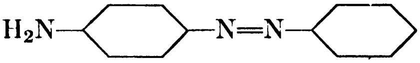
O. N. Witt, in 1876 (143), was the first to present an interpretation of these observations that afforded a basis for real progress. He concluded that certain groupings, or arrangements of atoms within the molecule, were responsible for the appearance of color in the visible region of the spectrum. He called these groupings *chromophores*, and among them he listed the following:

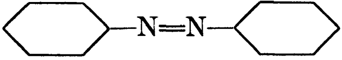
$$>C{=}C<,\ >C{=}O,\ >C{=}S,\ >C{=}NH,\ —CH{=}N—,$$
$$—N{=}N—,\ —N{=}O \text{ and } —NO_2$$

He also recognized that for the substance to be a dyestuff required salt-forming groups to give the molecule an affinity for the fiber. These groups he called *auxochromes*. Among them he included the following:

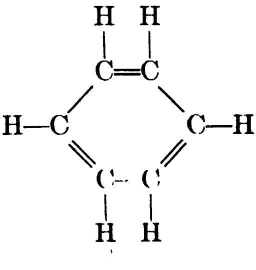
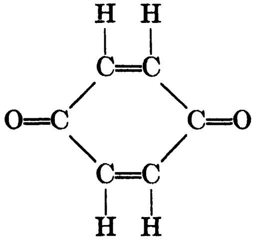
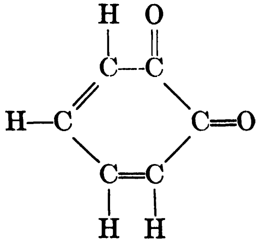
$$—OH,\ —NH_2,\ —NHR,\ —NR_2,\ —SO_3H \text{ and } COOH$$

The molecule without the auxochrome was called the *chromogen*. Thus the dyestuff aminoazobenzene,



contains the chromophore —N=N— known as the azo group, the chromogen , and the auxochrome NH_2. The auxochromes also cause an intensification as well as frequently a change or modification in the color.

Nietzki's rule (100) of 1879 states that an increase in the molecular weight deepens the color. Piccard (106), however, shows that this may not be true in all cases owing to the introduction of a second absorption band at the blue end of the spectrum.

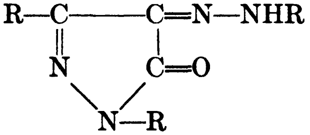
The quinone theory of Armstrong (7) proved to be particularly useful and stimulating. Although benzene  is colorless, *p*-quinone  is yellow and the stable form of orthoquinone  is red.

In fact in many cases the change from a benzenoid to a quinonoid structure is accompanied by the sudden appearance of color, and in the consideration of dyestuffs in general it is found that many of the typical color groups may be formulated in accordance with the quinonoid structure. The following groups are included:

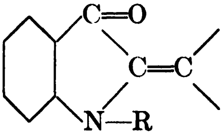
Nitro
Diphenylmethane
Triphenylmethane
Xanthene
Anthraquinone
Azine
Quinoline
Acridine

The existence of a quinone structure in most of the other groups of dyestuffs is not fully established, notably in the azo dyes.

Certain other ring structures bear a close resemblance to the orthoquinone structure:



Pyrazolone Type



Indigo Type

According to Cain and Thorpe (24),[*] "There is no doubt that the two best-established causes of color are the presence of conjugated and quinonoid systems and it may be suggested that these will be found to have a common origin."

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[*] Reprinted with permission from *Chemistry of the Synthetic Dyestuffs*, 7th Ed., published by Charles Griffin and Co.

Willstätter and Piccard (142) have shown more recently that comparatively unstable compounds formed from one benzenoid and one quinonoid unit, and linked by "partial" valencies, are more intensely colored than the corresponding free quinones.

A considerable number of studies have been made of the relation between the absorption spectra of dyes and their molecular structure, such as Brode's study (18), in which the effect of substituent groups in varying positions in the molecule was carefully measured. Definite effects were noted with respect both to the nature of the group and to its location in the molecule.

Interesting contributions are also being made bearing on the coordination complexes. Gardner (52) indicates that many properties that cannot be explained by the older concepts may be accounted for on the basis of such complexes. These space lattice relationships may bring very valuable results in the future, especially in view of their intimate connection with the physical orientation of the molecules and their arrangement in the crystal lattice. Pfeiffer (105), Pauling (102), Keggin (77), Mason (95), Drew and Landquist (41), Kunz and coworkers (85), Linstead and Bradbrook (90), and others have made significant contributions to this study.

One of the more recent conceptions, *resonance*, seems to supplement and bind together many of the earlier conceptions to give a rather convincing dynamic picture of the relation of structure to color. A substance is said to resonate when it is possible to construct for the molecule two different electronic structures that are equivalent, or very nearly equivalent, to each other.

The simplest possible resonating molecule is the hydrogen molecule ion $H_2{}^+$, which can exist at low pressures and is formed by bombarding hydrogen gas with high-speed electrons. The single electron that forms the bond joining the two hydrogen nuclei vibrates rapidly between them in complicated orbits which may or may not include the two nuclei as foci, but which bring the electron, part of the time, close to one nucleus, part of the time close to the other. To represent in a simple way these two possibilities one may draw the two electronic structures H· H and H ·H, which are equivalent. The molecule is said to resonate between these two.

According to Sidgwick, Taylor, and Baker (125): *

> The conception of resonance is the most important development which structural chemistry has had since it was extended to three dimensions by van't Hoff in 1874.
>
> The conditions for resonance to be possible between two structures are these:
>
> I. The relative positions of the atoms in space must be nearly the same in both.

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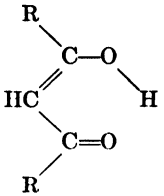
* Reprinted with permission from *The Organic Chemistry of Nitrogen*, published by the Oxford University Press, London.

II. The two must not differ too greatly in stability, or, in other words, both formulae must be reasonably probable.

III. The number of paired electrons must be the same in both. This last condition is practically always fulfilled, so long as we are not dealing with "odd molecules." The results of the resonance are the following:

1. The molecule has to some extent the properties of each constituent structure, though not necessarily to the same extent, the more stable form predominating.
2. The hybrid has a smaller energy content (a greater stability and heat of formation, a smaller heat of combustion) than either of the two structures.
3. The distances between the atoms are rather smaller than normal.

Examples of chelate compounds which meet these conditions are the β-keto-enols and the o-aldehydo-phenols. Here we have the two resonance structures, in one of which the hydrogen is attached to one of the oxygens, and in the other to the other:



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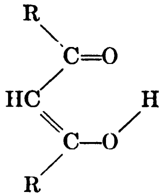

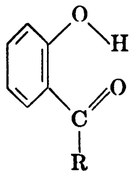

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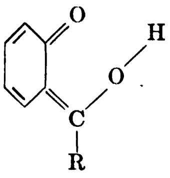
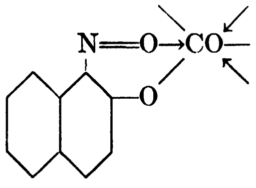


Examples of similar possibilities among dye and pigment structures are to be found in many classified groups. For example, the α-nitroso compound of β-naphthol (nitroso-β-naphthol) forms what appears to be a resonance hydrid with metals such as cobalt and iron (122):



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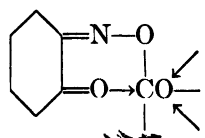
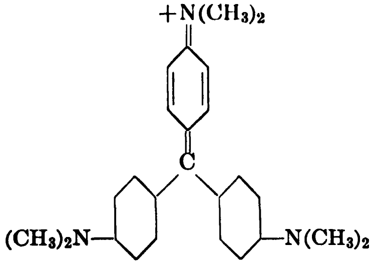


The actual complexes are made up of three such residues attached to one atom of cobalt. Wheland (140) points out:*

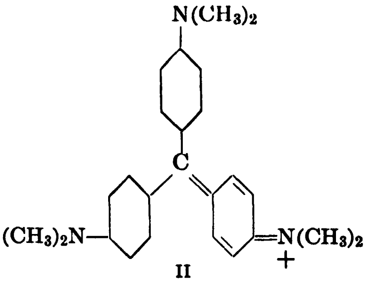
> Many of the most familiar dyes are salts in which the colored cations or anions resonate among structures that differ widely in the distribution of electric charge.

* Reprinted with permission from *The Theory of Resonance and Its Application to Organic Chemistry*, published by John Wiley and Sons, Inc.

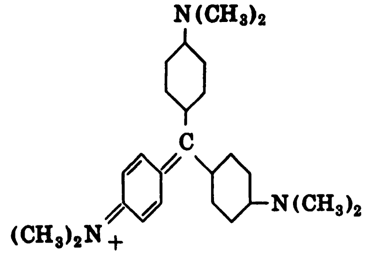
For example, in the ion of crystal violet the most important structures are presumably ones like I, II, and III, although numerous further structures like IV, V, and VI must also be involved. Indeed, if these latter structures were not possible, the resonance could be of only minor importance since then the condition [requiring that the electrons should not differ too widely in position] would not be satisfied. As a result, the states of the ion arising from the resonance among the structures like I, II and III would have practically identical energy; the absorption of light that would occur during a transition from one of these states to another would therefore be at a tremendously longer wavelength than observed.



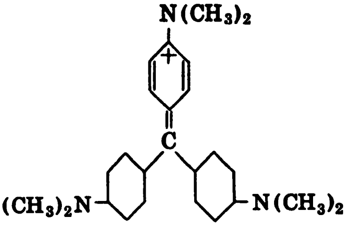
I



II

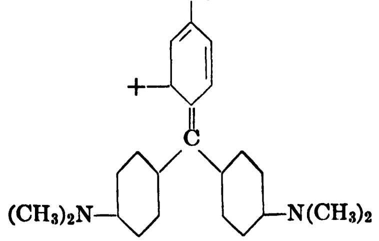


III

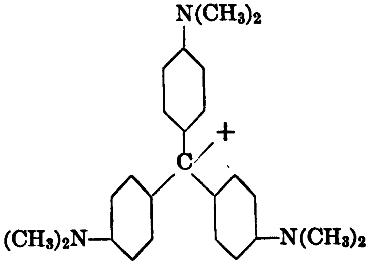


IV

When the further structures like IV, V, and VI are considered, however, the difficulty is removed, because structure I, for example, can resonate effectively with IV, which in turn can resonate with V, and so on until the structures II and III are finally reached.

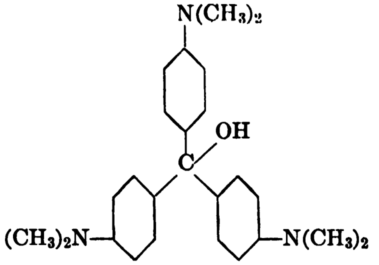


V



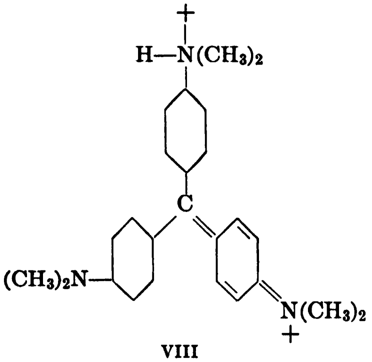
VI

The carbinol, VII, is the color base corresponding to the dye, crystal violet.

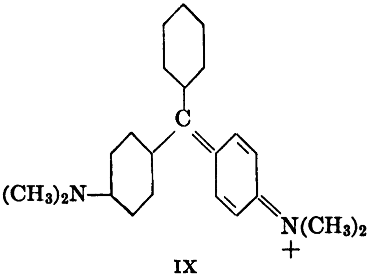


VII

The possibilities for resonance are much more restricted here than in the dye, and the structure is colorless. A further interesting fact in regard to crystal violet is that in strongly acid solution it loses its characteristic purple color and becomes green. This is because the ion acquires a proton under these conditions and takes on a double positive charge, as in VIII; the possibilities for resonance are then the same as in malachite green, IX.

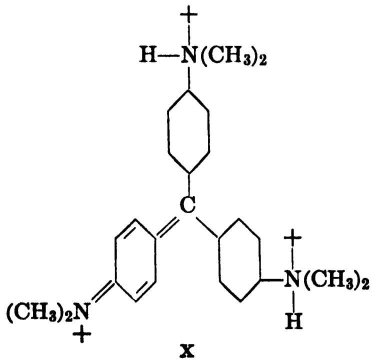


VIII

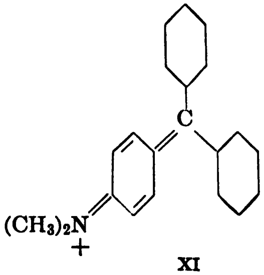


IX

In still more strongly acid solution, the color becomes yellow, as the ion X is formed: this ion corresponds to the simpler ion, XI, which also is yellow.



X



XI

Resonance, or the period of vibration, in a molecule is therefore dependent on the composition and structure and may in certain cases be altered at will. In many ways this introduction of a definitely active and dynamic condition into the interpretation of the relation between color and structure is more convincing than previous static conceptions, as the absorption of electromagnetic waves can best be understood on such a basis.

With special reference to pigments, it is probable that not only the molecular configuration but also the crystalline condition of the solid material must be considered in explaining the color of a pigment. Thus it is conceivable that the molecular structure may constitute the fundamental cause of color in the pigment, but wide variations in the hue, depth, intensity, and brilliance may be dependent to a marked degree on the physical structure.

Chapter IV

Color and Physical Structure

Consideration of the physical structure of organic pigments, as contrasted with chemical or molecular structure, is made necessary by the fact that particles which are formed by crystal growth, accretion, or aggregation exert a direct influence on incident electromagnetic (including light) waves, in addition to the usual absorption, by introducing the factors of both dispersion and reflection. The result is a modification in the apparent tone, strength, and brilliance of the material, and in its spectral characteristics, as compared with the effect produced on the electromagnetic waves by simple molecular absorption.

In this connection it may be noted that sodium, barium, and calcium lithols, which cover a rather extreme range of yellowish to bluish reds, give similar absorption curves (Fig. 85, Chapter X) when the measurements are made by transmission through solutions in sulfuric acid or pyridine, but give widely different curves when the measurements are made using reflectance methods with the pigments incorporated in the usual varnish or oil vehicles or in powder form. This suggests the conclusion that the difference in the color of the various metallic lithol reds may be due primarily to their differences in physical structure, which further involves the problem of particle size and crystal habit.

The relationship between structure and color as outlined in the preceding chapter has been dealt with largely on the basis of simple presence or absence of visual color, with but relatively little emphasis on other factors, or even on the part of the spectrum involved.

From a practical standpoint, however, there is less interest in considering a green in comparison with a red than in sharply differentiating between two greens or two reds which are relatively close in general tinctorial properties but differ in some way that may be of value in a particular method of use. It is in this phase of the subject that the major departure from typical dyestuff chemistry is encountered. For example, one red pigment (Exp. 2) in comparison with another of similar composition (Exp. 1), both being incorporated into an oil vehicle such as a lithographic varnish, may be found:

Slightly deeper and brighter in masstone.
Equal in overtone.
Considerably yellower in tint.
Five per cent stronger.
Appreciably less fast to light.
Somewhat harder in dry texture.
Appreciably less easy in grinding.

Assuming that these two colors are made from the same raw materials, in the same type of equipment, how can we account for the differences in characteristics noted? It would be logical to assume that the differences were brought about by variations in the methods of handling or details of operation, and it will therefore be of interest to examine these details somewhat more intimately and determine at several points in the operation what might be the result of certain variations in procedure. For example, during the precipitation of the pigment the efficiency of agitation or mixing may have been much higher in the case of 2 than of 1. An increased efficiency of mixing would tend to produce smaller particles than the mixing in 1. Such a variation in particle size might be sufficient to account for all the noted differences between 2 and 1.

In another test it may be assumed that all conditions remain the same except that the volumes of the solutions used in precipitating the pigment are 50 per cent larger in 2 than in 1. The formation of the particle in a higher state of dilution definitely tends to produce a smaller pigment particle.

In still another test it may be assumed that all conditions remain the same, including efficiency of agitation and volume, but 1 is heated, after precipitation, to the boil, whereas 2 is heated only to 50° C. In this case the opportunity for crystal growth to take place is much greater in 1, and this will result in the presence of fewer but larger particles.

These three sets of experiments illustrate conditions which might yield directly the two types of pigments described. It is therefore clear that the physical conditions, including particle size, and probably particle shape, are of primary importance in the control of uniformity in the manufacture of these products.

It may be of interest to go more closely into the actual mechanics of the formation of the particles of which these pigments are composed. For example, in the reaction between a solution of the sodium salt of eosin and a solution of lead nitrate, there is an immediate and copious precipitation of a flocculent, rapidly settling, deep red pigment.

It is reasonable to assume that the reaction between molecules of these materials resulted first in the formation of molecules of the pigment color. They were of molecular dimensions and would in that condition show no tendency to settle. In fact there would be little or no indication of the formation of an insoluble product as the solution would still be of the subcolloidal type and visually similar to a true solution. At this point two separate and distinct forces become active, one being crystal growth, which at this stage of extreme subdivision is undoubtedly very rapid in its action. The other is the force of flocculation or aggregation, which acts with tremendous speed in this particular instance.

The precipitate, which appears so quickly and settles so rapidly, has already passed through very definite and highly significant changes in size, and probably shape, of ultimate particle as well as in extent or degree of association of these particles to form clusters which are evident to the eye. Within a relatively short time, possibly 10 to 30 minutes, these actions become fairly well established and proceed at a greatly reduced speed.

If, at this point, the temperature should be gradually raised, the rate of change might again become appreciable and cause further noticeable alteration in color characteristics. Again there may be doubt as to which particle form is undergoing change. The color is, as a rule, finally filtered, washed, and dried, and possibly ground in a suitable mill or disintegrator.

Particle changes may continue under these conditions of moisture and high temperature, under the condition of gradual elimination of moisture, and particularly during disintegration. Drying may result in a further complication due to cementing the particles or flocculated clusters by soluble materials such as salts, or the cementing tendencies of fine particles even in the absence of soluble matter. In grinding the dried product, fracture of the sintered mass, by high velocity impact, may (1) only break up the sintered mass, (2) simply separate the dried clusters, (3) actually disintegrate the firm clusters, or, in excessively fine grinding, may possibly even (4) smash the finally developed ultimate particle. The last, however, is believed to be less likely.

The foregoing discussion indicates that continuous change is taking place from the instant the color molecule is formed until the product is finally ground and in the barrel. But, if this is true, how is it possible to produce material of satisfactory uniformity from batch to batch?

The strictly correct answer is that probably no two batches are ever made exactly alike and no two final products are ever exactly alike, but, with proper attention to those periods in the operations in which the rates of change are more rapid, it is possible to obtain products which fall within a sufficiently narrow range of property variation.

The problem of particle growth has been studied in a very interesting and realistic manner with the silver halide grains employed in photographic emulsions. In connection with this work it has been pointed out by Sheppard and Lambert (124):*

> The production of a precipitate, i.e., the formation of a solid phase, is broadly divisible into two periods or moments. The first consists in the inception or nucleation of the new phase; the second in the growth of grains, either by accretion from within or by aggregation of particles. Although these periods are ideally separable, in practice it is not always possible or desirable to separate them.
>
> The following tentative theory is proposed. In the first stage of digestion the process of Ostwald ripening is occurring, grains below a certain size are dissolved and grains above a certain size growing by accretion from solution. This process proceeds to exhaustion of the grains whose solubility is appreciably different from that of the largest. This would lead to practical cessation of grain growth. We find, however, that actually the grain growth goes on but at a new and decreased rate. This we assume to be due to recrystallization within the aggregates produced by collisions and coalescence. It has been observed already that this coalescence appears to increase rapidly once the "break" in the growth curve has been reduced. We suggest the following explanation of this.
>
> In the pure Ostwald ripening, each particle is surrounded by an electrostatic double layer. We regard this double layer as essentially a layer of imperfectly oriented ions of the solid plus ions of the solubilizing potassium bromide, these ions being more or less hydrated according as they are less or more completely oriented in the crystal lattice. The hydration of each ion is supposed to consist of a monomolecular sheath of oriented water, H_2O, dipoles, which are more or less numerous, according as the electric moment of the ion is not taken up by its attraction and fixation in the crystal lattice. It is therefore a maximum at some distance in the solution from the crystal and falls off very rapidly at the surface.
>
> This seems compatible with both Gouy's theory of a gradually diminishing double layer—since presumably there is an influx and efflux of hydrated ions—and with McBain's theory of a monomolecular double layer, since the only dimension that can be attributed to it is that of the pairs of ions of opposite sign.
>
> In the stage of Ostwald ripening these layers are not in the same state for the dissolving particles as for the growing particles, since in the former the layer is being renewed from within, in the latter from without (*A*).
>
> While the process of Ostwald ripening is proceeding, there is in principle a transfer of water from the growing grain to the dissolving grain. They are kept apart by the neutral water atmosphere thus created, so that very few collisions result in coalescence. When the process has declined, the double layers are similar in character as to hydration of the ions and as to relative efflux and influx of ions out of and into the double layer (*B*). These can coalesce on collision like two similar liquid globules,

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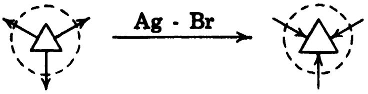
i.e., according to the fluctuation of the orientation and local surface charge giving a common double layer, and the two crystals - occasionally more—being in absolute contact (*C*).

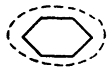
The double layer then will tend to reduce its potential (interfacial) energy, thus bringing the crystals into a maximum possible contact (*C*). There is still further reduction of this potential energy possible, by recrystallization out of the double



A. Ostwald Ripening.

B. Stage of No Growth.

C. Coalescence and Crystal Orientation.



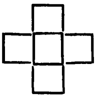
D. Recrystallization.

layer, i.e., assuming migration of the imperfectly oriented silver and bromine ions of the double layer. This means a recrystallization, by which a single crystal tends to form from the aggregate crystal (*D*).

It is conceivable that the particle thus finally built up by growth and accretion may represent what is sometimes referred to as *the ultimate particle.* Assuming this to be true, it is quite obvious that this condition of matter still does not represent the pigment products which are precipitated, filtered, washed, and dried in the plant. This is due to the fact that, simultaneously with the changes described above, other changes occur that appear to involve the tendency of these particles to come together in more or less tight clusters which separate from the solution and settle much more rapidly than the individual small particles. This action is generally called aggregation or flocculation, and its mechanism, in a broad way, is quite generally accepted. Its relation to the properties of organic or inorganic pigments, however, is not so generally recognized.

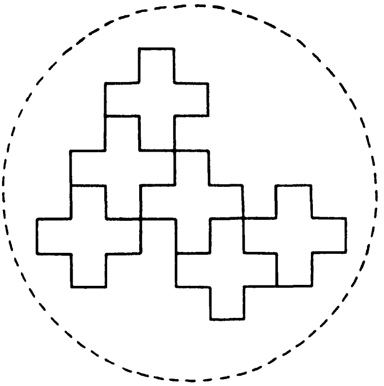
For example, it may be assumed that the ultimate particle is that described above. It is, then, conceivable that flocculation is brought about by a series of steps, in the first of which a few particles come together to form a more or less firm cluster which may be quite difficult to rupture or break up.

Ultimate particle—1 particle



α-Cluster—7 particles

The α-clusters as separate units may then come together in such a way that a larger β-cluster is formed, of a somewhat more fragile structure than the α-cluster but with planes of symmetry maintained:



β-cluster—42–100 or more particles

Since the planes of symmetry are preserved, it will be apparent that both α- and β-clusters might be confused microscopically, and even by other means of observation, with the indicated ultimate particle.

Figure 3 represents a fanciful structure, shown in perspective, which combines three methods of accretion, or combination of the α-clusters. The upper vertical portion shows a loose attachment which would be very fragile but would tend to tangle or aggregate readily with other similar groups. The right-hand arm illustrates a more dense type of aggregation, but, even so, a less dense type than shown in the left-hand arm. These forms, being more dense, tend to aggregate less readily than the vertical form. All three forms of aggregation, or accretion, maintain the planes or axes of symmetry throughout.

This β-cluster might possibly represent the stage of flocculation which would settle quite slowly, and a still more complex type of cluster might be required to correspond to the rapid settling material met with in actual practice, in which the planes of symmetry may not

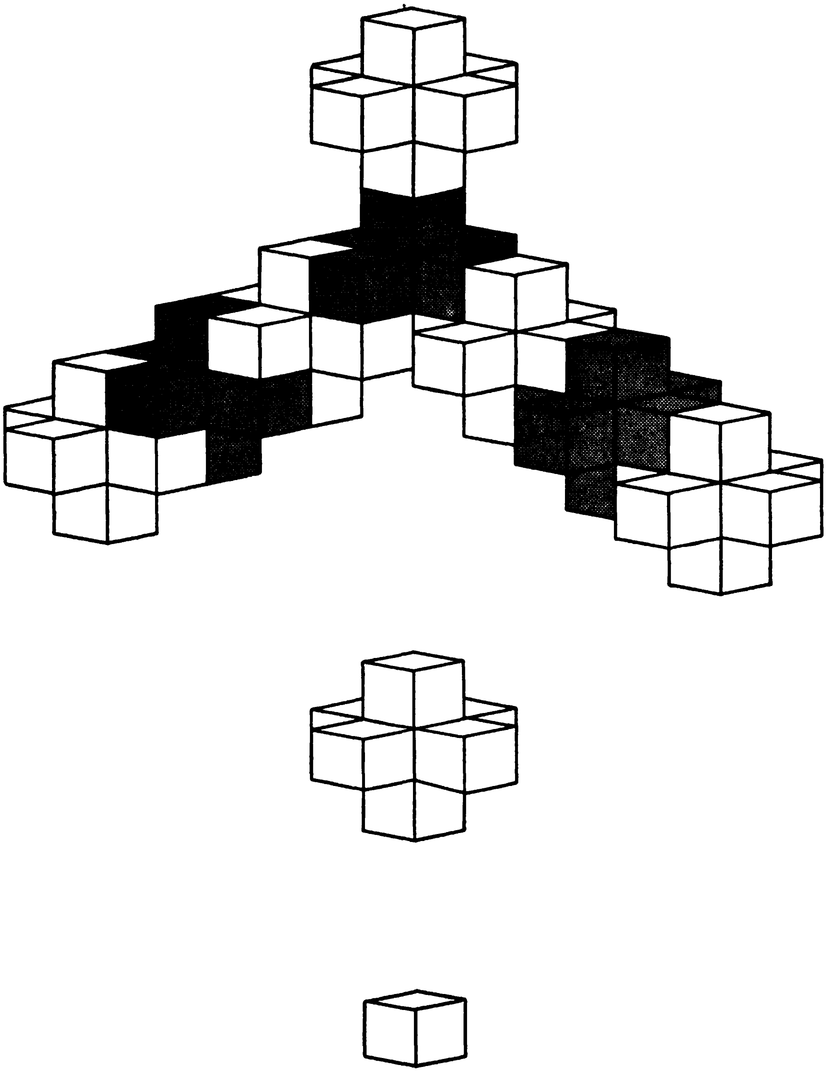
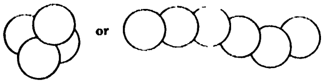


Fig. 3. Methods of Accretion.

be maintained. If the β-clusters are now represented by spheres, the γ-clusters might appear as follows:



γ-clusters—300–600 or More Particles

This conception of increasing complexity could, of course, be continued ad infinitum, but possibly the above series is sufficient for present purposes since each step is designed to represent a distinct phase.

The γ-clusters might be regarded as representing the condition of a pigment in the pulp form or in the condition of the filtered and washed cake. This might be the form in which the material is used in flushing operations or in aqueous vehicles of various sorts.

With regard to the effect of crystal shape on the color values of pigments, it is important to recognize the fact that the different crystal axes or planes of symmetry are related to different characteristics of the material. This has been illustrated particularly clearly by various studies, including those in which certain dyestuffs were found to show different colors on different crystal faces. It was possible to control conditions to modify the relative sizes of the crystal faces and in this way modify, at will, the color of the solid dye.

In discussing the effect of the nature of crystal faces on adsorption, Adam (2) states:*

> One source of uncertainty is that even on perfectly formed crystals, some faces adsorb very much more than others. This was known to Lehmann [87] and was extensively studied by Gaubert [53]. In recent years Saylor [122], France [48], Buckley [21], Bunn [22], and Royer [114] have carried on studies, especially on the effect of adsorption of "impurities" in the solution on the habit of crystals. A crystal will sometimes adsorb one dye on one set of faces, and another on a second set, no adsorption of the first dye occurring on the second set of faces, or vice versa. Thus lead nitrate adsorbs methylene blue on the (1.1.0) faces, another set of faces adsorbing none of this dye, but easily adsorbing picric acid. If the crystals are grown from a solution containing both dyes, one set of faces develops with a blue color, the other with a yellow.
>
> These different adsorptions are of great importance in determining the habit of crystals, for if a substance, colored or uncolored, is adsorbed on a set of faces, growth of the crystals perpendicular to those faces is retarded, because deposition on them is slowed down. These faces often appear finally as the only faces of the crystals, for the others have material deposited on them much faster, so that the faces on which deposition is slowest, or does not occur at all, are prolonged parallel to themselves until they finally meet.

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This condition, even though the study was made on crystals of macro dimensions, may account to an appreciable degree for the effects exerted by materials such as rosin soaps, Turkey Red oil, and other wetting and dispersing agents and assistants on the organic pigments. In addition, since rates of growth are dependent on conditions of temperature, concentration, and mixing, these conditions serve to control the type of crystal formation obtained in practice.

Moses and Parsons (99), in discussing regular structure in absence of distinct crystals, pointed out:*

> In the solidification of chemical compounds a regular arrangement of the particles takes place whether distinct crystals are formed or not. This can be proved in many ways: for instance,
>
> (*a*) The masses will often break in directions parallel to planes yielding solids absolutely constant in angles, and these solids can be broken from any part of the mass and of any size.
> (*b*) The velocity of transmission of light is the same along all parallel lines, but is not generally the same along lines not parallel.
> (*c*) The same constancy for parallel lines and variation for lines not parallel is shown for other physical characters such as expansion from heat, conductivity of heat or electricity, and even color and luster.

If the wet material described above is dried, as is the case with the greater proportion of organic pigment colors, a further, and in some cases, very significant change takes place. The final dry cake may be quite firmly set together. The condition at this point varies greatly with different products. One may give a cake which readily breaks down into a soft fluffy powder; another may be quite firm, breaking down with some difficulty to give a very fluffy powder; still another may be difficult to break down, and when disintegrated the final powder is dense and hard in texture. It is clear from this description that the γ-clusters, mentioned above, undergo a change which results in (1) a cementing together of the clusters, (2) a firm tangling or "felting" of the peripheral groups, or (3) some other variety of attachment which may vary greatly in its rigidity. The dry cake, in practical manufacture, is put through a disintegrator of some sort, possibly a so-called hammer mill or micropulverizer, which breaks down the lumps and possibly to some extent the γ-clusters.

A very interesting and practical question may be raised at this point. Which of these various stages in the crystal growth and in the flocculation is of primary importance in consideration of color properties and pigment characteristics? The answer is not so simple. It is probable

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that a frequent answer to this question would be "the ultimate particle." However, the above discussion makes it quite clear that the nature of the so-called ultimate particle is definitely in question. This problem can hardly reach a complete and satisfactory solution at the present time, partly for the reason that different pigments undoubtedly differ in the degree to which they are disintegrated in the much more intense dispersion to which they are subjected when they are incorporated into a vehicle such as a printing ink varnish or a paint when ground on the roller mill or stone mill or a ball mill.

The light microscope has given some of the necessary fundamental information in this field, which has been extended appreciably by use of the ultraviolet microscope. There is promise of further important advances in the use of the electron microscope, which affords a degree of resolution much higher than any previously reached. The spectrophotometers are also contributing much toward these problems. It would seem, however, that the instrument offering the greatest promise at the present time in the solution of problems of this nature is the X-ray or the electron diffraction apparatus. These instruments are capable of giving significant information on a number of particle characteristics:

1. Crystalline or amorphous condition.
2. Size of crystals.
3. Presence of other materials either crystalline or amorphous.
4. Identification of such materials.
5. Estimation of the amounts of individual materials.
6. Information on surface characteristics.

Various facts encountered in the practical handling of organic pigments will probably be found, eventually, closely related to these considerations. For example, in the study of the so-called flushed colors, which are not dried but incorporated into oil vehicles from the wet pulp, eliminating the cementing or caking stages mentioned previously, in certain instances the tinctorial value or strength of the final ink or color is increased over that obtained using the dried and ground pigment. In other cases no such increase is detectable.

Another example involves a very generally recognized condition. In order to obtain the full tinctorial strength of a pigment it must be disintegrated to a very fine state of division. There is, however, an anomalous condition involved in the type of disintegration employed. If, as an illustration, a pigment of the lithol type in the dry lump condition is passed through the usual type hammer mill, and then incorporated in a varnish vehicle, by grinding on a three-roll mill or ink mill, it will be found tinctorially weaker than a similar product wet thoroughly with the vehicle in the lump condition and then passed over the three-roll ink mill as in the previous case. It will be further found, if the same lump pigment is ground finer than in the first instance, by using a higher speed in the hammer mill or a finer screen, that the tinctorial power of the final ink will be even lower than that of the product first described. And the finer these materials are ground in the dry condition, the greater is the loss of strength. In some cases strength losses as high as 50 per cent can be obtained in this way.

As a rule, the pigments most sensitive to dry grinding are those which possess a rather hard texture, and one possible explanation of the strength loss may be the formation of air films in the mass of the pigment particles by shattering under the impact of the grinding. This may be supported to a certain degree by the fact that these pigments on dry grinding, followed by incorporation in the vehicle, become progressively lighter in masstone, whereas the same original lump materials, wet with the vehicle in lump form, or in a vacuum, and then ground on the ink mill, become progressively deeper.

Some of these variations in conditions are even apparent to the naked eye without the aid of the sensitive instruments discussed earlier. The complete solution of such problems, however, and their broad interpretation in terms of particle size, particle shape, aggregation, flocculation, cementing, caking, hardness, texture, surface conditions, and modifying materials must await the most skillful use of each type and adaptation to the study of a wide variety of pigment colors. This problem may become one of the long-range programs of the pigment industry. The importance of this conception in the manufacture of organic pigments can hardly be overestimated, as those factors which are important in the control of crystal growth, such as temperature, time, concentration, presence of salts, conditions of alkalinity or acidity, and efficiency of agitation or mixing, are the factors of major importance in the control of uniformity in manufacturing operations.

In addition to the physical condition of the pigment itself, the fact should also be kept very definitely and clearly in mind that tinctorial properties are directly dependent on the physical properties of the vehicle in which the pigment is used. The direct comparison of two pigments which may be very close in all respects in a specified vehicle, such as refined linseed oil, may show marked differences in their various characteristics when tested in other vehicles including varnishes, lacquers, or aqueous solutions, neutral or alkaline casein type, for example.

The influence of particle size may be more fully appreciated if the relations between physical properties and actual dimensions are more intimately examined. Moore (98)* has pointed out that the peculiar properties of colloids are due to their great development of surface, and as particles of matter are progressively subdivided the amount of "surface" increases tremendously. Since amount of surface is the capacity factor of surface energy, the surface energy at the same time increases enormously. As an illustration of this increase, Table I shows the results of dividing a cube having 1-cm sides by dividing the sides repeatedly into tenths.

TABLE I

SURFACE (98)

Length of Sides	Number of Cubes	Total Surface	Specific Surface (Surface Divided by Volume)	
1 cm	1	6 sq cm	6	
1 mm (10^{-1})	1,000	60 sq cm	6×10	
0.1 mm (10^{-2})	1,000,000	600 sq cm	6×10^2	ordinary suspensions and emulsions
0.01 mm (10^{-3})	1 billion	6,000 sq cm	6×10^3	size of cream globules
1 μ (10^{-4})	1 trillion	60,000 sq cm	6×10^4	slight Brownian movement
0.1 μ (10^{-5})	10^{15}	60 sq meters	6×10^5	limit of microscope; well-defined Tyndall effect
0.01 μ (10^{-6})	10^{18}	600 sq meters	6×10^6	typical colloidal solutions hemoglobin molecule
1 mμ $(1 \times 10^{-7}$ cm)	10^{21}	6,000 sq meters	6×10^7	
0.1 mμ $(10^{-8} = 1$ A)	10^{24}	60,000 sq meters	6×10^8	atomic dimensions

The relation between range of particle size and properties (98) is summarized in Table II.

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* Table I on this page and Table II on page 30 are reprinted with permission from Moore's article in the *Official Digest* of the Federation of Paint and Varnish Production Clubs.

In colloids the surface is enormous compared to the mass of the substance. Consequently, surface forces such as adsorption, capillarity, and surface tension become extremely large and of primary importance. Surface energy does not become noticeable until a specific surface of 10,000 or more is reached.

TABLE II

Particle Size and Properties (98)

$\left(1\ \mu\ [\text{micron}] = \frac{1}{1000}\ \text{mm}\right)$ $\left(1\ \text{m}\mu\ [\text{millimicron}] = \frac{1}{1{,}000{,}000}\ \text{mm}\right)$

Particle Size	0.1 μ	1 mμ	10 mμ	100 mμ	1 μ	10 μ	100 μ	1 mm
	Ultramicroscopic field				Microscopic field (real form may be seen)			
Molecular dispersions			Colloidal dispersions Turbidities		Mechanical suspensions			
	Pass through filter paper				Retained by filter paper			
	Very rapid		Brownian movement Slow		None			
	Oil emulsions in water do not separate				Oil emulsions in water separate into two layers			

Chapter V

Raw Materials

The raw materials which are fundamental to the dyestuff industry, and therefore also fundamental to the manufacture of organic pigments, are:

- Benzene
- Toluene
- Xylene
- Naphthalene
- Anthracene

Since the pioneer work of Hofmann and Mansfield (66) in the separation of these materials from coal tar, great technical progress has been made in increasing the amounts of the different individual products by changes in the details of manufacture and in broadening the sources of tars suitable for such treatment.

Typically, coal tar is a by-product of the coal gas industry appearing in the hydraulic mains, condensers, and scrubbers of the gas works. Large amounts are now recovered from coke ovens as well as from blast furnace gases and residues from the petroleum industry.

Distillation of these tars yields a series of fractions as follows:

A. First runnings	up to 110° C
B. Light oils	110 to 210° C
C. Carbolic oils	210 to 240° C
D. Heavy or creosote oils	240 to 270° C
E. Anthracene oils	270 to 400° C

and a heavy residue of pitch.

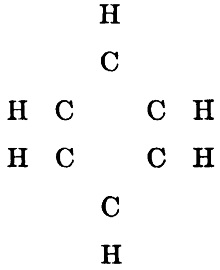
Further treatment of the "first runnings" and "light oils" yields benzene, toluene, and xylene. The carbolic and heavy oils yield naphthalene, along with a variety of phenolic compounds; and anthracene, with a large number of compounds of high molecular weight, is obtained from the "anthracene oils."

During World War II an interesting and very valuable development was made in the synthesis of toluene from petroleum products. Without it the required supplies of toluene for use in the manufacture of explosives and other necessary war materials could not have been readily obtained.

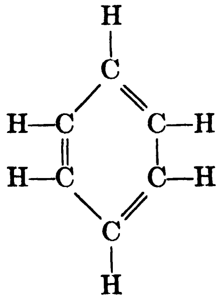
A rather popular question might be raised at this point as to why these raw materials are so essential to the manufacture of dyestuffs and pigments, especially in view of the fact that popular misconceptions in the past have indicated that these beautiful materials exist in coal and in the black sticky coal tar. Of course this is not true, but the materials obtained from coal tar can be chemically treated in various ways to produce these products. It is a matter of building up certain definite chemical structures. Some of the most interesting and even startling chemical and physical investigations have shown that the colors of the dyestuffs and pigments are due to certain definite structures built into the organic molecules.

It was established at an early date that benzene contains six atoms of hydrogen and six of carbon and may be represented as C_6H_6. This expression, however, gives no indication of the manner in which these atoms are connected with each other or held together. The solution of this problem was one of the most interesting pieces of chemical research ever carried out.

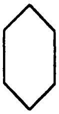
It was finally established (31), through the work of Kekulé (81), Claus, Armstrong (7), Baeyer (9), Thiele (130), and others, that the atoms in the benzene molecule form a ring, with the hydrogen atoms attached to the carbon atoms:



Further work established the structure, recognized today, in which the valencies of the atoms are taken fully into account and the molecule is shown to contain three so-called double bonds or points of unsaturation:

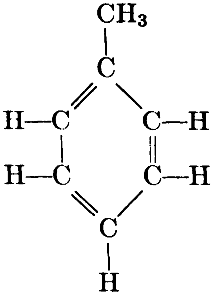


The benzene ring is usually more simply represented by

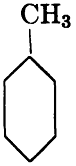


These investigations laid the foundation for an intelligent development of dye chemistry on a systematic basis as the importance of these structural relations was quickly and fully appreciated.

On the above basis the structure of toluene is:

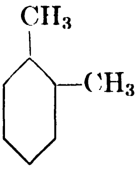


or

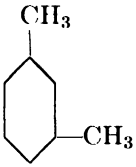


and only one such compound is possible as all the hydrogens are regarded as equal.

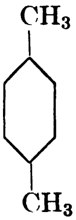
In the case of xylene three isomers are possible, and all are known, differing structurally only in the positions occupied by the methyl (CH_3) groups:



Ortho

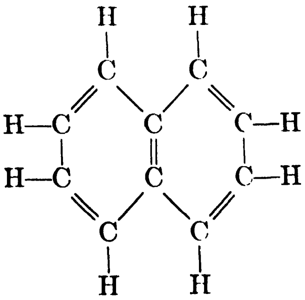


Meta

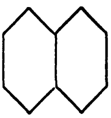


Para

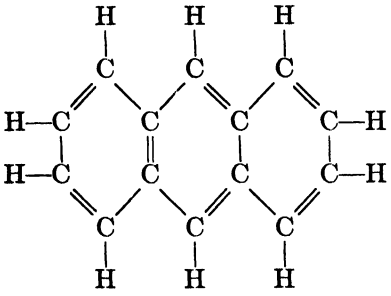
The structure of naphthalene is:



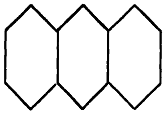
or



And that of anthracene is:



or



That the hydrogen atoms are active and can be replaced or substituted by other organic groups and inorganic groups or atoms is a feature of these structures that should be clearly recognized as it is essential to the subsequent consideration of reactions.

In addition to these aromatic compounds which are the basic raw materials for the making of both dyestuffs and organic pigments, many aliphatic compounds, including alcohols, aldehydes, acids, and such organic solvents as ethylene glycol, which are employed in producing intermediates and dyes varying widely in structure and nature are required.

A considerable number of inorganic materials are also essential to the production of organic pigments. They include such chemicals as acids, alkalies, nitrites, metal, and other salts and also the white insoluble materials used to dilute the full-strength colors to form so-called lakes. They include alumina hydrate (hydrous alumina), blanc fixe ($BaSO_4$), gloss white, which is a combination of alumina hydrate and blanc fixe, whiting ($CaCO_3$), barytes ($BaSO_4$), clay, and a variety of less frequently used materials. Alumina hydrate is the most important of these bases and is the only one which exerts appreciable absorption, or other chemical influence, on the lakes in which it appears.

Alumina Hydrate

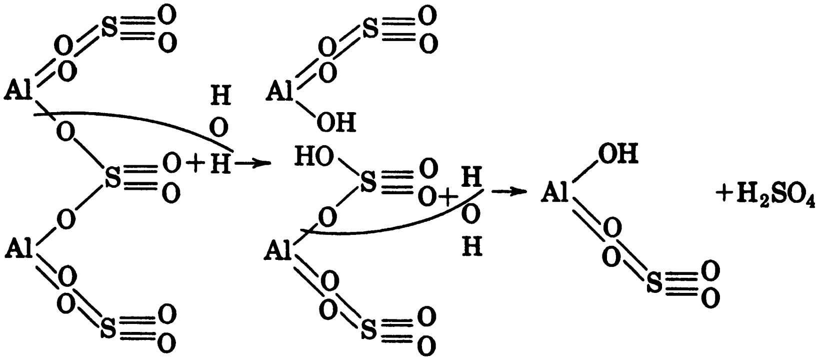
Alumina hydrate (hydrous alumina) is generally prepared by adding a solution of sodium carbonate (soda ash) to a solution of aluminum sulfate, with good agitation, filtering, and washing the precipitated base and, if the dry base is desired, drying at a low temperature. In practice, the preparation of this base is not so simple as the above would indicate, owing to the variations which appear in the nature of the base with variations in conditions of preparation. For example, if the percentage of sodium carbonate (soda ash), based on the weight of aluminum sulfate, is varied, rather marked differences will appear. Some of these differences are shown in Table III, which is based on the use of aluminum sulfate containing approximately fifteen molecules of water of crystallization and sodium carbonate of good commercial grade.

TABLE III

To 100 Parts of $Al_2(SO_4)_3 \cdot 15H_2O$

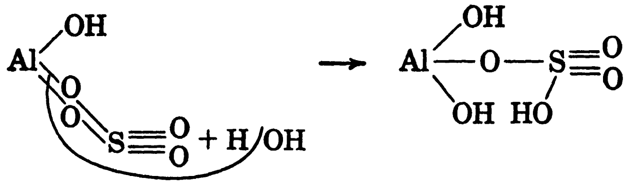
Na_2CO_3, Parts	Precipitation	*p*H	Loosely Combined Water	Power of Absorption	Oil Absorption
30	incomplete	acid	......	......	......
36	just complete	acid	highest	highest	lowest
40	complete	acid	lower	lower	higher
45	complete	neutral	still lower	still lower	still higher
50	complete	alkaline	still lower	still lower	still higher
60	complete	alkaline	still lower	still lower	still higher
70	complete	alkaline	lowest	lowest	highest

The variations in the characteristics of alumina hydrate bases are related in part to the degree of elimination of sulfate in the reaction with sodium carbonate. This action can be considered as an hydrolysis, progressively liberating sulfate, but with increasing difficulty, as the reaction proceeds. The successive changes may be indicated as follows:

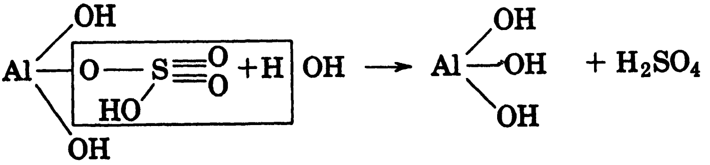


Two molecules of water have brought the aluminum sulfate into the condition of the monobasic sulfate, which is still soluble in water.

Another molecule of water yields the dibasic sulfate which is nearly or completely insoluble in water:



Removal of the last sulfate is much more difficult than the first, and cannot readily be carried to completion.



In a dry commercial alumina hydrate that still retains an appreciable content of SO_4, even though it may have been thoroughly washed, a considerable amount of loosely combined water remains attached to the molecule. Ignition results in a loss of approximately 50 per cent by weight, which indicates that the hydrate molecule holds about 2⅔ molecules of loosely combined water. The composition of a commercial alumina hydrate might, therefore, be indicated as

$$Al(OH)_3 3H_2O \cdot x Al(OH)_2 \cdot OSO_3H$$

where x is the variable factor.

Such variations in characteristics are subject to direct and quite satisfactory control and are therefore of real value in the development of lakes of certain required color values and working properties.

Other factors that exert a marked influence on the qualities of the alumina hydrate base include the temperature of precipitation and subsequent heat treatment, the concentration of solutions of reacting materials, and the rate of precipitation and agitation. By combination of these factors it is possible to obtain a wide range of desirable characteristics that are of great value in the field of lake pigments.

Gloss White

Gloss white is the name in use for a great many years to designate the combination of alumina hydrate and barium sulfate or blanc fixe, prepared by precipitating a solution of aluminum sulfate with sodium carbonate and then precipitating the sulfates and carbonates still in solution with barium chloride. The resulting white base, when dried at 120 to 160° F, contains approximately one part of alumina hydrate and three parts of barium sulfate. As a rule, a gloss white base gives a lake of lower oil absorption, lower consistency, and lower transparency in oil vehicles than a corresponding lake made on straight alumina hydrate.

Such bases have been employed to a great extent, however, in the preparation of pulp colors to be used with aqueous vehicles in surface coating of paper, paper boxes, and wallpaper. Under these conditions in many cases the gloss white base gives much more desirable working properties than a straight alumina hydrate base.

Gloss white is also subject to modification in properties by variation in the conditions of handling, but to a lesser degree than alumina hydrate. It is possible, however, to introduce modifications in the conditions employed not only during the precipitation of the alumina hydrate but also during the formation of the barium sulfate.

Blanc Fixe

Blanc fixe is the name used for many years to distinguish the precipitated form of barium sulfate from the finely ground mineral barytes. Its manufacture involves primarily the bringing together of solutions containing soluble barium and sulfate, and in many cases it represents a recovery of one material or the other.

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4$$

Barium sulfate is quite generally regarded as possessing certain definite characteristics but it is, nevertheless, subject to rather marked variation in properties, with changes in the conditions of precipitation and heat treatment. A higher degree of dispersion gives a product decidedly more transparent when used with oil vehicles.

Blanc fixe is generally used as an inert base under conditions which require no power of absorption, no increase, or perhaps a decrease, in oil absorption or consistency in oil vehicles, and an economical material for adjusting pigments of high strength to standard values.

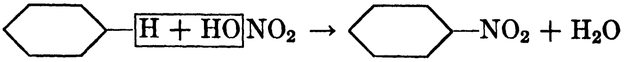
Chapter VI

Intermediates

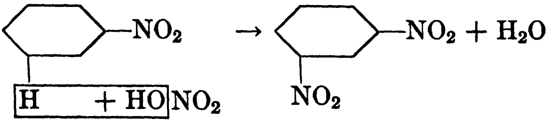
Intermediates are chemical compounds, typically colorless but in some cases colored, derived from raw materials which are converted into dyestuffs or into other intermediates by chemical treatment. In this field are to be found some of the finest examples of organic chemical investigations. The complexity of the problems has brought about a tremendous amount of research work which has resulted in the discovery of an extremely wide variety of typical reactions. It is not possible within the limits of this book to explore this phase of the problem thoroughly; but, since much of the chemistry of the intermediates is directly involved in the preparation of pigments and the whole subject possesses such an intimate relation to the full understanding of the nature of the organic pigments, discussion of the more important general reactions will be rather full.

NITRATION

Nitration, one of the basic reactions of intermediate chemistry, is used for the purpose of introducing into an aromatic molecule one or more nitro (NO_2) groups. These groups are of importance in pigment chemistry because of the special characteristics they impart to the resulting compounds and also because they can be readily converted, by reduction, into amino (NH_2) groups, which are of special value in this field. For example, nitrobenzene is formed in the mononitration of benzene. It may be shown as follows:



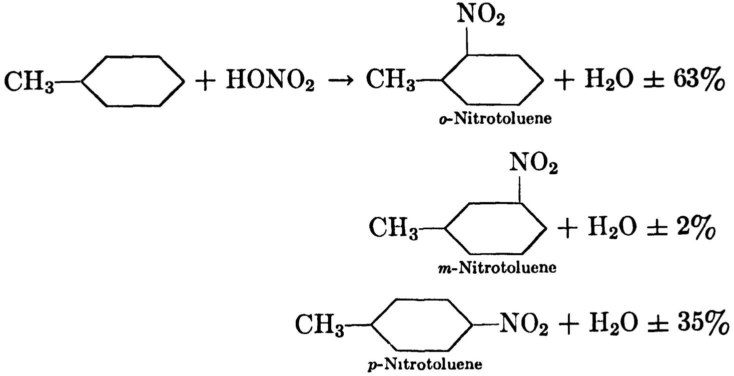
A second nitro group may also be introduced, in which case it enters almost exclusively (about 88 per cent) the meta position:



m-Dinitrobenzene

It is generally more difficult to introduce a second group in this way, and it may be extremely difficult or even impossible in some cases to introduce a third. On the other hand, in certain instances nitration to the tristage is readily accomplished.

In the nitration of toluene, isomers are formed. They are compounds whose molecules contain the same substituent groups but in different positions. For example:



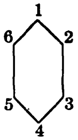
o-Nitrotoluene

m-Nitrotoluene

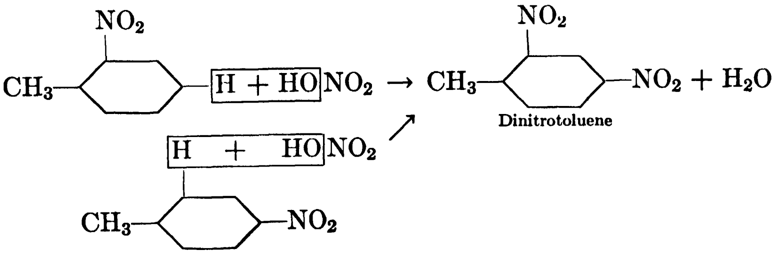
p-Nitrotoluene

Relative to position 1:

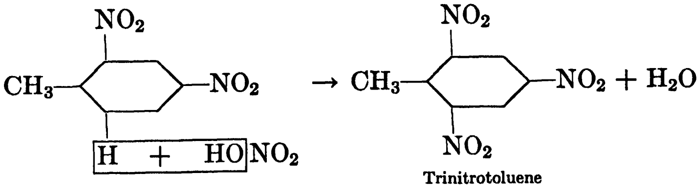
Position 2 is the ortho position.
Position 3 is the meta position.
Position 4 is the para position.
Position 5 is the meta position.
Position 6 is the ortho position.



Dinitration and even trinitration of toluene are readily accomplished.

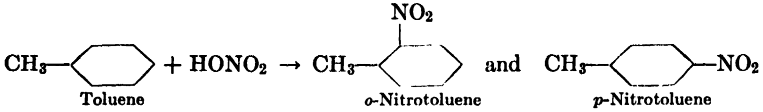


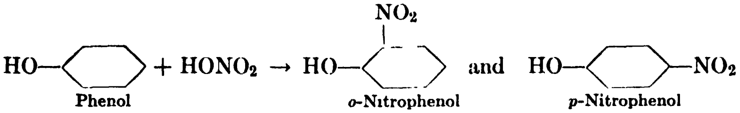
Dinitrotoluene



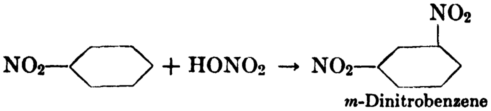
Trinitrotoluene

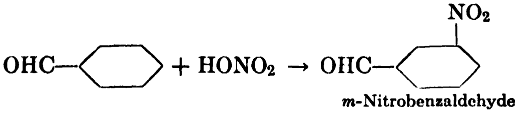
A great many materials may be nitrated, but it is also true that the ease of nitration is highly variable. In addition, the position occupied by the entering nitro group is dependent on the nature and position of the substituent groups already in the molecule. For example, a single alkyl group, or hydroxyl (OH) group, in a benzene molecule directs the entering nitro group to the ortho or para positions. On the other hand, the nitro group enters the meta position if the molecule already contains the nitro, aldehyde, carboxyl, or cyanogen group. For example:

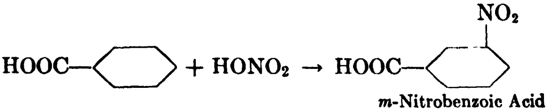


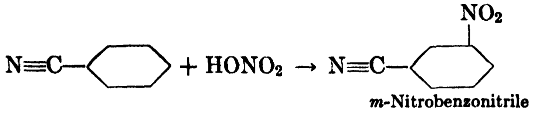


and

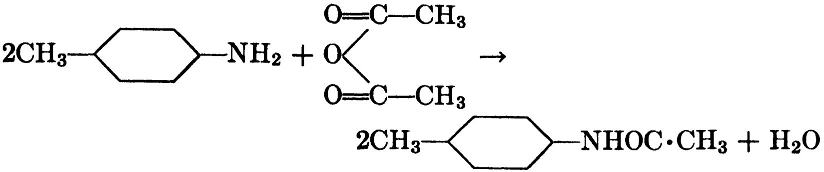


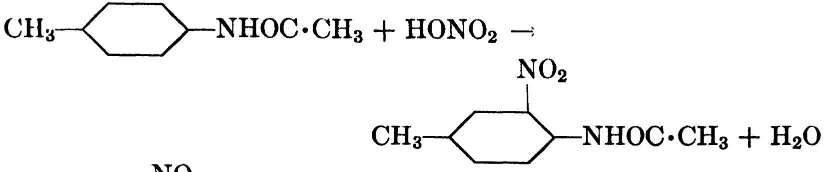


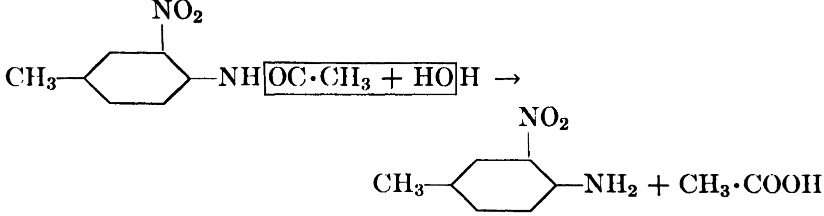




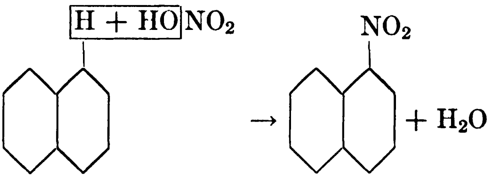
One particular type of compound, the one that contains an amino (NH_2) group, requires special care in nitration because of the readiness with which such compounds are oxidized. In many such cases it is necessary to protect the amino group previous to nitration by causing it to react with a material such as acetic anhydride. For example, in the preparation of *m*-nitro-*p*-toluidine, *p*-toluidine is acetylated, nitrated, and then the acetyl group removed by hydrolysis:





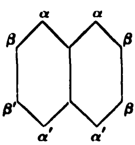


Nitration of naphthalene results first in the formation of α-nitronaphthalene almost exclusively, only a small amount of the β-isomer being formed:

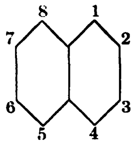


α-Nitronaphthalene

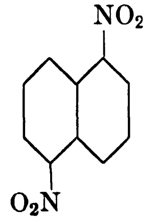
The positions in the naphthalene rings are indicated in two ways, as follows:



and

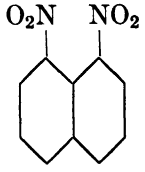


Dinitration yields the only two important dinitronaphthalenes:



1,5-Dinitronaphthalene

and



1,8-Dinitronaphthalene

Owing to these and many other variations in the properties of organic compounds, the nitration reaction is carried out in a variety of ways. For example, a few materials may be nitrated simply in an aqueous solution of nitric acid at ordinary temperature. The more usual procedure, however, is to nitrate in the presence of sulfuric acid, which serves to remove the water formed in the reaction and thus permit the reaction to go more readily to completion. In many cases higher temperatures are employed.

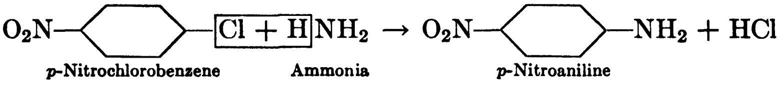
Mixtures of sulfuric and nitric acids, used in this way, are known as *mixed acids* and may vary from low to high concentrations for each acid. The power of a mixed acid as a nitrating agent is dependent directly upon its dehydrating value.

It is well known that an increase in the number of nitro groups in a compound tends to bring it closer to, or actually into, the class of explosives, of which trinitrotoluene (T.N.T.) is one of the best-known examples.

Nitrations are generally carried out, on the large scale, in iron equipment, the composition of the spent acid mixture being held above 68 per cent, as H_2SO_4, to avoid reaction with the metal.

REDUCTION—AMINO COMPOUNDS

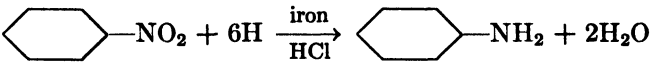
One of the largest and most important groups of intermediates is the group of the amino compounds (24), which are characterized by the presence of the amino (NH_2) groups. These compounds are generally prepared by reduction of the corresponding nitro compounds, but they may in some cases be produced by amidation of halogen derivatives as follows:



They are of special value in the preparation of the azo type pigments, although they also are used for many other purposes, such as the preparation of substituted amino intermediates and other dye or pigment types by condensation reactions.

Acid-Iron Reduction

An example of this class, the simplest and one of the most useful, is aniline, formed in the acid reduction of nitrobenzene:

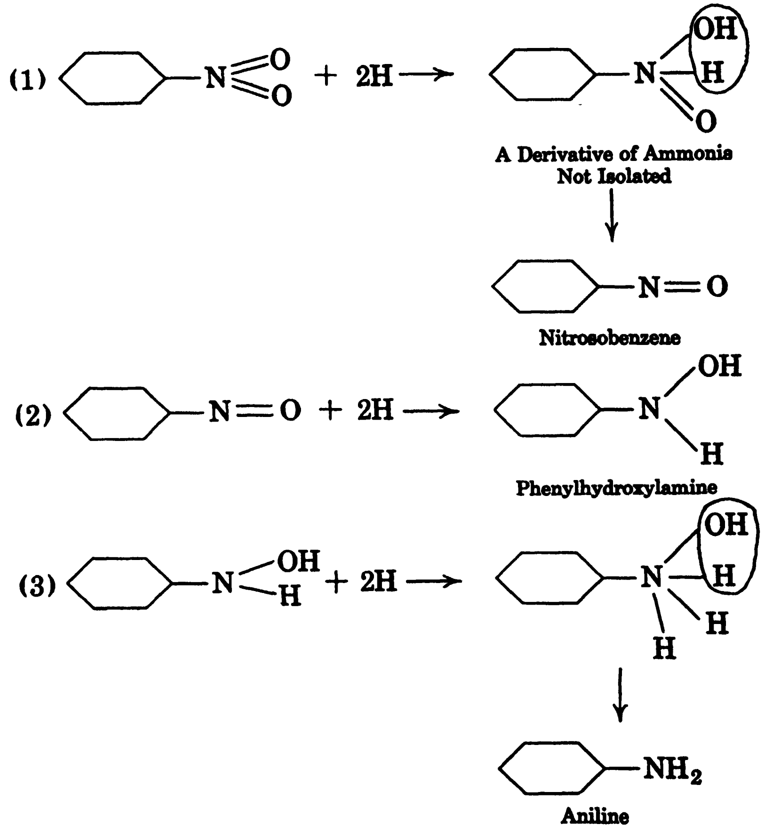


This reduction is generally carried out by using metallic iron in the form of filings, or borings, with only a small fraction of the theoretical quantity of acid.

The reaction as a whole may be considered as following the equation:

The amino compound in this case, aniline, is steam-distilled from the reaction mixture and obtained in very pure condition.

The mechanism of the acid-iron reduction may take place in steps, even though isolation of the intermediate products is not in all cases possible.

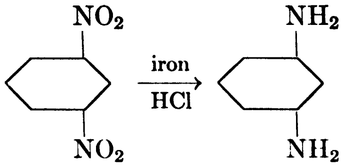


That but a small fraction of the theoretical amount of acid is actually required in practice may be accounted for by means of the following equations, which indicate regeneration of the ferrous ion:

$$\begin{array}{llll}
Fe & + 2HCl \rightarrow & FeCl_2 & + 2H^+ \\
FeCl_2 & + 2H_2O \rightarrow & Fe(OH)_2 & + 2HCl \\
Fe & + 2H_2O \rightarrow & Fe(OH)_2 & + 2H^+ \\
2Fe(OH)_2 & + 2H_2O \rightarrow & 2Fe(OH)_3 & + 2H^+ \\
2Fe(OH)_3 & + Fe \rightarrow & 3Fe(OH)_2 &
\end{array}$$

$$Fe \xrightarrow{ox} Fe^{++} \xrightarrow{ox} Fe^{+++} \xrightarrow{red} Fe^{++} \xrightarrow{ox} Fe^{+++} \xrightarrow{red} Fe^{++} \text{ etc.}$$

Most aromatic materials containing one nitro group can be treated in a similar manner to obtain the corresponding amino compounds. However, when two or more nitro groups appear in the molecule, complications may arise. By the above methods reduction of a dinitro compound yields a diamine.

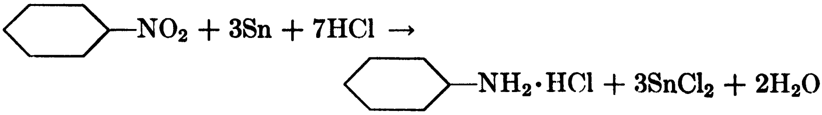


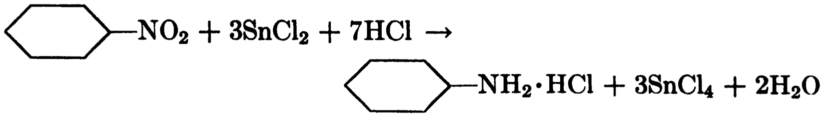
m-Dinitrobenzene *m*-Phenylenediamine

These operations in practice are conducted in large iron reducers provided with powerful agitation, and as a rule the reaction is carried out at or near the boiling point under a reflux condenser, the nitro compound being introduced slowly or in portions. Such reductions tend to go to completion and cannot be stopped at definite intermediate stages.

Acid-Tin Reduction

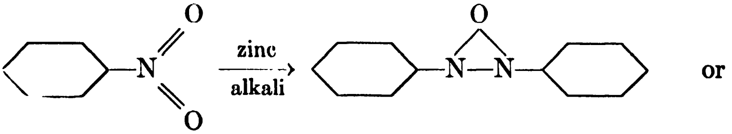
In the laboratory these reductions are frequently carried out with tin and mineral acid:



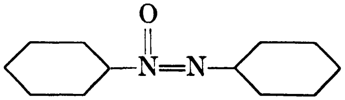


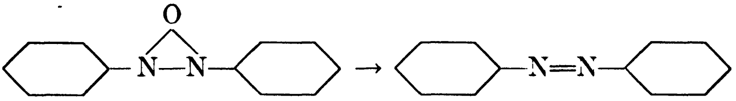
Alkaline Zinc Reduction

Reductions are employed, however, that are less vigorous than the acid-iron reductions and may be stopped at intermediate points. For example, an alkaline zinc reduction of nitrobenzene may be so controlled as to follow this course, each compound being readily isolated.

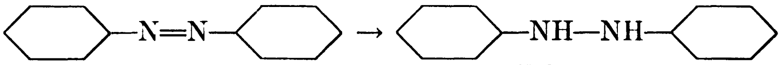


Azoxybenzene



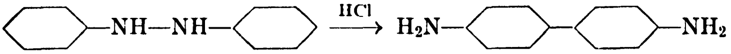


Azobenzene



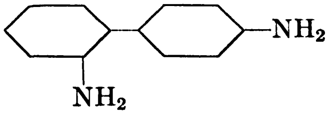
Hydrazobenzene

This final material, when heated with dilute acid, rearranges to form benzidine.

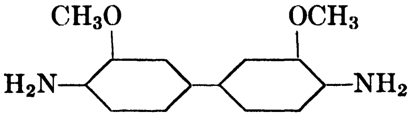


Benzidine

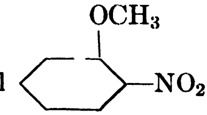
A small quantity of an isomer known as diphenylene is also formed.



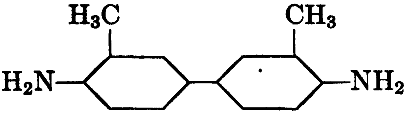
This type of structural change is known as the benzidine rearrangement and is also involved in the preparation of dianisidine



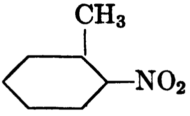
from *o*-nitroanisol



and tolidine

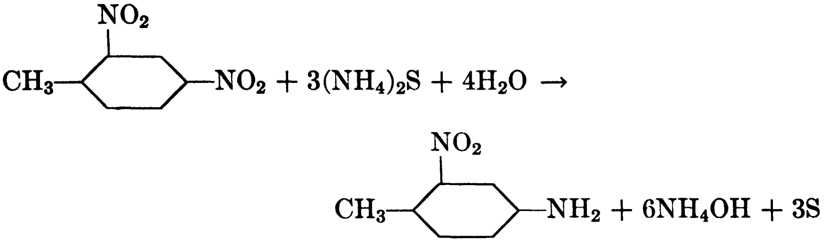


from
o-nitrotoluene

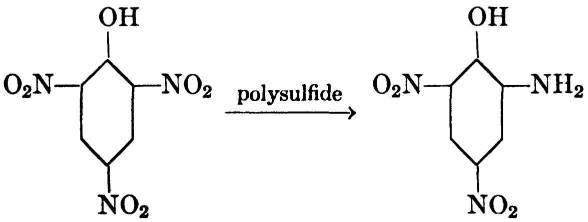


Alkaline Sulfide and Polysulfide Reduction

The use of mild reducing agents makes it possible to reduce one nitro group only in a molecule containing two or three. Alkaline sulfides and polysulfides are used for this purpose and, with good control of temperature and concentration, give excellent results. Orthonitro-*p*-toluidine may be prepared in this way from 2,4-dinitrotoluene as follows:



Another interesting reduction of this type is that of picric to picramic acid:



In the trade many of these amino compounds are known by so-called trade names, which are in general related to the colors they form rather than to their chemical nature. They appear as free amino compounds and in some cases as the acid salts. The following table includes many of the common and some of the less common commercial products. Molecular weights and melting points are given where possible.

TABLE IV

AMINO COMPOUNDS

(Courtesy of General Dyestuff Corporation, New York, N. Y.)

Trade Name and Chemical Composition	Mol. Wt.	M.P., °C
1. Fast Blue B Base Dianisidine	244	137–138
2. Fast Blue BB Base 1-Amino-2,5-ethoxy-4-benzoylaminobenzene	300	. . . . .
3. Fast Blue RR Base 4-Amino-1-benzoylamino-3,6-dimethoxybenzene	272	. . . .
4. Fast Blue Red O Base *o*-Nitro-*p*-phenetidine	182	110
5. Fast Black B Base 4,4-Diaminodiphenylamine	233	158
6. Fast Black G Base *p*-Aminodiphenylamine-*p*-azotoluene	303	. . . . .
7. Fast Black K Base *p*-Nitroaniline amidohydroquinone dimethyl ether	289	. . .
8. Fast Black LB Base *o*-Phenetol azo-1-naphthylamine	291	171
9. Fast Bordeaux BD Base 2-Amino-4-chlorobenzene-1,5-dimethyl ether	187.5	. . . . . .
10. Fast Bordeaux GP Base *m*-Nitro-*p*-anisidine	170	57.5
11. Fast Brown V Base 5-Methyl-4-methoxy-2-amino-2-chloro-4-nitroazobenzene	312	212
12. Fast Corinth B Base Benzidine base	184	115–120
13. Fast Corinth LB Base 1-Methoxy-2-benzoylamino-4-chloro-5-aminobenzene	276.5	.
14. Fast Corinth V Base *m*-Nitro-*p*-toluidineazo-*m*-xylidide	285	. .
15. Fast Dark Blue R Base Tolidine	212	129–131
16. Fast Garnet B Base *α*-Naphthylamine	143	50
17. Fast Garnet GBC Base *o*-Aminoazotoluene hydrochloride	262.6	80
18. Fast Orange GC Base *m*-Chloroaniline hydrochloride	164	137
19. Fast Orange GR Base *o*-Nitroaniline	138	71–72
20. Fast Orange R Base *m*-Nitroaniline	138	112–114
21. Fast Orange RD Base 3-Amino-4-chlorotoluene hydrochloride	177.5	30
22. Fast Red AL Base 1-Aminoanthraquinone	223	250
23. Fast Red B Base *p*-Nitro-*o*-anisidine	168	139
24. Fast Red BB Base *o*-Anisidine	123	liquid

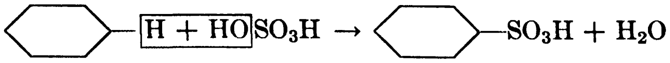
TABLE IV (*Continued*)

AMINO COMPOUNDS

Trade Name and Chemical Composition	Mol. Wt.	M.P., °C
25. Fast Red FG Base 4-Chloro-2-aminodiphenyloxide	219.5	....
26. Fast Red FR Base 4,4-Dichloro-2-aminodiphenyloxide	254	.....
27. Fast Red G Base *m*-Nitro-*p*-toluidine	152	116
28. Fast Red GG Base *p*-Nitroaniline	138	146–148
29. Fast Red 3GL Base *p*-Chlororthonitroaniline	172	105
30. Fast Red GTR Base 1-Methoxy-2-aminobenzene-4-ethylsulfone	215	.....
31. Fast Red ITR Base Diethylsulfamido-*o*-anisidine	258	245
32. Fast Red KB Base *p*-Chloro-*o*-toluidine hydrochloride	177.5	21–22
33. Fast Red RBE Base 6-Benzoylamino-4-amino-*m*-xylene hydrochloride	276.5	176
34. Fast Red RC Base *p*-Chloro-*o*-anisidine hydrochloride	202	82
35. Fast Red RL Base *m*-Nitro-*o*-toluidine	152	129
36. Fast Red TR Base *m*-Chloro-*o*-toluidine hydrochloride	177.6	base 29–30 23
37. Fast Scarlet B Base β-Naphthylamine	143	111–113
38. Fast Scarlet G Base *p*-Nitro-*o*-toluidine	152	167
39. Fast Scarlet GG Base 2,5-Dichloroaniline	162	50
40. Fast Scarlet LG Base 1-Methoxy-2,2-aminobenzene-4,6-benzylsulfone	277	.....
41. Fast Scarlet RC Base 4-Nitro-2-anisidine hydrochloride	204	117
42. Fast Scarlet TR Base 6-Chloro-2-aminotoluene hydrochloride	176.5	246
43. Fast Violet B Base 6-Benzoylamino-4-methoxy-*m*-toluidine	256	. . .
44. Fast Yellow G Base *o*-Chloroaniline	127.5	liquid
45. Variamine Blue B Base 4-Methoxy-4-aminodiphenylamine sulfate	312	100
46. Variamine Blue FG Base 4-Amino-3-methoxydiphenylamine	214	238
47. Variamine Blue RT Base 4-Aminodiphenylamine	183	79–80

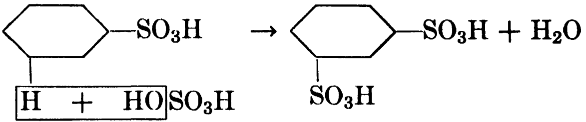
SULFONATION

Sulfonation is a reaction employed to introduce the sulfonic acid group (SO_3H) into organic molecules. Such compounds are typically water soluble. The mechanism of the reaction is quite similar to that of nitration, water being formed in a similar manner:



Benzene **Benzenesulfonic Acid**

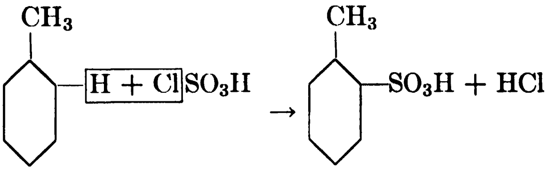
Introduction of a second group yields mainly the meta isomer as in nitration:



Benzene-*m*-disulfonic Acid

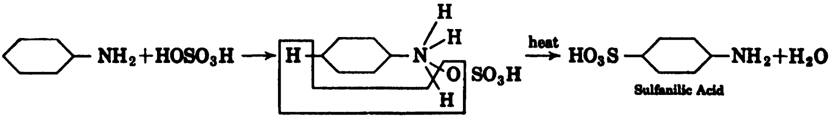
The ease or difficulty of sulfonation depends on the type of compound being acted upon. Certain materials, such as phenol, react readily with ordinary 95 per cent sulfuric acid. Others require acid of higher strength, such as 100 per cent, known as monohydrate, or the oleums, which go up to 100 per cent free SO_3, 122 per cent expressed as equivalent H_2SO_4. In addition, higher temperatures are employed in the more difficult reactions.

Chlorosulfonic acid is also employed for sulfonation, and in many cases it is a very active reagent. Hydrochloric acid is liberated freely and becomes objectionable unless conducted to an acid recovery or to the outside air.



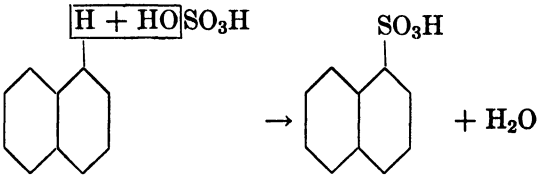
Toluene-*o*-sulfonic Acid

Another method of sulfonation that is applicable in the preparation of certain isomers is the *baking process.* In this method an amino compound, such as aniline, is stirred into concentrated H_2SO_4 in a shallow vessel, and the pasty acid sulfate is then heated to about 200–210° C in an oven for a period of several hours.



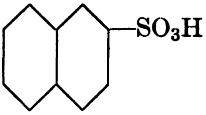
Sulfanilic Acid

Sulfonation is of particular interest in the naphthalene series because of the greater possibility of isomer formation and the fact that the production of a desired isomer can be satisfactorily controlled. For example, at low temperature the alpha isomer is formed:



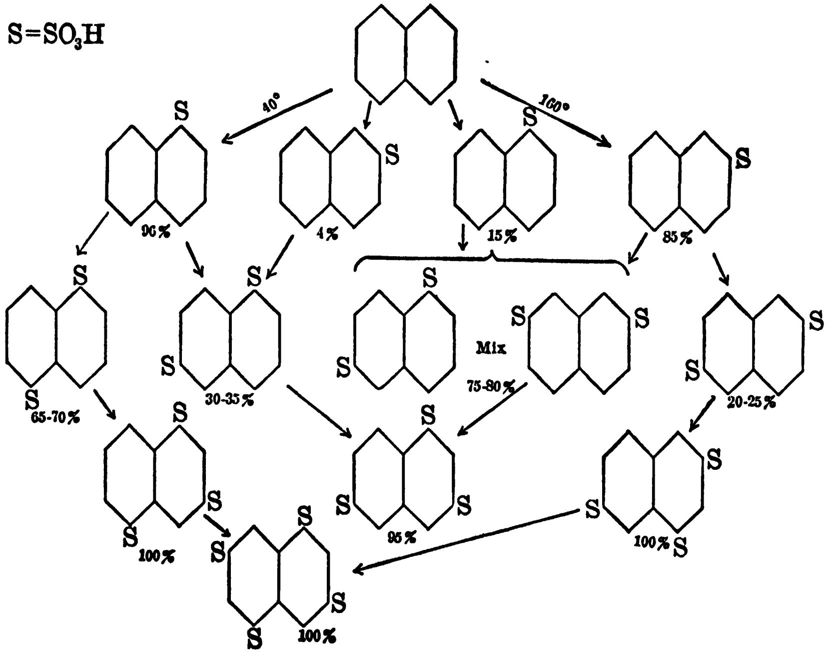
1-Naphthalenesulfonic Acid

Whereas, at high temperature, the beta is produced:



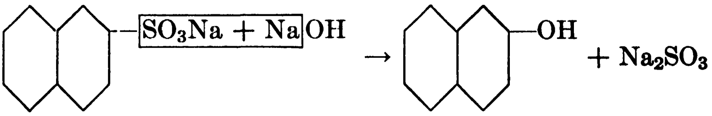
2-Naphthalenesulfonic Acid

Further sulfonation is complicated by the formation of several isomers. However, the conditions can be controlled to favor the production of desired isomers and separations of those formed are generally possible. The following outline (24) shows the products formed under the conditions indicated:



This scheme illustrates the complex conditions encountered in the direct sulfonation of naphthalene. It must be appreciated that similar conditions are met in the sulfonation of naphthalene derivatives such as the naphthylamines and the naphthols. Thus the number of possible intermediates reaches a high figure. When it is realized, moreover, that each individual product possesses characteristics different from those of any other intermediate, it becomes apparent that the number of possibilities for combinations to form dyestuffs is almost infinite and practically unlimited fields for the development of colors of varying properties and characteristics are opened up.

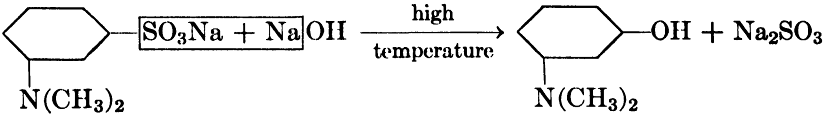
The sulfonic acids are also extensively used in the introduction of the hydroxyl group into aromatic molecules. For example, 2-naphthol (β-naphthol) is made by fusing 2-naphthalenesulfonic acid or its sodium salt with caustic soda at elevated temperatures:



2-Naphthol

HYDROXY COMPOUNDS

The hydroxy compounds represent another important group (24) among the intermediates as they are used in very large amounts in the manufacture of dyes and pigments. Several methods of preparation are available, but the most important involves the fusion of the sulfonic acids or their salts with caustic alkali at high temperature, for example:

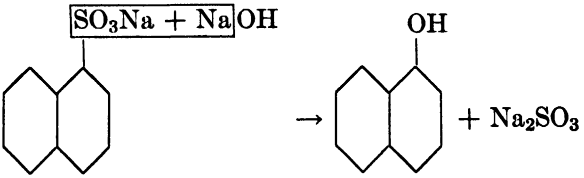


Dimethylaniline-*m*-sulfonate

Dimethyl-*m*-aminophenol

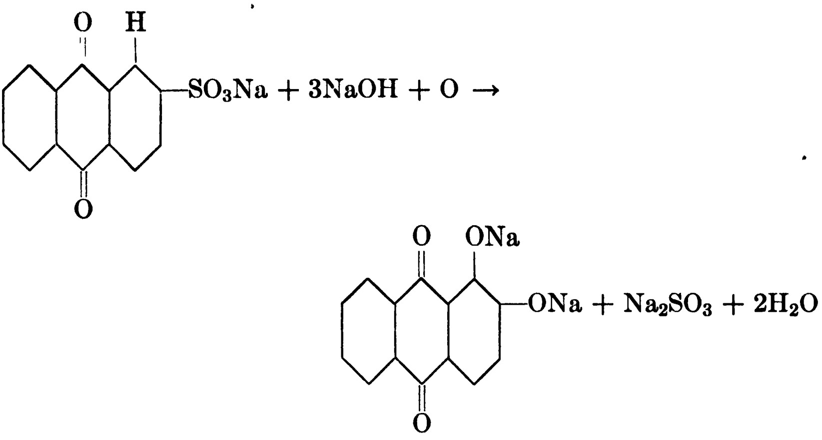
Such *m*-aminophenols are used in the manufacture of rhodamine dyestuffs which yield valuable phosphotungstic pigments.

The reaction is similar in the naphthalene series, as shown in the preparation of 1-naphthol (α-naphthol):

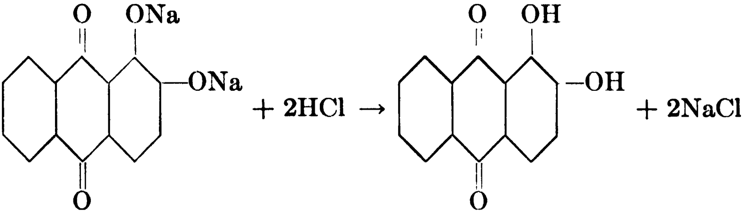


1-Naphthol

In the anthracene series, the preparation of alizarine by the fusion of anthraquinone-β-sulfonic acid with caustic alkali and the addition of an oxidizing agent such as sodium chlorate is another similar example:



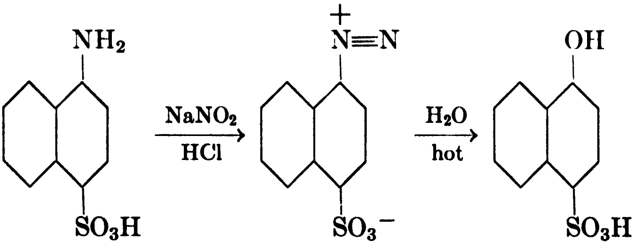
Na-salt



Alizarine

Wide variations in the concentration of the caustic alkali and the temperature of fusion are made to adapt this reaction to the specific requirements of individual compounds.

Another useful method involves boiling a diazonium salt with water. For example,



Naphthionic Acid

Diazonium Salt

1-Naphthol-4-sulfonic Acid (Neville and Winther's Acid)

Still another important method employs the hydrolysis of amine salts at high temperatures. α-Naphthyl ammonium sulfate (α-naphthylamine sulfate) under these conditions yields α-naphthol:

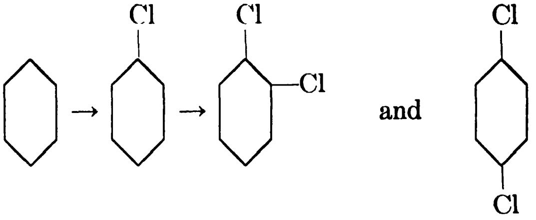
$$(C_{10}H_7NH_3)_2SO_4 + 2H_2O \rightarrow 2C_{10}H_7OH + (NH_4)_2SO_4$$

In the anthraquinone series, oxidation of nuclear hydrogen can be brought about by the action of fuming sulfuric acid. Since this application is primarily in the colors rather than in the intermediates, it will be indicated at this point only by a type reaction:

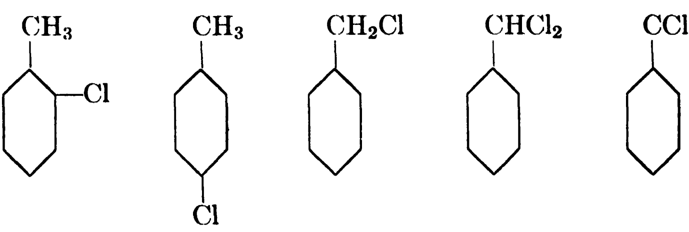
$$R \cdot H + SO_3 \rightarrow R \cdot OH + SO_2$$

HALOGEN COMPOUNDS (24)

In the great majority of cases halogenation is applied to the hydrocarbon rather than to more complex intermediate derivatives. Chlorine is generally introduced by means of gaseous chlorine, with the aid of a suitable catalyst such as iron or aluminum. Benzene is chlorinated to a mixture of about 80 per cent *o*-dichlorobenzene and 20 per cent *p*-dichlorobenzene:

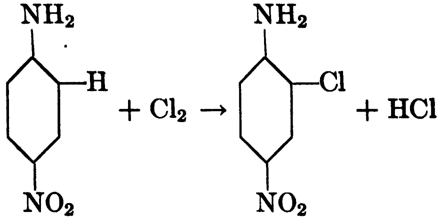


Chlorination of toluene may take place in the ring or in the side chain, giving the following products:



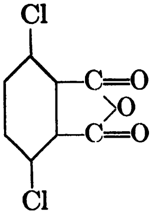
Catalysts, such as iodine or metallic chlorides, favor the ring substitution, whereas the action on the methyl group is favored by high temperature and sun or ultraviolet light.

A more complex intermediate such as *p*-nitroaniline may be chlorinated by passing gaseous chlorine into an aqueous acid solution of the intermediate until one molecule of chlorine has been absorbed. The reaction may be indicated as follows:

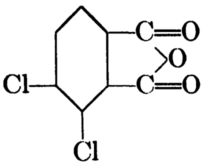


o-Chloro-*p*-nitroaniline

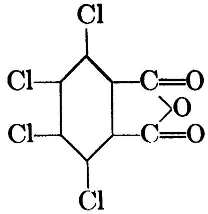
The chlorination of phthalic anhydride is of some importance and may be effected by passing gaseous chlorine into a solution of phthalic anhydride in fuming sulfuric acid in the presence of a small amount of iodine. The following products may be obtained:



p-Dichlorophthalic Anhydride



o-Dichlorophthalic Anhydride



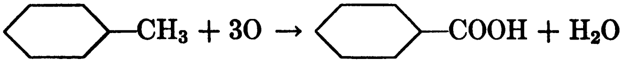
Tetrachlorophthalic Anhydride

Bromine may generally be introduced in similar fashion, using liquid bromine, but iodine cannot be entered in this way. Bromine and iodine may be introduced by the action of nitric acid and hydrobromic or hydriodic acid.

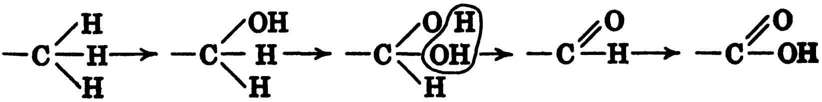
CARBOXYLIC ACIDS

Organic acids are characterized by the presence of the carboxyl (—COOH) group, which is introduced into organic molecules in a variety of ways (24).

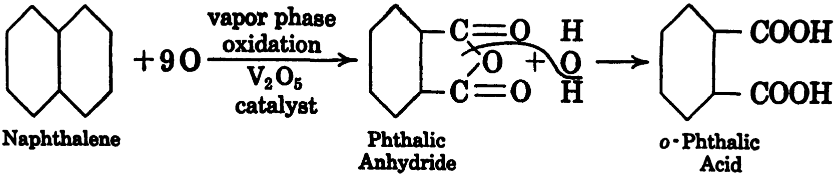
(1) Oxidation of a methyl (CH_3) group, as in the preparation of benzoic acid:



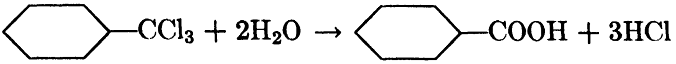
The course of the reaction may be as follows:



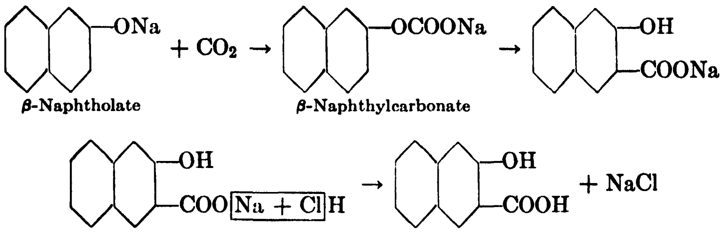
(2) Oxidation of a second carbon ring, as in the preparation of phthalic acid and anhydride (55):



(3) Hydrolysis of a CCl_3 group, as in the preparation of benzoic acid:

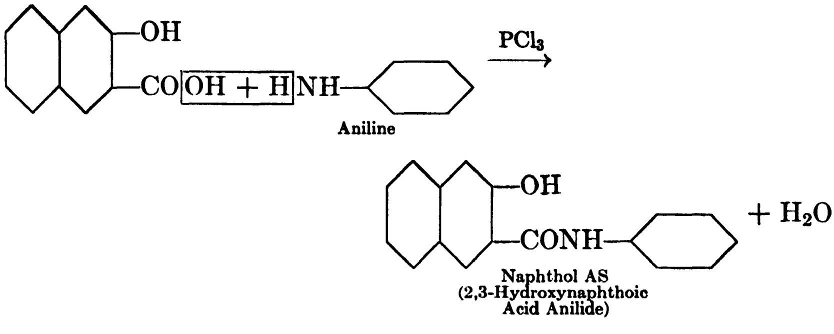


(4) Carbonation of a phenolate, as in the preparation of β-hydroxynaphthoic acid (2,3-hydroxynaphthoic acid):

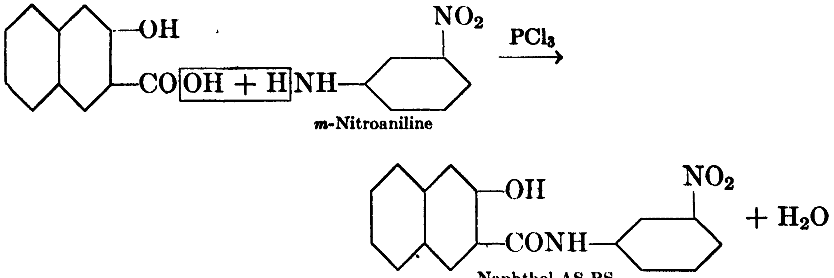


As the reaction may not go to completion, it is generally necessary to separate excess β-naphthol from the product which is finally obtained in quite pure form.

2,3-Hydroxynaphthoic acid, better known perhaps as β-oxynaphthoic acid, is the parent substance for a most interesting and valuable series of products known variously as Naphthol AS, Naphthanil, Naphthazole, and Naphthosol derivatives. They are formed by reaction between β-oxynaphthoic acid and amino compounds in the following manner:



Naphthol AS represents a type, and derivatives are generally identified by adding suitable letters to this type name, for example:



m-Nitroaniline

Naphthol AS-BS
(2,3-Hydroxynaphthoic Acid
m-Nitroanilide)

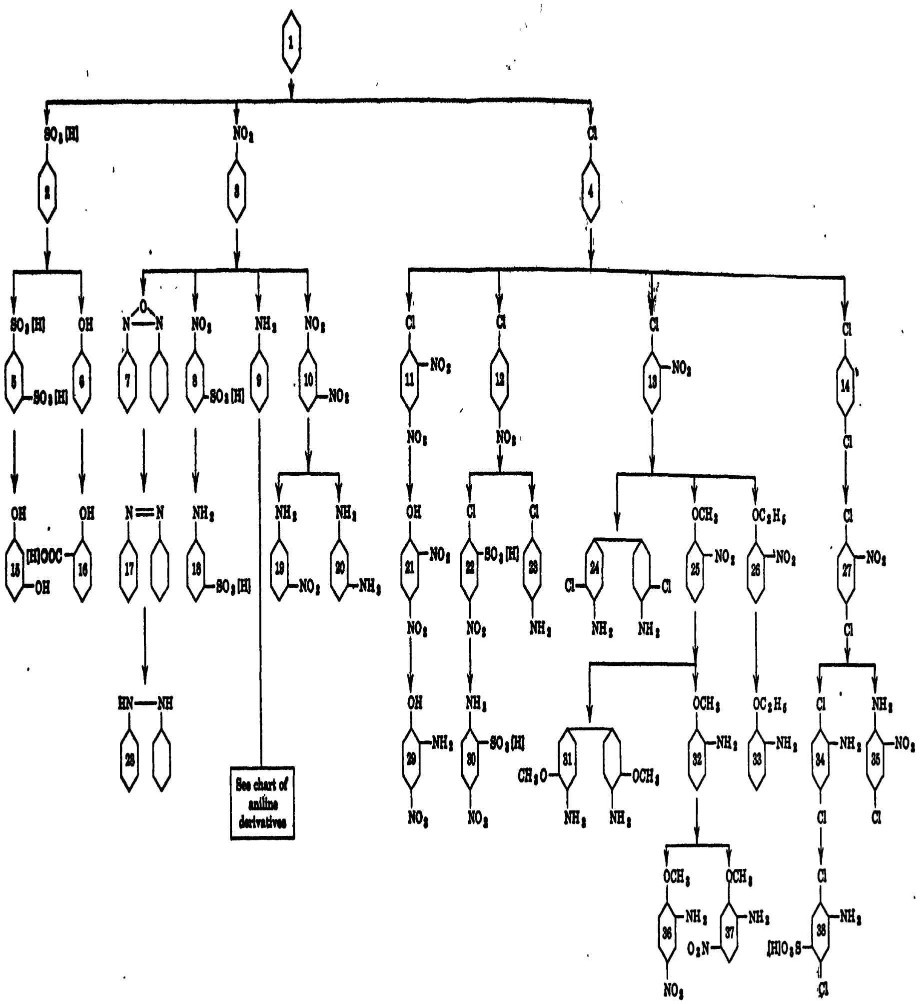
These compounds are soluble in caustic alkalies to varying degrees but all quite readily form alkali salts. In this condition they couple readily with diazonium salts to form azo dyestuffs or pigments.

Up to the present time they have been known commercially by their trade rather than by their chemical names, and until quite recently, in many instances, the actual composition had not been revealed by the manufacturer.

Table V, furnished by the General Dyestuff Corporation of New York, gives the trade name, chemical name, molecular weight, and melting point, where known, of most of these products which have been made available to the market.

It will be noted that certain items in the list are not derivatives of β-oxynaphthoic acid, such as No. 10, Naphthol AS–G, which is diacetoacetylorthotoluidide. Several types of compounds form salts and couple with diazonium salts in a manner similar to that of Naphthol AS. For this reason they have been included in the commercial listing as Naphthol AS types. Certain of these types will be discussed later in the chapter on azo pigments.

For a more complete and detailed review of the great variety of reactions that are of importance in intermediate research and manufacture, reference should be made to such works as Cain and Thorpe's (24) *Chemistry of the Synthetic Dyestuffs*, Charles Griffin and Company, London, 1933, J. C. Cain's (23) *Chemistry and Technology of the Diazo Compounds*, Arnold, London, 1920, and K. H. Saunders' (118) *The Aromatic Diazo Compounds*, Arnold, London, 1936, which deal primarily with the chemistry of the textile dyestuffs and intermediates.



1. Benzene
2. Benzene sulfonic acid
3. Nitrobenzene
4. Chlorobenzene
5. Benzene-*m*-disulfonic acid
6. Phenol
7. Azoxybenzene
8. Nitrobenzene-*m*-sulfonic acid
9. Aniline
10. *m*-Dinitrobenzene
11. 2,4-Dinitrochlorobenzene
12. *p*-Nitrochlorobenzene
13. *o*-Nitrochlorobenzene
14. *p*-Dichlorobenzene
15. Resorcinol
16. Salicylic acid
17. Azobenzene
18. Metanilic acid
19. *m*-Nitroaniline
20. *m*-Phenylenediamine
21. 2,4-Dinitrophenol
22. *p*-Nitrochlorobenzene-*o*-sulfonic acid
23. *p*-Chloroaniline
24. *o,o'*-Dichlorobenzidine
25. *o*-Nitroanisol
26. *o*-Nitrophenetol
27. 1,4-Dichloro-2-nitrobenzene
28. Hydrazobenzene
29. *p*-Nitro-*o*-aminophenol
30. *p*-Nitroaniline-*o*-sulfonic acid
31. Dianisidine
32. *o*-Anisidine
33. *o*-Phenetidine
34. 2,5-Dichloroaniline
35. 4-Chloro-6-nitroaniline
36. *p*-Nitro-*o*-anisidine
37. 5-Nitro-*o*-anisidine
38. 2,5-Dichloroaniline-4-sulfonic acid

Fig. 4. Benzene Derivatives.

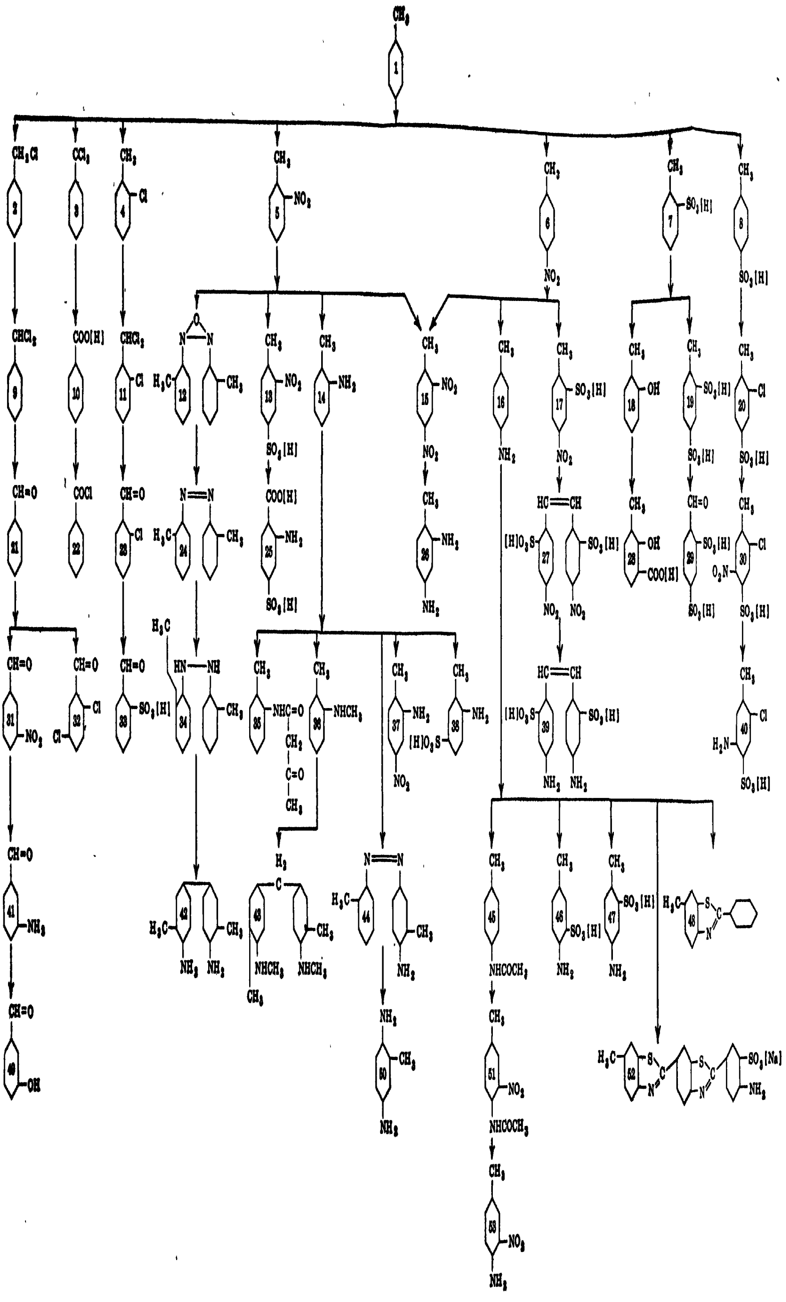
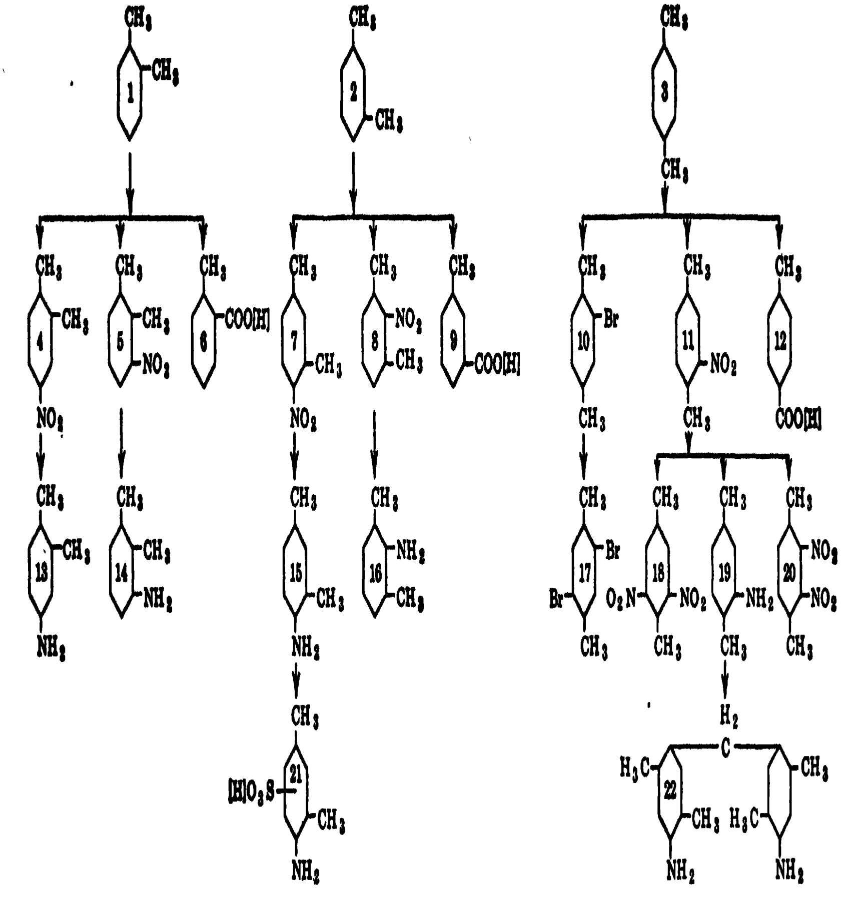


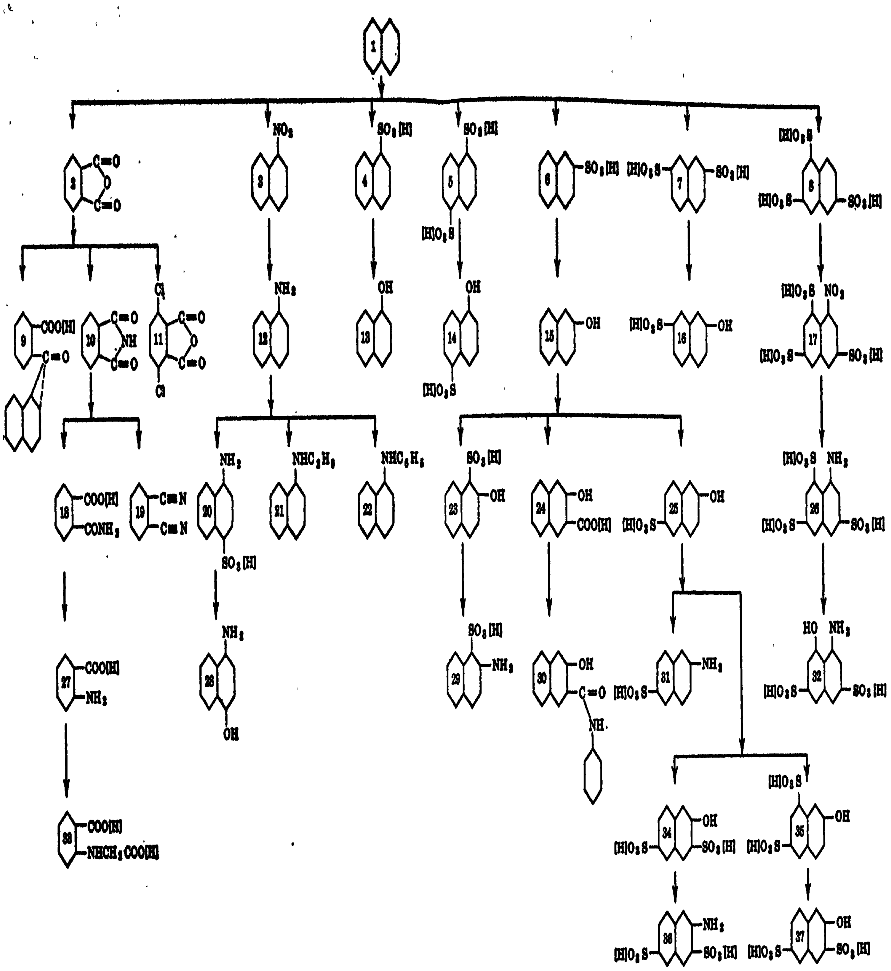
Fig. 6. Toluene Derivatives.

1. Toluene
2. Benzyl chloride
3. Benzotrichloride
4. *o*-Chlorotoluene
5. *o*-Nitrotoluene
6. *p*-Nitrotoluene
7. Toluene-*o*-sulfonic acid
8. Toluene-*p*-sulfonic acid
9. Benzal chloride (Benzilidene chloride)
10. Benzoic acid
11. *o*-Chlorobenzal chloride
12. Azoxytoluene
13. *o*-Nitrotoluene-*p*-sulfonic acid
14. *o*-Toluidine
15. 2,4-Dinitrotoluene
16. *p*-Toluidine
17. *p*-Nitrotoluene-*o*-sulfonic acid
18. *o*-Cresol
19. Toluene 2,4-disulfonic acid
20. *o*-Chlorotoluene-*p*-sulfonic acid
21. Benzaldehyde
22. Benzoyl chloride
23. *o*-Chlorobenzaldehyde
24. Azotoluene
25. *p*-Sulfoanthranilic acid
26. *m*-Toluylenediamine
27. Dinitrostilbenedisulfonic acid
28. Cresotinic acid
29. Benzaldehydedisulfonic acid
30. 2-Chloro-5-nitrotoluene-4-sulfonic acid
31. *m*-Nitrobenzaldehyde
32. 2,5-Dichlorobenzaldehyde
33. Benzaldehyde-*o*-sulfonic acid
34. Hydrazotoluene
35. Acetoacet-*o*-toluidide
36. Monomethyl-*o*-toluidine
37. *p*-Nitro-*o*-toluidine
38. *o*-Toluidine-5-sulfonic acid
39. Diaminostilbenedisulfonic acid
40. 2-Chloro-5-toluidine-4-sulfonic acid (C-acid)
41. Aminobenzaldehyde
42. Tolidine
43. Dimethyldiaminodi-*o*-tolylmethane
44. Aminoazotoluene
45. *p*-Acetotoluidide
46. *p*-Toluidine-*m*-sulfonic acid
47. *p*-Toluidine-*o*-sulfonic acid
48. Dehydrothio-*p*-toluidine
49. *m*-Hydroxybenzaldehyde
50. *p*-Toluylenediamine
51. *m*-Nitro-*p*-acetotoluidide (2-Nitro-*p*-acetotoluidide)
52. Primuline
53. *m*-Nitro-*p*-toluidine (2-Nitro-*p*-toluidine)



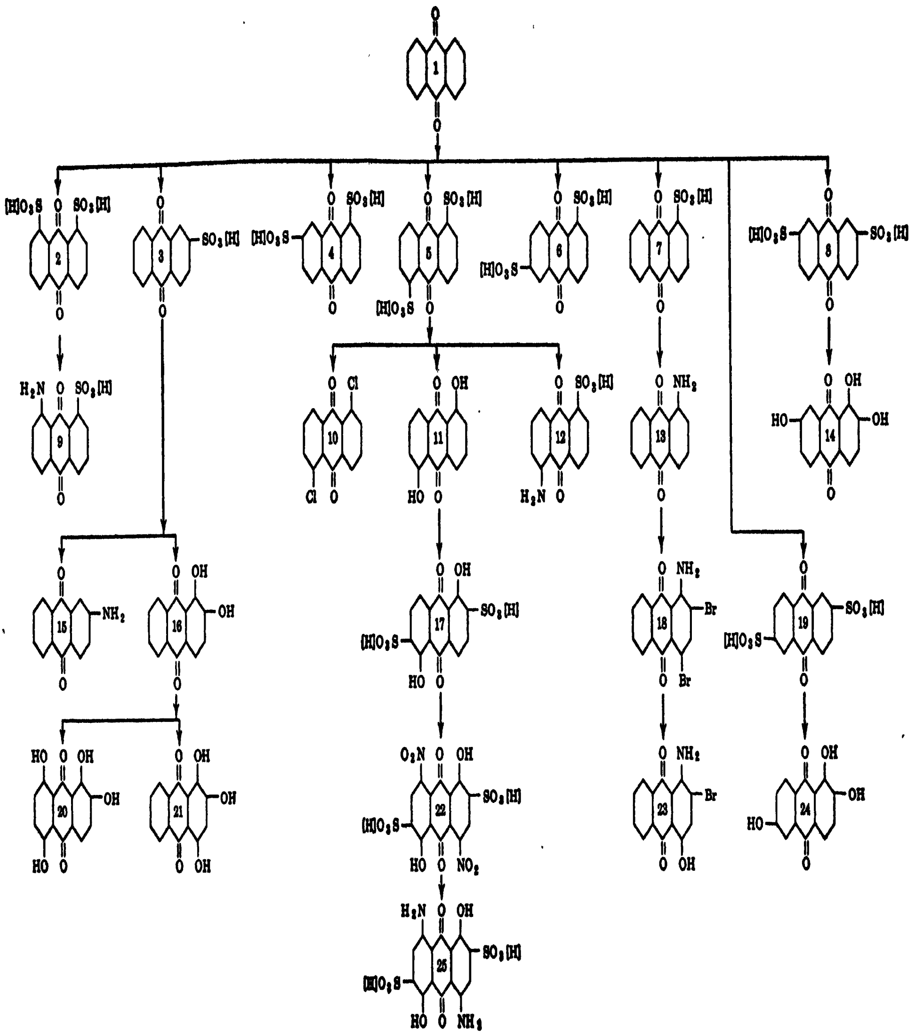
1. Orthoxylene
2. Metaxylene
3. Paraxylene
4. 4-Nitro-1,2-dimethylbenzene
5. 3-Nitro-1,2-dimethylbenzene
6. Orthotoluic acid
7. 4-Nitro-1,3-dimethylbenzene
8. 2-Nitro-1,3-dimethylbenzene
9. Metatoluic acid
10. 2-Bromo-1,4-dimethylbenzene
11. 3-Nitro-1,4-dimethylbenzene
12. Paratoluic acid
13. 4-Amino-1,2-dimethylbenzene
14. 3-Amino-1,2-dimethylbenzene
15. Metaxylidine (4-Amino-1,3-dimethylbenzene)
16. 2-Amino-1,3-dimethylbenzene
17. 2,5-Dibromo-1,4-dimethylbenzene
18. 3,5-Dinitro-1,4-dimethylbenzene
19. Paraxylidine (2-Amino-1,4-dimethylbenzene)
20. 2,3-Dinitro-1,4-dimethylbenzene
21. 4-Amino-1,3-dimethylbenzene-sulfonic acid
22. Diamino-di-*p*-xylylmethane

Fig. 7. Xylene Derivatives.



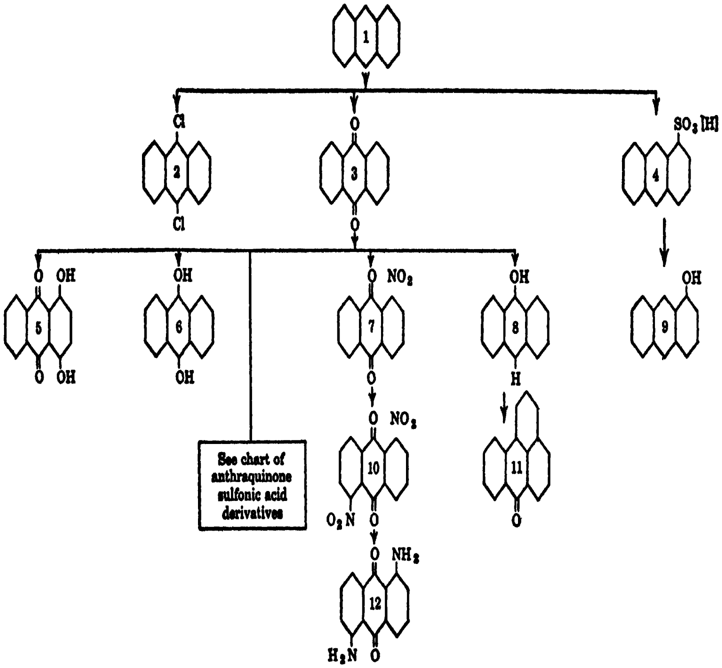
1. Naphthalene
2. Phthalic anhydride
3. α-Nitronaphthalene
4. α-Naphthalenesulfonic acid
5. Naphthalene-1,5-disulfonic acid
6. β-Naphthalene sulfonic acid
7. Naphthalene-2,7-disulfonic acid
8. Naphthalene-3,6,8-trisulfonic acid
9. α-Naphthoylbenzoic acid
10. Phthalimide
11. Dichlorophthalic anhydride
12. α-Naphthylamine
13. α-Naphthol (1-Naphthol)
14. α-Naphthol-5-sulfonic acid
15. β-Naphthol (2-Naphthol)
16. 2-Naphthol-7-sulfonic acid (Mono acid F)
17. 1-Nitronaphthalene-3,6,8-trisulfonic acid
18. Phthalamide
19. Phthalonitrile
20. 1-Aminonaphthalene-4-sulfonic acid
21. Ethyl-α-naphthylamine
22. Phenyl-α-naphthylamine
23. 2-Naphthol-1-sulfonic acid
24. 2-Hydroxy-3-naphthoic acid (β-Oxynaphthoic acid)
25. 2-Naphthol-6-sulfonic acid (Schäffer's acid)
26. Koch acid (α-Naphthylamine-3,6,8-trisulfonic acid)
27. Anthranilic acid (o-Amino-benzoic acid)
28. 4-Hydroxy-α-naphthylamine
29. 2-Naphthylamine-1-sulfonic acid (Tobias acid)
30. β-Oxynaphthoicanilide (Naphthol AS)
31. β-Naphthylamine-6-sulfonic acid (Bronner's acid)
32. H-acid (1,8-Aminonaphthol-3,6-disulfonic acid)
33. Phenylglycine-o-carboxylic acid
34. β-Naphthol-3,6-disulfonic acid (R-acid)
35. β-Naphthol-6,8-disulfonic acid (G-acid)
36. Amino R-acid (β-Naphthylamine-3,6-disulfonic acid)
37. β-Naphthol-3,6,8-trisulfonic acid

Fig. 9. Naphthalene Derivatives.



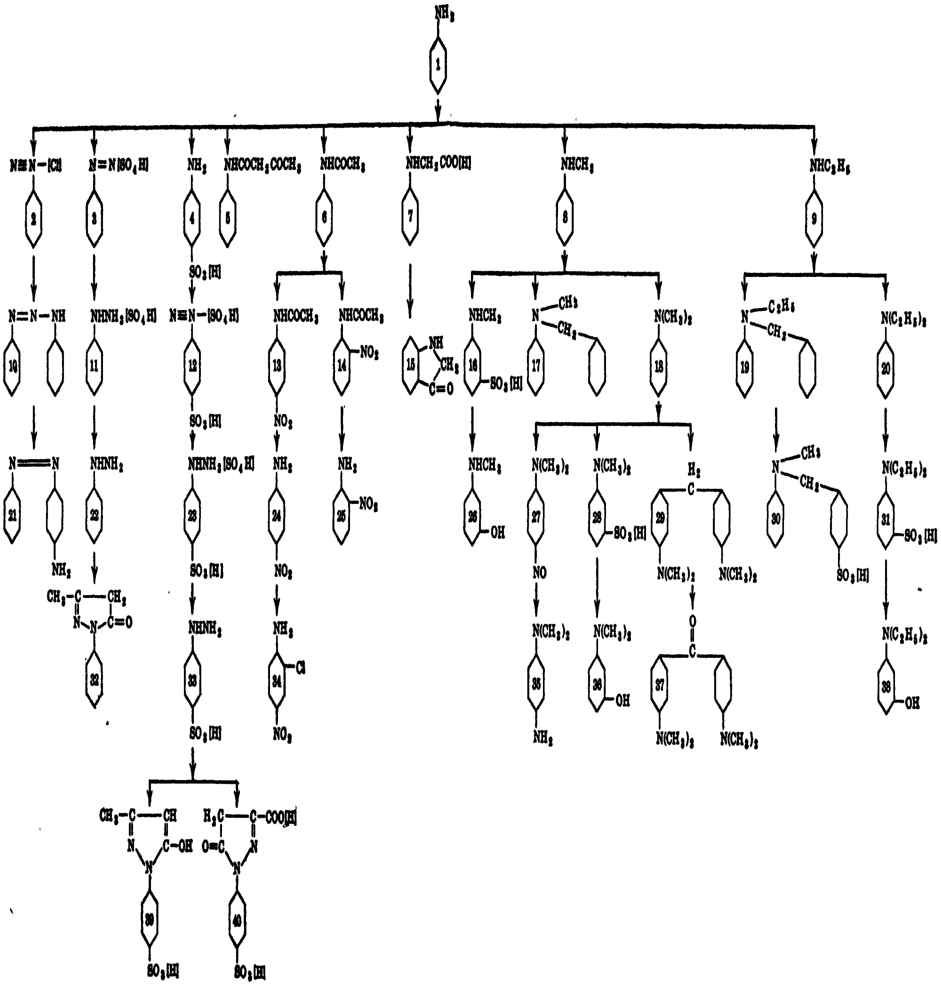
1. Anthraquinone
2. Anthraquinone-1,8-disulfonic acid
3. Anthraquinone-2-sulfonic acid
4. Anthraquinone-1,7-disulfonic acid
5. Anthraquinone-1,5-disulfonic acid
6. Anthraquinone-1,6-disulfonic acid
7. Anthraquinone-1-sulfonic acid
8. Anthraquinone-2,7-disulfonic acid
9. 1-Aminoanthraquinone-8-sulfonic acid
10. 1,5-Dichloroanthraquinone
11. Anthrarufin (1,5-Dihydroxyanthraquinone)
12. 5-Aminoanthraquinone-1-sulfonic acid
13. 1-Aminoanthraquinone
14. Anthrapurpurin (1,2,7-Trihydroxyanthraquinone)
15. 2-Aminoanthraquinone
16. Alizarine (1,2-Dihydroxyanthraquinone)
17. 1,5-Dihydroxyanthraquinone-2,6-disulfonic acid
18. 1-Amino-2,4-dibromoanthraquinone
19. Anthraquinone-2,6-disulfonic acid
20. Alizarine Bordeaux (1,2,5,8-Tetrahydroxyanthraquinone)
21. Purpurin (1,2,4-Trihydroxyanthraquinone)
22. 1,5-Dihydroxy-4,8-dinitroanthraquinone-2,6-disulfonic acid
23. 1-Amino-2-bromo-4-hydroxyanthraquinone
24. Flavopurpurin (1,2,6-Trihydroxyanthraquinone)
25. 1,5-Dihydroxy-4,8-diamino-anthraquinone-2,6-disulfonic acid (Alizarine Saphirol)

FIG. 10. ANTHRAQUINONE SULFONIC ACID DERIVATIVES.



1. Anthracene
2. 9,10-Dichloroanthracene
3. Anthraquinone
4. Anthracene-1-sulfonic acid
5. Quinizarine
6. Anthrahydroquinone
7. 1-Nitroanthraquinone
8. 9-Anthranol (9-Hydroxyanthracene)
9. 1-Anthranol (1-Hydroxyanthracene)
10. 1,5-Dinitroanthraquinone
11. Benzanthrone
12. 1,5-Diaminoanthraquinone

Fig. 8. ANTHRACENE DERIVATIVES.



1. Aniline
2. Benzenediazonium chloride
3. Diazobenzene sulfate
4. Sulfanilic acid (*p*-Aminobenzenesulfonic acid)
5. Acetoacetanilide
6. Acetanilide
7. Phenylglycine
8. Monomethylaniline
9. Monoethylaniline
10. Diazoaminobenzene
11. Phenylhydrazonium sulfate
12. *p*-Sulfobenzenediazonium sulfate
13. *p*-Nitroacetanilide
14. *o*-Nitroacetanilide
15. Indoxyl
16. Monomethylaniline-*m*-sulfonic acid
17. Benzylmethylaniline
18. Dimethylaniline
19. Benzylethylaniline
20. Diethylaniline
21. Aminoazobenzene
22. Phenylhydrazine
23. *p*-Sulfophenylhydrazonium sulfate
24. *p*-Nitroaniline
25. *o*-Nitroaniline
26. Monomethyl-*m*-aminophenol
27. Nitrosodimethylaniline
28. Dimethylaniline-*m*-sulfonic acid
29. Tetramethyldiaminodiphenylmethane
30. Benzylethylanilinesulfonic acid
31. Diethylaniline-*m*-sulfonic acid
32. 1-Phenyl-3-methyl-5-pyrazolone
33. Phenylhydrazine-*p*-sulfonic acid
34. *o*-Chloro-*p*-nitroaniline
35. *p*-Aminodimethylaniline
36. Dimethyl-*m*-aminophenol
37. Tetramethyldiaminobenzophenone (Mischler's ketone)
38. Diethyl-*m*-aminophenol
39. 1-*p*-Sulfophenyl-3-methyl-5-pyrazolone
40. 1-(*p*-Sulfophenyl)-5-pyrazolone-3-carboxylic acid

FIG. 5. ANILINE DERIVATIVES.

TABLE V

Naphthol AS Derivatives

(Courtesy of General Dyestuff Corporation, New York, N. Y.)

Trade Name	Chemical Composition	Mol. Wt.	M.P., °C
Naphthol:			
1. AS	β-Oxynaphthoic acid anilide	263	243
2. AS-AN	β-Oxynaphthoic acid *p*-nitroanilide	308	. . .
3. AS-BG	β-Oxynaphthoic acid 2,5-dimethoxyanilide	325	181
4. AS-BO	β-Oxynaphthoic acid α-naphthylide	313	223
5. AS-BR	β-Oxynaphthoic acid dianisidide	584	384
6. AS-BS	β-Oxynaphthoic acid *m*-nitroanilide	308	246
7. AS-BT	2,5-Dimethoxyanilide of 6-hydroxy-7-carboxydiphenylene oxide	363	217
8. AS-D	β-Oxynaphthoic acid *o*-toluidide	277	197
9. AS-E	β-Oxynaphthoic acid *p*-chloroanilide	315	259
10. AS-G	Diacetoacetyl-*o*-tolidide	380	202
11. AS-GR	β-Oxyanthracene carboxylic acid *o*-toluidide	326	270
12. AS-ITR	β-Oxynaphthoic acid-2,4-dimethoxy-5-chloranilide	358	196.5
13. AS-KL	. . .	. .	. .
14. AS-KR	.	.	.
15. AS-LB	*o*-Toludide of hydroxycarbazole	336	259
16. AS-LC	β-Oxynaphthoic-2,5-dimethoxy-4-chloroanilide	357	188
17. AS-LG	2,4-Dimethoxy-5-chloroanilide of terephthalylethanic acid	588	253
18. AS-L3G	Bis(2-methoxy-4-chloro-5-methylanilide) of terephthalyl diacetic acid (ethanic acid)	557	255
19. AS-L4G	2-Acetoacetylamino-6-ethoxybenzo-*p*-thiazine	278	200
20. AS-LT	β-Oxynaphthoic acid-2-methyl-4-methoxyanilide	309	194
21. AS-MXA	β-Oxynaphthoic acid *m*-xylidide	309	222
22. AS-OL	β-Oxynaphthoic acid *o*-anisidide	294	162
23. AS-PH	β-Oxynaphthoic acid *o*-phenetidide	308	159
24. AS-RL	β-Oxynaphthoic acid *p*-anisidide	293	230
25. AS-S	. . . .	. .	. . . .
26. AS-SG	5-Hydroxy(1,2-benzocarbazole)-4-carboxylic acid *p*-anisidide	382	261.5
27. AS-SM	(See Naphthol AS-SW) β-oxynaphthoic acid β-naphthylide	313	233
28. AS-SR	5-Hydroxy(1,2-benzocarbazole)-4-carboxylic acid 2,4-dimethylanilide	396	. . . .
29. AS-SW	β-Oxynaphthoic acid β-naphthylide	313	233
30. AS-TR	β-Oxynaphthoic acid 5-chlororthotoluidide	311	243

Chapter VII

Pigments from Natural Organic Colors

A book on organic pigments would be incomplete without a chapter on the natural organic pigments or the pigments prepared from natural organic coloring matter. This portion of the subject will be dealt with briefly, however, because natural pigments embrace an extremely broad field and discussion of them would require a great deal of space, and also because the chemistry of these natural products is similar to that of the synthetic products made more generally today. A few pigments have been selected from natural sources which have been significant in the historical development, or more particularly, in actual use. Some of these materials are of importance industrially at the present time, and most of them have been important within very recent years.

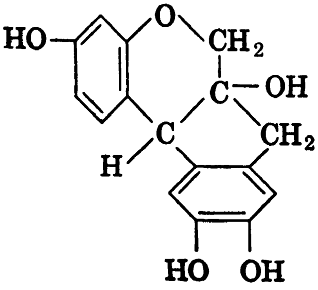
BRAZILWOOD

Brazilwood (54) is a natural red dye from the wood of *Caesalpinia brasiliensis.* That used in the Middle Ages came from Ceylon. It was known and called *brazil* many centuries before the discovery of the country, Brazil. The term *brazilwood* is derived from the word *brasa,* signifying "glowing like fire." Pernambuco wood, *Caesalpinia crista,* from Jamaica and Brazil, has about twice as much coloring matter, and various other trees of the family Leguminosae yield brilliant dyestuffs. The interior of the live wood is light yellow, but changes rapidly to deep red on exposure.

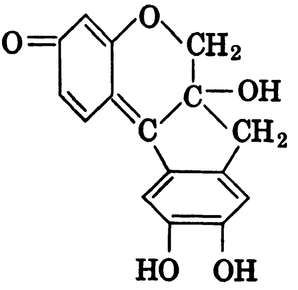
Other similar woods are Lima wood (resembling St. Martha and Nicaragua redwoods) from *Caesalpinia echinata* and sapanwood from *Caesalpinia sappan.* Brazilwood extract is made by boiling finely chipped wood with water and concentrating the liquor in vacuo. The leuco compound is brazilin, $C_{16}H_{14}O_5$. This forms, on exposure to air, brazilein, $C_{16}H_{12}O_5$, which is deep red to brown in color.

$$C_{16}H_{14}O_5 + O \rightarrow C_{16}H_{12}O_5 + H_2O$$

The formula proposed by Pfeiffer for brazilin is (97):

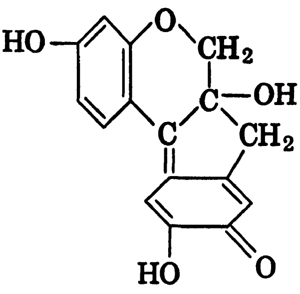


The corresponding structure for brazilein may be a choice between two possible quinonoid structures (97) proposed by Pfeiffer and Perkin.



(Pfeiffer)

and



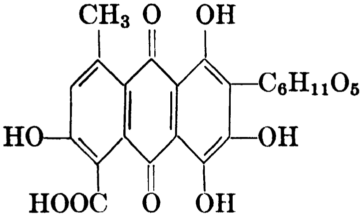
(Perkin)

Preference is given to Perkin's formula as it would be in accordance with the fact that oxidation of trimethyldesoxybrazilin results in oxidative attack on the pyrocatechol residue.

Brazilwood lakes (54), which are prepared with different mordants, vary in color from light cherry to deep red. One method formerly used was to extract the chips with hot alum solution, followed by precipitation with lye. The lakes are insoluble in water and in alcohol but are partially soluble in alkalies, which give them a brownish red color. They are decomposed by mineral acids and are not stable in strong light.

COCHINEAL

Cochineal (54) is a natural organic dyestuff made from the dried bodies of the female insect, *Coccus cacti*, which lives on various cactus plants in Mexico and in Central and South America. About 140,000 insects weigh one kg. After treatment with steam or dry heat, the ground mass yields about 10 per cent of pigment. It was first taken to Europe shortly after the discovery of those countries. Eiber says that it came in after the conquest of Mexico in 1523 and was first described by Mathioli in 1549. The coloring principle of cochineal extract is carminic acid, $C_{22}H_{20}O_{13}$, of which the accepted structure is (97):



Of the residue, $C_6H_{11}O_5$, it is known only that it contains four hydroxyl groups which can be acetylated, and that, although it is essentially a sugar group, it is not bound to the anthraquinone as a glucoside. Asymmetric carbon atoms are present, as carminic acid is dextrorotatory.

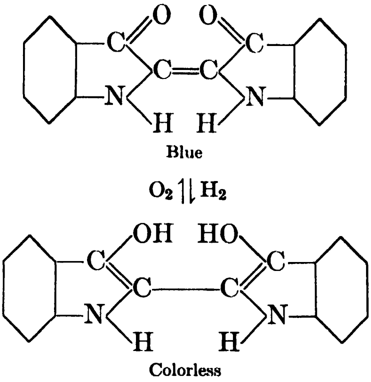
Carmine (54) is an aluminum and calcium salt of carminic acid, and carmine lake is an aluminum or aluminum-tin lake of cochineal extract. Crimson lake is prepared by striking down an infusion of cochineal with a 5 per cent solution of alum and cream of tartar. Purple lake is prepared like carmine lake with the addition of lime to produce the deep purple tone. The cochineal lakes are not permanent to light. They turn brownish and then fade rapidly in strong sunlight, particularly when used in water color. In oil, however, they are fairly stable and were used formerly in the preparation of fine coach colors.

INDIGO

Indigo (106) occurs as the colorless glucoside indican, $C_{14}H_{17}O_6N$, in various species of *Indigofera* (Papilionatae), as in *Indigofera tinctoria, pseudotinctoria, anil, disperma,* and *argentea.* The plant is originally indigenous to the region between latitudes 20 and 30 of Eastern Asia, but it thrives also in China, Japan, the Philippines, Central America, Brazil, and Java. Common woad, *Isatis tinctoria* (family of Cruciferae), was formerly cultivated in Europe but yields a smaller amount of indican than *Indigofera.*

In the preparation of the dye (54), the freshly cut plants are macerated, packed into large vats, and allowed to ferment. In this process the glucoside is hydrolyzed to indigo and sugar. The precipitate is strained, pressed, and dried into cakes. For use as a paint pigment it is not precipitated with a mordant but is ground directly to a fine powder.

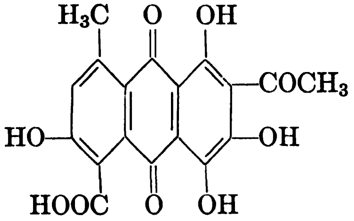
The colored and colorless forms of indigo are shown in the following structures:



Indigo has a fair tinting strength. In thin films it is green and blue by transmitted light. Physically it is much like Prussian blue, but chemically it is quite different. In an oil medium, no distinct particles can be seen at ordinary magnification. The dye appears to dissolve in the film and stain it. De Wild says, however, that at a magnification of 1500 intensely blue discrete particles appear. Though it can be worked in oil, it is better in tempera or water color. Indigo may fade rapidly when thin and exposed to strong sunlight; yet specimens of it have lasted for many centuries without apparent change. It is very stable chemically, being insoluble in water, ether, alcohol, lyes, or hydrochloric acid. It sublimes when heated to 300° C.

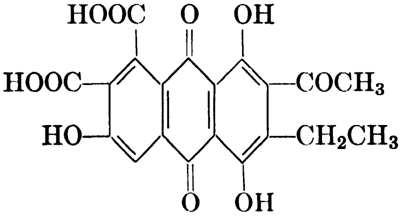
KERMES

Kermes (54) is one of the most ancient of the natural dyestuffs. It is derived from the dried bodies of the female insect, *Coccus ilici*, found on the kermes oak, which is indigenous to many parts of southern Europe. It is similar to the New World *cochineal* in origin, color, and chemical composition, and contains the coloring matter kermesic acid, $C_{18}H_{12}O_9$. It was well known to the Romans; Pliny called it *Coccum granum* and praised it highly. The word *kermes* is Arabic in origin and is the source of the English word *crimson*. Kermes dyes were precipitated with alum to form crimson lakes. Kermes lakes are not brilliant, and in the Middle Ages they were displaced by the lac lakes from India and, still later, by cochineal lakes from Mexico. The accepted formula for kermesic acid (97) is



LAC, LAC LAKE

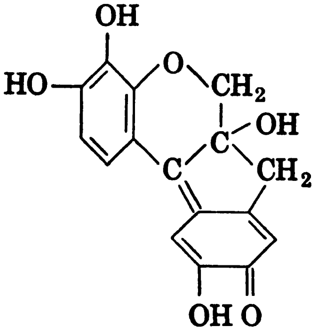
Lac, lac lake (Indian lake) is a natural organic red dyestuff prepared from the resin-like secretion of the larvae of the insect *Coccus lacca*, which lives on certain trees of the species, *Croton ficus*, in India, Burma, and the Far East. From the lac secretion, which also produces the *seed lac* or *shellac* of commerce, the red dye is extracted with hot dilute sodium carbonate solution when the shellac is purified. The lake is made by precipitation with alum. The coloring principle is laccaic acid or its salts, for which the following structure (97) is proposed:



It is similar in composition and color to the carmine dyes from cochineal, but the lac dye is somewhat faster, if duller, in shade.

LOGWOOD

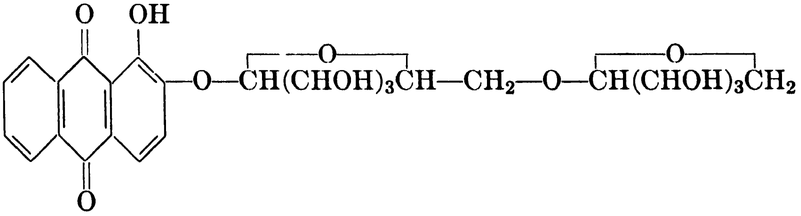
Logwood (54) is the name of a red dye that is extracted from wood of *Haematoxylon campechianum*, a tree of the Caesalpiniaceae family, which is indigenous to Mexico, Central America, and the West Indies. The interior of the live wood is yellow but it changes rapidly to dark brown on exposure to air. The leuco compound, haematoxylin, $C_{16}H_{14}O_6$, changes to red-brown haematein, $C_{16}H_{12}O_6$. It is extracted by boiling logwood chips in water under pressure. The accepted structure for haematein (97) is:



With sodium hydroxide a purplish blue solution is formed which changes to brown on exposure to air. Brown, reddish brown, black, and blue-black lakes can be prepared from logwood extracts with various mordants. All are insoluble in water and alcohol, are turned bluish violet by alkalies, and are decomposed by mineral acids with the formation of a blood-red solution. The lakes are rather fugitive to strong light.

MADDER

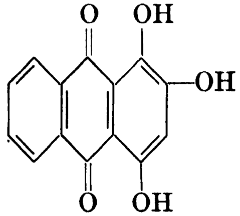
Madder is a natural dyestuff from the root of the herbaceous perennial, *Rubia tinctorum*, which formerly was cultivated extensively in Europe and in Asia Minor. Roots from plants 18 to 28 months old, grown in a calcareous soil, are best. The coloring matter, which is chiefly alizarin, occurs in the root in the form of a glucoside known as rubierythric acid (97):



It is extracted from the ground root by fermentation and hydrolysis with dilute sulfuric acid.

Madder lake and rose madder for artists' pigments are prepared from madder extract by adding alum and precipitating with an alkali.

The extract from the madder root also contains another natural dye called purpurin. This is 1,2,4-trihydroxyanthraquinone:

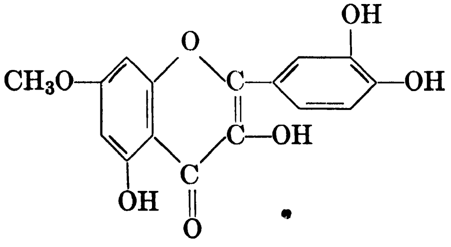


The presence of purpurin (54) distinguishes natural alizarin from the synthetic product. Pure purpurin gives lakes which are more orange and red than those of alizarin, and this accounts for the warm tones of madder lakes as compared with the pure alizarin lakes. Eibner says that the presence of purpurin causes madder lake to fluoresce a fiery yellow-red in ultraviolet light, whereas synthetic alizarin lakes show only a feeble violet luminescence.

Paint films colored with madder lake are nearly transparent and appear bright red, with a definite violet hue by transmitted light. Madder lake is among the most stable of the natural organic coloring matters. The color is turned purple by dilute sodium hydroxide but is only destroyed by much stronger reagents. According to Harrison (63), the alizarin lakes now far surpass lakes from the natural madder in purity, brilliance, and range of colors.

PERSIAN BERRIES

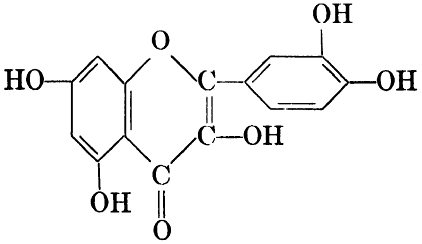
Persian berries (54) lake is a yellow lake made from the dried unripe berries of various shrubs of the buckthorn family, *Rhamnus*, found in the Near East and now imported from Smyrna and Aleppo. The coloring principle is rhamnetin $C_{16}H_{12}O_7$, which is extracted by boiling water. The structure is (97):



The lake is made by the addition of alum, followed by soda, and other colors are produced with other mordants. It is insoluble in water and in alcohol but is soluble in alkalies, forming a yellowish-brown solution. It is decomposed and decolorized by mineral acids but is moderately stable in light.

QUERCITRON

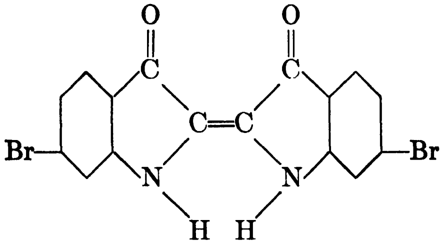
Quercitron lake is a yellow coloring matter made from the inner bark of a species of oak, *Quercus tinctoria*, that is indigenous to North America. The coloring principle is quercetin or tetrahydroxyflavonal the structure of which is:



The bark is extracted with water and the lake is made by adding alum and precipitating with chalk. It is soluble in water and in alcohol, but forms a yellowish-brown solution with alkalies and is decolorized by mineral acids. Yellow lakes of this nature are rapidly faded by sunlight but are said to retain their color well in artificial light.

TYRIAN PURPLE

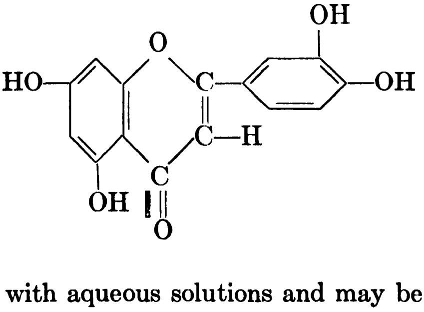
Tyrian purple (54), one of the most important and most costly of the organic coloring matters of the ancients, was prepared from several mollusks (whelks), including *Murex brandaris* and *Purpura haemostoma*, found on the shores of the Mediterranean and the Atlantic coasts, including the British Isles. Huge quantities of these mollusks were used for dying fabrics in ancient times, and on certain shores of the Mediterranean heaps of the shells still remain about the sites of ancient dye works. The color-producing secretion of the whelk is contained in a little vein or cyst, and when this is broken and squeezed by hand, it issues as a white fluid. Cloths to be dyed are dipped in this fluid and are exposed to strong sunlight, which causes the development of the color finally to purplish red or crimson. P. Friedländer, in his experiments on the extraction of purple from *Murex brandaris* collected at Trieste in 1908, obtained only 1.4 grams of the pure dye from 12,000 mollusks. He established the identity of the coloring principle as 6,6-dibromoindigotine (49):



The purple color is remarkably stable, resisting alkalies, soap, and most acids, and is only destroyed by hot nitric acid or chlorine. According to Pliny (10), the best quality was made at Tyre, probably the reason it is still called *Tyrian purple.*

WELD

Weld (54) is a natural yellow dyestuff obtained as a liquid or as a dry extract of the herbaceous plant, dyer's rocket, *Reseda luteola,* formerly cultivated in Central Europe. The coloring matter is luteolin or tetrahydroxyflavone:



It is extracted with aqueous solutions and may be made into lakes of various shades of yellow with different mordants. Although weld extract has lower tinctorial power than some other yellow dyes like quercitron, it yields the purest and fastest shades of all. Weld has a long history as a dye and lake pigment.

Chapter VIII

Synthetic Organic Pigments

The term *synthetic organic pigments,* in this book, is restricted in its application to those colored substances that have been made from the basic raw materials, or intermediates, by building the structures responsible for the presence of color, and then obtaining them in the insoluble forms required of modern pigments.

The previous chapter described a variety of pigments prepared from natural coloring matters or dyestuffs, and it must be understood that they represent a partial synthesis in the conversion of the dyestuff into the insoluble pigment form. These materials, as a group, however, are becoming less important as they are progressively replaced by the more desirable, fully synthetic types, and for this reason they are treated separately.

On this basis there are three general methods by means of which a synthetic organic pigment may be prepared:

1. By treating an intermediate, or raw material, in such a manner as to convert it into an insoluble colored product.
2. By combining two or more intermediates in such a way as to form an insoluble colored compound.
3. By forming the insoluble pigment from a dyestuff that has previously been made from one or more intermediates. The dyestuff, in this case, may be a soluble or an insoluble type.

All these procedures are represented among the groups of pigments dealt with in this chapter, although by far the greater number fall into the second and third classes.

The arrangement of material is based upon a rather practical type of classification, following, in a rough way, the Colour Index system, but collecting in a separate section the basic colors which are to be found in several different structural groups.

The basic dyestuffs, of all types, are readily converted into nonpermanent toners and lakes with tannic acid and tartar emetic, or into the permanent toners and lakes with the phosphotungstic or phosphomolybdic complex acids. In these respects they are similar.

The complete classification is outlined as follows:

Nitroso pigments
Nitro pigments
Azo pigments
Basic dye pigments, permanent
Basic dye pigments, non-permanent
Acid dye pigments of basic type
Xanthene dye pigments
Anthraquinone pigments
Vat color pigments, Indigoid
Vat color pigments, Anthraquinone
Phthalocyanine pigments

Historically, the earliest synthetic pigments used in commercial quantities were to be found largely in the nitro, azo, non-permanent basic dye, acid dye of basic type, and xanthene groups. Many of these pigments were of the non-permanent or fugitive-to-light type, especially the yellow, green, and blue lakes. Comparatively few of the products had reasonably good resistance to either outside or interior exposure.

After the first world war greater attention was devoted to improvement in the quality of organic pigments for many industrial uses, such as the development of the permanent type of basic color pigments, anthraquinone pigments, and a few of the vat color pigments of both the indigoid and anthraquinone types. More recently, the major development has been in the field of the new phthalocyanine pigments which appear mainly in blue and green forms.

Possibly the most valuable and significant improvements during the past few years, however, have been the revolutionary improvements in the characteristics and qualities of well-known standard types of pigments. They have included marked improvements in brilliance, large percentage increases in tinctorial power, considerable improvements in texture for a variety of uses, and exceptionally favorable changes in the so-called working properties which include low consistency, good flow, and ready wetting or dispersion with oil vehicles, all of which are of great importance in the fields of printing inks and paints.

This last feature of development, which is obviously based on the recognition of the valuable characteristics of certain individual pigments or types of products, has been and is of primary significance, as it undoubtedly will continue to be in the future. The real point of significance is that there is no such thing as a perfect pigment, for either general or specific use. Any material now employed can readily be improved for some particular purpose, and occasionally an improvement appears which is broadly applicable to a variety of products and a variety of uses.

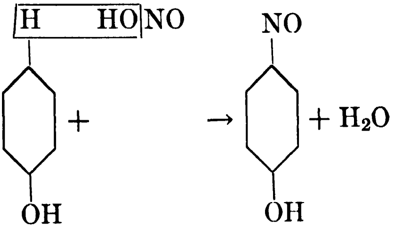
It may be quite clearly recognized that, in general, improvements have followed the requirements of industrial use, occasioned by new types of vehicles, new methods of application, and new ideals of artistic accomplishment, and it may repeatedly happen in the future, as it has in the past, that the unsatisfactory pigments of today may become or lead to the high-grade products of tomorrow.

The field of pigments would appear to be almost unique in the degree to which modification and improvement may be and are consistently applied to the old standard types of commercial products. It is doubtful if there are any considerable number of organic pigments on the market today of the identical quality of the products of ten years ago, and the percentage would still be low if a five-year period should be considered.

NITROSO PIGMENTS

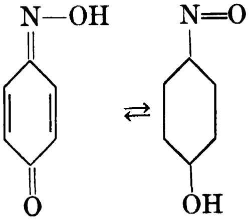
The nitroso pigments are characterized by the presence of the nitroso (—NO) group. Their preparation depends on the reaction between phenols and nitrous acid. They are of special interest because of the tautomeric nature of the products or, as will be seen, the existence of these materials in the form of resonance hybrids.

The direct reaction of phenol with nitrous acid may be represented as:



p-Nitrosophenol

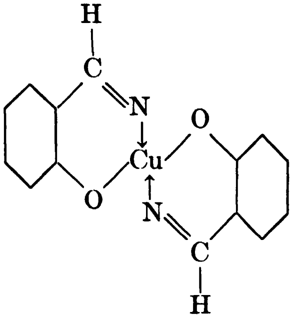
with the presence also of an equilibrium condition between *p*-nitrosophenol and quinone-monoxime.



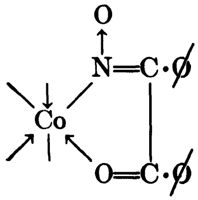
According to Sidgwick (125):*

> Certain oximes will form stable complexes with metals, particularly with those of the transitional triads of the Periodic Table and adjacent groups, and are widely used for the detection and estimation of those metals. Thus the reagent used for the estimation of nickel and palladium is dimethylglyoxime ($HON{=}CCH_3{-}CCH_3{=}NOH$).

Complexes of this type, including copper, cobalt, and nickel, may be illustrated as follows (125):



1



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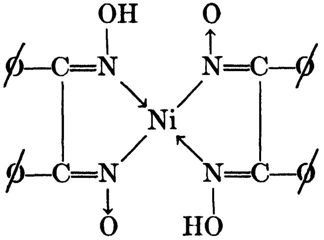
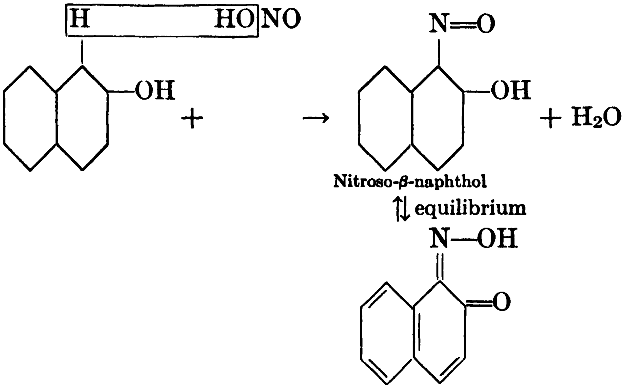


3

The most important phenol used in formation of nitroso pigments is β-naphthol, where the para position to the hydroxyl group is occupied and so substitution takes place in the alpha position:

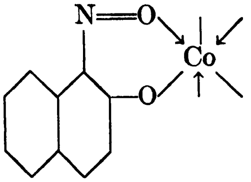


Nitroso-β-naphthol

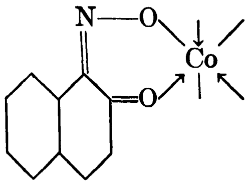
1,2-Naphthaquinone

* Reprinted with permission from *The Organic Chemistry of Nitrogen*, published by the Oxford University Press, London.

These compounds, in accordance with the typical oxime reactions, form complexes with such metals as cobalt or iron, which have a chelate structure and may be shown in two possible forms as the cobalt derivatives:

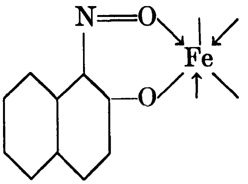


and

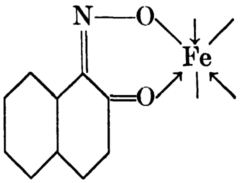


The actual structure of these complexes appears to be that of a resonance hybrid of these two formulas.

Some of these metallic complexes are deeply colored. Nitroso-β-naphthol, by reaction with an iron salt, gives a bright fast green known as Naphthol Green Y. The structure may be represented as

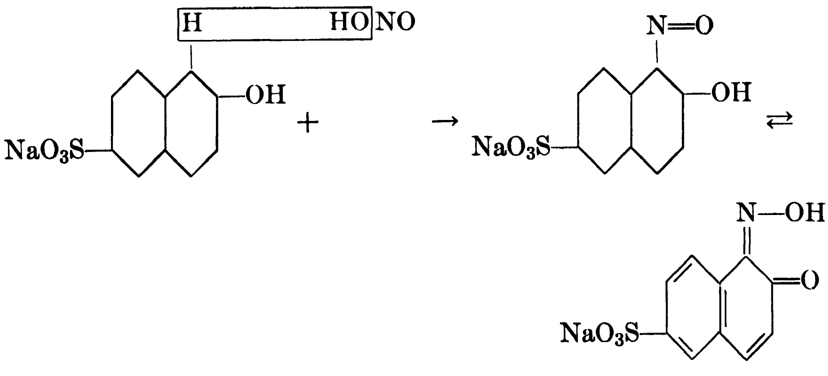


and

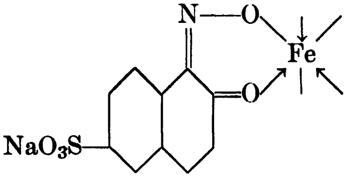


It is a pigment of considerable stability toward light and heat, but has not been extensively used because it lacks brilliance and has a tendency to form a hard gritty product on drying.

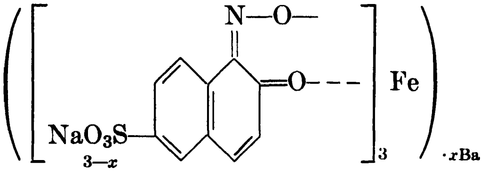
The most widely used pigment in this group has been the Naphthol Green B, which is made from Schäffer's acid (2-naphthol-6-sulfonic acid). The dyestuff is a water-soluble compound readily precipitated in the form of a metallic (Ba) lake on alumina hydrate or gloss white. Its formation may be indicated as follows:



Treatment with iron gives the soluble dyestuff



which can be precipitated on a suitable base such as alumina hydrate with a solution of barium chloride:



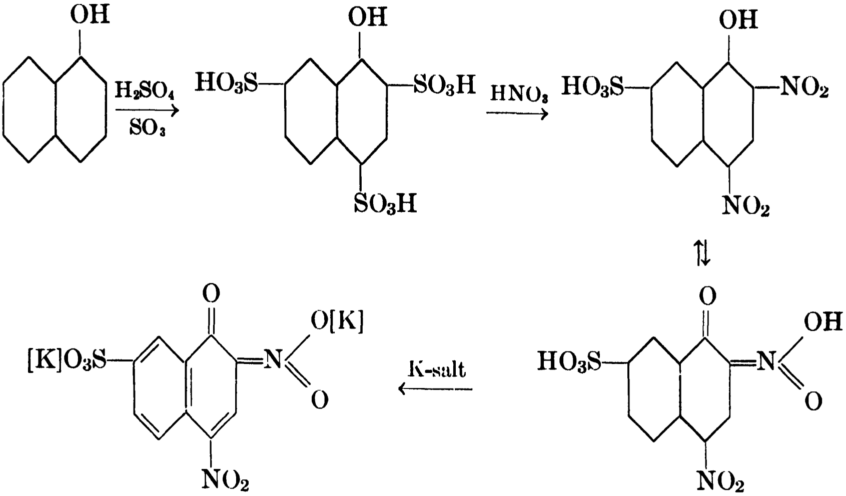
The exact nature and composition of this color complex are not well established. It may involve reaction with each of the three sulfonic acid groups in the dye complex or with only two.

Naphthol Green B is a rich green pigment of a bluish tone and high in tinctorial power, but is rather unstable in contact with water. In the past it was a very useful color, but it has been largely replaced within recent years by products of greater brilliance, better stability, and broader application.

NITRO PIGMENTS

The nitro pigments are characterized by the presence of nitro (—NO_2) groups. In such cases there is no apparent chromophore group aside from the nitro group itself, but it should be kept in mind that in most cases it is possible to represent the structure in a tautomeric form which is analogous to an orthoquinone. This will be indicated in each of the following cases.

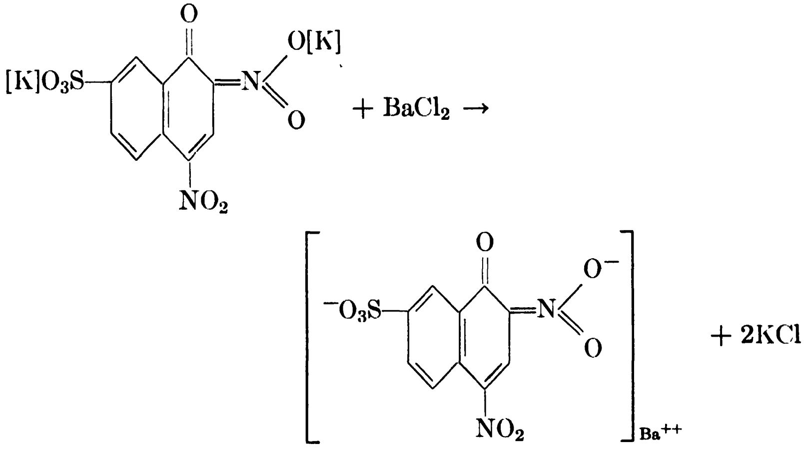
The most widely known and useful pigment in this group, Naphthol Yellow S, is made by nitrating 4-nitroso-1-naphthol-2,7-disulfonic acid, or by nitrating 1-naphthol-2,4,7-trisulfonic acid. The latter procedure may be illustrated as follows:



Naphthol Yellow S

C.I. 10 *
Sch. No. 7 †

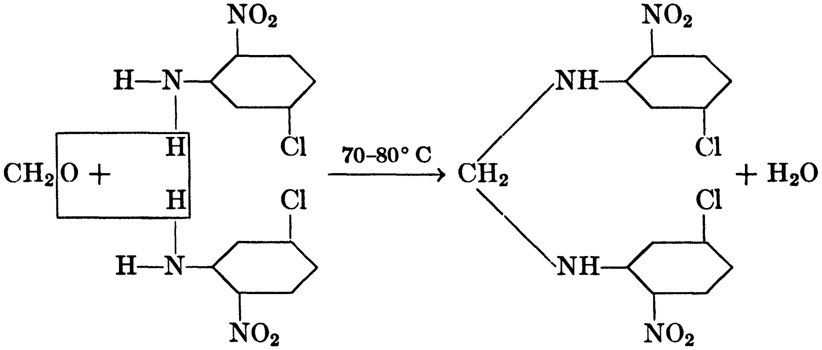
As the dyestuff is readily precipitated by heavy metal salts the pigment is generally formed by treating the dye, in solution, with barium chloride:



This pigment has been extensively used in the manufacture of yellow lakes of excellent tinctorial properties and of fair permanency to light.

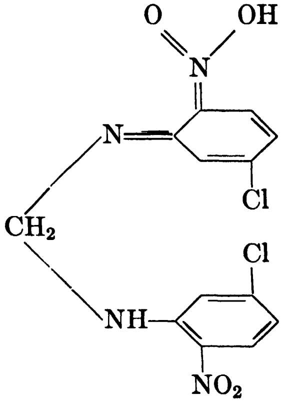
* C.I. = Colour Index (32).
† Sch. = Schultz Number, *Farbstofftabellen*, 14th Ed.

Two nitro type dyestuffs that have been quite extensively used as pigments are made by condensation of formaldehyde with nitroamino compounds. For example, 3-chloro-6-nitroaniline gives Pigment Chlorine GG.



C.I. 13
Sch. No. 8

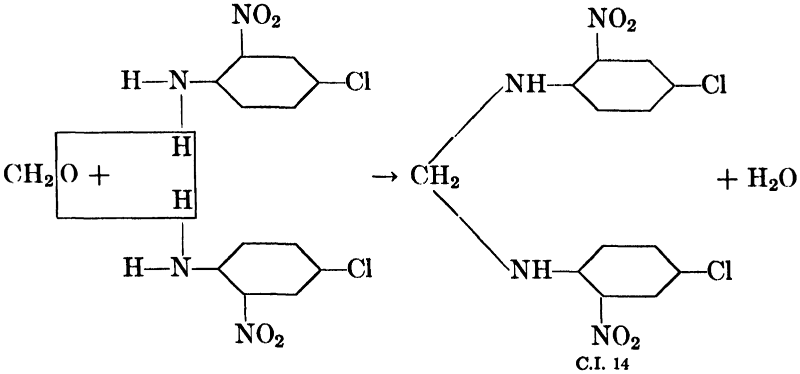
The dye molecule in this case can also be represented in the quinonoid form



but the inactivity of the substance renders this simple change in structure rather less likely.

Pigment Chlorine GG has been used for pure greenish yellow lakes that are very fast to water. The lakes darken, however, on exposure to light.

In a similar manner 4-chloro-2-nitroaniline is condensed with formaldehyde to form Lithol Fast Yellow GG,



C.I. 14

which has been used in color lakes, for lithographic printing, and as a non-poisonous substitute for lead chromate in wallpaper and distemper colors. Its resistance to heat is not good.

AZO PIGMENTS

The azo pigments are characterized by the presence of the azo (—N=N—) group. Including many of the most interesting as well as the most valuable of the synthetic pigments, they also exhibit the widest range of colors and the greatest diversity of chemical and physical properties of any color group. This is due directly to the very general application of the diazo and the coupling reactions and the almost unlimited variety of intermediates available for use.

Fundamentally these colors are formed by the coupling of a diazo (or diazonium) salt with a second component, which may be either a phenolic or an amino compound (24):

$$R\cdot N_2\cdot Cl + HR'OH + NaOH \longrightarrow R\cdot N_2\cdot R'OH + NaCl + H_2O$$

or

$$R\cdot N_2\cdot Cl + HR'NH_2 \xrightarrow{\text{acid}} R\cdot N_2\cdot R'NH_2 + HCl$$

The Diazonium Salt (118)

The first diazonium salt was accidentally discovered in 1858 by Peter Griess, who recognized it as a member of an unknown class of compounds. In attempting the conversion of picramic acid to hydroxypicramic acid, by treating picramic acid with warm nitrous acid, Griess also conducted the treatment in the cold. The resulting product had none of the expected properties, and similar treatment of other amines soon convinced him that he had discovered a reaction of general application.

Since that time three methods of preparation have been found especially useful in practice.

1. **The Direct Method.** In this procedure a solution of a metallic nitrite is introduced rapidly into a cold solution of the amine in dilute mineral acid.

2. **The Inverted Method.** Mixed alkaline solutions of a metallic nitrite and a salt of a sulfonated or carboxylated amine are run into an excess of cold dilute mineral acid.

3. **The Acid-Solution Method.** The amine is dissolved in a concentrated acid (sulfuric, phosphoric, or glacial acetic) and diazotized with nitrosylsulfuric acid. This method is particularly applicable to amines of very weak basic character.

Three other methods are of interest but of less practical value in this field:

1. Witt's method of dissolving the amine in nitric acid and adding metabisulfite, which forms nitrous acid by reduction:

$$Na_2S_2O_5 + 2HNO_3 \rightarrow Na_2S_2O_7 + 2HNO_2$$

2. Griess' method, treating the amine, suspended or dissolved in water or alcohol, with nitrogen trioxide:

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

3. Knoevenagel's method, treating the amine, dissolved in water, acids, or alcohol, or suspended in an inert solvent, with alkyl nitrite:

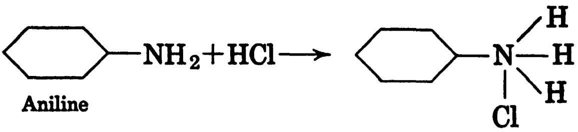
$$R\text{—}ONO + HCl \rightarrow RCl + HONO$$

In general the diazonium compounds are unstable, decomposing gradually even at low (0–5° C) temperatures, and at higher temperatures the reaction may become very rapid. For this reason the diazo reaction, in commercial use, is conducted at low temperatures and as a rule with ice present.

Higher acidity also tends to retard decomposition. The presence of an excess of acid is generally regarded as essential. Theoretically two molecules of acid are required to complete the diazotization of an amine, but more may be required if the acid is a weak acid, such as acetic acid, or if the amine itself has a very low degree of basicity.

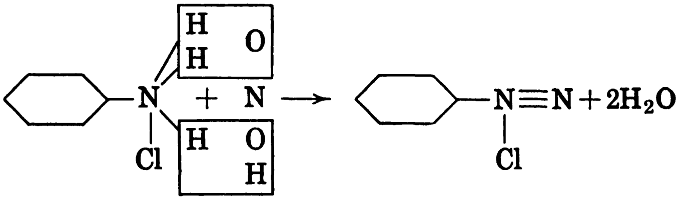
The basic reaction of diazotization may be represented in this way:

$$H\boxed{Cl + Na}NO_2 \longrightarrow HONO + NaCl$$



Aniline

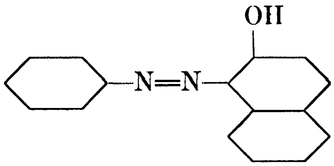
Aniline Hydrochloride



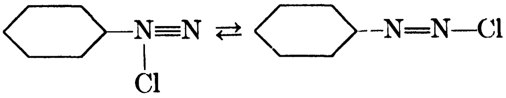
Nitrous Acid

Benzene Diazonium Chloride

However, since reaction of the diazonium salt with a naphthol, for example, yields a compound of the following accepted structure



it is evident that a rearrangement must occur at some point. This is frequently indicated by an equilibrium between the diazonium salt and the diazo salt:



Diazonium Form

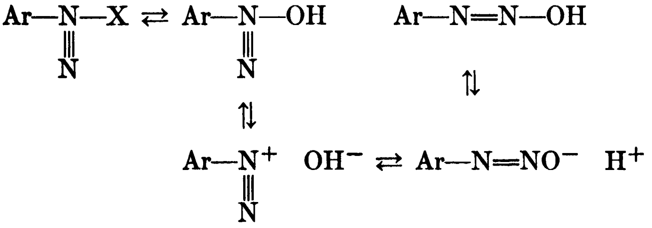
Diazo Form

This mechanism would indicate the direct reaction of the diazo form with the phenolic compound, the equilibrium causing progressive conversion until the diazonium salt has been changed completely into the diazo form.

A great deal of work has been done in the study of the diazonium compounds and the so-called diazotates by Blomstrand, Hantzsch, Bamberger, Cain, and others, and a great deal has been learned of their reactions, stabilities, colors, and other properties. A completely satisfactory solution of the problems of structure and reaction, however, has not yet been achieved. Saunders (118) gives an excellent review of this important work. For example, Blomstrand suggested the structure of the diazo compounds to be $R-\underset{\underset{N}{|||}}{N}-X$ where X is the ion of a strong monovalent acid or its equivalent, largely on the basis of the great difference in stability between the diazo and the azo compounds. Blomstrand's structure was opposed by E. Fischer (47) and was almost forgotten when, in 1895, it was rediscovered by Bamberger (11) and Hantzsch (61), who recognized how correctly it interpreted the facts. Hantzsch proposed the name *diazonium* for the radical.

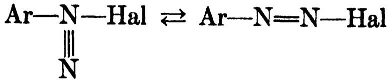
The Blomstrand formula suggests analogy to the ammonium compounds and to derivatives of ammonium hydroxide. However, treatment of the diazonium salts with alkalies brings about far more deep-seated changes than the liberation of the required hydroxide. An hydroxide having the structure $Ar-\underset{\underset{N}{|||}}{N}-OH$ has never been isolated, nor can it be certain that it has been obtained, free from isomers, in solution. To obtain this hydroxide, Hantzsch acted on a pure diazonium chloride in dilute aqueous solution at 0° C, with a slight excess of moist silver oxide. The filtered solution is strongly alkaline and couples readily with β-naphthol.

Without the special precautions described by Hantzsch internal rearrangement sets in as rapidly as the hydroxide is liberated by the action of the alkali. The diazonium salt is changed into that one of the isomeric diazo compounds which occupies the middle zone in the table of metamorphosis and which, unlike the diazonium form, possesses the capacity to couple completely and rapidly. The equilibrium is not directly between the diazonium salt and the normal diazo compound, but between the ions of the dissociated hydroxides:



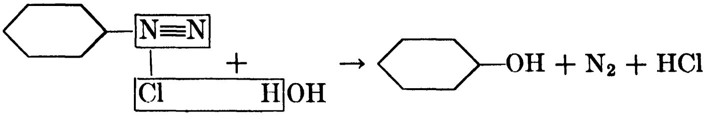
$$\begin{array}{lcl} Ar-\underset{\underset{N}{|||}}{N}-X \rightleftarrows Ar-\underset{\underset{N}{|||}}{N}-OH & & Ar-N{=}N-OH \\ \qquad\qquad\qquad\quad \uparrow\downarrow & & \qquad \uparrow\downarrow \\ \qquad\qquad\quad Ar-\underset{\underset{N}{|||}}{N^+}\ \ OH^- & \rightleftarrows & Ar-N{=}NO^-\ \ H^+ \end{array}$$

The suggestion has been made by Hantzsch that in certain diazonium halides the simpler equilibrium can exist in the solid state:



$$\underset{\underset{\displaystyle N}{|||}}{Ar-N-Hal} \rightleftarrows Ar-N=N-Hal$$

In the field of organic pigments there are two reactions that should be particularly recognized as sources of difficulty in the diazo operations. One involves the replacement of the diazo or diazonium group with an hydroxyl group:

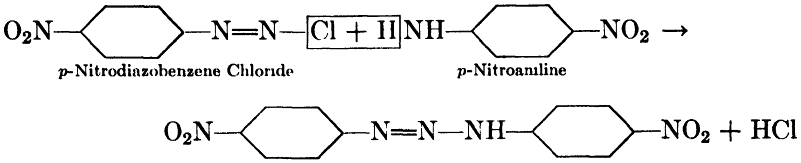


Various investigations have shown that in acid solution the decomposition of a diazo compound which is in complete solution follows the ordinary law for a unimolecular reaction, namely:

$$K = \frac{1}{t} \log \frac{A}{A - X}$$

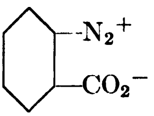
This action makes it essential to handle diazo solutions at low temperatures, and without unusual delay, in order to avoid losses of material and serious effects on the quality of final products.

Another side reaction which sometimes causes difficulty involves the formation of diazoamino compounds:

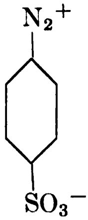


This may be brought about by conducting the diazo reaction in the presence of a deficiency of acid or nitrite, allowing a direct reaction between the diazonium salt already formed and the unchanged amine. In the diazotization of *p*-nitroaniline this reaction is of interest, as a deficiency of acid or nitrite may cause the formation of the diazoamino compound which is insoluble and yellow in color. In this case the failure of the operation to yield a clear diazo solution is, of course, not corrected by further addition of acid or nitrite.

In order to avoid or minimize the effects of these interfering side reactions it is essential that the established conditions of operation, such as factors of time and concentration, degree of acidity, and invariable excess of nitrous acid, be rigidly maintained. The diazonium compound derived from the aminocarboxylic and sulfonic acids of benzene occupy a special position because there is a strongly basic group and an acidic group in the same molecule, so that the diazonium compounds exist as internal salts or "zwitterions" of the betaine type. Thus anthranilic acid gives the diazonium compound I, and sulfanilic acid gives II:



I

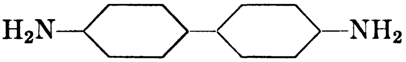


II

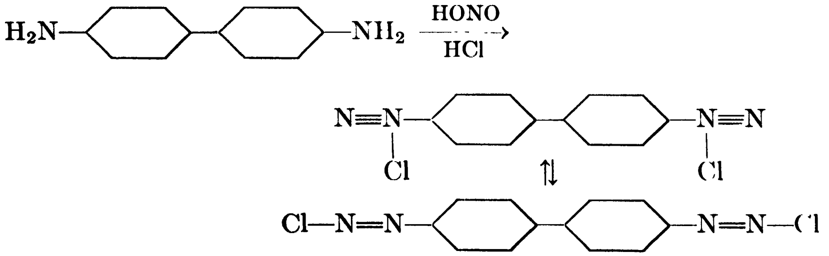
These compounds are water soluble, but the solutions naturally show no electrolytic conductivity, although the compounds are salts.

Tetrazo Compounds

Diamino compounds of the benzidine type



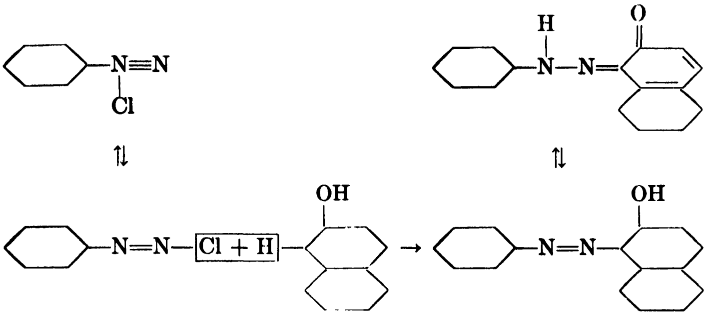
react with nitrous acid in mineral acid solution to convert both amino groups into diazonium groups.



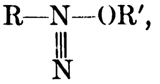
These compounds couple in the usual way with two molecules of a phenolic, acetoacetic, or pyrazolone type of second component to yield a complex diazo pigment that is generally in the range of yellow or orange. The hansa and benzidine yellows and oranges are products of these reactions and will be outlined more completely in a later section.

The Coupling Reaction

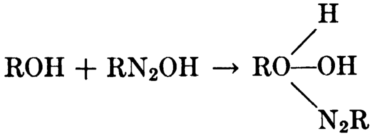
Reactions between diazo compounds and phenolic or amino compounds are generally called coupling reactions and usually yield colored products. In the field of organic pigments the phenolic type of coupling is of primary importance and interest. It may be represented as follows:



Diazo Naphthol Azo Color

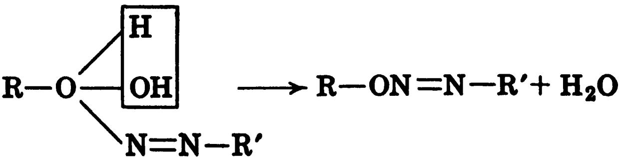
The reaction mechanism (24) suggested by Dimroth (39) is the formation in alkaline solution of a diazo oxide (diazotate), R—N=N—OR′ or  $R—\underset{\underset{N}{|||}}{N}—OR'$, from the diazo compound and the phenol. The oxide then spontaneously rearranges into the ordinary azo compound.

Auwers and Michaelis (8) regard the intermediate reaction as an addition complex with an oxonium structure:



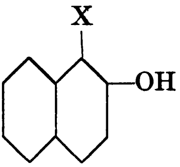
$$ROH + RN_2OH \rightarrow RO\begin{matrix} \diagup H \\ —OH \\ \diagdown N_2R \end{matrix}$$

The dye is then formed by elimination of water, followed by the same rearrangement:

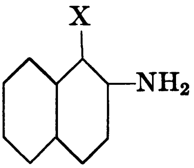


$$R—ON{=}N—R' \longrightarrow HO—RN{=}N—R'$$

Position of Coupling. With an hydroxyl group or amino group in the 2-position in a naphthalene compound, such as 2-naphthol or 2-naphthylamine, combination takes place in position 1.

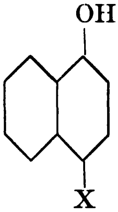


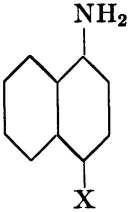
or

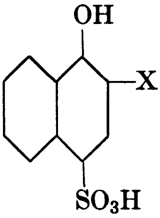


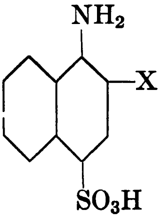
If this position is occupied, no formation of the azo compound takes place.

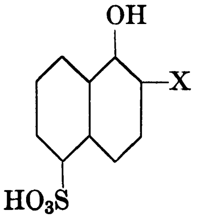
In other compounds the situation becomes more complex. For example (24), in the cases of 1-naphthol and 1-naphthylamine, combination takes place in position 4. If this is occupied or if the position 3 or 5 is occupied by a sulfonic acid group, combination takes place in position 2. The cross indicates the position of the entering azo group in the following compounds:

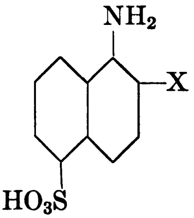


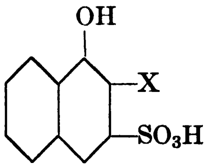


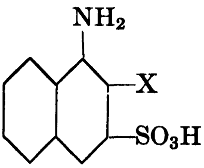






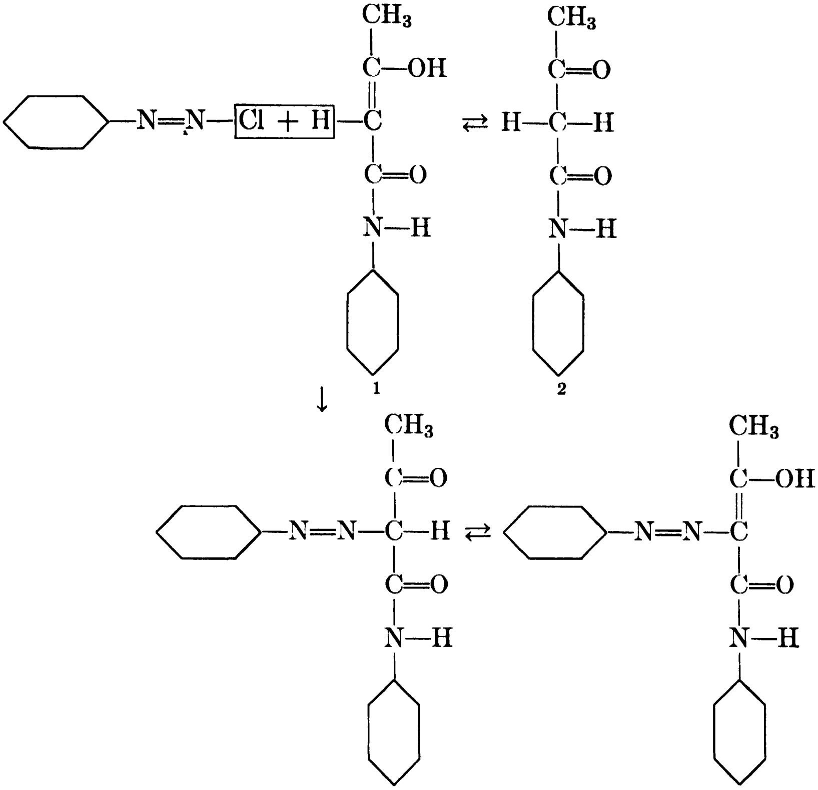






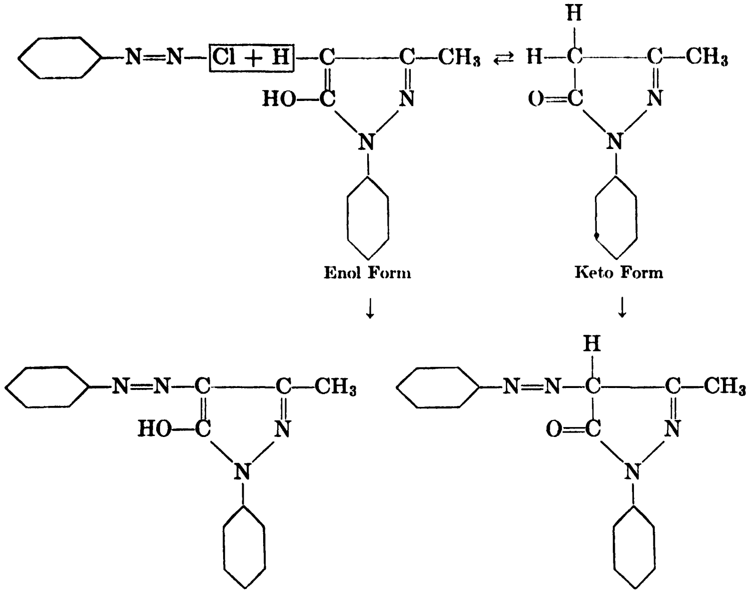
This is sufficient to indicate the complexity of conditions when dealing with second components possessing involved structures.

Another type of coupling reaction is that between diazo compounds and the acetoacetic arylides (see page 97), such as that between aniline and acetoacetanilide.



Within recent years this reaction has become of considerable importance in the production of hansa and benzidine yellows. In this type of reaction the acetoacetanilide derivative exists as an equilibrium mixture of the keto 2 and enol 1 forms, the latter being the active form.

In still another type of coupling reaction the diazo compounds react with pyrazolone derivatives:



This type of reaction is of importance in the manufacture of Tartrazine, Fast Light Yellow, Pigment Chrome Yellow, and other compounds in the yellow and orange range. They are generally quite permanent to light and other influences.

PIGMENTS

The azo pigments undoubtedly represent the largest and most important group of the synthetic organic pigments. Although they are almost entirely restricted to the range of yellows, oranges, and reds, the pigments are so diverse in type, tinctorial characteristics, and physical properties that their usefulness is extended to nearly all fields of color use. For convenience these products may be classified in three major groups, each of which includes a considerable number of representative types:

1. *The pigment type* is insoluble in the reacting medium directly on formation and contains no salt-forming groups. Toluidine red is an example. This group also includes the para reds, hansa yellows, part of the pyrazolone colors, benzidine yellows, and the coupling products from members of the Naphthol AS series of intermediates.

Pigment type as used in this classification, for lack of a more significant term, covers a group of colors that are rather definitely and completely of an organic or hydrophobic nature, and in the great majority of instances show a strong tendency toward solubility in organic solvents. The benzene and naphthalene residues hold substituent groups such as alkyl or aralkyl groups, phenolic or ether groups, nitro groups, and so on, but no sulfonic acid, carboxylic acid, amino, or substituted amino groups which might react with suitable metallic or acid agents to form insoluble products.

The degree of solubility in organic solvents is closely parallel to the bleed or solubility in oils and varnishes, and in a few instances, such as that of the α-naphthylamine-β-naphthol coupling, the solubility may be so great as seriously to reduce the value of the material as a pigment. The greater number of the pigments included in this group, however, are sufficiently low in organic solubility to permit their use in oils and varnishes with no apparent bleed, and many are excellent oil and varnish colors.

Permanency or fastness to light is quite generally good in this group, and certain individual items have earned a very high rating. This is particularly true of the permanent orange, hansa yellows, and certain of the Naphthol AS series of couplings.

2. *The soluble dye type* usually contains a sulfonic acid group, giving solubility to the dyestuff and permitting conversion into an insoluble heavy metal salt. Persian orange lake is an example of this type. In many instances pigments of this group are quite sensitive to water, and very sensitive to alkalies, with the result that they are of little value under conditions of appreciable alkalinity. In spite of this defect, many have been found well adapted to use in printing inks, in surface coatings with aqueous vehicles, and, in the form of alumina hydrate or gloss white lakes, are extensively employed where transparency is an important factor.

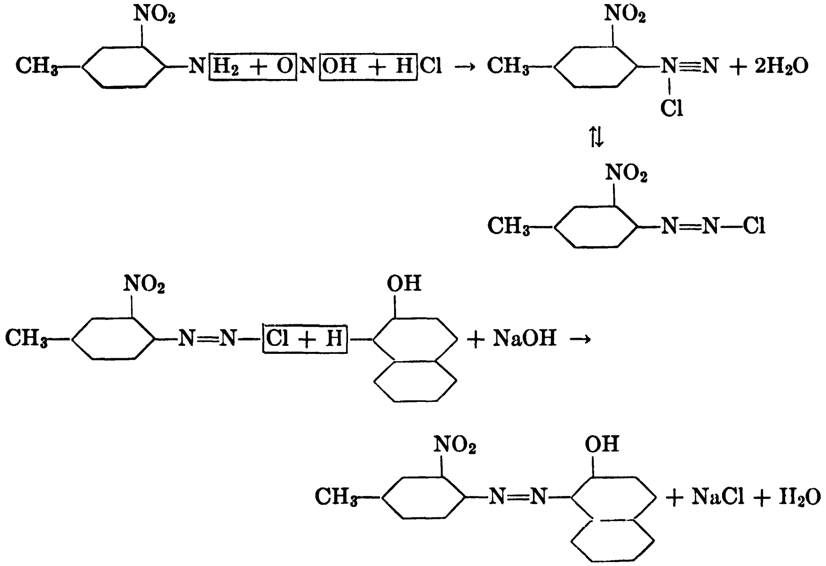
3. *The difficultly soluble dye type* usually contains a sulfonic acid group which, although the sodium salt of the dye is insoluble, or soluble with difficulty, may be converted into a heavy metal salt. Lithol red is an example of this type.

Members of this group include many of the most useful and interesting of the organic pigments. Their properties are to a considerable degree dependent on the presence, in the molecular structure, of the acid groups —SO_3H and —COOH. Formation of the metallic salts of these groups confers upon the pigment molecule a marked insolubility in organic solvents and oils, and as a rule the stability of the salt toward mild alkali is sufficiently great that many of the products are suitable for use under mildly alkaline conditions such as those encountered in soap wrapper and package printing. These products find use in nearly every field of pigments, and items of especially soft texture are employed in rubber.

These three groups will be discussed in some detail.

1. Pigment Type

One of the most important members of this group is toluidine red. The pigment is made by diazotizing 2-nitro-*p*-toluidine (*m*-nitro-*p*-toluidine) and coupling the diazo compound with alkaline 2-naphthol (β-naphthol).



Toluidine Red
C.I. 69
Sch. No 73

If only the above reaction were considered, one would expect toluidine red to be a definite chemical individual with characteristic properties and a perfectly definite color or hue. Such, however, is not the case. A great variety of toluidine reds is available on the market with substantial variations in hue, brilliance, tint, and strength, and even variations in stability to baking in enamels. The explanation of the existence of these variations is to be found in the fact mentioned previously, that the physical structure as well as the chemical nature of the compound is of great importance in determining the color properties of a pigment.

For example, variations in the conditions employed in the preparation of toluidine reds may modify very greatly the tinctorial properties with no appreciable change in the chemical nature of the final material. Diazotization may be conducted at different temperatures, and at different acid concentrations; the temperature of coupling as well as the rate of coupling may be changed; concentrations of both diazo and naphthol solutions may be altered; the alkalinity of the naphthol solution in which coupling occurs, as well as the chemical nature of the alkali, may be changed; dispersing or other agents may be employed before, during, or after coupling; the reaction mixture after coupling may be heated to various temperatures; variations in washing and conditions of drying may be made; and during all these steps variations may be made in the type and rate of agitation to be employed. In short, almost an infinite variety of conditions may be used in the preparation of the color, and each variation will alter, to a greater or less extent, its properties.

In many instances noted above the effect will be on the physical condition of the ultimate color particle or the aggregates formed by flocculation. The change in physical condition is accompanied by corresponding changes in tinctorial properties. The effect of changes in concentration is clearly shown in the photomicrographs (Figs. 11, 12, 13 and 14) made by the Research Division of the Imperial Paper and Color Corporation and not previously published. The results are summarized in Table VI. Magnification is in all cases 1750.

TABLE VI

EFFECT OF BATCH CONCENTRATION—TOLUIDINE RED

No.	Concentration	Color Values		
		Masstone	Strength	Tint
2979	Double	Very deep, opaque	Weak	Blue
2971	Normal	Lighter, more transparent	Much stronger	Yellow
2980	One-half	Deep, dull, much more transparent	Very much stronger	Much yellower
2972	One-eighth	Deep, very dull, still more transparent	Still stronger	Still yellower

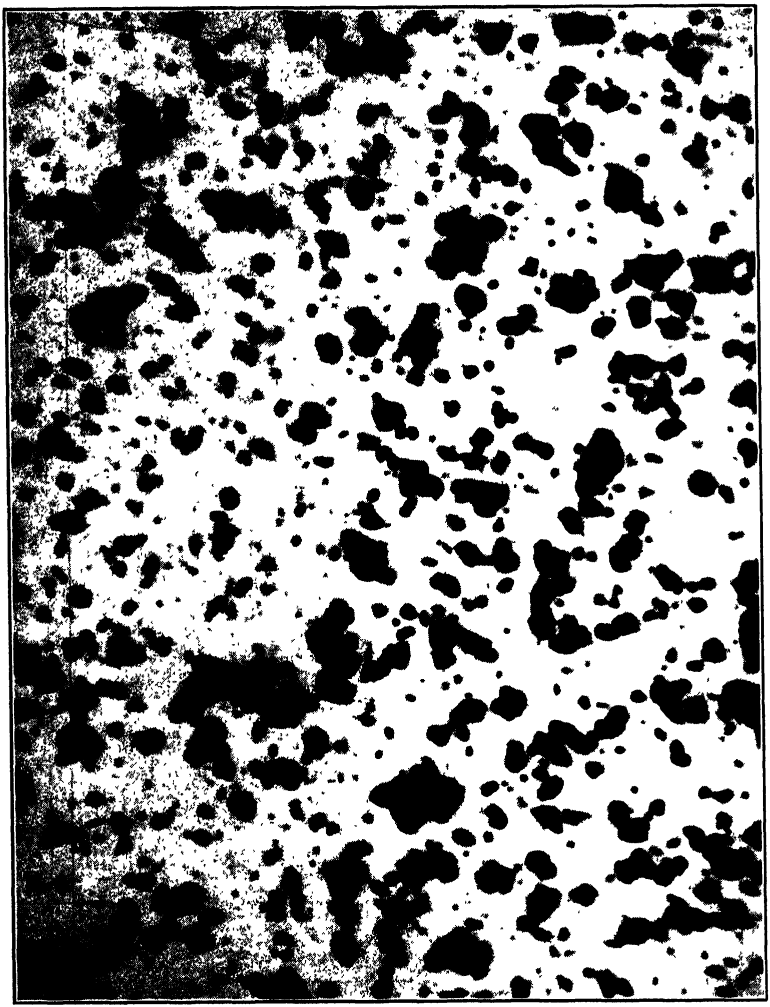


FIG. 11. Toluidine Red. Double Concentration. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division, A. F. Brown, General Manager.*)

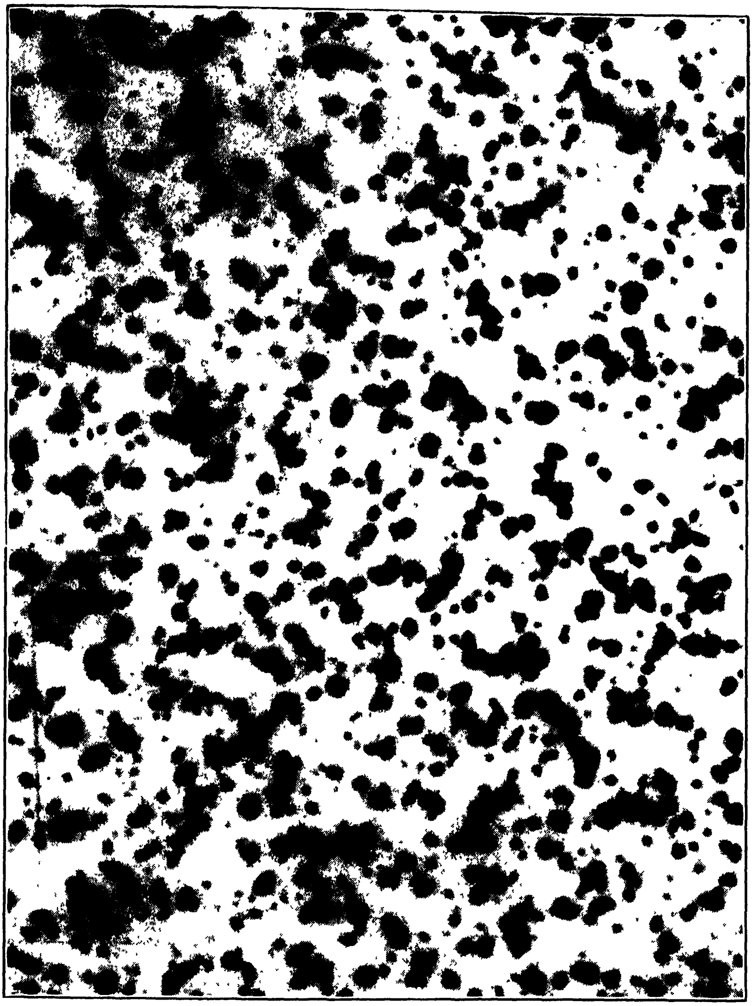


FIG. 12. Toluidine Red. Normal Concentration. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

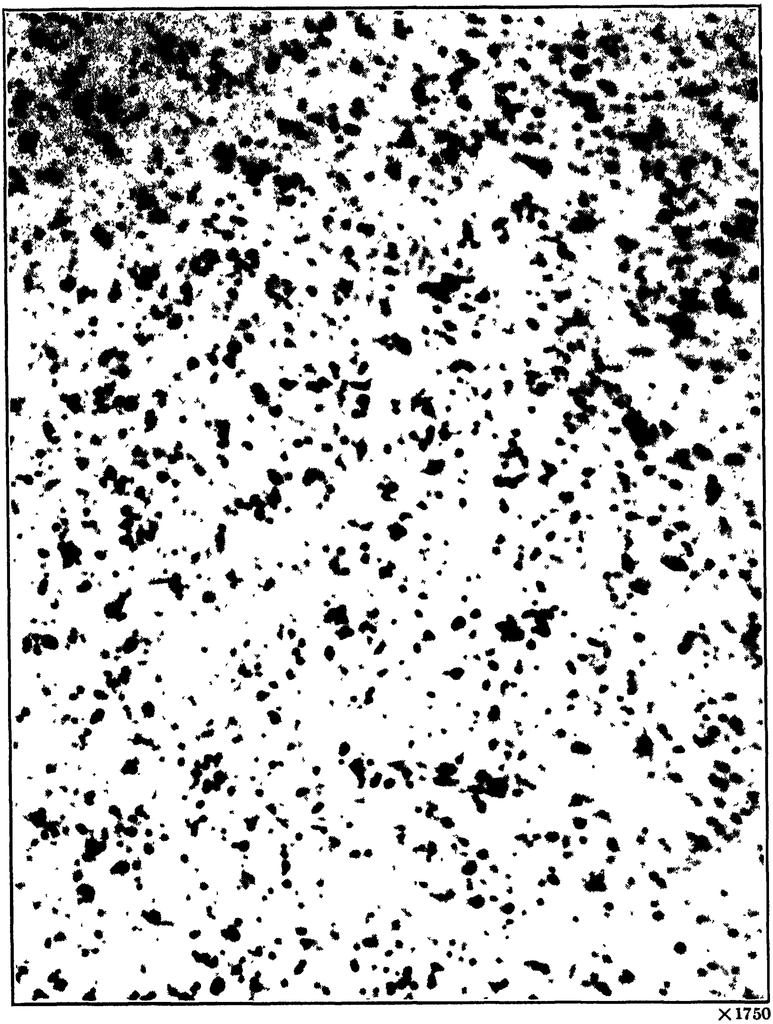
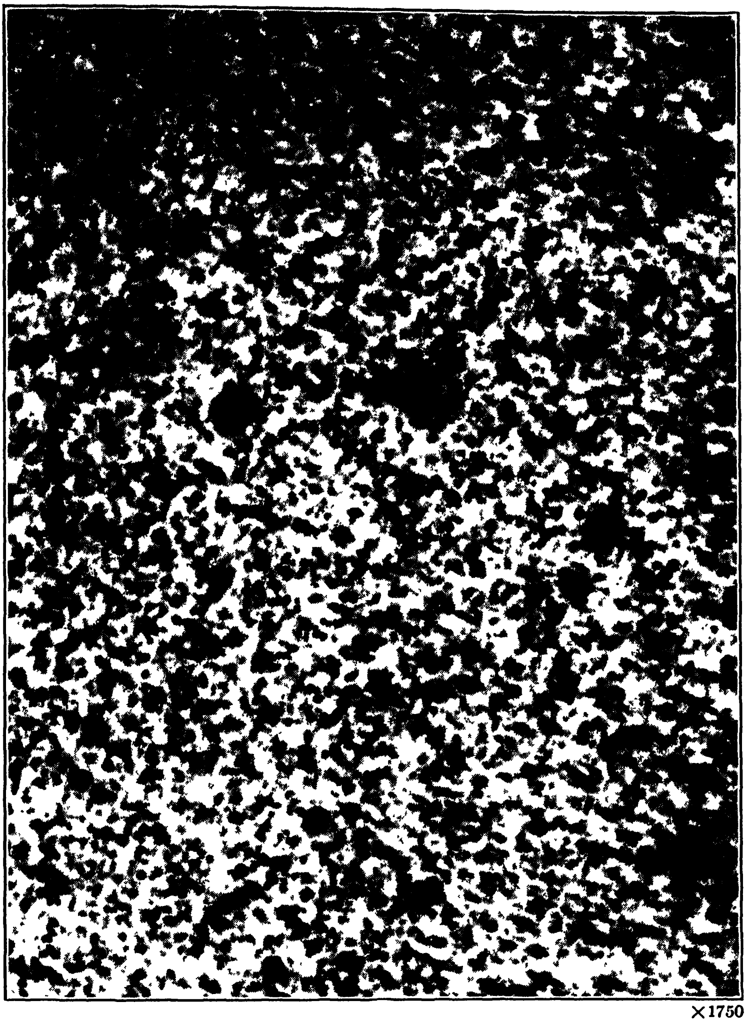


FIG. 13. Toluidine Red. One-half Concentration. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)



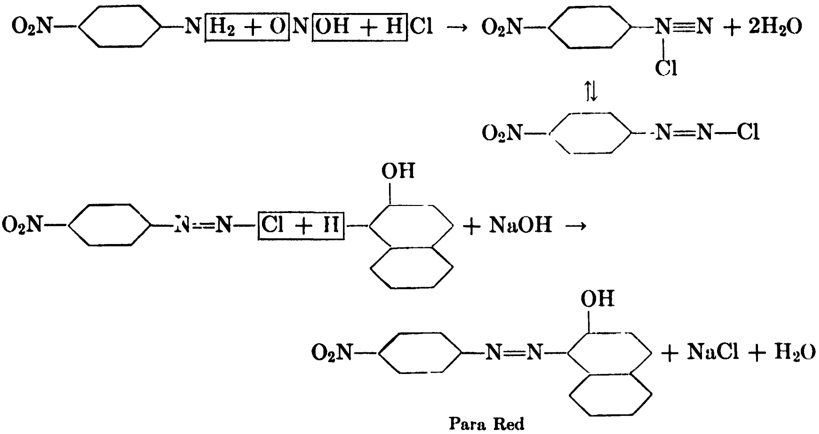
×1750

FIG. 14. Toluidine Red. One-eighth Concentration. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

In other cases changes may be brought about in the product by introducing resins or other materials which may alter the physical condition of the particles, or by their presence modify the working characteristics of the product in certain vehicles. In still other cases modifications may be made by using other intermediates in conjunction with those indicated above, and then both chemical and physical changes will result.

The toluidine reds are pigments of excellent properties, being brilliant, strong, soft, very permanent toward light, and resistant to acid and alkaline conditions. They have been found useful in many fields in which pigment colors are employed.

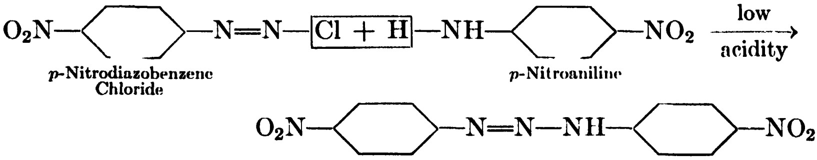
Para Reds. The para reds, made by coupling diazotized *p*-nitroaniline with alkaline β-naphthol, are very similar to toluidine reds in methods of preparation, except that a great deal more care is required in the diazotization step. A deficiency of acid or of nitrite in this operation, or an elevated temperature, results in the formation of the diazoamino compound, which not only causes a loss in direct yield but also introduces into the final product a yellow azo color of undesirable characteristics. The preparation may be indicated as follows:



Para Red

C.I. 44
Sch. No. 56

The side reaction may be shown in this way:

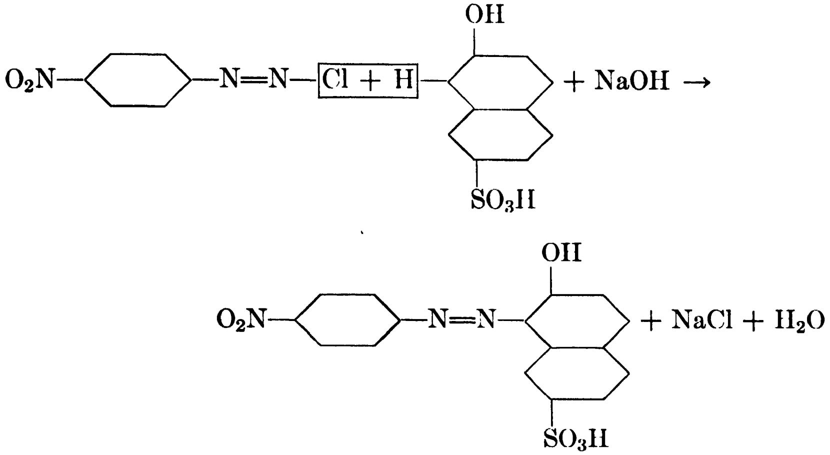


p-Nitrodiazobenzene Chloride

p-Nitroaniline

Diazoamino Compound

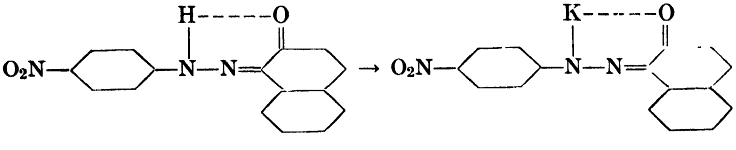
The para reds show a range of tinctorial characteristics similar to the toluidine reds, but the very deep red and blue-toned types are generally made with replacement of part of the β-naphthol by *mono-acid* (mono-acid F or 2-naphthol-7-sulfonic acid). The coupling of this material with diazotized *p*-nitroaniline gives, directly, a product with pigment properties and does not require conversion into a metallic derivative, although such a conversion is frequently made.



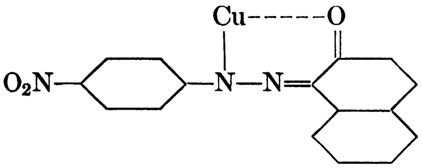
These deep-colored products are, as a rule, much harder in texture than the lighter yellow types.

The para reds are deeper and much less brilliant than the toluidine reds and considerably less permanent toward light. They have been found very valuable, however, in a great variety of fields of color use and represent one of the most important groups of organic pigments.

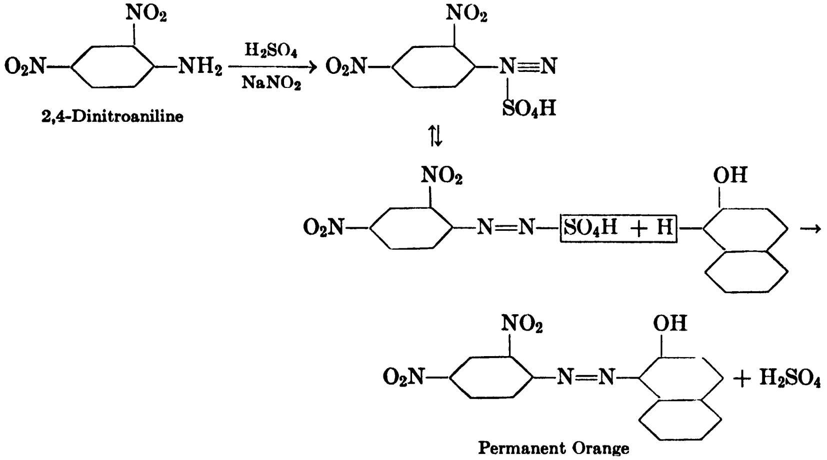
One unusual feature of the para reds is their ability to react with strong alkali, especially potassium hydroxide in alcohol solution, to give a violet color. The test is used frequently as a method of identification and, although not entirely specific, is valuable. The mechanism of the reaction is not entirely clear but is regarded as being an example of chelate ring formation:



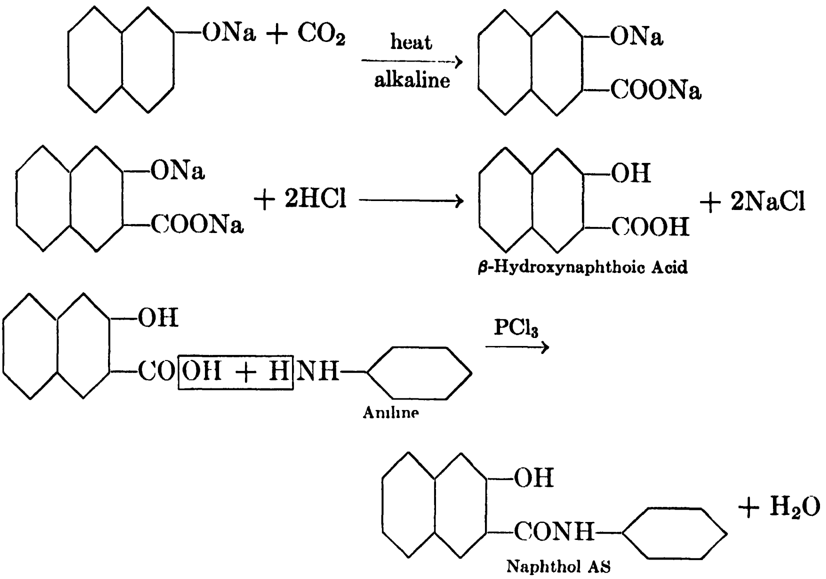
A similar explanation may be logically applied to the formation of the so-called para brown when para red is treated with copper salts in the later stages of preparation. This product is a rather clean brown pigment of good strength and may be represented in the following structure:



Permanent Orange. Permanent orange, made from diazotized 2,4-dinitroaniline and β-naphthol, is an example of the more difficult diazotization of an amino compound in which the basicity of the amino group has been so greatly diminished by the presence of two nitro groups that the material is not appreciably soluble in a dilute acid solution. In such a case it is rather common practice to carry out the diazotization in a strong acid solution, dissolving the amino compound in strong sulfuric acid and then adding the nitrite in dry powder form, or dissolving the nitrite in the acid, forming nitrosylsulfuric acid (HSO_3NO) before adding the amino compound. In either case the progress of the diazotization may be followed by placing a few drops of the mixture in a small beaker of water. Until diazotization is nearly complete a precipitate of unchanged yellow amino compound will immediately appear. The final diazo solution is prepared by running the strong acid solution into ice or a heavy slurry of ice and water.



β-Hydroxynaphthoic Acid and the Naphthol AS Series. Derivatives of β-naphthol are to be found in two very important types of second components, β-hydroxynaphthoic acid, formed by carbonation of β-naphthol, and the members of the Naphthol AS series, formed by condensation of β-hydroxynaphthoic acid with various amino compounds. The reactions may be illustrated as follows:



Both these compounds couple with diazonium salts to yield useful azo pigments, the coupling being in the alpha position as in the case of β-naphthol.

The β-hydroxynaphthoic acid couplings are as a rule converted to metallic salts, and will therefore be considered in a later section.

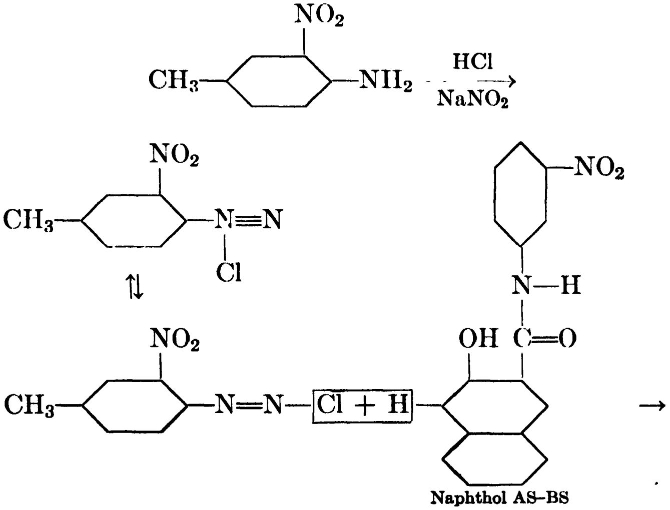
Naphthol AS Pigments. The Naphthol AS derivatives form pigments directly on coupling and therefore fall into this section. The Naphthol AS series is composed of thirty or forty derivatives, differing, generally, only in the amino compound condensed with β-hydroxynaphthoic acid. Several compounds, however, are classified commercially in this series which are not derivatives of β-hydroxynaphthoic acid. Among them are derivatives of:

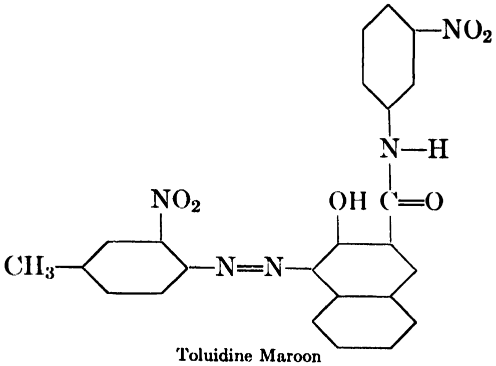
Acetoacetic acid
6-Hydroxy-7-carboxydiphenylene oxide
β-Oxyanthracene carboxylic acid
Hydroxycarbazole
Terephthalylethanic acid
(Terephthalyl-diacetic acid)
5-Hydroxy(1,2-benzocarbazole)-4-carboxylic acid

In chemical characteristics and tendencies toward color formation these materials are very similar to the true derivatives of Naphthol AS. Table V gives the more important characteristics of those Naphthol AS derivatives which have been or might be of importance in the organic pigment field.

The Naphthol AS derivatives are generally quite insoluble in water. In caustic alkali solutions they quite readily form the alkali salts, but in many cases the salts are not very soluble in water. For this reason it is common practice to treat the alkaline solution or suspension with acetic acid and carry out the coupling in the fine suspension in mildly acid condition. Coupling can be brought about satisfactorily in alkaline solution, but often the more desirable color is obtained from acid couplings. Assistants or modifying agents such as dispersing agents of various types may be employed in either the diazo or naphthol solutions to modify the physical characteristics of the resulting pigments. Such products are becoming of interest in the fields requiring soap and alkali resistance and good fastness toward light, and their importance is expected to be greatly increased by future developments.

The most important member of this group up to this time is the so-called Toluidine Maroon, a coupling of diazotized *m*-nitro-*p*-toluidine and Naphthol AS-BS, which is the *m*-nitroanilide of β-hydroxynaphthoic acid.

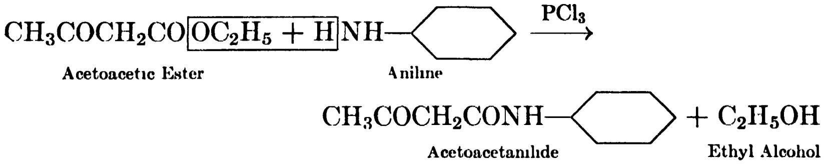




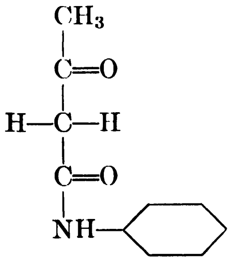
Toluidine Maroon

This product has been extensively used as a maroon in automotive lacquers. It possesses excellent properties of permanency toward light and weathering. Products of this type are generally highly resistant to alkalies and acids and have been found useful in the printing of soap wrappers and cartons.

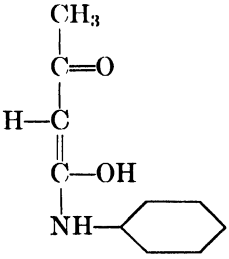
Acetoacetic Arylides. Another type of second component which is of considerable importance in the pigment field is formed by condensing an amino compound with acetoacetic ester. (See page 83.) For example, acetoacetanilide is formed in the condensation of aniline with acetoacetic ester:



Such acetoacetic compounds are soluble in alkaline solution and undoubtedly exist as an equilibrium mixture of the keto and enol forms:

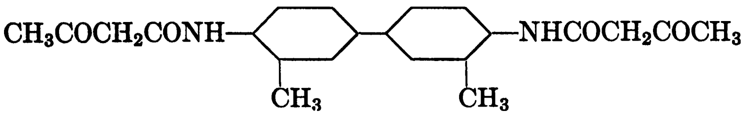


Keto Form



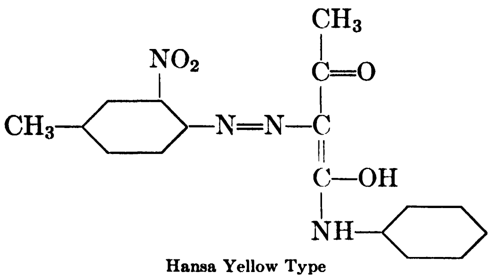
Enol Form

Naphthol AS-G, which is not a true naphthol, is a more complex compound of similar nature:



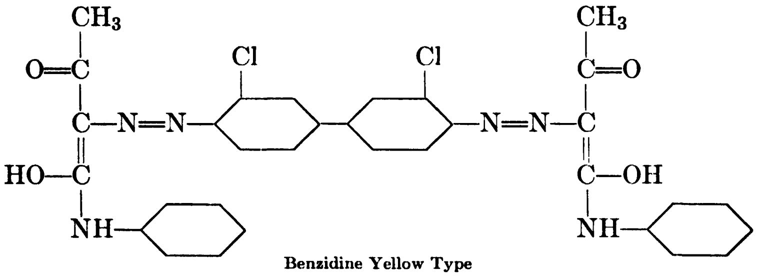
It is a condensation of *o*-tolidine with acetoacetic ester and couples with two molecules of diazonium salt. These materials are soluble in alkaline solutions and couple with diazonium salts in either alkaline or acid condition. It is apparent that these compounds make possible a variety of pigment types, as shown in the following formulas:

Azo Type



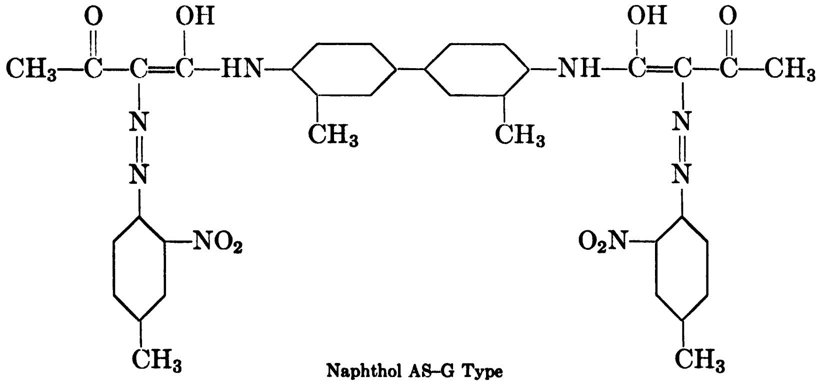
Hansa Yellow Type

Tetrazo Type



Benzidine Yellow Type

Diacetoacetyl Type



Naphthol AS-G Type

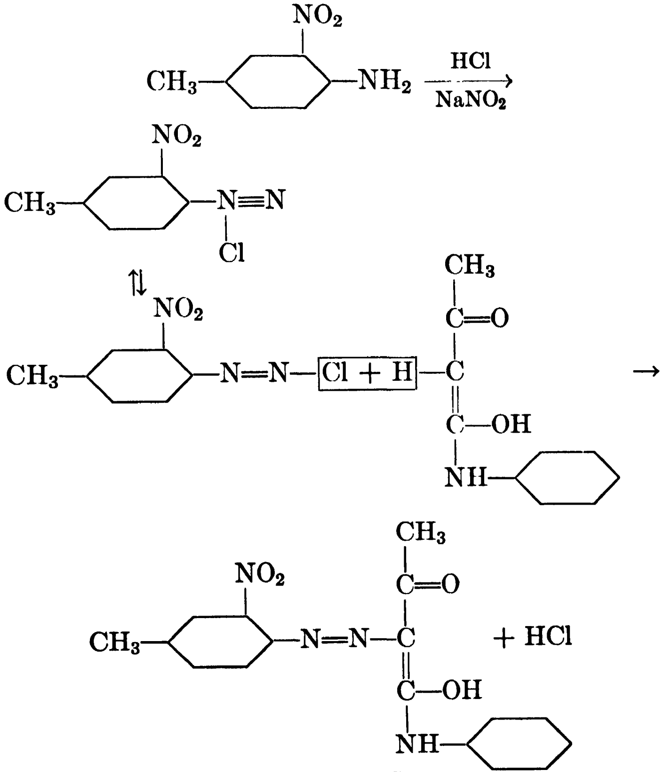
Other acetoacetanilide derivatives which have been tried include:

Acetoacet-2,5-dichloroanilide
Acetoacet-*o*-phenylanilide
Acetoacet-α-naphthalide
Acetoacetbenzylanilide
Acetoacet-*p*-nitroanilide
Acetoacet-*p*-phenetidide

The list will undoubtedly be considerably extended in the future.

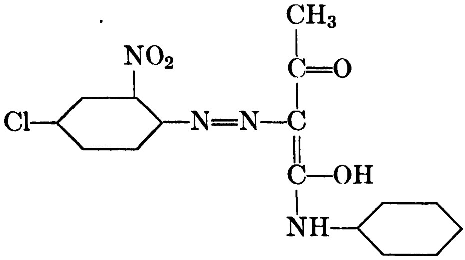
Azo Type (the Hansa Yellows). The hansa yellows become insoluble pigments immediately on formation and require no conversion to metal salts. They are, however, rather sensitive materials and the color characteristics are quite definitely dependent on conditions of operation. In general, they show a very excellent fastness to light and good brilliance, but lack of tinctorial power, or strength, makes them rather expensive.

Hansa Yellow G is the most important hansa yellow and is made by coupling diazotized *m*-nitro-*p*-toluidine with acetoacetanilide:

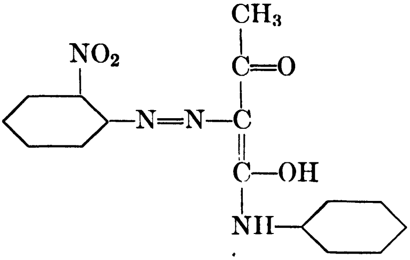


Hansa Yellow G

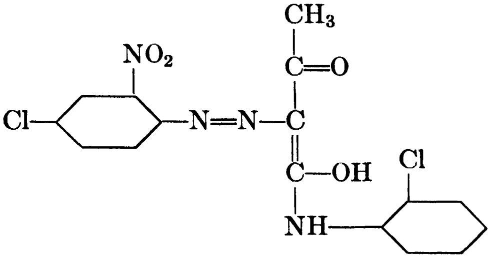
Hansa Yellow 3G is a greener and weaker product made by coupling 4-chloro-2-nitroaniline with acetoacetanilide:



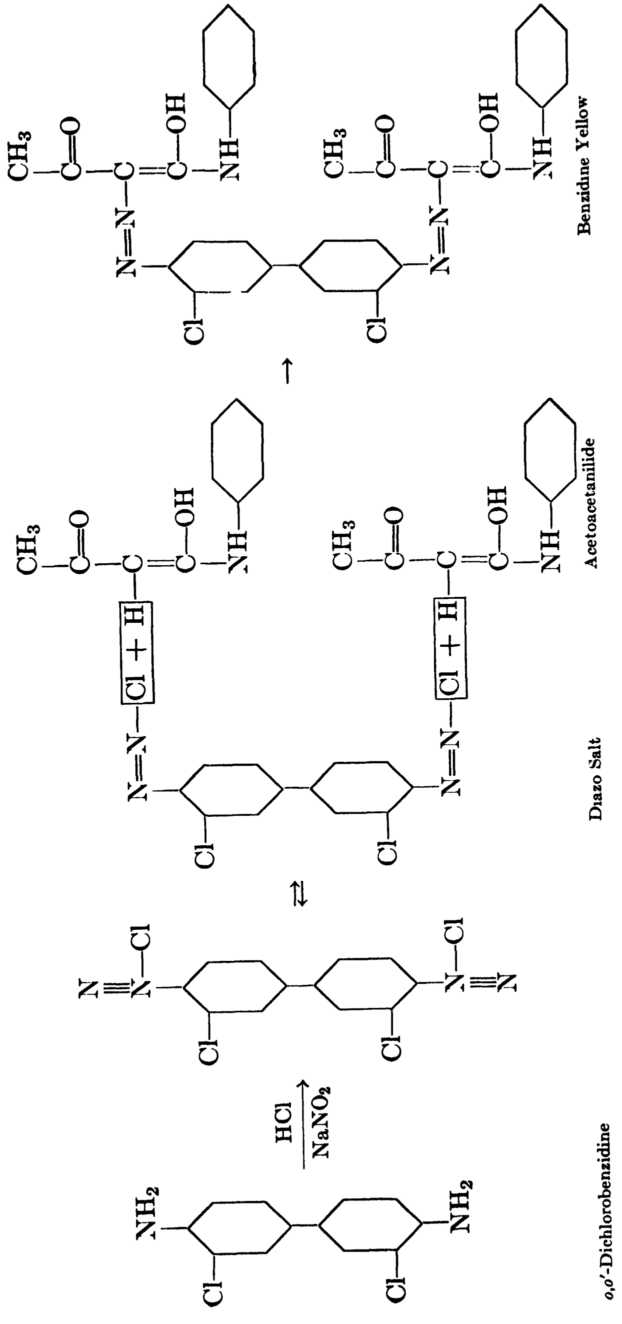
Hansa Yellow 5G is a much greener and weaker product, made by coupling diazotized *o*-nitroaniline with acetoacetanilide:



Hansa Yellow 10G is a product of extreme green shade and very low strength, made by coupling diazotized 4-chloro-2-nitroaniline with acetoacet-2-chloroanilide:

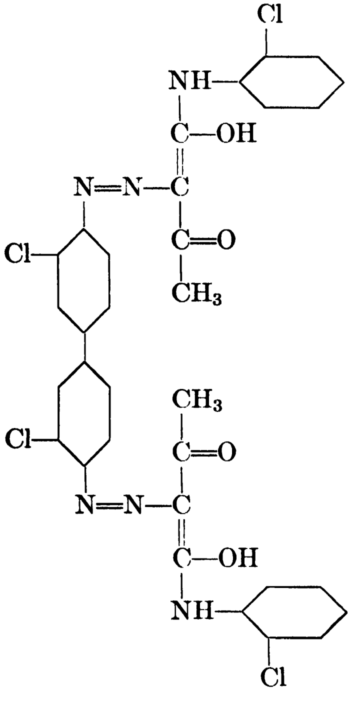


Tetrazo Type (the Benzidine Yellows). The benzidine yellows are, typically, couplings made using the tetrazo compounds of benzidine derivatives and acetoacetanilide or its derivatives. Pigments of this type have become important commercially during the past few years because of their high tinctorial power, clear brilliant tones, and excellent fastness to light. The most important color is that made from *o,o'*-dichlorobenzidine and acetoacetanilide:


o,o'-Dichlorobenzidine
HCl
NaNO₂
Diazo Salt
Acetoacetanilide
Benzidine Yellow

These are essentially normal coupling reactions. The formation of the tetrazo compound is clean cut, the material is very stable in solution, and couples smoothly with the acetoacetanilide. Coupling may be carried out in either acid or alkaline solution, but the product of the alkaline coupling is much redder in tone than that made under a condition of slight acidity.

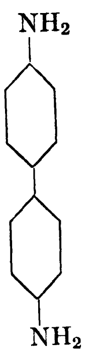
Another benzidine yellow of excellent properties is formed by the coupling of the tetrazodichlorobenzidine and acetoacet-*o*-chloroanilide. Its structure is:



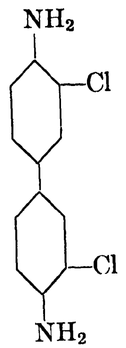
Benzidine derivatives which have become of value commercially, up to this time, are comparatively few in number, being essentially restricted to benzidine, *o,o'*-dichlorobenzidine, dianisidine, and tolidine.

It is clear, however, that many other derivatives can be made readily; and, as the importance of this type of compound in pigment and dye chemistry is more fully recognized, it is probable that many useful products will become available.

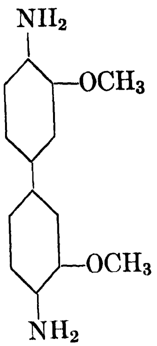
The benzidine yellows are used to some extent as non-toxic substitutes for the cheaper chrome yellows, and their very high relative strength nearly eliminates the cost differential on a strength basis particularly in the printing ink industries, but to a much lesser extent in the finishes industries. They are very adaptable colors, being much stronger than the hansa yellows, although appreciably less lightfast, exhibit a wide range of greenish to reddish yellow tones, as well as covering power or transparency, and are generally soft colors with excellent working properties.



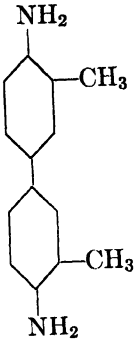
Benzidine



Dichlorobenzidine

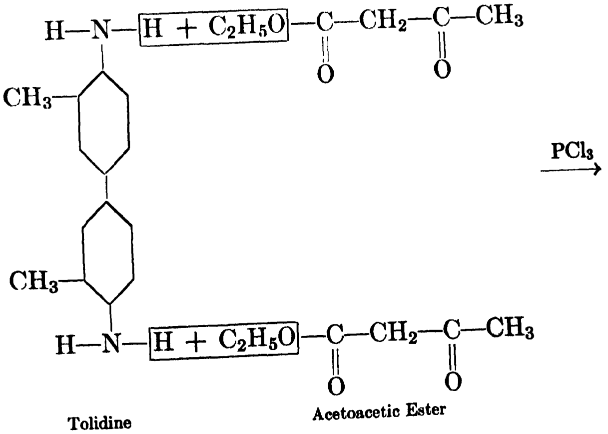


Dianisidine



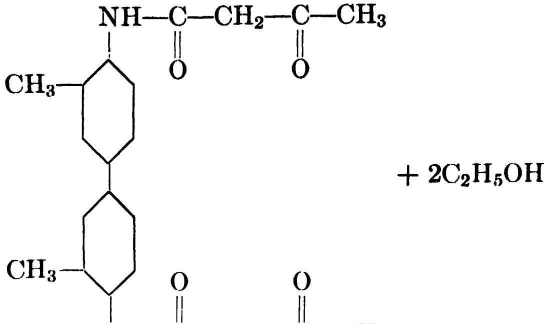
Tolidine

Diacetoacetyl Type (Naphthol AS-G Type). Naphthol AS-G was originally listed in the class of Naphthol AS derivatives because its properties and reactions were similar to those of the arylide derivatives of β-hydroxynaphthoic acid. It is soluble in alkaline solution and couples smoothly with two molecules of a diazonium salt. It is obtained in the condensation of orthotolidine and two molecules of acetoacetic ester.



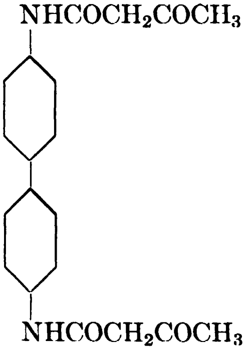
Tolidine

Acetoacetic Ester

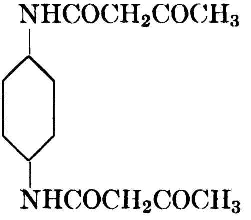


Diacetoacet-*o*′-tolidide Ethyl Alcohol

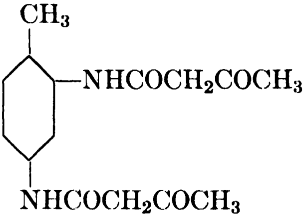
Similar products may be prepared from other diamino compounds, and derivatives of benzidine (1), *p*-phenylenediamine (2), and *m*-toluylenediamine (3) are now on the market:



(1) *N,N*′-Diacetoacet-benzidide

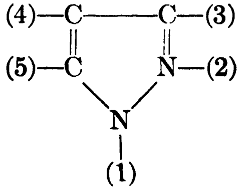


(2) Diacetoacet-*p*-phenylenediamine

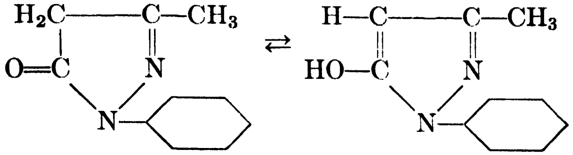


(3) Diacetoacet-*m*-toluylenediamine

Pyrazolone Pigments. The pyrazolone pigments, in addition to being azo compounds, are characterized by the presence of the pyrazolone ring structure:



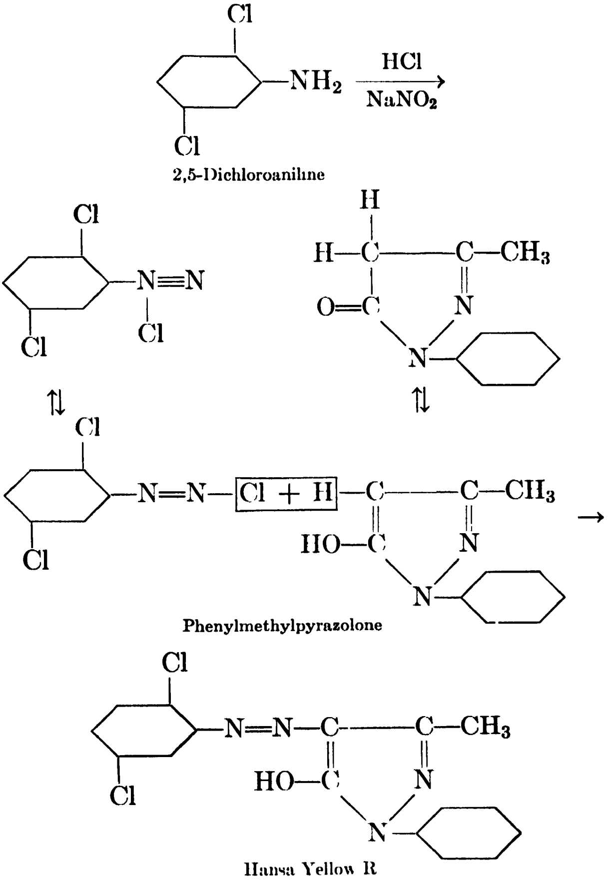
The pyrazolones are typically soluble in alkaline solution and couple readily with diazonium salts. They exist as an equilibrium mixture of the keto and enol forms, which, in the case of the most common 1-phenyl-3-methyl-5-pyrazolone, may be shown as follows:



Keto Form Enol Form

The hydrogen atom on the carbon in position 4, adjacent to the carbonyl (C═O) or the alcohol (C—OH) group, is active in coupling, and linkage to the azo group is at this point.

Hansa Yellow R, which is much redder in tone than the regular hansa yellows made with acetoacetyl compounds, is made using 2,5-dichloroaniline and 1-phenyl-3-methyl-5-pyrazolone:

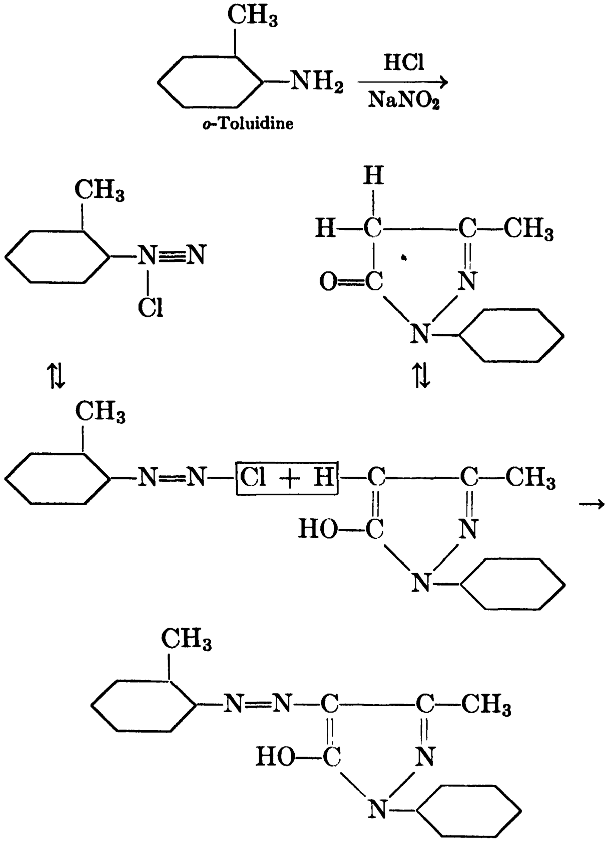


2,5-Dichloroaniline

Phenylmethylpyrazolone

Hansa Yellow R

Pigment Chrome Yellow L (C.I. 638, Sch. No. 21) is another example of this type, made from *o*-toluidine and 1-phenyl-3-methyl-5 pyrazolone:

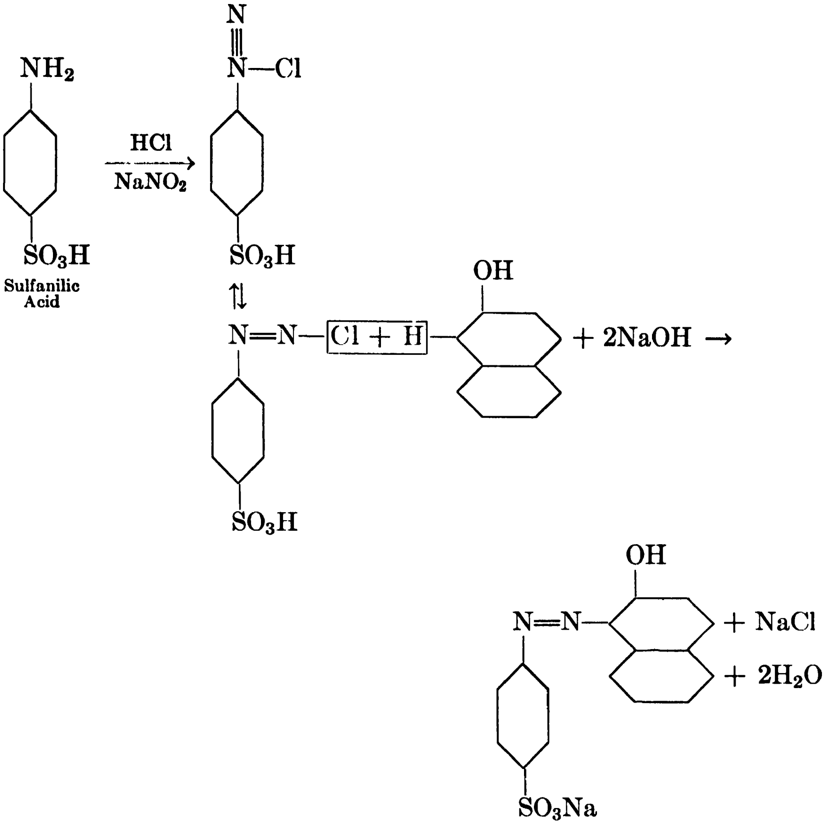


Pigment Chrome Yellow L

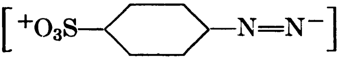
2. Soluble Dye Type

This group is composed of the azo pigments that are made by forming insoluble metal salts of soluble azo dyestuffs. Members of this group are among the most important of the organic pigments and represent some of the oldest as well as the most valuable individual pigments.

Persian Orange. Persian orange is, and has long been, a very useful pigment even though its permanency toward light is quite deficient. The dyestuff from which this pigment is made, Orange II, is obtained by diazotizing sulfanilic acid and coupling the diazo compound with β-naphthol. The diazonium salt is indicated as a normal type for convenience, but it actually occurs in the form of a so-called Zwitterion or internal salt.

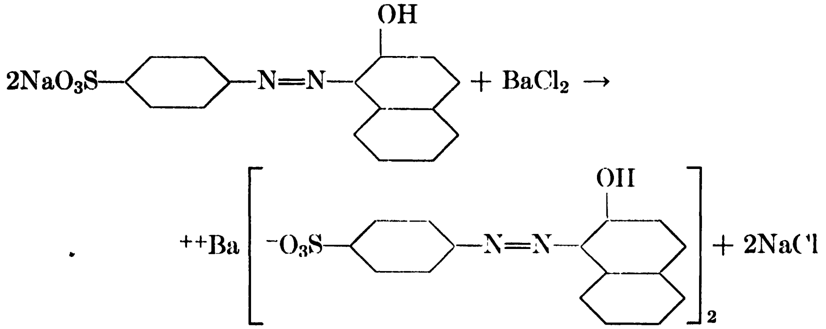


Orange II
C.I. 151
Sch. No. 145



The Zwitterion

Orange II is very soluble in water and is usually salted out from solution, filtered off, and dried before use in the preparation of pigments. Both toners and lakes are made from this dyestuff. In making a lake the dyestuff is dissolved in water, run into a suspension of washed alumina hydrate, and then precipitated on the base by introducing a solution of barium chloride or some other suitable metal salt such as aluminum.



The pigment is precipitated in intimate mixture with the alumina hydrate base, and a final product of very uniform physical condition is obtained. Here again a great variety of products is encountered, particularly from the point of view of transparency. In this case, however, the question of physical variation is not fully established as the modifications are more definitely brought about by chemical means. For example, modifications can be obtained by variations in the preparation of alumina hydrate, as well as by using different metal salts, such as aluminum chloride, in the precipitation of the dyestuff. It is doubtful, in this case, if there is an appreciable absorption or adsorption of color by the hydrate base, although such an action may be present to a minor degree.

Orange II can, however, be precipitated in the form of the toner or full-strength color, and in this form is more susceptible to modification from the physical point of view than in the form of the lake as described.

A question is frequently raised as to whether lakes of this type are true chemical compounds or adsorption complexes, and support has been given to both sides of the discussion.

In the study of the adsorption of Orange II on hydrous alumina, Weiser and Porter (138) employed an alumina prepared by treating a solution of aluminum chloride with ammonia, and then washing by decantation, with the aid of a centrifuge, until peptization was just started. Observations on the adsorption of the dye by the hydrous alumina were made at constant initial and at varying *p*H values. They found the Orange II to be somewhat less strongly adsorbed than either oxalate or sulfate, which might be expected as the dye acts only as the salt of a monobasic acid under the conditions of the experiment. They concluded:*

> In view of the fact that the curves representing the amount of Orange II taken up by the hydrous oxides are continuous, both when the initial concentration is

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* Reprinted with permission from *The Journal of Physical Chemistry.*

varied and when the initial hydrogen ion concentration is kept constant and the dye content varied, there seems little reason to doubt but that the lake formation process is a typical adsorption phenomenon, the composition of the lake depending on the physical character of the hydrous oxide, the concentration of the dye and the hydrogen ion concentration of the bath.

Reinmuth and Gordon (112) made a number of preparations under sufficiently varied conditions as to eliminate the possibility of hitting upon a coincidence of conditions which might lead to the formation of a heterogeneous product in which the dye radical and the metal ion might accidentally appear in equivalent quantities. According to their equation:

$$\mathrm{AlCl_3} + \underset{\text{Dye}}{\mathrm{3NaX}} \rightarrow \underset{\text{X = dye radical}}{\mathrm{AlX_3}} + \mathrm{3NaCl}$$

one might anticipate the possibility of a metathetic reaction between aluminum chloride and the dye, with the equilibrium shifted almost completely to the right if the product AlX_3 proved to be but slightly soluble.

Precipitations were carried out using equivalent ratios of dye to $AlCl_3 \cdot 6H_2O$ of 2:1, 1:1, and 1:2.

$$1:1 \text{ ratio} = \begin{cases} 13.5 \text{ grams Orange II} \\ 2.5 \text{ grams } \mathrm{AlCl_3 \cdot 6H_2O} \end{cases}$$

The products, washed and dried, were analyzed for dye content by the $TiCl_3$ reduction, a slight modification of the Knecht and Hibbert method. Aluminum was determined by ignition, and moisture by drying at 120 to 125° C to constant weight. Average analyses for all three products, reduced to a dry basis, are summarized in Table VII (112).*

TABLE VII

Orange II Lakes

	Calculated for AlX_3	Ratios of Reactants		
		1 dye: $\frac{1}{3}AlCl_3$	2 dye: $\frac{1}{3}AlCl_3$	1 dye. $\frac{2}{3}AlCl_3$
Per cent Al	2.67	2.88	2.77	2.91
Per cent X	97.33	97.05	97.48	96.33
	100.00	99.93	100.25	99.24

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* Reprinted with permission from Reinmuth and Gordon's chapter in *Colloid Symposium Annual*, Vol. II, edited by H. B. Weiser and published by John Wiley and Sons.

It seems safe to assume that the figures just quoted indicate a relationship other than coincidental between the quantities of dye radical and aluminum in the products formed.

Similar results were obtained in the interaction of the free acid of Orange II and $AlCl_3 \cdot 6H_2O$:

$$\mathrm{Al}\boxed{\mathrm{Cl_3 + 3H}}\mathrm{X} \rightarrow \mathrm{AlX_3 + 3HCl}$$

and of the free acid of Orange II and the hydrous alumina gel.

Voet (133)* has followed up this and other work and established a definite relationship between the type of lake formed with alumina hydrate and the *p*H conditions. The Orange II dye was carefully purified and fresh solutions used in each test. The alumina hydrate was carefully precipitated, using C.P. chemicals, and very thoroughly washed. Finally a suspension was made containing 37.2 grams of Al_2O_3 per liter, and allowed to age for several months at room temperature. The *p*H was 6.50.

Lakes were prepared by adding a measured volume of dye solution to a measured volume of the alumina hydrate suspension. The solutions in Pyrex bottles, sealed with rubber stoppers, were placed in a thermostatic shaker filled with water at 40° C. After the period of interaction the solutions were centrifuged for 15 minutes. A measured volume of the top layer was removed carefully and recentrifuged. Dye concentrations were determined by means of a Hellige-Duboscq optical colorimeter. The quantity of dye taken up by the alumina hydrate was found by subtracting these estimated quantities from the amount of dye originally added to the solution.

The *p*H of the solutions was measured with a glass electrode. All reported *p*H values refer to the final stage of suspension. Adjustments of the *p*H were made by addition of the required quantities of hydrochloric acid or sodium hydroxide. Figure 15 shows the amount of dye taken up by the alumina hydrate plotted against the final concentration, at two *p*H levels. Figure 16 shows the amount of dye taken up by the alumina hydrate plotted against the *p*H.

Influence of Dye Concentration: To the alumina hydrate suspension, equal volumes of dye solutions of the different concentrations were added, the *p*H of which had been previously adjusted to a standard. The amount of dye taken up was established after 72 hours of interaction at 40° C. It was found that, in solutions of a final *p*H of 5.5, as well as in more acid solutions, all the dyestuff present is carried down by the hydrate independent of the initial dye concentration.

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* The discussion on this page and on pages 111 and 112 is based on Voet's article.

Influence of pH: Although the importance of the *p*H may be observed from the curves of Fig. 15, the influence of the *p*H on the amount of dye taken up by the hydroxide is plotted separately in Fig. 16 for a solution containing 1.9 per cent of Orange II. It was found that only a slight amount of dye is taken up in neutral and basic solutions, while a tremendous increase is observed in more acid solutions.

When the curve of Fig. 15, measured at a *p*H of 7.16, is considered, it becomes evident that its shape is that of a regular adsorption isotherm. Consequently, the mechanism of interaction between Orange II and alumina hydrate, at a *p*H of 7.16, is adsorption.

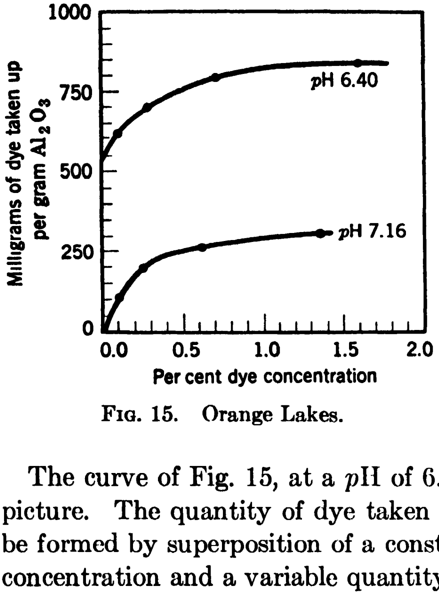


FIG. 15. Orange Lakes.

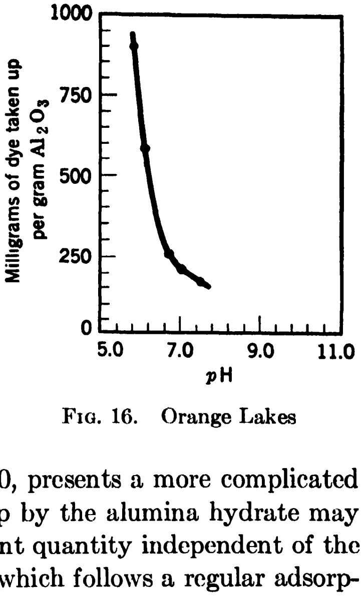


FIG. 16. Orange Lakes

The curve of Fig. 15, at a *p*H of 6.40, presents a more complicated picture. The quantity of dye taken up by the alumina hydrate may be formed by superposition of a constant quantity independent of the concentration and a variable quantity which follows a regular adsorption isotherm.

Finally, at still higher acidity, it is observed that all the dye present in the solution is carried down by the hydrate.

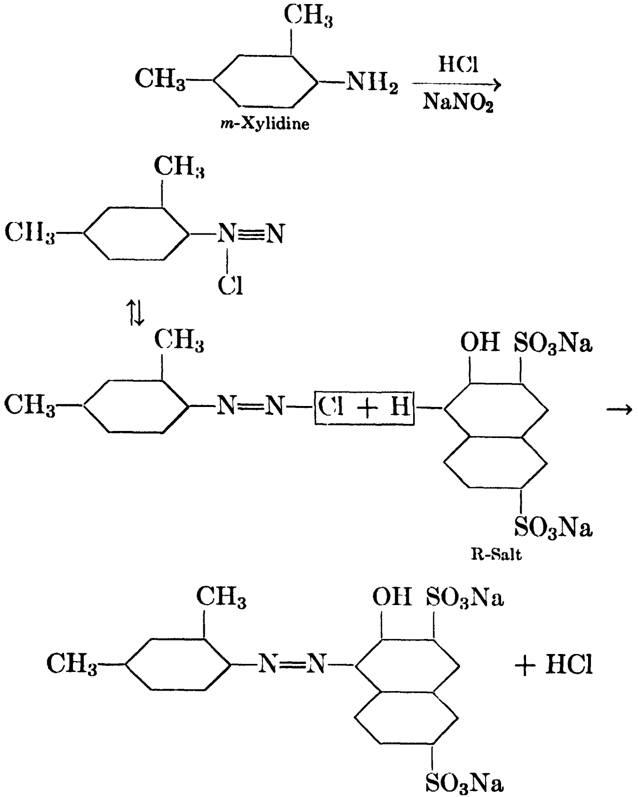
This rather complicated picture becomes comparatively simple when it is borne in mind that precipitated alumina hydrate is readily dissolved in acid. Consequently it is to be expected that, at a *p*H below 7.0, the hydrate will dissolve. The speed of this process is greatly increased at greater hydrogen-ion concentrations. As a result of the dissolution of alumina hydrate, aluminum ions are formed which are able, as previously mentioned, to form the insoluble aluminum salt of Orange II. Thus, at a *p*H directly below 7.0, the amount of dye carried down by the hydrate is made up by superposition of a precipitated and an adsorbed part. At a still higher acidity, where a large quantity of aluminum ions is present, practically all the dyestuff carried down will be in the form of the aluminum salt. At a *p*H above 7.0, in the absence of precipitating ions, the entire amount taken up is adsorbed.

Physically and chemically a very distinct difference is observed between adsorbed lakes formed at a *p*H above 7.0 and precipitated lakes formed in the presence of aluminum ions at a *p*H lower than 7.0. Adsorption complexes have a yellowish shade, while precipitated lakes are more reddish. On prolonged washing with distilled water of 25° C the filtrate of a precipitated lake was only very slightly colored and had a *p*H of 5.0, while under similar conditions the filtrate from the adsorption complex was markedly colored and had a *p*H of approximately 4.0.

Finally, a color lake was prepared that was known to contain only the aluminum salt of Orange II by adding an equivalent quantity of aluminum chloride to a solution of Orange II, and then mixing the wet precipitate with an alumina hydrate gel. The resulting product could not be distinguished physically or chemically from a color lake made by interaction of Orange II and alumina hydrate at a *p*H below 5.5.

A further study revealed the type of adsorption occurring at a *p*H above 7.0. Analysis of adsorption lakes showed that no sodium was present in the lake. This observation eliminates a direct adsorption of the dye and leaves as an explanation of the adsorption phenomena either an exchange adsorption or an hydrolytic adsorption. Hydrolytic adsorption, however, must also be disregarded since no change in *p*H is observed as a result of adsorption. Consequently, exchange adsorption is the remaining possibility. This is proved directly by analysis, which showed that sulfate ions previously adsorbed by the hydroxide are released upon adsorption of Orange II acid, in such a way that one sulfate ion is exchanged for every two Orange II ions. It is interesting to note that the apparent contradictions, mentioned in the literature, are non-existent. Marker and Gordon (94) rightly claimed a chemical combination, since their experiments were made in acid solutions, while Bancroft and Farnham (13) were justified in claiming an adsorption, since it may be deduced from their reports that they studied neutral or slightly basic solutions.

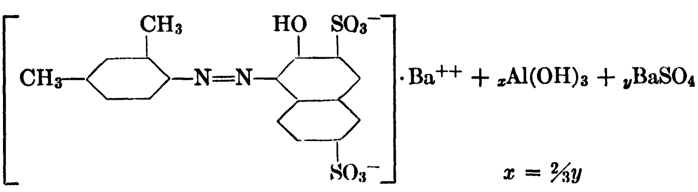
Scarlet Lake. One of the more important scarlet lakes is that made by precipitation of Scarlet 2R on alumina hydrate or gloss white base. Scarlet 2R is made by coupling diazotized *m*-xylidine with R-salt (2-naphthol-3,6-disulfonic acid):



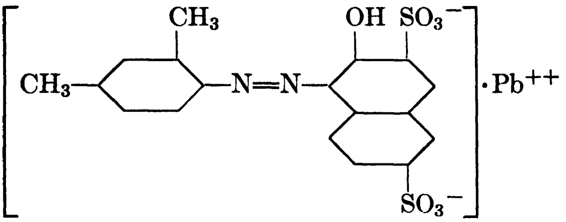
Scarlet 2R (Ponceau 2R)

The resulting dyestuff is very soluble in water but is readily salted out of solution. It comes on the market in dry form.

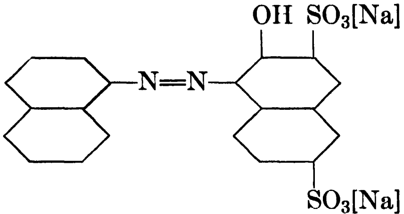
The lake is commonly made by dissolving aluminum sulfate in water, adding the dye, adding soda ash to precipitate the alumina hydrate, and then precipitating the dye and all soluble sulfates with barium chloride. The product is the barium lake on a so-called gloss white base (1 part alumina hydrate, 3 parts blanc fixe).



The scarlet lakes have been and are extensively used in printing inks and for many surface coating purposes. They are quite fugitive to light but give colors of excellent brilliance and working characteristics. Freedom from bleed in nitrocellulose lacquers makes it a useful color in lacquer coatings. Scarlet 2R is not, as a rule, precipitated as a toner, or full-strength product, but the lead toner has been used to some extent in the past. These operations are carried out, generally, at higher temperatures, as the brilliance and other qualities of the products are greatly improved under such conditions. The composition of the lead toner may be represented as follows:

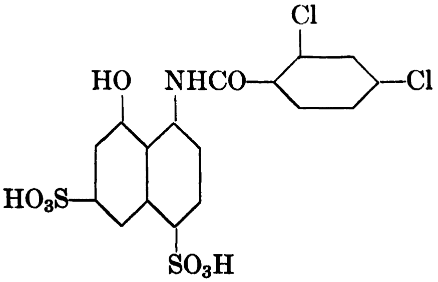


Other types of dyestuffs handled in a similar manner include other ponceaux and scarlets as well as the important Bordeaux B, made from α-naphthylamine and R-salt:

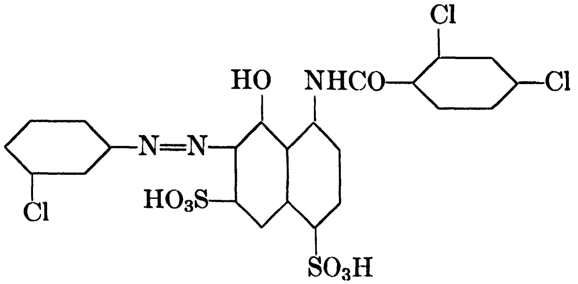


C.I. 88
Sch. No. 112

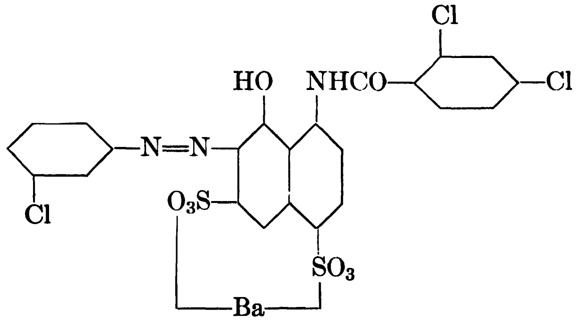
Anthosine Lakes. A group of pigments in the form of alumina hydrate or gloss white lakes of exceptional beauty have been made, in relatively small amounts, using the dyestuffs known as anthosines. These dyestuffs, which in some tinctorial characteristics resemble the rhodamines, are made by coupling diazo compounds with dichlorobenzoyl-K-acid.



Curtis (33) indicates that Anthosine B is formed by coupling the diazo compound from *m*-chloroaniline with dichlorobenzoyl-K-acid:

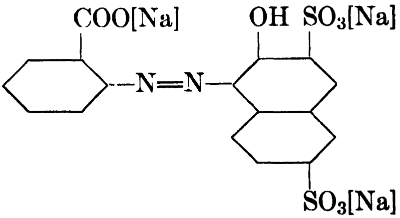


and the pigment formed by precipitating this soluble dyestuff on a suitable base, with barium chloride or another metal salt, may be represented as



Anthosine 3B is prepared in a similar manner from *m*-toluidine, and Anthosine 5B from *m*-xylidine.

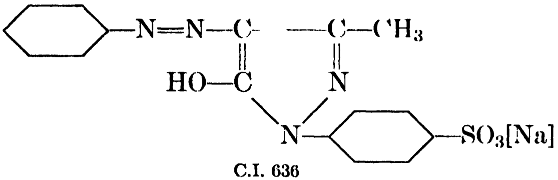
Solochrome Red B (for Pigment Scarlet 3B)



C.I. 216
Sch. No. 202

Pigment Scarlet 3B is a very useful pigment because of its high degree of light-fastness and its exceptionally clean bluish red tone. Its excellent properties are improved materially by the use of zinc oxide in its preparation.

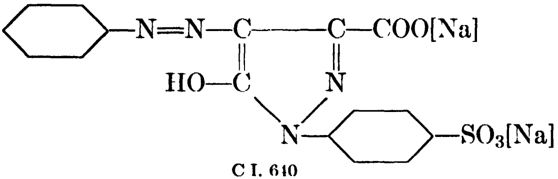
Fast Light Yellow 3G (Pyrazolone Color)



C.I. 636
Sch. No. 19

The toner or lake of this color is characterized by a very light brilliant tone with excellent light-fastness.

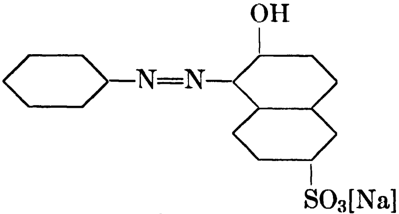
Tartrazine (Pyrazolone Color)



C.I. 640
Sch. No. 23

Tartrazine is employed in the preparation of a wide variety of excellent yellow lakes, some showing almost complete transparency in printing ink vehicles, relatively good permanency toward light, and satisfactory working properties.

Crocein Orange



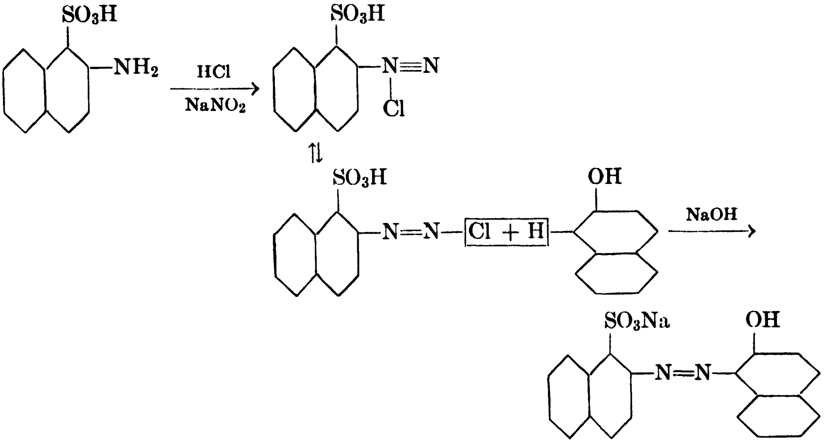
C.I. 26
Sch. No. 37

3. Difficultly Soluble Dye Type

The difficultly soluble dyes are those colored compounds that contain acid groups, such as —SO_3H or —COOH, but in the form of their sodium or alkali salts are practically insoluble in water. Several of these compounds are of the greatest importance in the organic pigment field as they include the lithols, C-Reds, rubines, maroon toner, and Lake Red D.

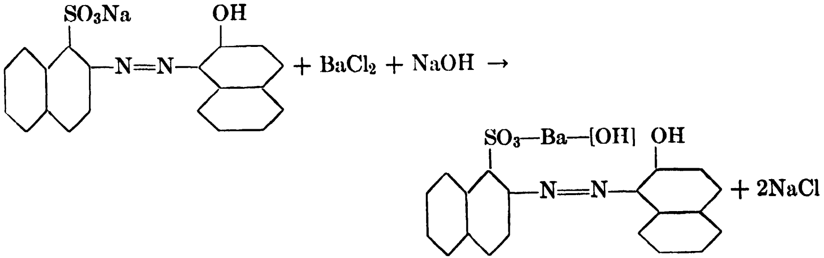
Lithols. The lithols are the most important single group of organic pigment colors. Their importance is due not alone to their excellent characteristics for color work but also to their wide range of tinctorial values. For example, the sodium lithols are light, yellow-toned pigments in the orange range. The barium lithols are much redder, stronger, and bluer in tone. The calcium lithols are extremely bluish in tone and generally deeper than the barium colors, while the strontium lithols are generally intermediate between the barium and calcium products. The lithols are of only fair light-fastness, the sodium toners being considerably less permanent than the barium and calcium.

Lithols, as a class, are prepared by coupling the diazonium salts of Tobias acid (2-naphthylamine-1-sulfonic acid) with β-naphthol, and then converting the resulting practically insoluble sodium lithols into the corresponding barium, calcium, or strontium products. The reactions are as follows:



Sodium Lithol

C I. 189
Sch. No. 173



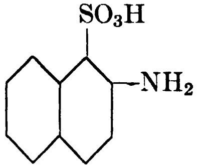
Barium Lithol

The reaction indicated in the second equation is carried out, as a rule, without isolation of the sodium toner, simply by addition of the soluble metal salt to the sodium toner suspension and then heating to complete the reaction and bring about the physical change required to establish desirable pigment characteristics.

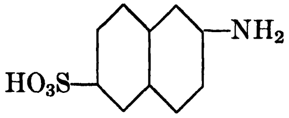
The suggested structure of the barium toner, as the basic barium salt, is justified by the fact that analysis usually indicates the combination of one atom of barium with one molecule of color and the fact that the final color suspension is generally alkaline. Another possibility is that the barium atom may retain one chlorine atom, and still another that a chelate ring might satisfy the second barium valence. An intricate analytical study would be required to establish definitely the actual structure in this case.

Although the equations on page 117 indicate one sodium and one barium lithol, the market is supplied with a considerable variety of each type in addition to those representing the calcium and strontium types.

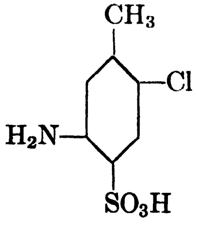
The great number of distinctive products is made possible by the sensitivity of the compounds and reactions involved, and by variation in materials, or conditions employed. For example, Tobias acid is a chemical individual



which, in pure form, has very definite properties. However, in commercial practice, a variety of Tobias acids are available, distinguished by different degrees of purity, and by different isomeric or non-isomeric impurities or additions. It is common to modify the Tobias acids by the addition of other aminosulfonic acid compounds such as Brönner's acid, 2-naphthylamine-6-sulfonic acid:



and in some cases the intermediate for C-Red, 2-chloro-5-toluidine-4-sulfonic acid:



The presence of these and other modifiers and impurities bring about widely varying conditions for the formation of the typically insoluble diazonium salt and for the formation of the ultimate color particles.

It is thus possible to accomplish wide variation in the diazonium salt particle, as well as in the final color particle, by modification of the Tobias acid and also by modification in the details of procedure, such as in concentration of solutions, efficiency of agitation, order of chemicals addition, degree of acidity, and time factors at various points. The effect of variation in speed or efficiency of agitation, for example, is shown in the photomicrographs of Tobias acid in Figs. 17 and 18, made by the Research Division of the Imperial Paper and Color Corporation and tabulated in Table VIII.

TABLE VIII

Tobias Acid—Effect of Agitation

Fig.	No.	Agitation	Crystals	Comments
17	3506	Rapid	Long and narrow with parallel sides (planks)	They convert, on standing, to the type of 3507.
18	3507	Slow	Pyramids	Become more perfect on standing.

When Tobias acids of the types represented by 3506 and 3507 were diazotized, the results were as shown in Figs. 19 to 23 and tabulated in Table IX.

TABLE IX

Tobias Diazo Crystals

Fig.	No.	Tobias Acid	Diazo Crystals
19	3500	From 3507	Relatively large flat planks.
20	3501	From 3500	Starting to decompose under light and heat. Shows bubbles of N_2 gas.
21	3502	From the type of 3506	Slightly smaller and narrower than those made under slow agitation.
22	3503	From the type of 3506	Shows bubbles of N_2 gas.
23	3510	From the type of 3506	

In many cases the large and small diazonium crystals, on coupling with β-naphthol, gave products of essentially identical characteristics.

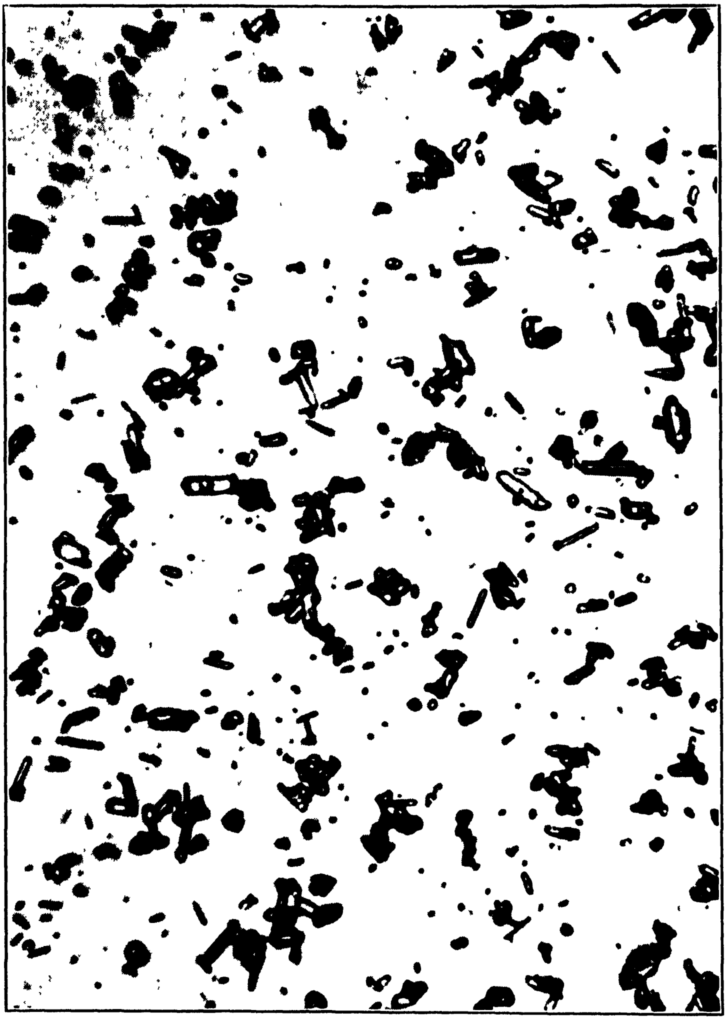


FIG. 17. Tobias Acid. Rapid Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 18. Tobias Acid. Slow Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 19. Tobias Diazo Crystals. Fresh, Slow Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 20. Tobias Diazo Crystals. Aged, Slow Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 21. Tobias Diazo Crystals. Rapid Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 22. Tobias Diazo Crystals. Rapid Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

FIG. 23. Tobias Diazo Crystals. Rapid Agitation. (*Courtesy of Imperial Paper and Color Corporation, Pigment Division.*)

Rosin Soap Lakes. According to Allen (4) the use of rosin and rosin soap as dispersing agents and for the purpose of obtaining a slightly improved masstone or printing tone effect has been long known. However, within the last fifteen years, what can best be designated as rosin soap lakes of azo dyes have reached a very important place in the pigment industry. Their greatest use is as derivatives of lithol red pigments, for the printing ink trade, although some other azo dyestuffs may be converted into such lakes and substantially all of them find some use in the pigment-consuming industries.

The distinctive feature of the composition of rosin soap lakes is that substantial amounts (15 to 30 per cent being the preferred range) of metallic rosinates are incorporated into the finished pigment color, without loss of tinting strength (5). In other words, the metallic rosinate functions as a non-diluting substratum.

The properties which characterize the rosin soap lakes are higher oil absorption, definitely increased brilliancy of shade, greater depth and brightness of masstone, and higher and a more glossy finish on the printing tone obtained from printing inks into which they have been incorporated.

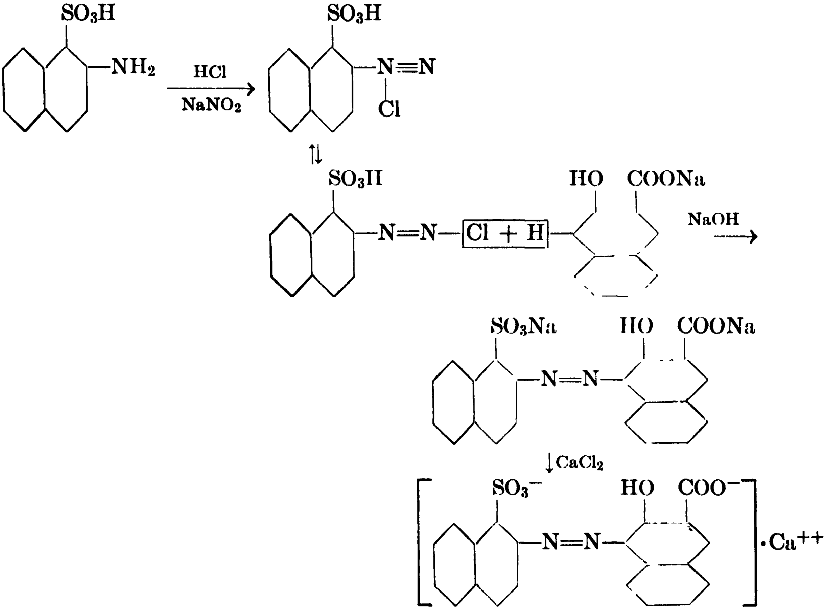
The preparation of rosin soap lakes is, at least up to the present, limited to derivatives of difficultly soluble acid azo dyestuffs. (See page 116.) As is well known, conversion of these products into satisfactory pigment colors involves their conversion into alkaline earth salts. This transformation involves, in addition to mere precipitation, the heating, usually to boiling, of the suspension, which is accompanied by a definite color change, in the case of red dyes, in the direction of the blue, accompanied by increase in brilliancy and tinctorial power. This color change, sometimes referred to as *development,* determines to a very considerable extent the tinctorial qualities of the final pigment color and is subject to considerable variation by alteration in the details of processing. This shade alteration, in course of conversion to the alkaline earth salt, is apparently that to which Curtis (33) refers when he says that the process is employed to convert difficultly soluble dyestuffs into their barium salts. The reaction is used with certain red dyestuffs and the shade or hue is altered toward the blue. This process yields certain shades which cannot be obtained with equal purity by other methods.

If alkali rosinate, together with free alkali, is present at the time of this transformation, the color change is much more pronounced, sufficient, for example, to compensate in tinctorial strength for any diluting action of the soluble rosinate and produce, in addition, a more brilliant product. The higher oil absorption and higher finish, produced by the resulting inks, presumably result from the physical properties of the incorporated alkaline earth rosinates.

The qualities of rosin soap lakes are now well recognized in the pigment producing and consuming trade, where they occupy an important position. Unfortunately the Bureau of Commerce statistics do not report these items separately so that nothing more exact can be stated than that they represent an important commercial development.

No satisfactory explanation of the nature of the chemical or physical changes, involved in the formation of these interesting products, can be given in our present state of knowledge. The suggestion of Gardner (52) that complexes may be formed is helpful, but the real explanation of the nature of this change must be the subject of further research before even the more familiar facts can be satisfactorily interpreted.

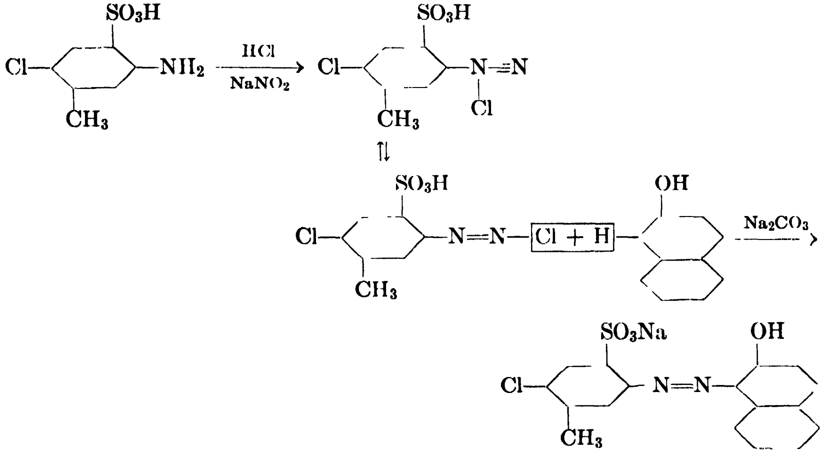
Maroons. A group of maroon pigments, derived from Tobias acid, has become of considerable importance during the past few years as they are of sufficiently good fastness to light to permit their use in automotive lacquers. One of the earliest was prepared by coupling the diazonium salt of Tobias acid with β-oxynaphthoic acid and converting the resulting dye to the calcium salt.



Other valuable pigments are prepared by using metals such as manganese and iron in place of all or part of the calcium in the above structure. As a class these products are rather hard in texture but of excellent tinctorial power. The manganese and iron products are much less brilliant than products containing calcium, but offer other offsetting advantages in durability and hiding power.

Red for Lake C. The so-called C-Reds are pigments of excellent properties, showing a high degree of fastness to light, good brilliance and strength, and very satisfactory working characteristics. They have been used for many years for brilliant yellowish-toned reds. The sodium and barium products are of the greatest commercial importance while the aluminum product is highly transparent and of a yellow tone. The calcium derivative has very poor pigment properties.

C-Red Sodium Toner. This pigment is made by coupling diazotized 2-chloro-5-toluidine-4-sulfonic acid with β-naphthol.



Sodium C-Red

The sodium toner is an orange rather than a red pigment. It is known as bronze orange and is used in printing ink to impart a strong bronze surface.

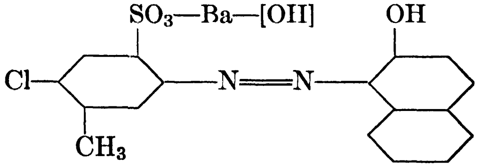
Sodium C-Red is a very interesting pigment, as it has the property of absorbing or retaining up to nearly 15 per cent of water, which appears to be held loosely as water of crystallization. This amount represents approximately three molecules of water. The material can be dried to a moisture content of 3 to 5 per cent and still very readily pick up moisture from a humid atmosphere. Elimination of the last few percentages of water, however, destroys the power of absorption.

The bronzing characteristic of the pigment is in direct proportion to the content of retained moisture, the anhydrous or low moisture material being nearly free from bronze when incorporated into printing ink varnishes.

C-Red Barium Toner. The barium toner can be made by adding barium salts directly to the sodium C-Red suspension but, as a rule, the filtered and washed material is used for this purpose.

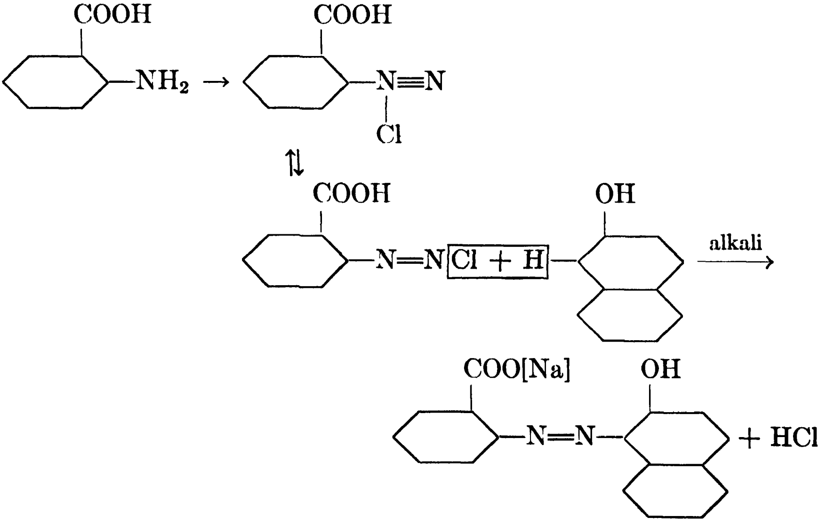
An interesting control is used in the preparation of the barium C-Reds. The deep types are prepared by adding the barium salt to the hot suspension of sodium C-Red, while the light types are treated with the metal salt at low temperatures and then heated.

The composition of the barium toner may be represented as:

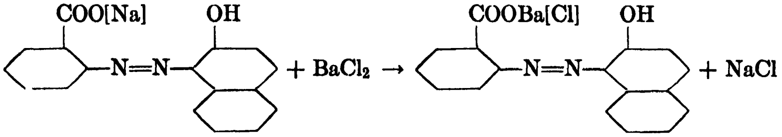


although this is not definitely established.

Red Lake D. Red Lake D, which is formed when diazotized anthranilic acid is coupled with β-naphthol, is a red of excellent tinctorial power and of pleasing tone. It has, however, the great disadvantage of being unstable in the presence of cobalt driers, becoming darker and much less brilliant:

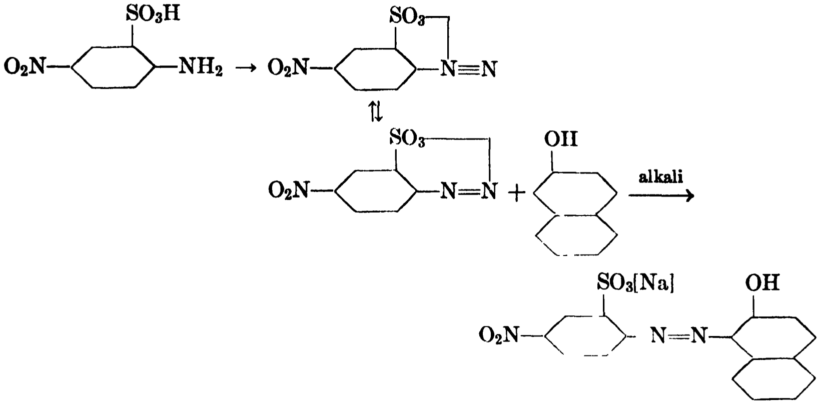


The barium toner may be indicated as follows:

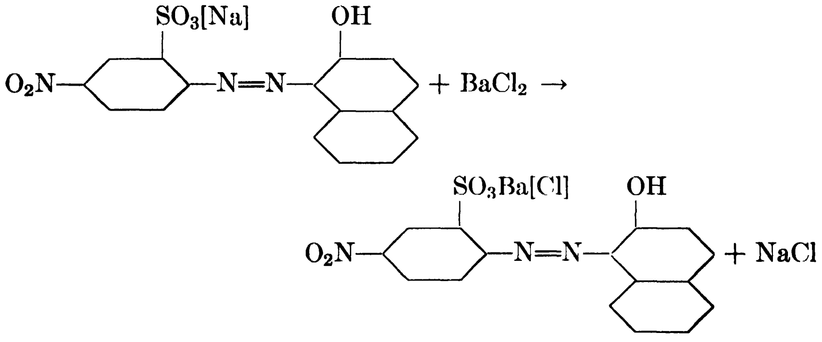


This color has been used in the past in the form of a brilliant bluish red lake, but over a period of years the decline in actual use has been marked.

Red Lake P. Red Lake P is made by coupling diazotized *p*-nitroaniline-*o*-sulfonic acid with β-naphthol:

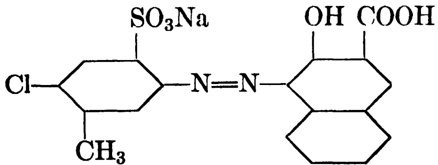


and the dyestuff may be converted to the barium lake as follows:



Red Lake P has been used in the past in considerable quantities, but present commercial use is small.

Another color of excellent tinctorial characteristics is Lithol Red 2B, formed by coupling the diazo salt from 2-chloro-5-toluidine-4-sulfonic acid with 2,3-hydroxynaphthoic acid in alkaline solution:



C.I. 166

The barium toner of this dyestuff shows exceptional fastness to light.

TABLE X. PROPERTIES OF AZO PIGMENTS.

(Reprinted with permission from Allen's Chapter 5 of *Protective and Decorative Coatings*, Vol. II, edited by J. J. Mattiello and published by John Wiley and Sons)

	Permanency as a Full Tone Color	Permanency as a Tinting Color	Specific Gravity	Grinding Properties	% Pigment in Raw Linseed for Soft Paste	Color Permanency under Baking Temperatures	Bleed in Linseed Oil	Bleed in 95% Alcohol	Bleed in Hot Paraffin	Resistance to 5% Alkali
Permatone Orange	Very permanent; good for exterior exposure.	Good	1.460	Excellent	42.00	Good	Slight	Slight	Yes	Good
Toluidine Toner	Very permanent; good for exterior exposure.	Good	1.430	Excellent	38.00	Good	V. slight	V. slight	Yes	Good
Lithol Red, Light (Sodium Salt)	Fair; not for exterior exposure.	Poor	1.280	Good	40.00	Good	V. slight	V. slight	Yes	Good
Lithol Red, Medium (Barium Salt)	Fair; not for exterior exposure.	Poor	1.470	Good	40.00	Good	Yes	Yes	Yes	Good
Lithol Red, Deep (Calcium Salt)	Fair; not for exterior; better than Ba and Na.	Poor	1.610	Good	40.00	Good	Yes	Yes	Yes	Good
Orange Toner	Very permanent; excellent for exterior.	Good	1.570	Excellent	40.00	Good	Slight	Slight	Yes	Good
Fire-Blazing Red	Permanent; excellent for exterior.	Good	1.560	Excellent	40.00	Good	Yes	Yes	Yes	Good
Para Red, Light	Fair; not satisfactory for exterior.	Poor	1.400	Good	48.00	Fair	Yes	Yes	Yes	Good
Para Red, Deep	Fair; not satisfactory for exterior.	Poor	1.520	Good	40.00	Fair	Yes	Yes	Yes	Fair
Lithol Rubine	Good; not satisfactory for exterior exposure.	Fair	1.60	Fair	42.00	V. good	None	None	None	Fair
Permanent Red 2B	Good permanency; slight tendency to bronze on exposure.	Good	2.608	Good		Good	None	Slight	None	Slight
Pigment Scarlet	Good.	Fair	1.650	Good	50.00	V. good	None	None	None	Poor
Lake Red C (Ba Toner)	Fair; not for exterior.	Poor	1.720	Good	45.00	Fair	None	None	None	Good
2R, Scarlet Lake	Poor; not for exterior.	Fugitive	2.410	Good	75.00	Good	None	None	None	Poor
R.M.T.A. Red	Not for exterior.	Poor	1.850	Good	48.00	Good	None	None	None	Poor
Pigment Rubine G (Barium, Strontium, or Calcium Lake)	Good; not satisfactory for exterior exposure.	Fair		Good		Good	None	None	None	Poor
Pigment Rubine 3G (Barium, Strontium, or Calcium Lake)	Good; not satisfactory for exterior exposure.	Fair		Good		Good	None	None	None	Poor

The properties of the azo pigments (3) that make them valuable in industry are summarized in Table X, which is based on the average or general characteristics of representative members of the different groups. The data indicate the permanency, or fastness to light, of the pigments in both full tone and tint, specific gravity, grinding properties, oil absorption, baking stability, bleeding tendencies in linseed oil, 95 per cent alcohol and hot paraffin, and resistance to dilute (5 per cent) alkali. These are the properties which determine, to a great extent, the use or uses to which the material may best be put. Such fields of use may include general application in exterior finishes, as paint, lacquer, or enamels; poster work, which also requires a high degree of fastness to light and weathering; interior work, such as magazine or book illustration, tinting of paper, interior surface finishes, wallpaper surface coating, which now demands a high degree of light fastness, surface coating of paper for use in covering of boxes; and many other uses in rubber wax, linoleum, and so on.

PHOSPHOTUNGSTIC, PHOSPHOMOLYBDIC, AND PHOSPHOTUNGSTOMOLYBDIC PIGMENTS (BASIC DYE PIGMENTS, PERMANENT)

During the later years of the last and the early years of the present century the advantages to be gained in the use of more permanent colors in all lines of decorative art were being more clearly recognized. This was particularly true in the textile field, in which a definite effort was being made to improve the resistance of color used on fabrics to the destructive action of light rays.

For many years the very fugitive basic dyestuffs had been extensively used because of their beauty, strength, and extremely wide range of hue. In the effort to improve textile colors in general, therefore, special attention was directed to these brilliant and useful dyes.

At that time the basic dyestuffs were fixed on the fiber, as a rule, with tannic acid and tartar emetic, the resulting colors being very attractive in appearance but sensitive to light and other influences, such as washing. However, in the studies made to obtain more permanent dyeings, an investigation was made of the reaction which had long been known and used in biochemical work, that of formation of insoluble products when amino compounds, such as pyridine, are treated with the complex inorganic acids formed when a mixture of disodium phosphate and sodium tungstate or molybdate are treated, in solution, with a strong mineral acid, such as hydrochloric acid.

When this technique was applied to the fixing of basic dyes on the textile fibers a marked increase in the permanency to light was noted.

Previous to this discovery the basic dyestuffs were used to some extent in the preparation of pigments, being precipitated and fixed by means of tannic acid and tartar emetic or other reagents, such as rosin soap, fatty acid soap, phosphates, and green or white earth. These pigments exhibited advantages and defects similar to the textile dyeings, that is, brilliance and strength but great sensitivity to light and water.

When this discovery was applied to the formation of pigments, the extremely favorable results obtained became the foundation upon which has since been built the present very valuable and extensive class of colors known by the all-too-complicated names of phosphotungstic, phosphomolybdic, and phosphotungstomolybdic toners and lakes. These products possessed excellent permanency to light and, in addition, retained to a great degree the brilliance, beauty, and strength of the earlier more fugitive types.

Immerheiser and Immerheiser and Beyer made the first commercial development, applying for patents in 1914, which were issued in 1917. One patent covered the use of phosphomolybdic acid (70) and the other of phosphotungstic acid (71). In spite of the great interest in this new type of pigment and its recognized value to the industry, further application of the discovery was delayed for several years by the first World War. The elements tungsten and molybdenum were in such great demand for the production of high-speed steels required in the manufacture of military equipment that the high prices placed on these metals were sufficient to delay their extensive use in pigment colors until about 1920.

In 1921 a patent (88) was issued to Lendle, extending the use of the phosphotungstate and phosphomolybdate complexes to the precipitation of the basic colors containing acid groups. The real object of this development was the replacement of the expensive vat colors used in the tinting of paper stock.

Another patent of even greater significance was issued to Linz (92), which indicated that the complex acids could be prepared in a simple manner, more easily adaptable to commercial purposes than the methods previously in use. This patent revealed that isolation of the complex acid is not necessary but that it can be employed directly in the original solution, changing an operation of considerable expense and difficulty to one that is both practical and economical.

In 1927 a patent (64) was issued to Hartman covering the use of mixed phosphotungstic and phosphomolybdic acids, as well as the phosphosilicates.

These five patents may be regarded as the basic patents on which the development of phosphotungstic, phosphomolybdic, and phosphotungstomolybdic pigments has been carried successfully forward.

Among the more recent patents, the following may be mentioned as of rather special interest. In 1928 a patent (69) was issued to I. G. Farbenindustrie Akt.-Ges., involving the use of colorless amino compounds with the phosphotungstic complexes. In 1929 a patent (109) was issued to Rabe, Wenk, and Hartman, involving the reduction of the $24(WO_3—MoO_3)P_2O_5 \cdot 3H_2O$ complex. In 1932 a patent (20) was issued to Buchwald, involving the use of leuco forms of the basic dyestuffs, forming the pigment and then oxidizing. In 1933 a patent (147) was issued to Zschimmer, covering the use of reduced complex acids, and one to Zschimmer and Pohl (148), emphasizing the effect of *p*H of the complex acid solution. In 1934 a patent (72) was issued to Immerheiser and Zschimmer, covering the heating of the pigments under pressure. In 1935 a patent (25) was issued to Calcott, Carleton, and Stryker, covering the use of alkylamines with the complex acids.

The Basic Dyes

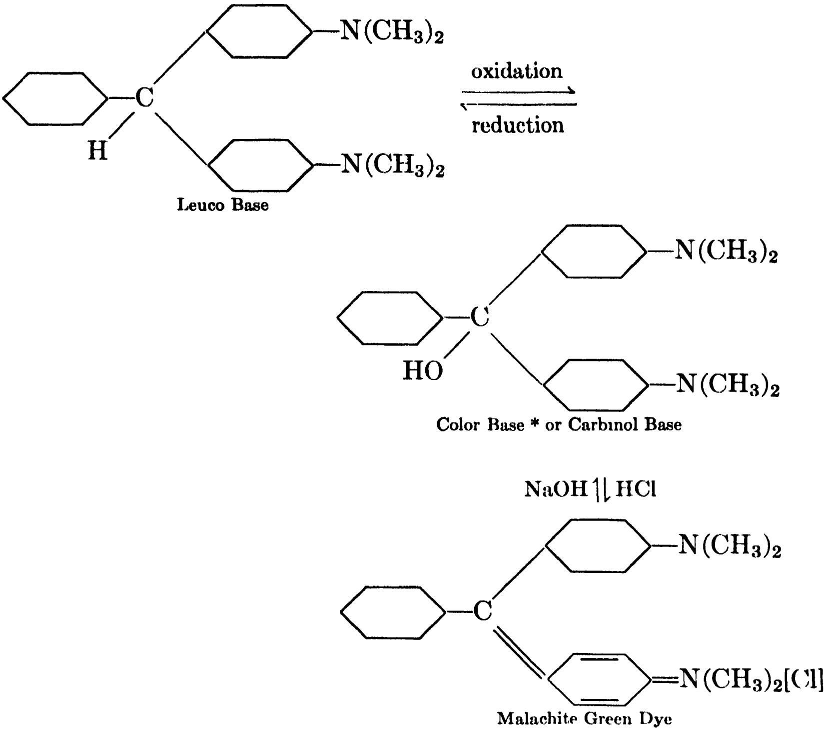
The basic dyes are synthetic organic coloring matters that are typically basic or alkaline in chemical nature, owing to the presence in the dye molecules of free or substituted amino groups: $—NH_2$, $—NHCH_3$, $—N(CH_3)_2$, $—N(C_2H_5)_2$, and others. Such groups readily form salts with the acids and acid salts, and the basic dyes appear on the market as a rule in this form. For example, this type of salt formation may be shown as follows:

$$R—NH_2 + HCl \rightarrow (RNH_3)Cl$$

or

$$R—NH(C_2H_5) + HOOC—COOH \rightarrow (RNH_2(C_2H_5))OOC—COOH$$

Salts of this type are generally soluble in water, which is also characteristic of the basic dyes. A typical basic dye and its acid salt are the following:



Leuco Base

Color Base * or Carbinol Base

Malachite Green Dye

Malachite Green generally appears in the market as the oxalate rather than as the hydrochloride.

Crystal Violet illustrates another factor which will be referred to later in this chapter. It is possible for more than one basic group in a basic dyestuff to enter into salt formation. This may be indicated as in the following reversible reactions, by progressive saturation of the substituted amino groups by direct addition of acid molecules, and their subsequent removal in the reverse reactions by gradual addition of alkali. The resulting changes in molecular constitution are accompanied by definite alterations in the color of the dyestuff in solution as shown below:

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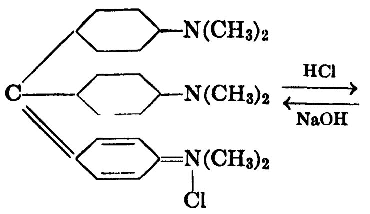
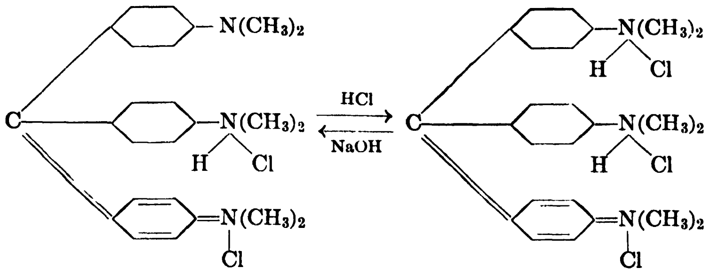
* The carbinol type is generally referred to as a "color base" even though it is usually colorless or but slightly colored because only salt formation is required to bring out the full color of the dye.



Violet Color



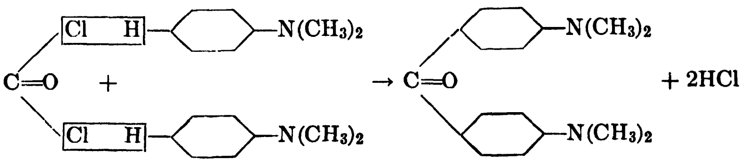
Green Color
Yellow Color

These changes take place very readily in dilute solution, the colors being clear and the reactions reversible as indicated. They are entirely consistent with the discussion of resonance given in Chapter III, the addition of acid molecules preventing the corresponding basic groups from contributing to the resonance of the structure.

Many interesting procedures are involved in the manufacture of basic colors. A few of the more important products are illustrated in the following outlines of formation.

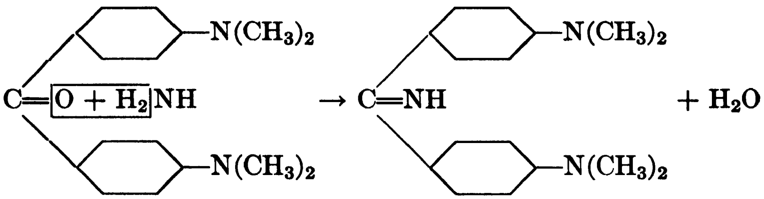
Auramine O. Auramine O is one of the most valuable basic yellows in textile use, but in the pigment field it is of less importance than the greener type Thioflavin. It is a ketonimine dyestuff.

Phosgene reacts with bases such as substituted anilines to give materials similar to Michler's ketone·



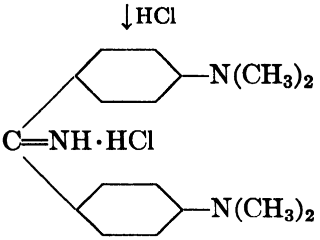
Phosgene Dimethylaniline Michler's Ketone

The ketone reacts with ammonia to give the color base:



Auramine Base

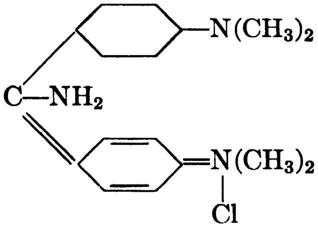
and the acid salt of the base is the final dye:



Auramine O

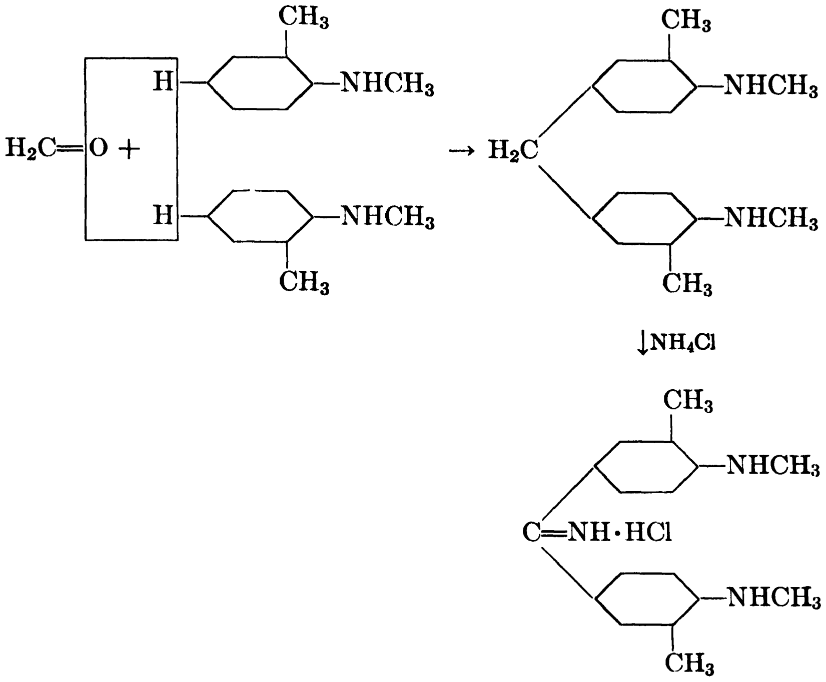
C.I. 656
Sch. No. 494

Auramine can be represented in the quinonoid form to account for its color:



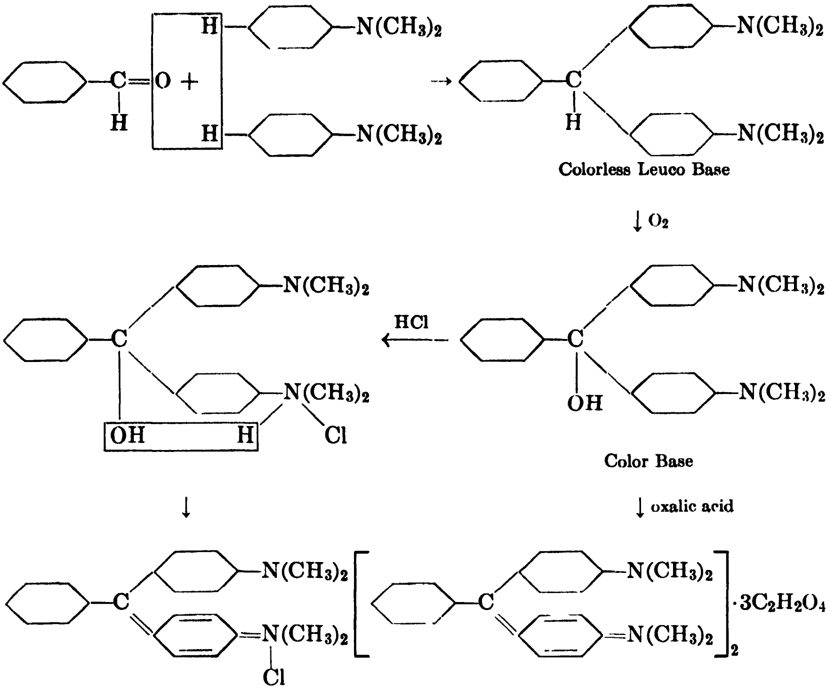
but all such compounds are deeply colored, while auramine is yellow. It is possibly better to consider the color as a resonance hybrid inasmuch as the three nitrogen atoms make such a mechanism highly probable.

Auramine G. Auramine G is a ketonimine dyestuff closely related to Auramine O in general properties and structure but much greener in tone. It is prepared from monomethylorthotoluidine, formaldehyde, and ammonium chloride:



Auramine G has been used commercially but in a much smaller volume than the redder type Auramine O.

Malachite Green. Malachite Green is one of the most widely used basic colors of the triphenylmethane class, owing largely to its rich bluish green tone and relatively low cost. It is made from dimethylaniline and benzaldehyde. Formerly the zinc chloride double salt ($3C_{23}H_{25}N_2Cl + 2ZnCl_2 + 2H_2O$) (32) was the usual market type, but at the present time the oxalate ($2C_{23}H_{25}N_2 + 3C_2H_2O_4$) is more generally used.

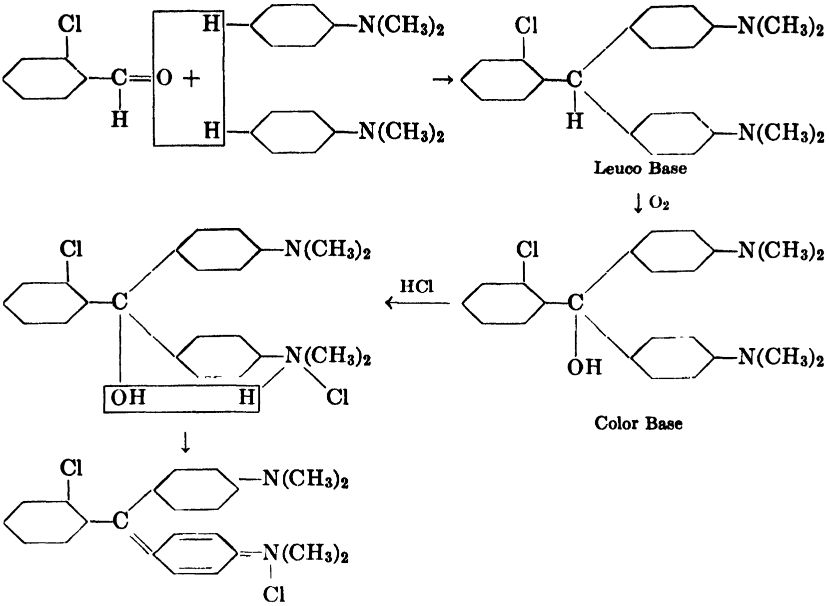


Malachite Green (Chloride)

Malachite Green (Oxalate)
C.I. 657
Sch. No. 495

Setoglaucine (Rhoduline Blue 6G). Setoglaucine or Rhoduline Blue 6G is a very brilliant greenish basic blue, of the triphenylmethane class, which has proved valuable in the form of organic pigments. The pigment is sometimes referred to as Permanent Peacock Blue owing to its resemblance in color values to the fugitive Peacock Blues made from erioglaucine.

The dyestuff is prepared by condensing *o*-chlorobenzaldehyde with dimethylaniline and then oxidizing the leuco base to the color base:

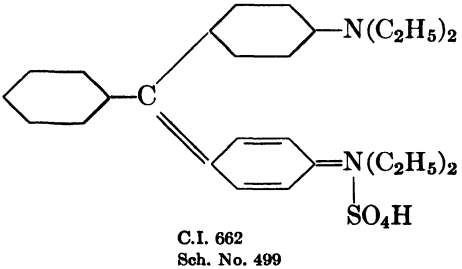


Setoglaucine

C.I. 658
Sch. No. 496

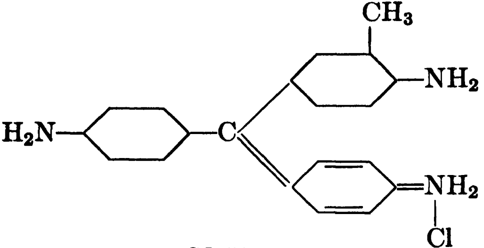
It has been pointed out by Kaeswurm (74) that the meta and para isomers of this color are of no value.

Brilliant Green. Brilliant Green is a basic dyestuff of the triphenylmethane class, much yellower and cleaner in tone than Malachite Green. It is prepared from diethylaniline and benzaldehyde and usually appears on the market in the form of the sulfate. The reactions are similar in form to those used in the preparation of Malachite Green.



C.I. 662
Sch. No. 499

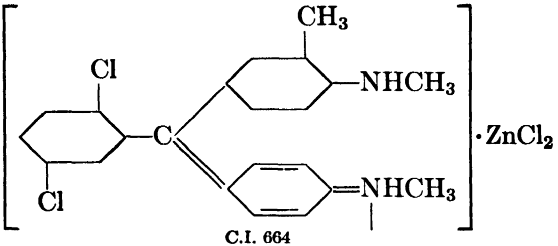
Magenta (Fuchsin). Magenta or Fuchsin is not a true chemical individual but a group of products formed by heating a mixture of aniline, *o*-toluidine, *p*-toluidine, and their hydrochlorides in nitrobenzene, with iron and zinc chloride. The dyestuff is a triphenylmethane derivative that can be approximately represented by the following structure:



C.I. 677
Sch. No. 512

Magenta has been used to a considerable extent in the past in shading of other colors and to some extent in the making of pulp colors for surface coating work.

Brilliant Glacier Blue. Brilliant Glacier Blue is a basic dyestuff of the triphenylmethane class, of a much redder tone than setoglaucine. It is prepared by condensing 2,5-dichlorobenzaldehyde with monomethyl-*o*-toluidine, oxidizing the leuco base and converting the color base into the zinc chloride double salt:

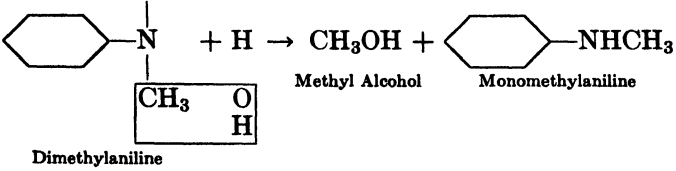


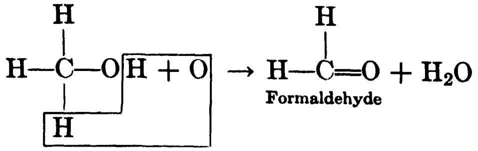
C.I. 664
Sch. No. 501

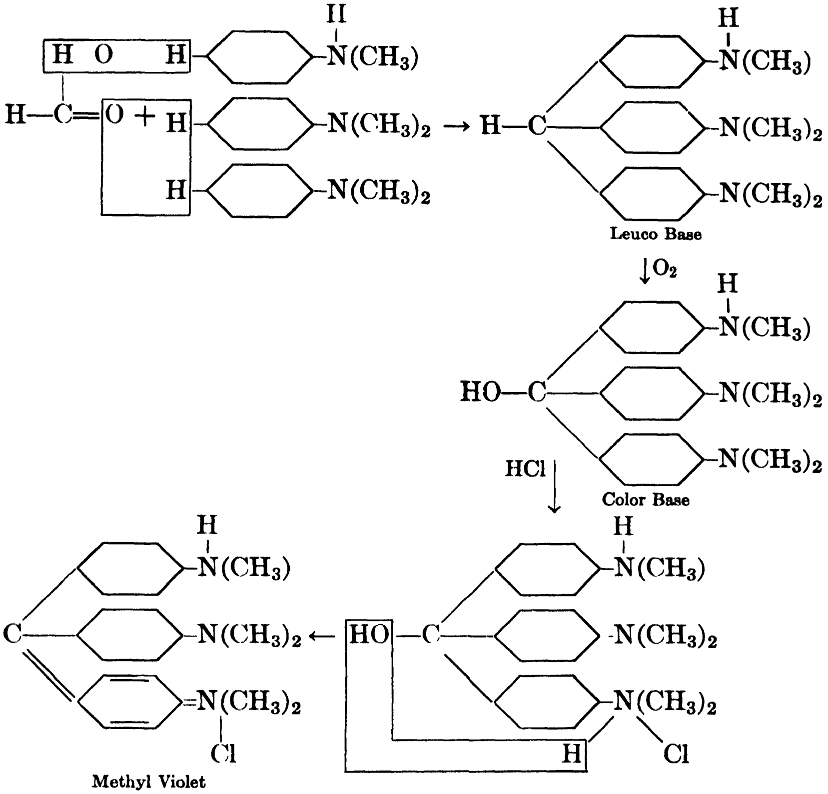
In pigments, this color is one of the less important products.

Methyl Violet. Methyl Violet (24), a basic dyestuff of the triphenylmethane class, is a mixture of the hydrochlorides of the more highly methylated *p*-rosanilines, the average being represented by the pentamethyl derivative. It is formed in the oxidation of dimethylaniline with cupric chloride in a mixture of dimethylaniline, phenol, salt (NaCl), and copper sulfate.

The mechanism of the reaction may be accounted for in the following way:

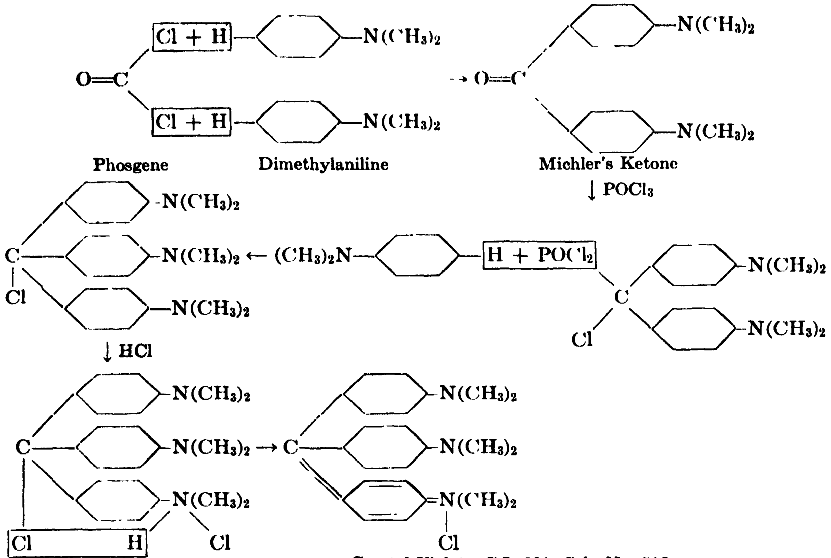






Methyl Violet, because of its relatively low price and useful color characteristics, has been used extensively in the manufacture of both fugitive and light-fast pigments, and is one of the most valuable of the basic colors in this field. The fugitive type has found its greatest use in carbon papers and typewriter ribbons, while the permanent type is widely used in printing ink, paper, and rubber.

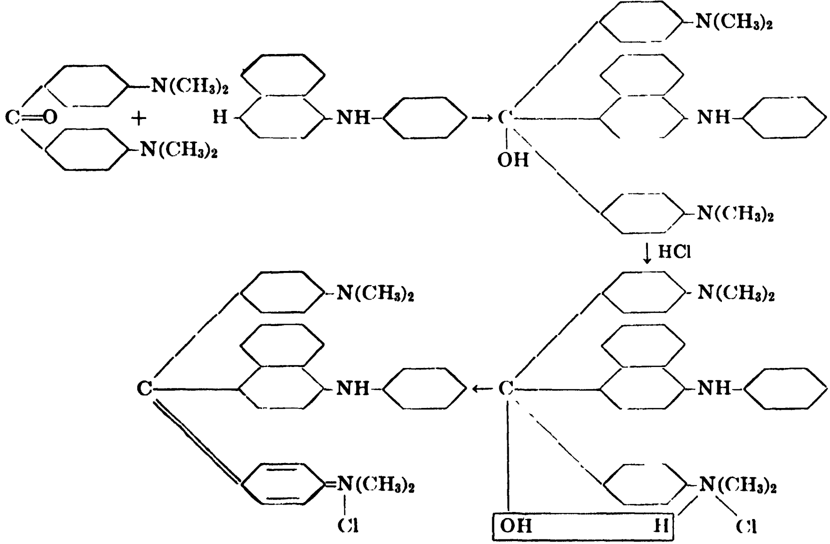
Crystal Violet. Crystal Violet is a basic dyestuff of the triphenylmethane type which has not been used extensively in pigment work, but is nevertheless a color of exceptional beauty and is readily prepared in a high state of purity. It is made by the phosgene method, forming Michler's ketone and then the dichloride, an addition product of phosphorus oxychloride, which reacts with dimethylaniline to form the dyestuff.



Crystal Violet—C I 681. Sch. No. 516

Crystal Violet, as a pigment, is a much greener and more brilliant type of violet than that prepared from Methyl Violet.

Victoria Blue B. Victoria Blue B, a dyestuff of the triphenylmethane type, has been for many years important in the field of pigment colors. It is a blue of a reddish hue, showing excellent strength. Michler's ketone is condensed with phenyl-α-naphthylamine:



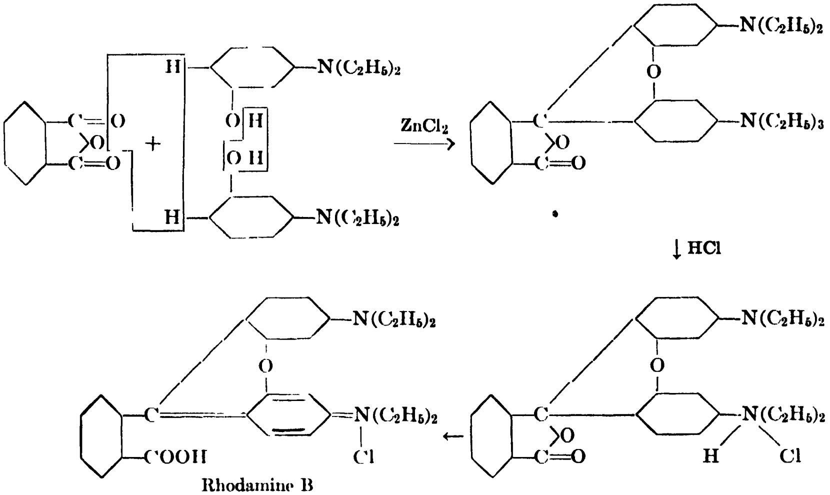
Victoria Blue B.—C.I. 729. Sch. No. 559

Victoria Blue B yields pigments which are reddish in hue, of excellent strength, and have been found valuable in many fields of pigment use, including printing ink, paper and rubber.

Victoria Pure Blue BO* is a dyestuff of quite similar color values which gives pigments of greatly improved characteristics.

Rhodamine B. Rhodamine B is one of the most beautiful of the basic colors, having an unusually brilliant bluish undertone. It is a dyestuff of the xanthene class.

Diethyl-*m*-aminophenol is condensed with phthalic anhydride in the presence of zinc chloride:



Rhodamine B

C.I. 749
Sch. No. 573

In the textile field the rhodamines have long been regarded as among the most beautiful of dyestuffs, and their characteristics of brilliance, purity of tone, tinctorial power, and favorable working properties have been retained in both their fugitive and permanent types of pigments.

Rhodamine 6G. Rhodamine 6G is also a basic dyestuff of the xanthene class, of great beauty and much yellower in hue than Rhodamine B. It is prepared by condensing monoethyl-*m*-aminophenol with

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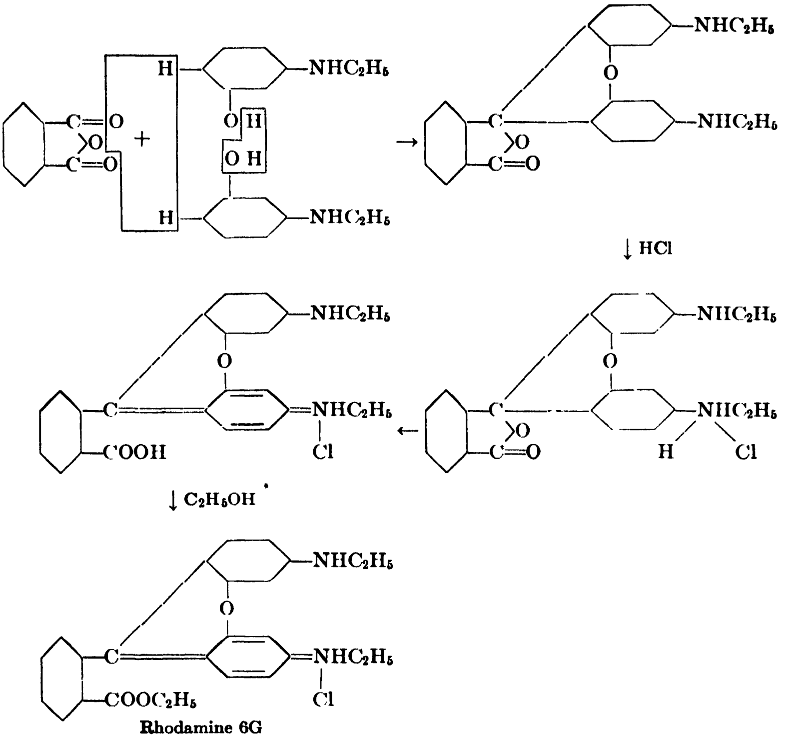
* E. I. du Pont de Nemours and Co., Wilmington, Del.

phthalic anhydride, and then forming the ethyl ester with ethyl alcohol and hydrochloric acid:



Rhodamine 6G

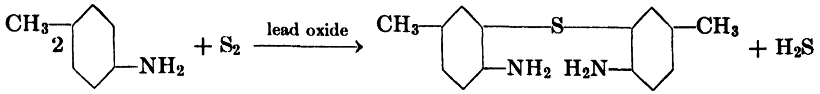
C.I. 752

Sch. No. 571

The pigments prepared from Rhodamine 6G are quite similar in characteristics and in usefulness to Rhodamine B, but, since the carboxyl group is esterified, the stability of the molecule is appreciably increased.

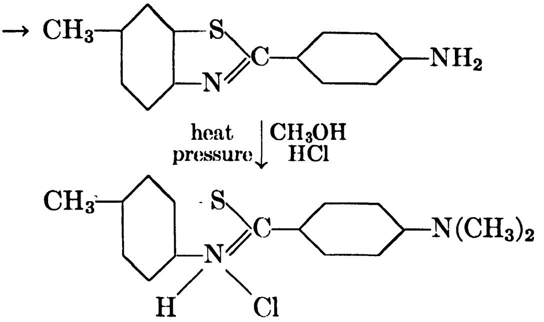
Thioflavin T. Thioflavin T is a yellow basic dyestuff of the thiazine class. It has practically no value as a straight pigment but has great value in combination with other green or blue pigments in making greens of a very brilliant type. The straight pigment is quite weak and lacking in cleanness. Its hue, however, is very greenish in tone, and, in combinations with greens, the resulting mixed pigments show a surprising brilliance and strength. This is one of the most striking instances in the entire pigment field of the effect of hue on brilliance in a blended color.

Thioflavin T is made from *p*-toluidine by heating with sulfur in the presence of lead oxide over a long period at temperatures up to about 220° C. At lower temperatures thiotoluidine is formed:



p-Toluidine   Thiotoluidine

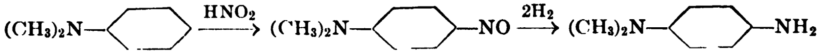
but the high temperature product is dehydrothio-*p*-toluidine:



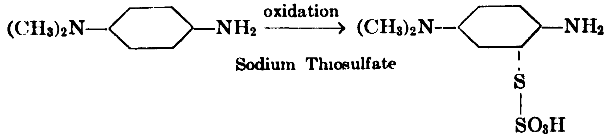
Thioflavin T

C.I. 815
Sch. No. 618

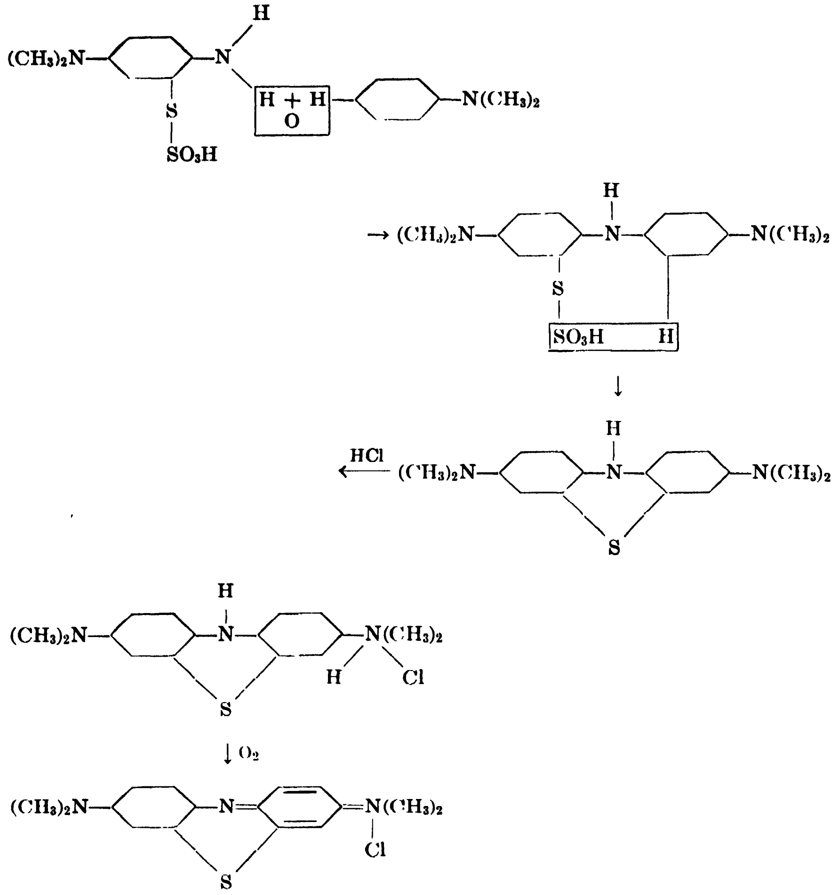
Methylene Blue. Methylene Blue is a basic dyestuff of the thiazine class. It is of special importance in the textile field but of little value as a pigment, owing to the relatively low tinctorial power and instability of the products. It is prepared from *p*-aminodimethylaniline by an interesting series of reactions:



Dimethylaniline   *p*-Nitrosodimethylaniline   *p*-Aminodimethylaniline



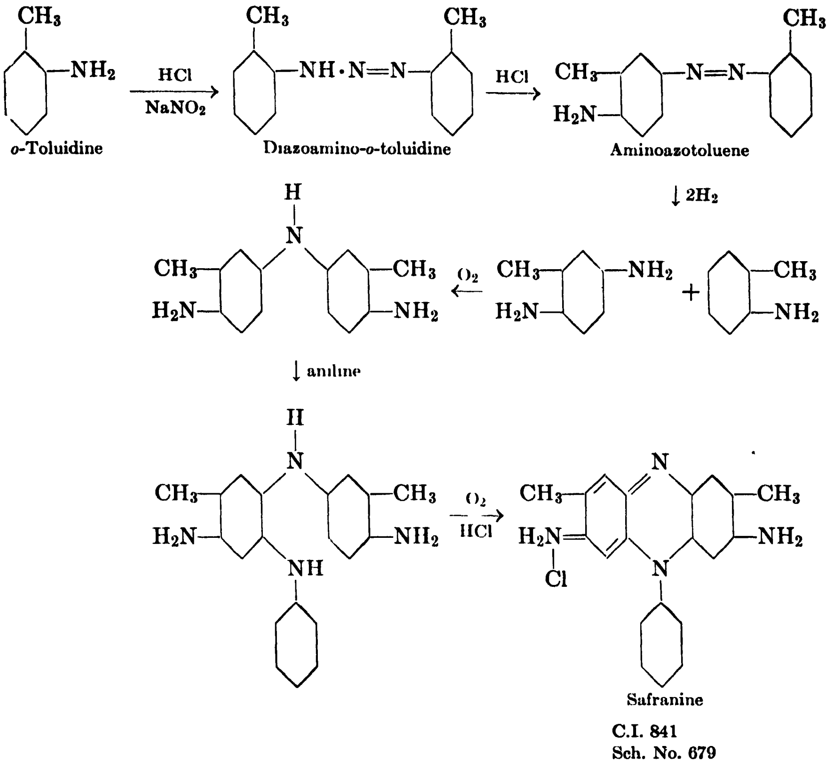
p-Aminodimethylaniline-*m*-thiosulfonic Acid



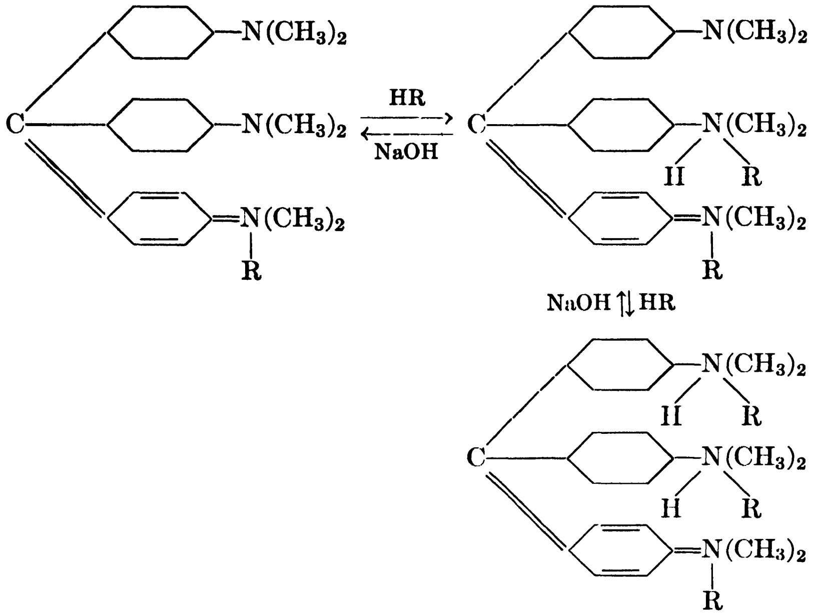
Methylene Blue

C.I. 922
Sch. No. 659

Safranine. Safranine is a red basic dyestuff of the azine class. It has been used extensively in textile work but has not proved of great value in the pigment field. As a pigment it is of a yellowish red hue and quite lacking in brilliance. It is prepared from o-toluidine and aniline in the following manner:



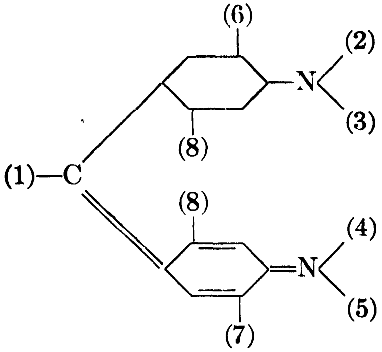
Pigment Formation. In considering the mechanism of the formation of the phosphotungstic and phosphomolybdic pigments it is necessary to regard the complex acids as acting in a manner similar to that illustrated above with the more simple acids. If the complex acid is represented by HR, the possible salts formed with Crystal Violet might be represented as follows:



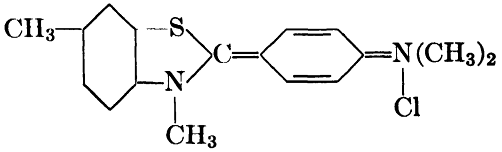
It is quite uncertain in the practical preparation of the complex pigments just how significant the above reactions may be. The products are immediately precipitated even before the addition of a molecule equivalent of the complex, which might indicate the union of only one molecule of complex with six molecules of dye, but other facts appear to cast at least an element of doubt on this conclusion. For example, in order to produce first-class modern pigments, it is quite essential to employ excess of the complex and, generally, to heat the final precipitated product in order to bring out an entirely satisfactory degree of resistance to light in the finished pigment. What happens chemically under these conditions is not definitely known. There may be good reason for the view that the changes which have taken place in the ultimate pigment particles are purely physical, involving crystal growth, or change in the size and shape of the particle. However, there appears to be good ground for the opinion that, if the reactions are completed under more vigorous conditions, there may be progressive salt formation between the excess of complex acid in the solution and the free basic groups of the precipitated pigment.

It might appear to be a simple matter to settle this point by resort to analytical methods, to establish the relation between basic dye molecules and molecules of the complex acid combined definitely with them. The difficulty is that the structural identity of the complex acid has not yet been satisfactorily established. It is probable, moreover, that the complex, as used, is not a single chemical individual but an equilibrium mixture of several. This phase of the problem will be discussed more fully under the section dealing with the complex acids.

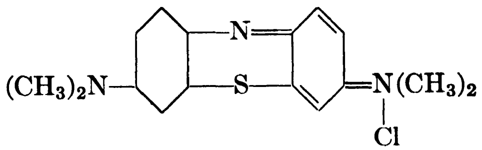
The basic dyestuffs are of varied chemical structure, the greater number and in general those of greatest importance being found among the diphenylmethane and the triphenylmethane series. Other classifications include the azine, xanthene, thiazine, and thiazole groups. It is of interest to note (108) that with few exceptions these dyes may be related to a single typical structure, the various individual dyes appearing as derivatives. Table XI illustrates this relation. The numbers refer to the positions in the following structure:



Exceptions include the important Thioflavin:



the less important Methylene Blue:



and Safranine:

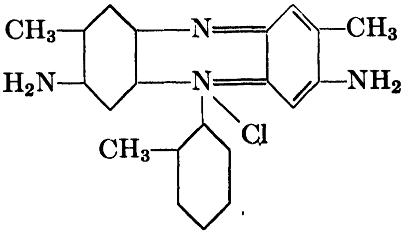


TABLE XI

BASIC DYESTUFFS OF SIMILAR STRUCTURE

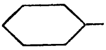
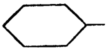
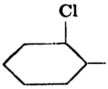
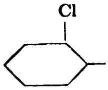
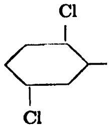
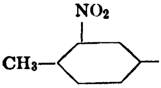
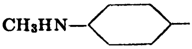
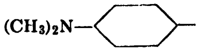
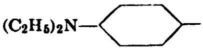
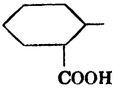
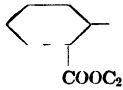
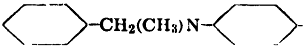
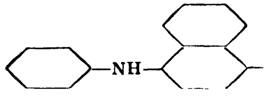
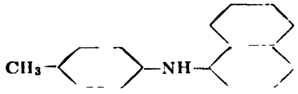
Dyestuff	Substituents in Positions								
	1	2	3	4	5	6	7	8	8
Magenta		H	H	H	H	CH_3	H	H	H
Auramine	HN=	CH_3	CH_3	CH_3	CH_3	H	H	H	H
Malachite Green		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Brilliant Green		C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	H	H
Setocyanine		H	CH_3	H	CH_3	CH_3	CH_3	H	H
Rhoduline Blue		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Glacier Blue		H	CH_3	H	CH_3	CH_3	CH_3	H	H
Turquoise Blue		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Methyl Violet		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Crystal Violet		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Ethyl Violet		C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	H	H
Rhodamine B		C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	—O—	

TABLE XI (*Continued*)

BASIC DYESTUFFS OF SIMILAR STRUCTURE

Dyestuff	Substituents in Positions								
	1	2	3	4	5	6	7	8	8
Rhodamine 6G		H	C_2H_5	H	C_2H_5	H	H	—O—	
Benzyl Violet		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Victoria Blue		CH_3	CH_3	CH_3	CH_3	H	H	H	H
Night Blue		C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	H	H

Complex Phosphotungstic, Phosphomolybdic, and Phosphotungstomolybdic Acids

Although the complex acids, formed by combination of the phosphate radical with the oxides of tungsten and molybdenum, are the real foundation of the permanent colors prepared from the basic dyestuffs, this is the part of the problem in which the greatest degree of uncertainty is encountered. The literature bearing on the chemistry of these complexes is extensive, but inconclusive, in establishing the true structure under the conditions ordinarily employed in manufacture.

Hsein Wu (67) * has given a survey of the historical developments in this field of study which indicates the difficulties encountered in reaching a complete solution to the problem.

Gmelin (58) discovered that phosphoric acid forms a yellow precipitate in acid solution with ammonium molybdate. The phosphorus content was so small that he regarded it as unessential.

Sonnenschein (127) showed that phosphoric acid was an integral part of the precipitate and suggested its use for the quantitative determination of phosphoric acid.

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* The discussion on pages 153 to 162 is based largely on the article by Dr. Hsein Wu in the *Journal of Biological Chemistry*. Adapted with permission.

TABLE XII

BASIC DYESTUFFS—GENERAL INFORMATION (108)

	Colour Index	Empirical Formula	Mol. Wt.	Spectrum in Water	Fastness on	
					Wool	Cotton*
Magenta	677	$C_{20}H_{20}N_3Cl$	409	546 15 and 489 2	5	4
Auramine	322	$C_{17}H_{22}N_3Cl \cdot H_2O$	322	.....	4–5	4–5
Malachite Green	657	$C_{23}H_{25}N_2 \cdot 1\frac{1}{2}C_2H_2O_4$	464	616.9	3	4
Brilliant Green	662	$C_{27}H_{33}N_2SO_4H$	482	623.0	3	4
Setocyanine	663	$C_{25}H_{28}N_2Cl_2$	392	612.3	...	4
Rhoduline Blue	658	$C_{23}H_{24}N_2Cl_2$	399	630 8	..	5
Glacier Blue	664	$C_{23}H_{23}N_2Cl_3$	398	612 3	3	3
Turquoise Blue	661	$C_{24}H_{26}N_3O_2Cl$	424	630.4	..	
Methyl Violet	680	$C_{24}H_{28}N_3Cl$	394	587 0 and 535.0	4–5	4–5
Crystal Violet	681	$C_{25}H_{30}N_3Cl \cdot 9H_2O$	569	591 0 and 540 5	4–5	4–5
Ethyl Violet	682	$C_{31}H_{42}N_3Cl$	492	596 9 and 546 5	.	. .
Rhodamine B	749	$C_{28}H_{31}N_2O_3Cl$	479	555.0 and 517.0	3–4	3–4
Rhodamine 6G	752	$C_{26}H_{27}N_2O_3Cl$	451	525.4 and 491.3	3–4	3–4
Benzyl Violet	683	$C_{31}H_{34}N_3Cl$	484	591.0 and 540.5	5	4–5
Victoria Blue	729	$C_{33}H_{32}N_3Cl$	729	619.2 and 567.0	5–4	...
Night Blue	731	$C_{38}H_{42}N_3Cl$	576	568.2 and 627.3	(5)	(5)
Thioflavin	815	$C_{17}H_{19}N_2SCl$	319	....	3	3
Methylene Blue	922	$C_{16}H_{18}N_3SCl$	320	667.8 and 609.3	..	2
Safranine	841	$C_{20}H_{19}N_4Cl$ $C_{21}H_{21}N_4Cl$	351 364	......	5	3

* Cotton mordanted with tannic acid and tartar emetic.

Debray (37) prepared the free phosphomolybdic acid by digesting the yellow precipitate with aqua regia, and found the ratio of P_2O_5 to MoO_3 to be 1 to 20.

Rammelsberg (110) found the ratio to be 1 to 22.

However, the unanimous opinion of Finkener (46), Pemberton (104), von der Pfordten (135), Gibbs (56), and Hundeshagen (68), that the compound contains $1P_2O_5$ to $24MoO_3$, is now generally accepted.

Gibbs (56) undertook further work on the complex acids. He boiled 24 molecules of $Na_2WO_4 \cdot 2H_2O$ with 2 molecules of Na_2HPO_4 and acidified the mixture with HNO_3. The complex acid was precipitated with mercurous nitrate, and the mercurous phosphotungstate was decomposed with HCl. The free acid complex thus obtained contained $1P_2O_5$ to $24WO_3$.

Sprenger (128), Kehrmann and Freinkel (80), and Brandhorst and Kraut (16) obtained the same compounds by slightly different methods. All these analytical results showed the ratio P_2O_5 to WO_3 to be as 1 to 24.

Besides the compounds containing $1P_2O_5$ to $24MO_3$ ($M = W$ or Mo), Gibbs reported others with the ratio P_2O_5 to Mo_3 as 1 to 22, 1 to 20, 1 to 18, and 1 to 16. These compounds were obtained only in the form of salts; and because the conditions under which they were formed were not well defined, the purity was not definitely established, and the analytical procedure for the determination of phosphate was not rigidly accurate, much of the work is of doubtful significance.

Péchard (103) reported several complex acids other than 1 to 24 acid. He mixed theoretical quantities of M-tungstic and phosphoric acids and claimed to have obtained acids of the ratio P_2O_5 to WO_3 as 1 to 20, 1 to 16, and 1 to 12. There is, however, no convincing evidence that his compounds had the composition he assigned to them.

In 1887 Kehrmann (78) prepared a new phosphotungstic acid by boiling 1 molecule of sodium tungstate with 4 molecules of phosphoric acid. He at first assigned to the compound formed the ratio 1 to 16. As a result of further work this was later (1892) corrected to 1 to 18. In collaboration with Böhm (79) he succeeded in isolating the corresponding molybdenum compound. He also observed that the 1 to 24 phosphotungstic acid is transformed into the 1 to 18 acid by free phosphoric acid on long standing. Kehrmann and his collaborators observed that the 1 to 24 and 1 to 18 phosphotungstic acids were converted by carbonates into new complexes containing respectively $1P_2O_5$ to $17WO_3$. These complex salts corresponded to hypothetical acids of the composition $7H_2O \cdot P_2O_5 \cdot 22WO_3$ and $5H_2O \cdot P_2O_5 \cdot 17WO_3$, but when these salts were boiled with mineral acids the 1 to 24 and 1 to 18 acids were regenerated.

Compounds containing much smaller amounts of WO_3 or MoO_3 are also known. The $1P_2O_5$ to $15MoO_3$ was reported by Rammelsberg (110), the $1P_2O_5$ to $5MoO_3$ by Rammelsberg, Zenker (146), Debray (37), Wernke (139), and Friedheim, the $1P_2O_5$ to $4MoO_3$ and the $1P_2O_5$ to $2MoO_3$ by Friedheim, and the $1P_2O_5$ to $7MoO_3$ by Gibbs and Kehrmann (57).

All these compounds, if they exist at all, are formed either from the higher acids by decomposition with insufficient alkali or from the molybdate and tungstate with insufficient acid. They have been prepared only in the form of salts, as they are converted by mineral acid into the 1 to 24 or the 1 to 18 acid.

The work of Hsein Wu (67) has placed the chemistry of these complex acids on a much more definite basis. Methods were developed for the preparation of the various tungsten and molybdenum complexes, analytical procedures were brought into a much more satisfactory position, various reduction products were studied, and a more rational and systematic interpretation of the composition and properties of the individual complexes arrived at. It was shown that the complex phospho compounds of molybdenum and tungsten fall into two well-defined groups.

Group I. This group includes the complexes containing $1P_2O_5$ to $24MO_3$ and $1P_2O_5$ to $18MO_3$ (M = W or Mo). They can exist either as free acids or as salts. They are all colored, with the exception of the 1 to 24 tungsten compound. They are very sensitive to reduction and precipitable with pyridine in dilute solutions. They are converted by alkali into compounds of Group II.

Group II. This group includes a number of the salts with different P_2O_5 to MO_3 ratios. They exist only in the form of salts, being converted by mineral acids into compounds of Group I. They are all white or colorless. They are not sensitive to reduction and are not precipitable with pyridine in dilute solutions.

The properties and reactions that have been found useful in distinguishing the complex acids are shown in Table XIII.

The formation of the complex acids depends on four factors: (1) acidity or hydrogen-ion concentration; (2) concentration of phosphoric acid; (3) concentration of tungstic acid or molybdic acid; and (4) temperature.

Acidity is the most important factor. A definite hydrogen-ion concentration is apparently required to condense the simple tungstic acid or molybdic acid into a complex structure, which then combines with phosphoric acid. A higher acidity is required to form $(MO_3)_{24}$ than $(MO_3)_{18}$, and for the molybdenum compound than for the corresponding tungsten compound. The concentration of tungstic or molybdic acid and that of phosphoric acid exert their effects in accordance with mass action, but they are relatively unimportant. Boiling temperature is required to form the complex acid of the 1 to 18 series, but the 1 to 24 acids are formed even at ordinary temperatures.

TABLE XIII

PROPERTIES AND REACTIONS OF COMPLEX ACIDS (67)

Reaction	W		Mo	
	1 to 18	1 to 24	1 to 18	1 to 24
Color	Lemon-yellow.	Colorless.	Bright yellow.	Orange.
NH_4 salt	Soluble.	Insoluble.	Soluble.	Insoluble.
With uric acid	Blue coloration in alkaline solution.	Brown coloration in acid. Blue in NaOH (but not in Na_2CO_3) solution. Fading rapidly.	Blue coloration in alkaline solution.	Blue coloration in alkaline or in acid solution with complex in excess. Violet with uric acid in excess.
With SO_2	Blue coloration, growing slowly in acid. Only a trace of color in alkaline solution.	Almost no reaction. Very faint violet coloration.	Blue coloration in alkaline or neutral solution.	Blue coloration in alkaline solution with the complex in excess. Lavender-blue with SO_2 in excess.
With ferrous salt	Blue in alkaline. Almost none in acid solution.	Brown in acid. Blue in alkaline solution. Fading rapidly.	Blue in alkaline as well as in acid solution.	Blue in alkaline as well as in acid solution with the complex in excess. Lavender-blue with the ferrous salt in excess.

The acidity of a mixture of sodium molybdate and phosphoric acid is not enough to form any complex acid of Group I. Whatever proportion of the two compounds is used, the solution contains only colorless complex molybdate (Group II) even after long boiling. Addition of hydrochloric acid to an equimolar mixture of Na_2MoO_4 and H_3PO_4, in an amount equivalent to the quantity of Na_2MoO_4 used, produces a mixture of the 1 to 18 and the 1 to 24 acids. The formation of the 1 to 24 acid increases with increasing acidity.

The acidity of a mixture of 1 molecule of $Na_2WO_42H_2O$ with 4 molecules of H_3PO_4 suffices to transform all the tungstate into the 1 to 18 acids, but none of the 1 to 24 acid is formed. If, however, hydrochloric acid is added, the 1 to 24 acid will be formed almost to the exclusion of the 1 to 18 acid.

Mixed complex acids containing molybdenum and tungsten, both of the 1 to 18 and of the 1 to 24 series, were prepared. The methods of preparation were similar to those of the compounds containing only one metal. Their properties lie between those of the pure molybdenum and the pure tungsten compounds, and resemble more the pure compounds of the predominant element. Thus the soluble ammonium salts of the mixed complex acid of the 1 to 18 series with high content of molybdenum are easily transformed into insoluble salts of the 1 to 24 series, whereas those with high tungsten content may be heated to 70° C without danger of transformation. The sensitiveness to reduction of these compounds runs roughly parallel to their molybdenum content, if one uses as a measure of sensitiveness the intensity of the color produced from a given weight (20 mg) of the ammonium salt, with an excess of sodium sulfite (10 cc of 10 per cent solution).

The number of mixed complex acids must be very large, and here the possibility of isomerism is far greater than in the pure molybdenum or tungsten compounds. By using sodium tungstate and molybdate in different molecular ratios, about twenty different ammonium salts of the 1 to 18 series were obtained. When these salts were reduced with reagents that do not affect the pure tungsten compound, the amount of color produced was far more than could be accounted for by the amount of molybdenum in the form of pure molybdenum compound in them. Their reduction products also showed a great variation in color, whereas the pure molybdenum and pure tungsten compounds give colors that are only slightly different from each other.

The color changes from bluish-green to violet as the proportion of tungsten is increased. The preparations showed no change by recrystallization from lukewarm water. They must therefore be either different chemical individuals or mixtures of two adjacent members of the series; for example,

$$3H_2O \cdot P_2O_5 \cdot 10WO_3 \cdot 8MoO_3$$

and

$$3H_2O \cdot P_2O_5 \cdot 9WO_3 \cdot 9MoO_3$$

These compounds not only would be isomorphous but all their properties would also be so similar that their separation would be practically impossible. A few compounds of the 1 to 24 series were also obtained, which likewise gave different colors on reduction.

Mixed complex acids of the 1 to 24 series were prepared from mixtures of tungstate and molybdate by essentially the same methods as were used for pure acids of the 1 to 24 acid series.

The mixed complex acids of the 1 to 18 series include the chief component of the phenol reagent of O. Folin and W. Denis (in which Hsein Wu was primarily interested). The conditions of their formation were found to be as follows:

1. In the absence of strong acid (HCl) the complex formed is one with high tungsten content (not very sensitive to reduction), no matter how much molybdate is used. It appears that under this circumstance the MoO_3 is not sufficiently condensed to form a long chain; the excess MoO_3 remains in the form of colorless compounds of Group II.
2. A strong acid (HCl) must be used in order to incorporate all the molybdic acid used in the complex. The greater the proportion of molybdenum used in the mixture, the larger the amount of acid required.
3. In the presence of molybdic acid a considerable amount of strong acid may be used without the formation of the complexes of the 1 to 24 series. However, when much strong acid is used, the 1 to 24 complexes are formed with corresponding decrease in the yield of the 1 to 18 series.

Reduction of the Complex Acids (67). The phosphotungstic and phosphomolybdic acids are very sensitive to reduction, remarkably so in comparison with the corresponding simple acids. The complex acids are, indeed, akin to chromic acid in their power of oxidation and in their color; and in these respects they, rather than the simple acids, represent molybdenum and tungsten in their periodic relation with chromium.

The complex acids yield, on moderate reduction, highly colored compounds which resemble the corresponding unreduced compounds in all respects except color. Thus the reduced phospho-24-molybdic and phospho-24-tungstic acids form difficultly soluble ammonium salts. The salts of the reduced phospho-18-molybdic and phospho-18-tungstic acids are soluble, but they can be salted out with ammonium chloride. All are precipitated with pyridine in acid solution and all are extractable with ether. The methods used for the isolation and purification of the unreduced compounds are also applicable to the reduced compounds.

The complex acids rated in the order of increasing sensitiveness to reduction are:

1. Phospho-24-tungstic acid
2. β-Phospho-18-tungstic acid
3. α-Phospho-18-tungstic acid
4. Phospho-24-molybdic acid
5. Phospho-18-molybdic acid

The last two acids react with a variety of mild reducing agents in acid as well as alkaline solutions, whereas the first three are reduced only when the solution is rendered alkaline.

The salient feature of the reduction of the complex acids is that the sensitivity is localized in one or two atoms of the metal in the 1 to 18 series, and probably the same number in the 1 to 24 series. This now finds support in the fact that complex salts of the 1 to 17 and 1 to 22 series, formed respectively from the 1 to 18 and 1 to 24 acids with the loss of one and two atoms of the metal, are totally inert.

Mild reducing agents (ferrous salt, sulfite, uric acid, and others) affect only the sensitive atoms, and the resulting products are still complex acids. If, however, the reduction is carried further, for example, by means of zinc and hydrochloric acid, the complete structure is disintegrated and all the atoms of the metal originally in the complex can be reduced just as those in the simple acids would be reduced under the same circumstances. The reduced complex acids are readily restored to the original by oxidation, for example, with bromine water. This shows that none of the atoms of the metal is detached from the complex.

Basicity of the Complex Acids. The basicity of the complex acids is of vital importance in consideration of the structure of the pigment colors, as there is undoubtedly a relation between the number of free acid groups in the free complex acids and the number of molecules of basic dyestuff which will enter into salt formation.

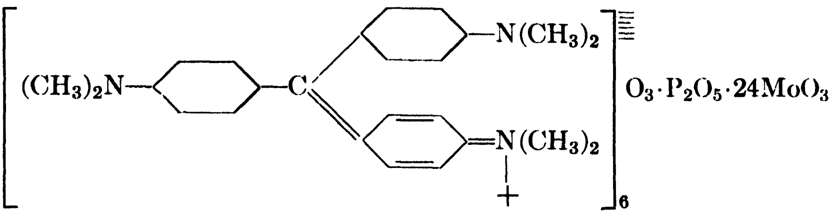
The phospho-24-molybdic acid is represented as

$$3H_2O \cdot P_2O_5 \cdot 24MoO_3$$

and the corresponding ammonium salt is

$$3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3$$

This indicates a basicity of 6, or six acid hydrogen atoms in the complex group, as illustrated in the following formula for the straight molybdate toner of Crystal Violet:



Calculations based on this type of composition are shown in Table XIV as they apply to several of the more important basic colors. It is apparent in this tabulation that the molecular structures are extremely complex, that the tungstate molecule is much heavier than that

TABLE XIV

PHOSPHOTUNGSTATE AND MOLYBDATE TONERS OF BASIC DYESTUFFS

	Dye, Mol. Wt.	Empirical Formula	Molecular Weight		%
			As Tungstate	As Molybdate	
Rhodamine B $C_{28}H_{31}N_2O_3Cl$	479	$C_{168}H_{186}N_{12}O_{98}P_2Mo_{24}$	8416	6304	74.9
Rhodamine 6G $C_{26}H_{27}N_2O_3Cl$	451	$C_{156}H_{162}N_{12}O_{98}P_2Mo_{24}$	8248	6136	74.4
Auramin $C_{17}H_{22}N_3Cl \cdot H_2O$	322	$C_{102}H_{132}N_{18}O_{80}P_2Mo_{24}$	7366	5254	71.3
Thioflavin $C_{17}H_{19}N_2SCl$	319	$C_{102}H_{114}N_{12}S_6O_{80}P_2Mo_{24}$	7456	5344	71.6
Brilliant Green $C_{27}H_{33}N_2 \cdot C_2H_2O_4 \cdot H_2O$	493	$C_{162}H_{198}N_{12}O_{80}P_2Mo_{24}$	8068	5956	73.8
Malachite Green $2C_{23}H_{25}N_2 \cdot 3C_2H_2O_4$	464	$C_{138}H_{150}N_{12}O_{80}P_2Mo_{24}$	7732	5620	72.6
Rhoduline Blue 6G $C_{23}H_{24}N_2Cl_2$	404	$C_{138}H_{144}N_{12}O_{80}P_2Mo_{24}$	7966	5854	73.4
Victoria Blue B $C_{33}H_{32}N_3Cl$	512	$C_{198}H_{192}N_{18}O_{80}P_2Mo_{24}$	8641	6502	75.4
Brilliant Glacier Blue $C_{23}H_{23}N_2Cl_3$	435	$C_{138}H_{138}N_{12}Cl_{12}O_{80}P_2Mo_{24}$	8152	6040	74.1
Crystal Violet · $C_{25}H_{30}N_3Cl \cdot 9H_2O$	570	$C_{150}H_{180}N_{18}O_{80}P_2Mo_{24}$	7990	5878	73.5
Methyl Violet $C_{24}H_{28}N_3Cl$	400	$C_{144}H_{168}N_{18}O_{80}P_2Mo_{24}$	7942	5830	73.4

containing molybdate, that the yield of a straight molybdate product would be only about 72 to 75 per cent of that of the straight tungstate, and that the content of phosphorus, or P_2O_5, is so small that analytical values based on phosphorus would be very inaccurate. It must be emphasized that these values are assumed to be approximately correct only for pure 100 per cent dyestuffs and do not apply closely to the commercial products. The possibility of the direct addition up to six molecules of basic dyestuff to the complex acid is therefore indicated.

In the case of the 1 to 18 complex acid, analytical data have established the composition of the ammonium salt quite satisfactorily as

$$3(NH_4)_2O \cdot P_2O_5 \cdot 18WO_3$$

which indicates the same degree of basicity as that shown by the 24-acid.

Structure of the Complex Acids. Very significant and valuable contributions, based on X-ray studies, have been made by Pauling (102) and Keggin (77), and rather fully reviewed by Emelius and Anderson (43) and by Gardner (52). This recent work has shown the above 24-acids to be tribasic complex 12-acids of structures $H_3(PW_{12}O_4)$, $H_3(PMo_{12}O_4)$, etc. Simple dye salt formation thus will not explain the complete structure of these pigments. Undoubtedly, some of the dye molecules are coordinated with the complex acids in producing these dyes and pigments.

Phosphotungstomolybdic Complex Pigments

On the basis of the foregoing discussions of the chemical characteristics of the basic dyestuffs and the complex phosphotungstic and phosphomolybdic acids, it is now possible to consider the nature of the reactions which enter into the formation of the pigment colors resulting from their union.

The following is a typical preparation of such a pigment, using the basic dyestuff Crystal Violet.

Dye Solution. Dissolve 10.1 parts of Crystal Violet in 5000.0 parts of water containing 2.0 parts of 70 per cent acetic acid, maintaining the temperature at 120° F.

Complex Solution. Prepare the complex acid separately as follows: Dissolve 15.0 parts of sodium tungstate, 5.0 parts of sodium molybdate, and 3.4 parts disodium phosphate in 1000.0 parts of water at 60° C. Add 13.0 parts of concentrated HCl.

Precipitation. Run the complex solution, under agitation, into the dye solution at a uniform rate in 15 minutes. Heat to boiling. Allow to cool partially. Filter. Wash free of acid and salts. Dry. This example may well serve as the basis for the following discussion of the reactions and factors involved in the preparation of phosphotungstomolybdic complex pigments in general.

Crystal Violet was selected not because of its importance or significance as a commercial product but because it possesses a rather symmetrical structure and contains three substituted amino groups that may be regarded as available for reaction. A critical examination of the above directions will reveal that the following conditions exist.

1. Dye Solution. The original dyestuff contains approximately one mole of combined hydrochloric acid, and a further addition of slightly over one mole of acetic acid has been made. It is therefore probable that the dye is present in the warm solutions, at least partially, in the form of the salt of two of the basic groups. The percentage of the color present in this form is rather in doubt, owing to the ease of hydrolysis of the acetic acid salt and the increased hydrolizing influence of the elevated temperature.

2. The Phosphotungstomolybdic Complex Solution. Inasmuch as the final mixture is decidedly acid with excess hydrochloric acid, it is very probable that the complex solution, as prepared, is made up mainly of the 1 to 24 complex acid. Owing, however, to somewhat elevated temperature, the presence of small amounts of the 1 to 18 complex acid may be expected, as well as appreciable amounts of tungstic acid, molybdic acid, and phosphoric acid which are not quantitatively combined to form the complex. And it is of interest in this connection to note that all these acids are capable of precipitating basic dyes under suitable conditions.

3. Formation of the Pigment. Precipitation starts almost immediately with the first addition of complex solution, and is complete before the addition is finished. The only change noted, during or after the final heating, is a slight alteration in the rate of settling or a change in the flocculation of the precipitate.

It is quite logical to assume that the salt formed by a complex acid and a triacid base may not under all conditions be represented by the same chemical individual, but that variations in acidity, concentration, and temperature, for example, might increase or diminish the tendency toward complete satisfaction of all the acid groups in the complex acid and the basic groups in the basic dye molecule.

Allen (4) has proposed a very interesting structure, based upon the principle of coordination valencies, to represent such a typical pigment color. It should prove very useful in stimulating speculation in this direction. The structure is shown in Fig. 24. This structure is based on the assumption that the acid groups of the complex acid are completely neutralized and that but one basic group in each molecule of basic dyestuff enters into salt formation. Such a result appears entirely possible in the initial precipitation, owing to the fact that the basic dyestuff is in excess during that period. However, during the later

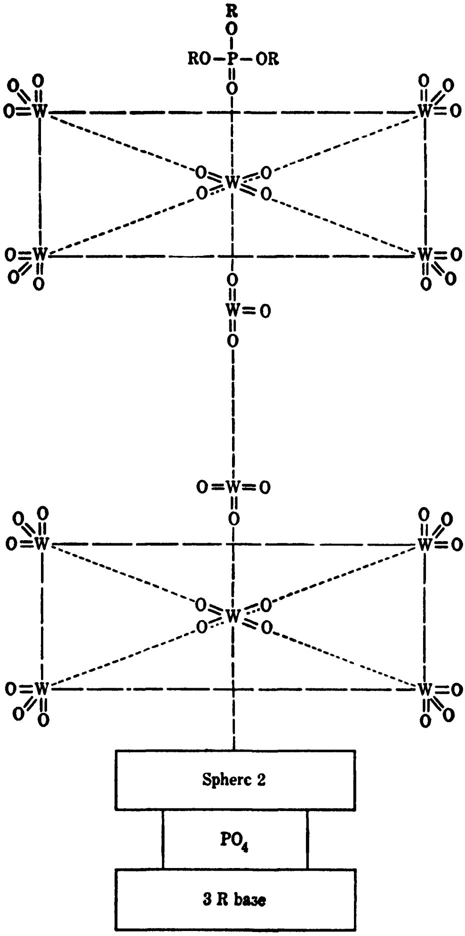
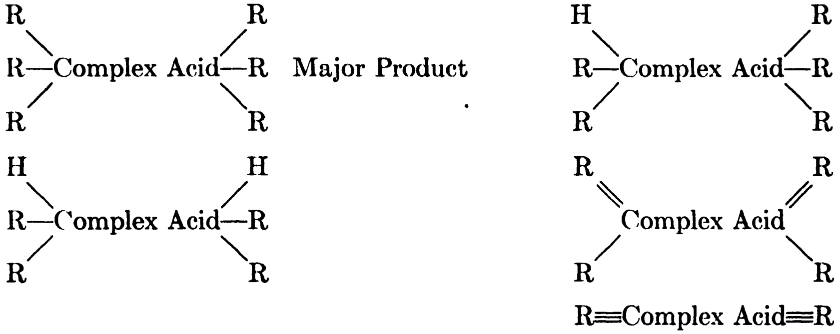


Fig. 24. Basic Dye Phosphotungstic Complex. (*Courtesy of E. R. Allen, Technical Director, Pigment Division, E. I. du Pont de Nemours & Co., Newark, N. J.*)

part of the precipitation and the heating period the excess complex acid and the excess of the simple acids have an opportunity to bring about changes in the initial structure that may be of definite significance. For example, the pigment color undergoes modification, which results in increased permanency to light, diminished tinctorial strength, and increased yield of the final product.

Some of these changes are unquestionably physical in nature; others appear to be definitely chemical. Physical change is evidenced by more rapid settling, greater ease of filtration, and progressively softer texture, whereas in this case a chemical change is quite definitely indicated by a slight increase in the weight of the final product. Similar changes can be caused in other ways. For example, an increase in the acidity or increase in the amount of complex acid used will alter results in the same direction.

In the original precipitation it is conceivable that materials of the following type may be represented in the insoluble pigment suspension:



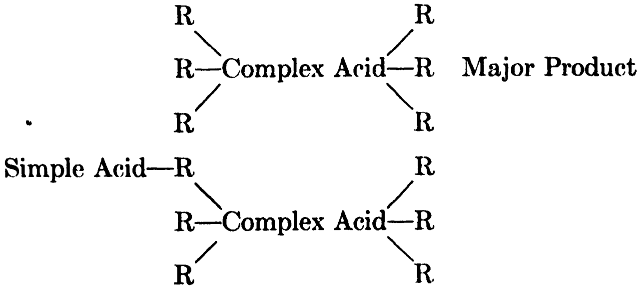
R— simple tungstate

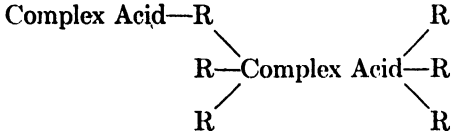
R— simple molybdate

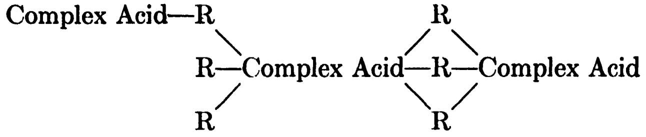
R— simple phosphate

It is readily seen that the structures indicated represent only a small fraction of those possible of consideration, from a structural standpoint; but with almost a complete lack of direct evidence it is hardly desirable to complicate the treatment further.

It is then possible that the influence of heat in the presence of an excess of the precipitating agent may result in the formation of a mixture containing varying amounts of the following types:







Changes of this nature could readily account for many of the facts known about pigments in this classification. It is, however, unfortunate that analytical information, sufficiently accurate and reliable to establish the true conditions, is not available. It is, however, quite clear that rigid theoretical or stoichiometric relations cannot be assumed in reactions as complex as those under discussion.

In practical manufacture of these pigments rather definite relations are established between the amounts of complex used with the various dyestuffs, which may to some degree depend upon the molecular weight of the dye or the number of free or substituted amino groups, but the significance of the figures is to a considerable degree questionable. If a standard type of product were made from each basic dyestuff by all producers, these figures would possess real significance. As a matter of fact, a wide variety of products can be and are made from the same dyestuff, with varying proportions of reacting materials and various conditions of operation, the different products having particular values for special uses. It is therefore next to impossible to establish what are often loosely referred to as "optimum conditions," as those which might be considered perfectly satisfactory for one type of product will be definitely undesirable for another, the desirable characteristics of which may be very different from those of the first.

Straight Phosphomolybdate Pigments

In 1937–1938 the Sino-Japanese War and disturbed European conditions, culminating in 1939 in the outbreak of World War II, caused a sharp rise in the price of tungsten, which is notoriously sensitive to military influence. This is reflected in the diagram (Fig. 25) of the world production and price of tungsten ore yearly from 1909 to 1943, inclusive, taken from the chart prepared by the Wah Chang Trading Corporation through the courtesy of Mr. K. C. Li.

A threefold increase in tungsten production followed the discovery of tungsten in China and during the high demands of World War I.

The depression of 1920–1921 reduced production to prediscovery levels, which persisted at low values until disturbed conditions prior to 1939 again brought about a sharp rise in the curve. The price of tungsten has shown only one instance of extreme rise, which reached its peak in 1916 during World War I.

A natural consequence of these increased values and material shortages of tungsten was a greatly increased interest in the use of molybdenum and the production of straight molybdate pigments (92). To a certain degree the fact was overlooked that for several years molybdenum had been lower in price than tungsten and that during that time the contents of molybdenum in the mixed tungsten-molybdenum pigments had been raised to the highest points believed to be consistent with desirable quality.

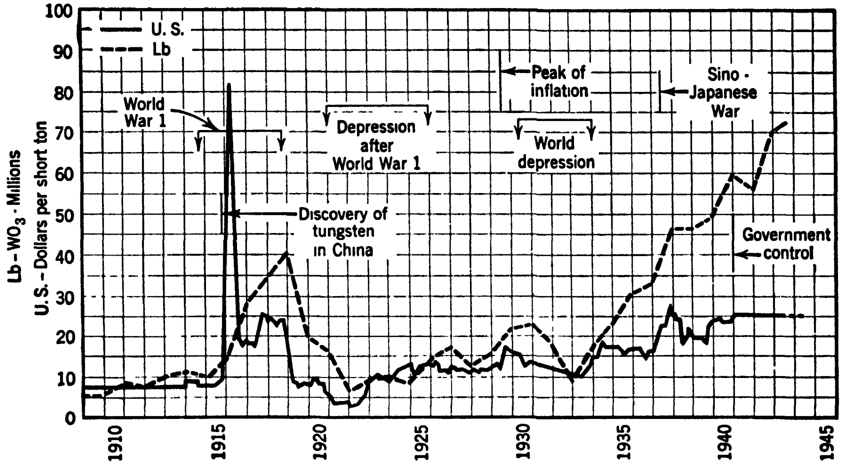


FIG. 25. Tungsten Ore—World Production. (*Courtesy of Mr. K. C. Li, Wah Chang Trading Corporation.*)

In general the properties of these materials are modified in desirable directions up to certain percentages of molybdenum, beyond which certain less desirable features appear. However, it is equally true that for certain purposes straight molybdic types may be desirable and perhaps even more desirable than the straight tungsten or mixed products.

It would appear to be the logical procedure, therefore, as a future policy, to study primarily the uses to which the straight molybdate products may be put advantageously rather than to attempt the complete replacement of tungsten for all purposes. The effect of increasing percentages of molybdenum in a typical pigment preparation is described here.

The straight tungstate may show a very decided fading under a certain definite condition of exposure to light. With increasing percentages of molybdenum, the degree of fading is steadily diminished up to a point (varying from 5 to 60 per cent of molybdenum, depending on the dyestuff used), at which, instead of fading or actual loss of color depth, the exposure begins to show a definite darkening. Beyond this point the darkening becomes more and more pronounced, with progressive loss of brilliance in the exposed color.

Simultaneously with the above changes a steadily increasing strength or tinctorial power of the product is noted, which is, however, almost directly offset by decrease in the yields of pigment obtained.

Intensive study of the effects of *p*H control, concentration of solutions, temperatures, and proportions of reacting materials will make it possible, undoubtedly, to employ larger proportions of molybdenum and will lead, conceivably, to complete replacement of tungsten. Present information, however, points quite clearly to the conclusion expressed by J. E. Loughlin (93) that the phosphomolybdic lakes and toners must not be considered as substitutes for phosphotungstates but should be considered and treated as a distinct line of colors.

Comments on Manufacture. In the manufacture of phosphotungstic, phosphomolybdic, and phosphotungstomolybdic pigments certain factors must receive consideration.

Solubility of the Basic Dyestuffs. A considerable variation exists in the solubilities of the basic colors. Some are readily soluble in the form of their normal commercial salts in cold water up to the percentages required in manufacture. Others require the use of more dilute solutions and higher temperatures for satisfactory results, and a few show a tendency to come out of solution or form a gel if the temperature falls below certain values.

Desirable conditions must be established for each dyestuff employed. In general, favorable results are obtained by adding acetic acid to the dye solution. In this case, again, each individual dyestuff must be studied to establish the most favorable conditions.

Complex Acid Solutions. An extremely wide range of possible variations appears in this step of the operation. A straight tungstate, a straight molybdate, or a mixed precipitating agent may be used. In addition the *p*H of the solution may be widely varied as well as the concentration. These conditions must be definitely established on the basis of the type of product desired. For example, permanency toward light is favored by increasing proportions of molybdate up to a certain point, which must be determined, by increasing the acidity or lowering the pH of the solution, and by increasing the actual amount of the precipitating agent used.

Strength or tinctorial power is favored by increasing proportions of molybdate, by decreasing acidity or higher pH, and by decreasing the actual amount of precipitating agent used.

Texture, as a rule, is improved by decreased amounts of molybdate, increased acidity, and increased amounts of precipitating agent.

Higher yields are favored by increased proportions of tungstate, increased acidity, and increased amounts of precipitating agent.

These are general conditions and their effects are subject to modification by other conditions affecting the operations.

Temperature of Precipitation. As a rule the precipitations are made at temperatures sufficiently elevated to insure complete solution of the dyestuffs. Aside from this restriction, higher precipitation temperatures favor increased permanency to light, decreased strength, and increased yields.

Heat Treatment. Heating of the batch after precipitation to higher temperatures brings about very definite and marked changes in the nature of the final pigment. Marked increase in permanency is noted, as well as loss in strength, increased yield, and improved texture. The extent of the heat treatment to be adopted must depend definitely on the type of product being developed.

Filtration, Washing, and Drying. These operations are essentially normal for colors of this type, except for those of a decidedly colloidal nature, in which cases special precautions may be required.

Grinding. As a group these pigments are not to be classed among the products of soft texture, and some are decidedly hard. They show a rather universal sensitivity to dry grinding. Losses in strength depend on the fineness of the grinding, and also to a considerable extent on the hardness of texture of the particular color, the harder products showing greater losses than those of softer texture.

Conclusion. It is evident from the above that a very great variation in the properties of these materials is possible, and it is this characteristic which has contributed much to the usefulness of these pigments in a wide variety of fields.

Preparation of Lakes. In the manufacture of lakes or reduced colors the usual practice is to prepare the toner or full-strength color and then add the desired base, such as blanc fixe, gloss white, or clay, previous to pressing. This procedure is desirable owing to the loss of permanency toward light in those colors made by striking the color directly on the base.

USES

Extension of the use of the phosphotungstic and phosphomolybdic pigments has been retarded to a very considerable extent in the past by their relatively high prices. This situation, however, has been corrected in some degree, and the desirable characteristics of the products have encouraged an ever-broadening demand in a great variety of the color-consuming industries.

The printing ink industry probably represents the field of greatest interest and use, but the paint, enamel, rubber, wax, and paper industries all use appreciable quantities of these materials.

Printing Ink (144)*

The phosphotungstic acid toners and lakes form a very valuable series of pigments for use in printing ink. They are much more resistant to the action of sunlight, alkalies, heat, and water than the lakes produced from the same dyestuffs by precipitation with the usual tannic acid-tartar emetic mixture.

The high cost of the concentrated basic dyestuffs and the sodium tungstates and molybdates used in the preparation of the tungstated colors makes their cost per pound rather high. However, considering their brilliancy and permanency and the amount of reduction they will stand, they are relatively inexpensive pigments. A short description of the more important of these colors follows.

Permanent Blue Toners.

Victoria Blue. A small amount of alumina hydrate is generally added to improve the working and grinding qualities of the toner. This toner is very resistant to the action of light, receiving a rating of approximately twelve on the permanency scale in which madder lake is taken as twenty or eosin as one. Even when considerably reduced the pigment still possesses good resistance to light. It is insoluble in water, oil, and hot paraffin, but is somewhat soluble in alcohol and acetic acid. It is fairly resistant to the action of dilute acids and alkalies and may be used in the manufacture of alkaliproof (not necessarily soap-proof) inks. It is a good lithographic and offset ink pigment and is also suitable for use in tin printing inks as it will stand baking at the usual temperature of 270° F for 20 minutes without discoloration. It is a rather difficult pigment to grind and is likely to produce short-bodied inks unless it is ground in rather long vehicles or reduced considerably with alumina hydrate or gloss white. It is a slow-drying pigment.

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* The discussion on pages 170 to 172 is based largely on the work of Herbert J. Wolfe. Adapted with permission.

Rhoduline Blue (*Setoglaucine*). Generally some base, such as alumina hydrate, is incorporated with the toner to impart body and working qualities to the resulting pigment. This pigment is generally greener in hue and less brilliant than the fugitive Peacock Blues derived from Erioglaucine, although the deficiency in brilliance is now less pronounced than formerly. These products are not in reality highly permanent colors, as they rapidly become duller and darker, and eventually fade on exposure to sunlight. The advantage they possess over the Erioglaucine lakes lies in the fact that they darken before they bleach and therefore keep up the appearance of intensity of color even though the original hue has changed. The pigment is practically insoluble in water and may be safely used in lithographic and offset inks. It will also withstand baking at a temperature of 270° F for a period of 20 minutes without serious change of shade, and hence may be used in tin printing lacquers. It is insoluble in oil and hot paraffin and is unaffected by exposure to weak alkaline solutions. Strong acids and alkalies quickly destroy the color. It is somewhat soluble in alcohol and similar solvents. It is rather slow-drying.

Permanent Green Toners. Several types of green toners appear in the trade, some made from Malachite Green, some from Brilliant Green, and others from various combinations of Malachite Green, Brilliant Green, and Thioflavin or Auramine. These products are relatively fast to light, water, oil, hot paraffin, and alkalies. Dilute acids do not affect the colors although strong acids turn them yellow and finally destroy them altogether.

Like the permanent blues, these colors are rather hard to grind and are poor driers. They are, however, excellent pigments for use in lithographic and offset inks and will withstand baking at the usual temperatures met with in practice, in common with other colors of this type. They find wide application in glassine and cellophane inks because of their brilliancy and great tinctorial strength.

Permanent Red Toners.

Rhodamines. In both the manufacture and the use of the permanent rhodamine pigments great care must be exercised to prevent contamination with other less brilliant colors, as their chief value lies in their brilliancy and cleanness of hue. They are somewhat easier to grind than the other phosphotungstic colors, but in most respects they resemble the others very closely.

Magenta. This product is used more especially for shading or modifying the other materials in this class.

Permanent Violet Toner. This pigment is not, strictly speaking, a permanent pigment. Its permanency rating, on the scale of madder lake as twenty and eosin as one, is approximately ten.

The pigment darkens and blackens on exposure before it actually fades. It is insoluble in water, oil, and melted paraffin. It is fairly alkali-resistant and also withstands the action of dilute or weak acids. Strong acids quickly destroy the color. As with the other colors of this class, it is rather difficult to grind and is likely to produce short, buttery inks unless it is ground in a long vehicle or considerably reduced with gloss white or alumina hydrate. It is a crystalline pigment, which accounts for its high bronze and hardness. The pigment is a poor drier and tends to powder off the stock, which is another good reason for grinding it in a long binding vehicle.

Paint

The phosphotungstic and phosphomolybdic complex pigments are not used for outside paint work because of an insufficient degree of permanency toward sunlight and also because of a tendency toward intensive checking of the films during outside exposure. For inside work, however, many of these pigments are of value if used in rather high color concentrations.

Rubber

For satisfactory use in rubber it is essential that a pigment possess a very soft texture. In milling the pigment into rubber, no real grinding action takes place, but the shearing action between the rolls tends to cause the rubber to stretch and flow. In this process the pigment is progressively pulled apart. Pigments for use in rubber should, therefore, be especially prepared to exhibit extreme softness. Such products may possess very poor color values and working characteristics, when tested in the usual way in varnishes and oils, but the color values and tinctorial power, in rubber, will be greatly improved.

Paper

The type of pigment required in the tinting and shading of paper bears little resemblance to those employed in other branches of pigment use. In many respects it more closely resembles the form of the soluble dyestuff. For example, when a pigment of this type is placed in water it disperses quickly to form what appears to be a true solution, from which the pigment does not settle out, or only very slowly.

The preparation of these products involves highly specialized operations, particularly in the finishing stages. But it is of primary interest at this point to emphasize the necessity of forming the products in a state of unusually high dispersion. This, of course, results in difficulty in normal filtration operations, but control of the dispersion can be maintained at such a point that final products of useful characteristics can be obtained under practical working conditions.

Dispersion of suitable type and degree can be achieved in various ways, such as by employing efficient agitation, fairly high dilution, not too rapid rate of precipitation, low excess of complex, mild heat treatment, and a minimum quantity of a suitable dispersing agent.

The final washed material may be obtained as a dry product by incorporation into a mixture of water-soluble material such as sugar or dextrin, with, possibly, the addition of further dispersing agent, or it may be treated with a suitable dispersing agent and then dried.

BASIC COLOR PIGMENTS, NON-PERMANENT TYPE

The basic dyestuffs have been used for a great many years, in the form of fugitive lakes and toners, for such purposes as wallpaper printing, surface coating of paper, distempers and kalsomines, and for the manufacture of carbon paper and typewriter ribbons. The last uses are still important but the others have largely disappeared.

The basic colors themselves, as employed in textile dyeing, are fugitive to light and rather sensitive to washing. When they are precipitated in the form of fugitive lakes and toners, the same disadvantages exist. Such precipitations are brought about by treating the dye solutions, which may or may not contain inert material such as alumina hydrate, gloss white, blanc fixe, barytes, whiting or clay, with solutions of tannic acid or tannin, quebracho extract, tannic acid and tartar emetic, rosin soap, fatty acid soaps, sulfonated oils, synthetic tans such as Tamol and Katanol, green or white earth, phosphates, casein and arsenious acid.

As a class these products are very brilliant in tone, and strong, but fugitive to light, sensitive to washing and to organic solvents such as alcohol, and, if dried, of a generally hard texture. Many have been used in the past only in the form of pulp colors.

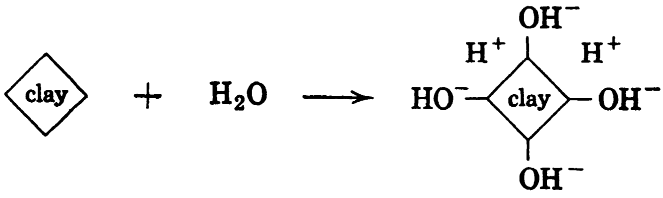
Earth Lakes

Green earth is a natural material made up largely of silicates that are in a form suitable to favor absorption of basic dyestuffs. White earth is a somewhat similar material of a brighter, cleaner appearance but possessing a lower power of absorption than green earth.

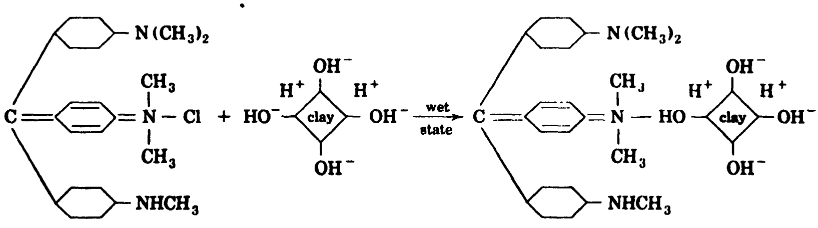
In the preparation of green earth lakes the dye solution is run into an agitated suspension of green earth in an amount that will be completely absorbed. The lake is then filtered and washed, and may be dried if necessary. Green earth lakes are, as a rule, rather low in strength, containing only 3 to 5 per cent of actual dye. Their permanency toward light is somewhat better than that of the straight basic colors, but they are still in the highly fugitive class.

The mechanism of dye absorption by white and green earths may be compared with the mechanism in the absorption of basic dyes on primary and secondary clays suggested by Kress and Trucano (84).* Reaction I indicates a colloidal dispersion of the clay: it acquires an overall negative charge by preferentially adsorbing hydroxy ions from the slurry. Reaction II shows the formation of the moist Methyl Violet pigment from the reaction of clay, water and dyestuff.

Reaction I

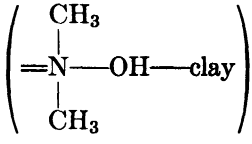
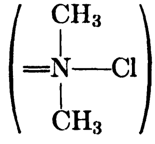


Reaction II



Methyl Violet

Pigment

The resulting pigment has a new bond linkage  $\left(=\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{N}}\text{——}OH\text{——}\text{clay}\right)$ in its structure instead of the original  $\left(=\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{N}}\text{——}Cl\right)$ linkage of the dyestuff. The resonating action of these two linkages will be different and therefore will give curves of different characteristics, as shown in

---

* Reactions I and II reprinted with permission from the *Paper Trade Journal.*

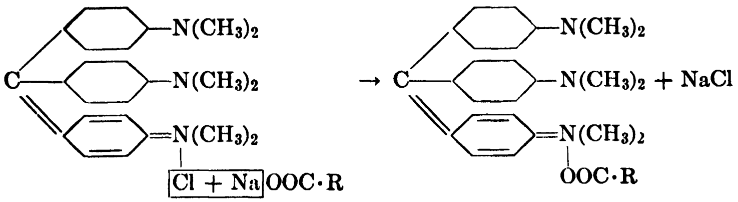
the experimental work. Upon air-drying the pigment, the water is evaporated from the surface of the clay particles, causing a shift in the equilibrium reaction. A compound is formed similar to the original dyestuff, which is deposited on the clay surface. The dry pigment will give a reflection curve characteristic of the original dyestuff.

This method of lake formation has been largely superseded by those giving products of greater uniformity and stability.

Fatty Acid Lakes

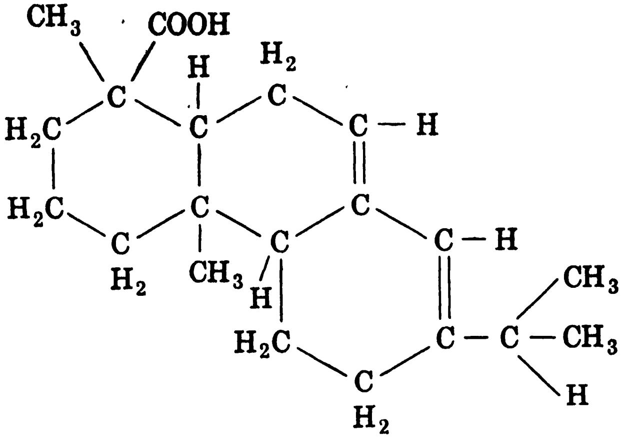
In the preparation of fatty acid lakes and toners the fatty acid, such for example as stearic or oleic acid, in the form of an alkaline soap solution, is run into the dye solution under agitation. One objectionable feature in this operation is the tendency toward frothing which at times causes much inconvenience. After a suitable period of stirring, and possibly gentle heating, the precipitate is filtered off, washed slightly and then held in pulp (paste) form. The products are generally used in pulp form and are very brilliant. Being entirely organic in composition, they bleed badly in oils and in contact with other organic solvents, a feature which is very troublesome. These products are now rarely used.

The mechanism of pigment formation appears to be a simple salt formation between the fatty acid and the basic dye molecule:



Basic Dye Fatty Acid Soap Fatty Acid Pigment

Rosin soap products are handled in a very similar way and possess most of the advantages and the objectionable features of the fatty acid lakes. Rosin is composed chiefly of abietic acid, which is insoluble in water, soluble in alcohol, and readily forms the soluble alkali salts or soaps with alkali hydroxides or carbonates. The generally accepted structure is:



Abietic Acid

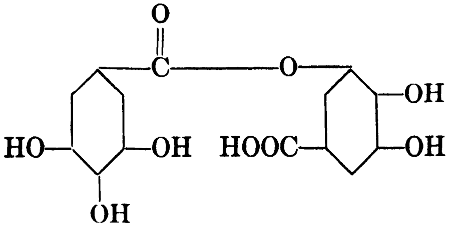
Arsenious Acid Lakes

The arsenious acid lakes were formerly used to a considerable extent in the printing of bright patterns in wallpaper, but, because of their poisonous nature, this practice was discontinued many years ago. In the preparation of these materials, arsenious oxide was dissolved in hot sodium carbonate solution to give sodium arsenite, and this was added to the dye solution under agitation, or, in some cases, the reverse feed was employed. The products were used largely in pulp form.

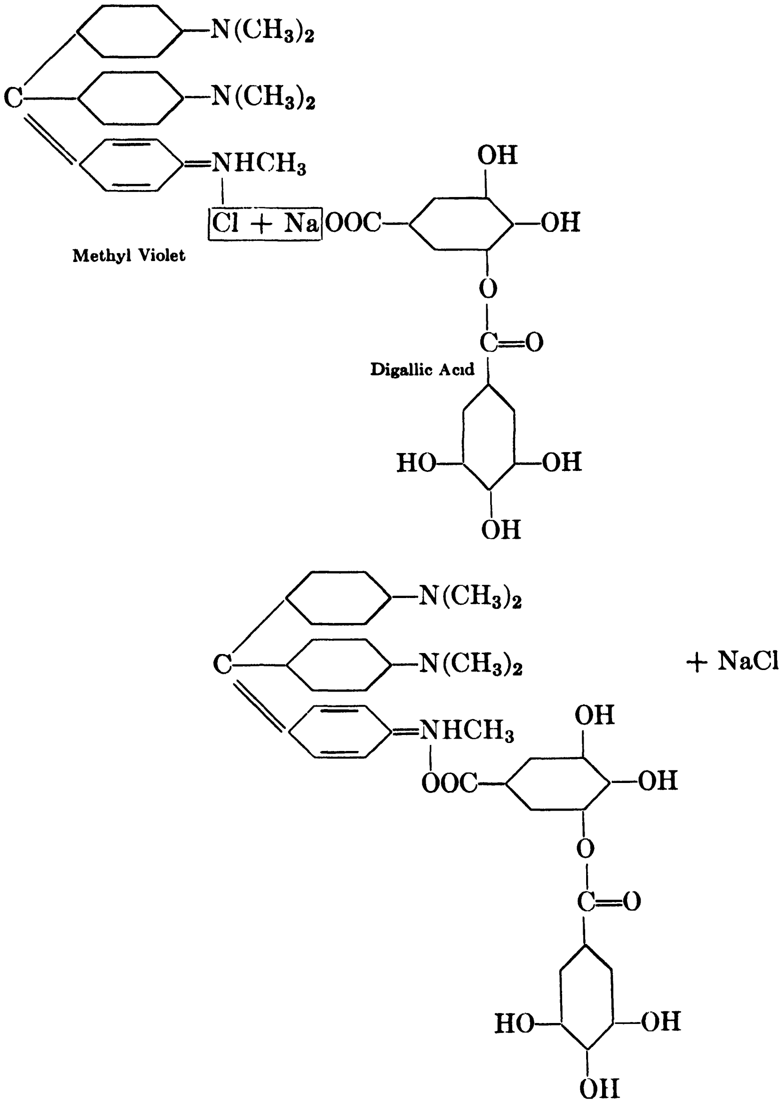
Tannic Acid Lakes and Toners

The tannic acid-tartar emetic type of basic color lakes and toners is of major importance at the present time. These materials are used in considerable quantity in the manufacture of carbon papers and typewriter ribbons. The color of primary importance in this field is made by using Methyl Violet. The Methyl Violet solution is treated with a solution of tannic acid, or tannin, sufficient nearly to complete the precipitation of the dye. A solution of antimony salt, such as tartar emetic, is then added and the precipitation becomes complete. The product is filtered, washed, and dried. In order to lower the cost of manufacture, quebracho, in powder or extract form, may be employed in place of tannic acid or tannin.

The chemistry involved in the formation of the tannic acid lakes is not entirely clear, but it appears to involve (1) the reaction between tannic acid and the basic dye molecule, probably in a mechanism similar to that involving the fatty acids, and (2) the reaction between the antimony salt and the tannic acid portion of the pigment molecule. The active constituent of tannic acid is generally regarded as digallic acid, which is a major constituent of tannins:



(1)

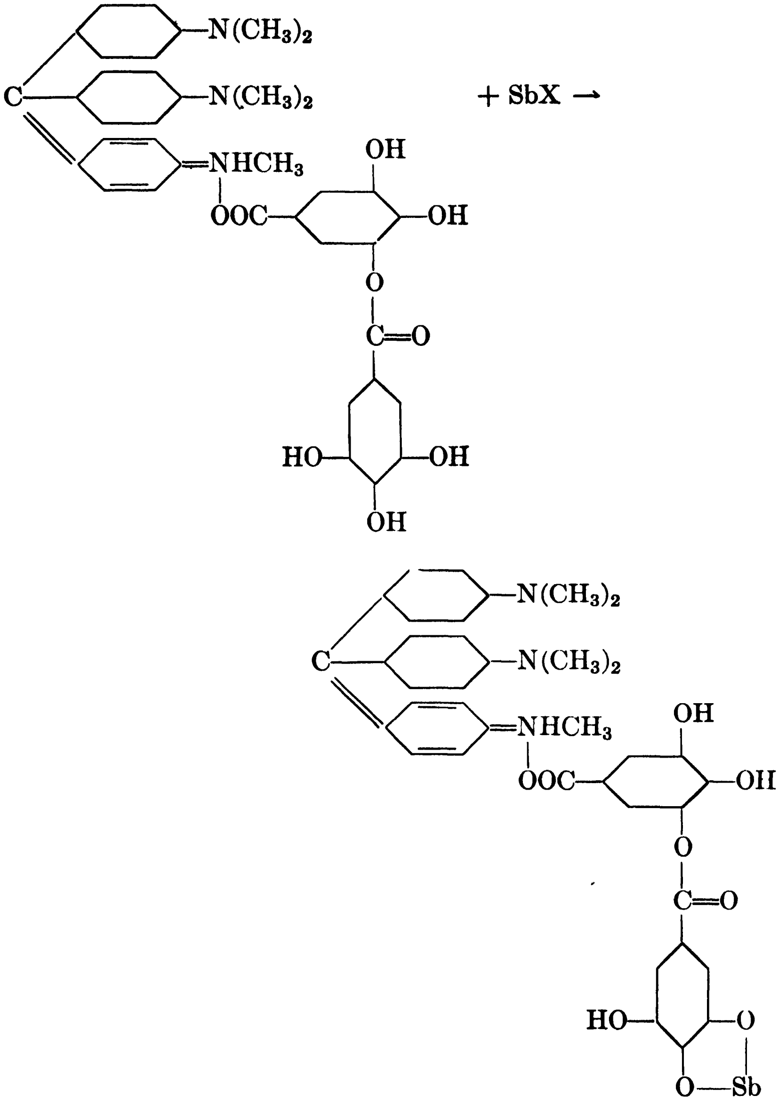


Methyl Violet

Digallic Acid

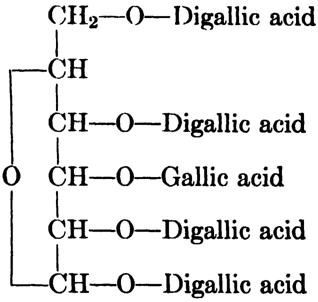
Dye-Digallate

(2)

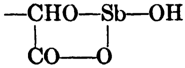


Antimony-Dye-Digallate

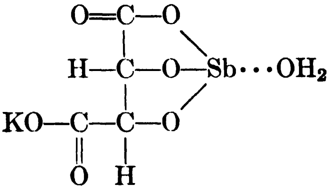
Chinese tannin (75) is a mixture of compounds of glucose with varying numbers of gallic acid and digallic acid molecules. The five hydroxyl groups of glucose are replaced by gallic acid, *m*-digallic acid, or possibly trigallic acid residues. On the average each sugar molecule has nine gallic acid residues. The varying nature of the tannin is largely due to the presence of glucose molecules galloylated to different extents and in different ways. The structure * of such a component might be somewhat as follows:



The above reaction with an antimony salt, such as tartar emetic, is used only to illustrate the combination of the three ingredients, dye, tannic acid, and antimony, to form the pigment. At the present time the antimony is considered to be held in the form of a complex by the free hydroxyl groups. According to Whitmore (141):†

> Tartar emetic is usually formulated as potassium antimonyl tartrate,
>
> $$KOOC(CHOH)_2COOSbO \cdot \frac{1}{2}H_2O$$
>
> It is difficult to believe, however, that the hydroxyl groups take no part in the formation of the compound. It would seem more reasonable that a ring,
>
> 
>
>
> is involved.

Recent studies by Reihlen and Hezel (111) indicate that it is a coordinated compound having the structure:



The presence of the antimony salt improves the brilliance and physical properties of the final pigment and appreciably decreases its tendency to bleed in various vehicles.

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ACID DYE PIGMENTS OF THE BASIC TYPE

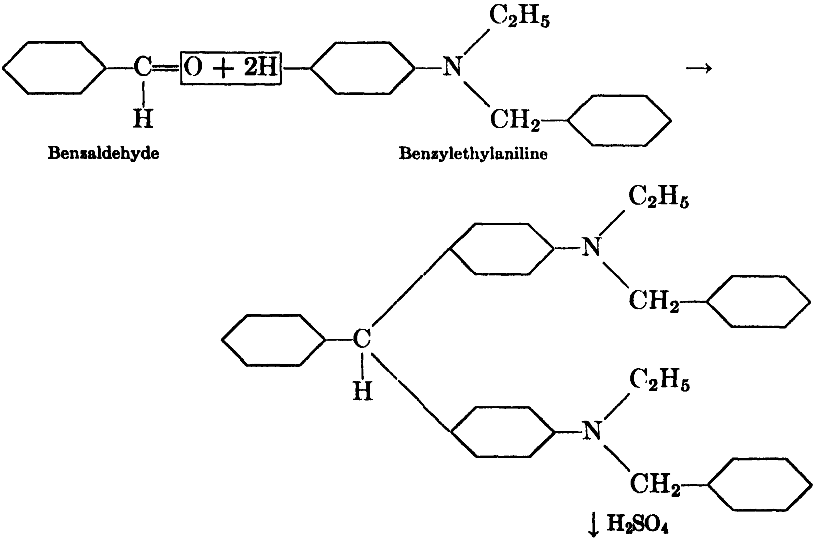
The acid dye pigments of the basic type are those which are made from dyestuffs largely of the di- and triphenylmethane class, containing both amino, or substituted amino groups, and sulfonic acid groups. As a class, these dyestuffs, and the corresponding pigments, are very brilliant and of great tinctorial power but, being closely related to the basic dyestuffs, are quite fugitive toward light, and decidedly sensitive to alkalies, which greatly detracts from their usefulness.

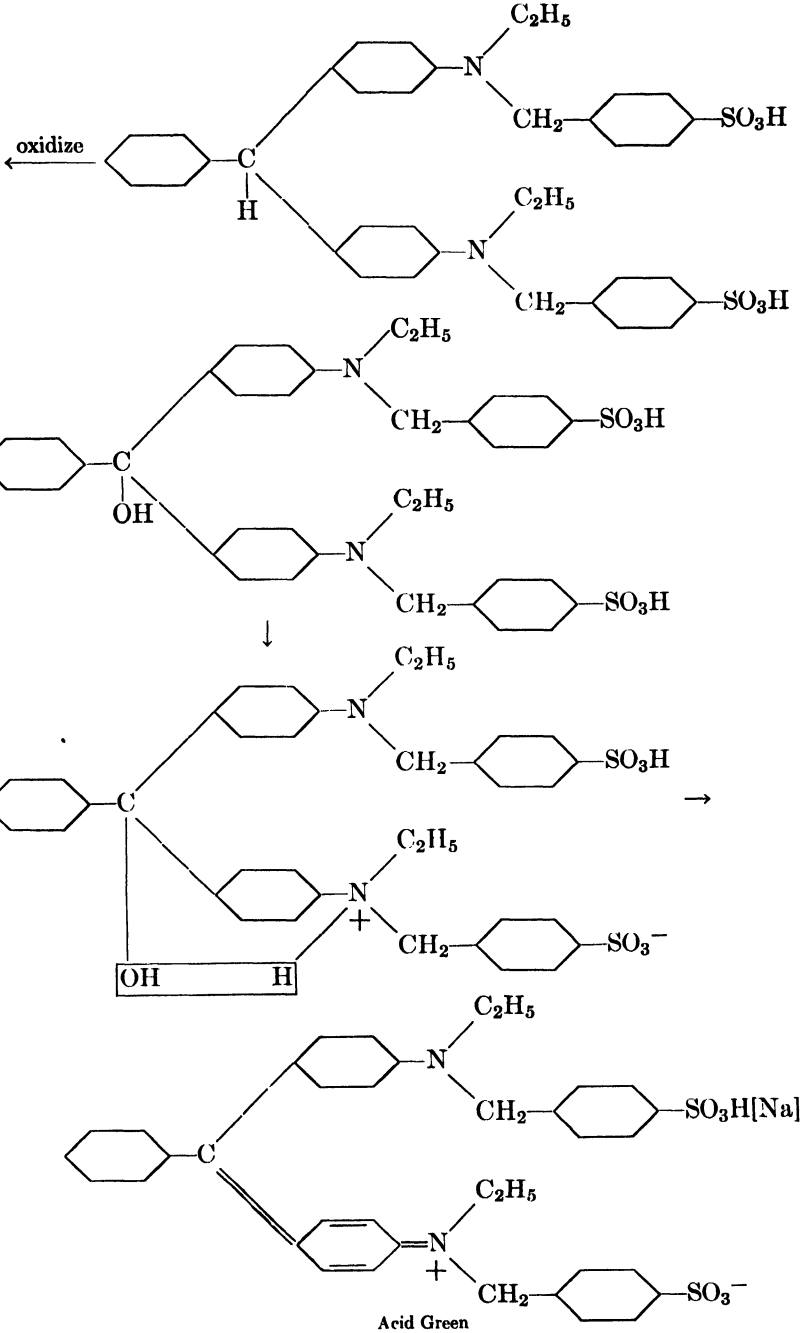
Most of these products contain more than one sulfonic acid group and are therefore very soluble in water and difficult to precipitate, the difficulty being in direct proportion to the number of sulfonic acid groups present. In the majority of cases it is impossible to prepare toners, or full-strength colors, as an absorbing base, such as alumina hydrate, is required to permit complete precipitation.

Three groups of these pigments have been found of real importance commercially, those prepared using Acid Green, those from Alphazurine or Erioglaucine, and those from Alkali Blue.

Acid Green Pigments

The Acid Green pigments are made to cover a range from the deep blue type obtained from straight Acid Green to the light clean yellowish green type made by using combinations of Acid Green and various yellow acid dyestuffs, such as Quinoline Yellow, for example. Acid Green is made by condensing benzaldehyde with *n*-benzyl-*n*-ethylaniline and sulfonating the product. Oxidation then yields the dyestuff:





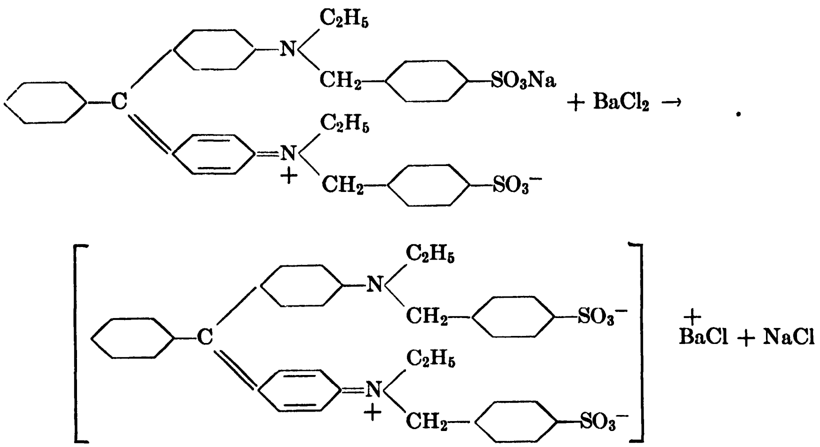
Acid Green
C.I. 669
Sch. No. 504

The dyestuff is here indicated with the "Zwitterion" or inner salt structure.

The lake is usually formed by precipitating the dyestuff on an absorptive base such as alumina hydrate or gloss white. As pointed out previously, the character of the pigment may be altered to a considerable degree by modifications in the preparation of the base. For example, the oil absorption, texture, strength, bleeding, and general working properties in vehicles can be varied over a rather wide range, depending on the nature of the base used.

Generally the base is prepared separately and well washed to eliminate soluble sulfates which would otherwise introduce blanc fixe into the final lake. The dye solution is added to the base suspension and then an excess of metal salt, such as barium chloride, added. Within a short time the dye is almost completely precipitated, but a longer period gives a more thorough and complete absorption of the soluble or dispersed color by the hydrate base. The product is then filtered, washed, dried, and ground to a fine powder.

The exact mechanism of metal salt formation is not fully established, but it may be represented as follows:



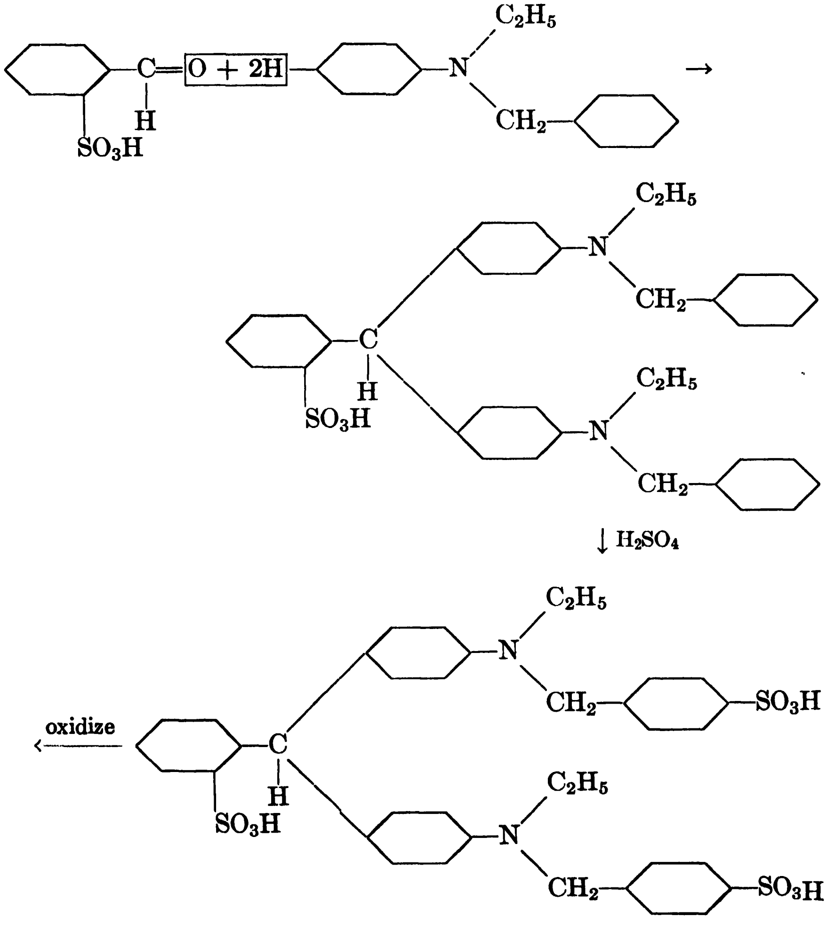
A lake of this type is quite sensitive to alkalies and to light, but, in spite of these deficiencies, very large amounts of these products have been used in the past. At the present time they are being used in only small amounts because they have been replaced by colors of better fastness and bleeding properties.

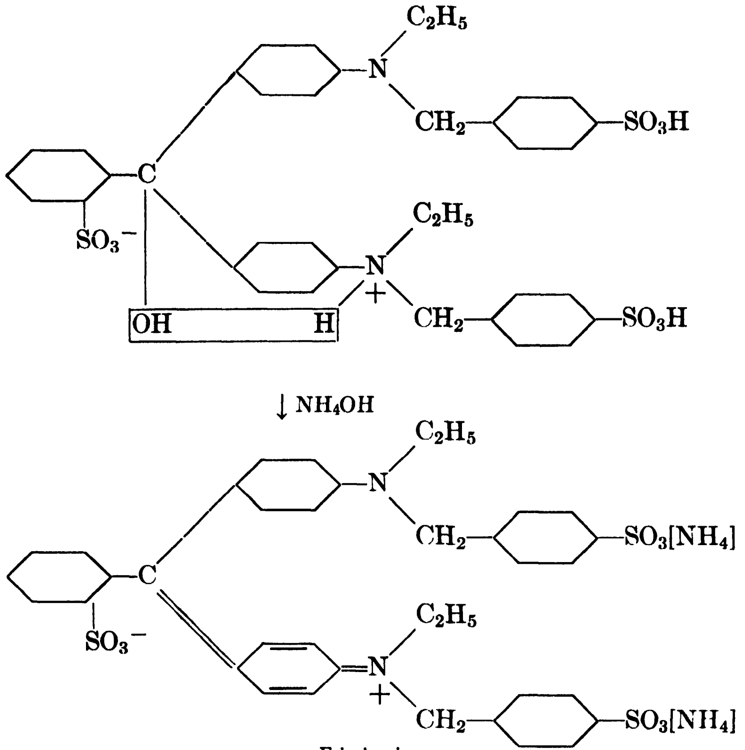
The lakes of yellower type, containing yellow lakes in conjunction with the Acid Green lakes, are, in general, made like the above, with mixtures of the green and yellow dyes. The final products show the same disadvantages, although sometimes to a less degree, as those indicated above.

Peacock Blue Lakes

The Peacock Blue lakes have been used commercially for many years in spite of their very low resistance to light and very marked sensitivity to alkalies. They are made from the dyestuff Erioglaucine, also known as Alphazurine and Patent Blue.

Erioglaucine is prepared by condensing *o*-formylbenzenesulfonic acid (benzaldehyde-*o*-sulfonic acid) with *n*-benzyl-*n*-ethylaniline, sulfonating, oxidizing, and converting to the ammonium salt:





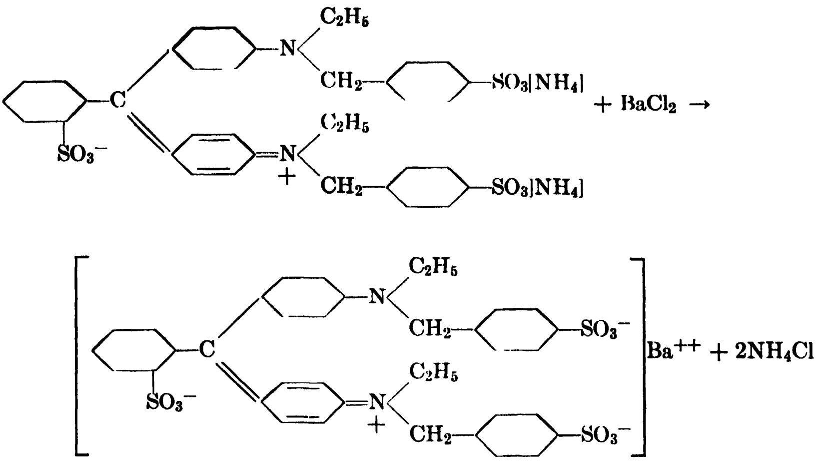
Erioglaucine

C.I 671
Sch. No. 506

The Peacock Blue lakes are generally formed on straight alumina hydrate base rather than on a gloss white, owing to the necessity of having a high power of absorption to accomplish a nearly complete precipitation of the dye. The type of hydrate base to be used is determined in each case by the type of lake desired.

Precipitation of the dyestuff can be accomplished with barium chloride, and sometimes with aluminum chloride, with or without the addition of Turkey Red oil.

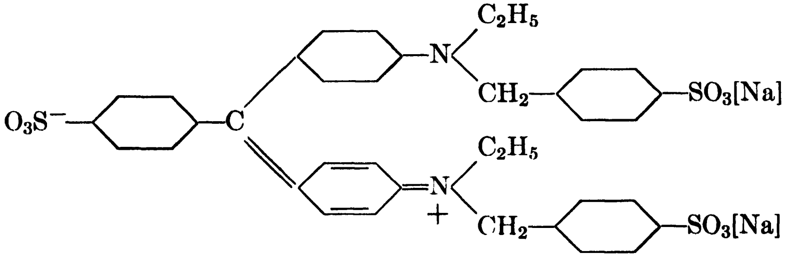
Lake formation, disregarding the hydrate base, may be represented as follows:



The product is not sufficiently insoluble to precipitate completely, but in the presence of alumina hydrate the amount of color in solution steadily decreases until only a very slight stain remains. The pigment may then be filtered off, washed, dried, and ground in the usual way.

Peacock Blue lakes are made with a considerable variation in strength, the usual range being 10 to 30 per cent of actual dyestuff. The weaker lakes show less tendency to bleed when in contact with water, or fountain solution in printing, but they have a greater tendency to liver in ink on storage. They are typically unstable in alkaline solutions, or large volumes of water, owing to the ease with which the barium in the lake is replaced, thereby restoring the soluble form of the dyestuff.

Another very similar dyestuff is Light Green SF Yellowish:

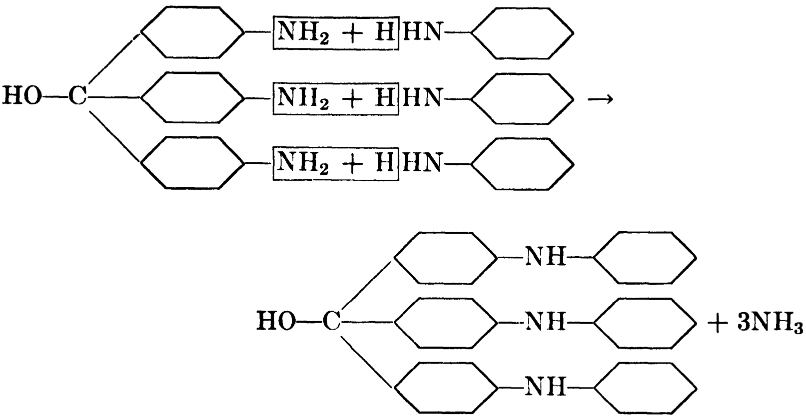


C.I. 670
Sch. No. 505

Alkali Blue

Alkali Blue * is the sodium salt of the monosulfonic acid of phenylated rosaniline, and because of the presence of only one sulfonic acid group its solubility is much lower than that of the alkali salts of Erioglaucine or Acid Green. It derives its name from the fact that, in dyeing, it is taken up by the fiber from an alkaline bath.

The molecule of Alkali Blue is built up by phenylation of *p*-rosaniline, which, as a rule, also contains an appreciable amount of the ortho derivative. If the rosaniline is considered to be entirely para, the reaction may be represented by the following:



The phenylation is carried out by adding the required quantities of aniline, rosaniline, and benzoic acid to the kettle, heating to 135–150° C, and holding at this temperature until phenylation is complete. The function of the benzoic acid is to speed the rate of phenylation. It is believed to act as a condensing agent, but its actual function has not been established. Although acetic acid may be used instead of benzoic acid, it has been found less effective.

Numerous factors affect the shade of the product. The quality of the rosaniline used is of great importance since the various isomers and the impurities in the rosaniline phenylate to varying degrees, and thus affect the shade. The color of the aniline blue varies with the degree of phenylation from a violet, for monophenylated compound, to a blue for the diphenylated, and a greenish blue for the triphenylated product. The presence of excess aniline not only increases the rate of

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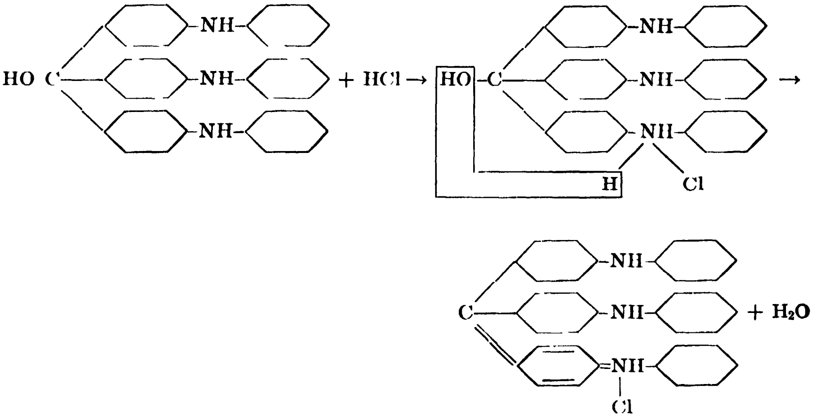
* According to Victor L. King, Ph.D., Technical Director of the Calco Chemical Division of the American Cyanamid Company.

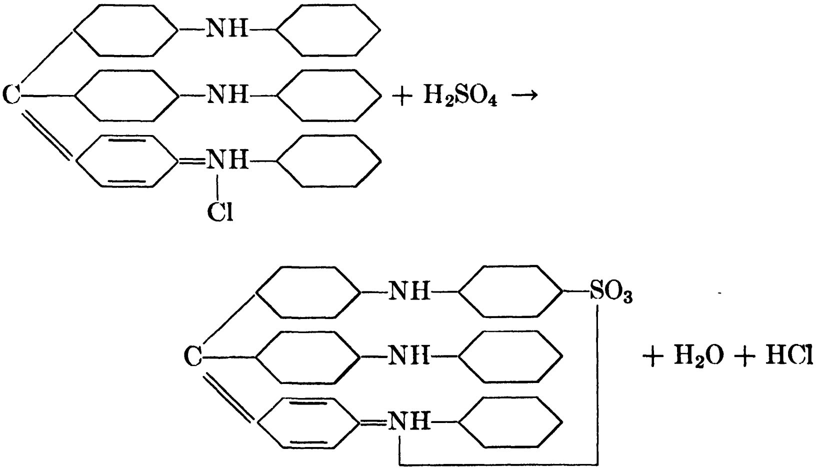
phenylation, thus tending to give a higher degree of phenylation, i.e., greener shades, but also tends to give brighter shades.

Drowning of the finished phenylation in hydrochloric acid, which dissolves the excess aniline and lower phenylated impurities, precipitates the (spirit-soluble) aniline blue as follows:



Aniline (Spirit) Blue

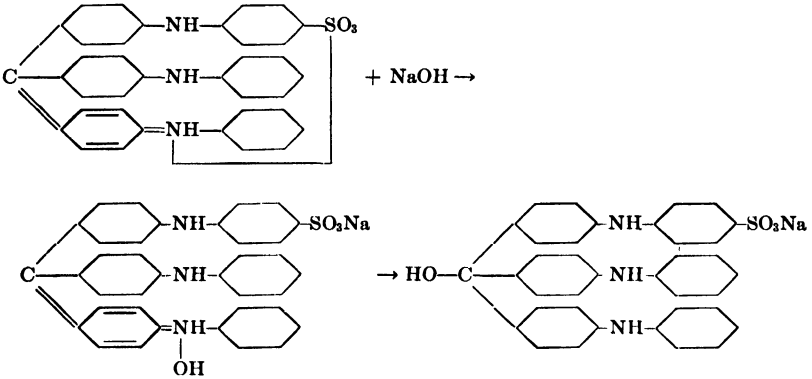
The rate of drowning must be controlled to prevent the formation of lumpy agglomerates that will occlude aniline, and the agitation adjusted to avoid a too finely divided product that is difficult to wash. After isolation, the aniline blue is sulfonated under controlled conditions with concentrated sulfuric acid:



The spirit blue is added to the sulfuric acid at low temperature to avoid oversulfonation, which would give a more soluble product, and hence be more difficult to isolate. Higher temperatures give a greater degree of sulfonation.

The sulfonation mixture is drowned in water, which dissolves the sulfuric acid and precipitates the relatively insoluble monosulfonic acid, which is then washed free of excess acidity.

The monosulfonic acid is converted to the sodium salt by solution in caustic soda:



Alkali Blue

The Alkali Blue is isolated by evaporation of the solution.

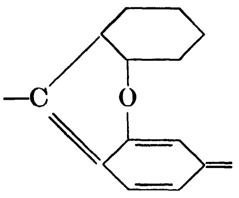
By sulfonation beyond the monosulfonic acid stage, increasingly soluble products are obtained that, because of their solubility, are unsuitable for use as pigments. These products, however, find wide application in the manufacture of laundry and ink blues and in the dyeing of textiles.

Alkali Blue found its original application in the dyeing of silk and wool. It is moderately fast to milling and light and is not affected by dilute acids. Alkaline milling decolorizes the dye, but the color can be restored in a dilute acid bath. At the present time, alkali blue is used primarily as a pigment for inks. For this purpose the highly insoluble monosulfonic acid itself is used. The product press cake is dispersed, or "flushed," in lithographic varnish which by its affinity for the product effects a separation of the water in the cake. This vehicle-dispersed pigment is used as a toner for carbon black inks. These toners give a luster and mask the characteristic brownish tinge of carbon black inks. The alkali blue toners are extremely well-dispersed inks with excellent working properties. They are used extensively in lithographic and offset inks. Their great tinctorial power, good working properties, and relatively low cost make them ideal colors for toning black inks.

The monosulfonic acid is also used extensively in metal printing, since it stands temperatures up to 270° F without appreciable color change, as well as in coloring glassware and cellophane.

XANTHENE PIGMENTS

The xanthene pigments are characterized by the structure

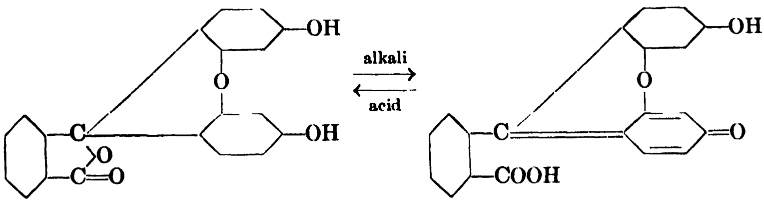


and include some of the most beautiful and interesting of the synthetic dyestuffs and pigments. The rhodamines are representative of the basic-type xanthene colors, and the fluoresceins, eosins, phloxins, erythrosins, and rose bengals are representatives of the acid type.

The first group or basic types are discussed in the sections on phosphotungstic and molybdic pigments and on basic color pigments, nonpermanent type.

Acid Type

The acid type of xanthene colors is represented by the dyestuffs and pigments which are derivatives of Fluorescein. These may exist in the phenolic form and in the quinonoid form in equilibrium:



Phenolic Form

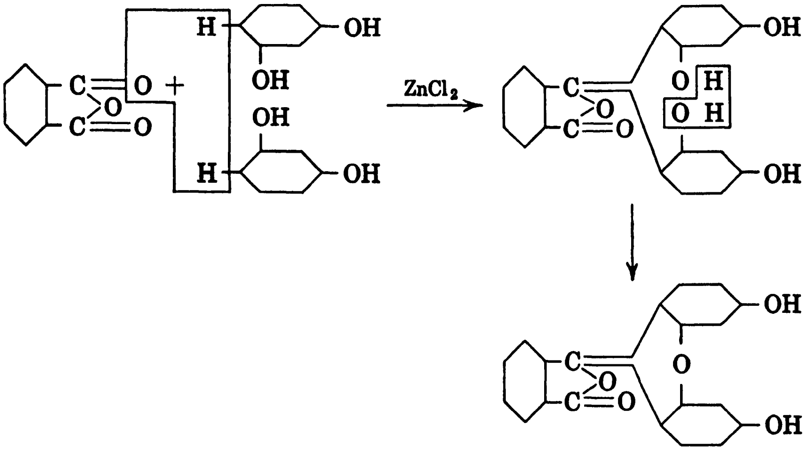
Quinonoid Form

Fluorescein

The quinonoid form is highly colored and readily forms salts with alkalies.

Eosin, typical of the acid type and the most important dyestuff in this group, is used in the manufacture of pigments. It will be discussed later.

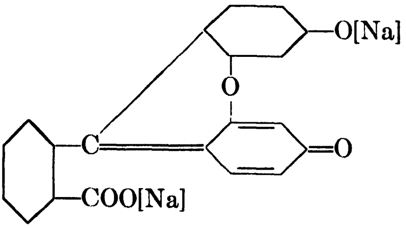
Fluorescein is first prepared by condensing resorcinol and phthalic anhydride, with zinc chloride as the condensing agent:



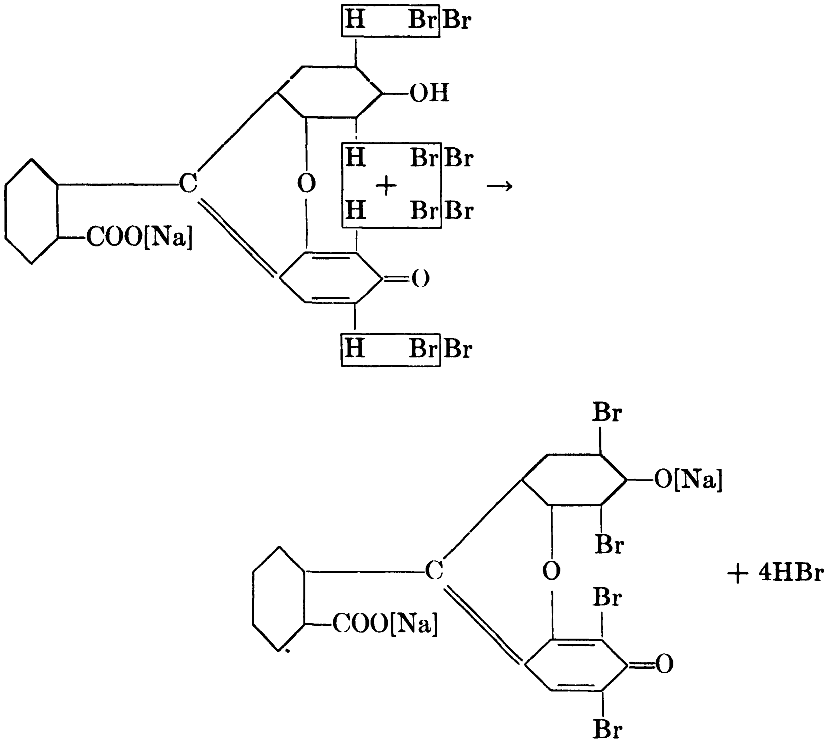
Fluorescein

C I 766
Sch No 585

The sodium salt of Fluorescein appears in commerce as Uranin:



Caro found in 1871 that Fluorescein will react with bromine, yielding a dyestuff which he called Eosin:



Eosin

C I 768
Sch. No 587

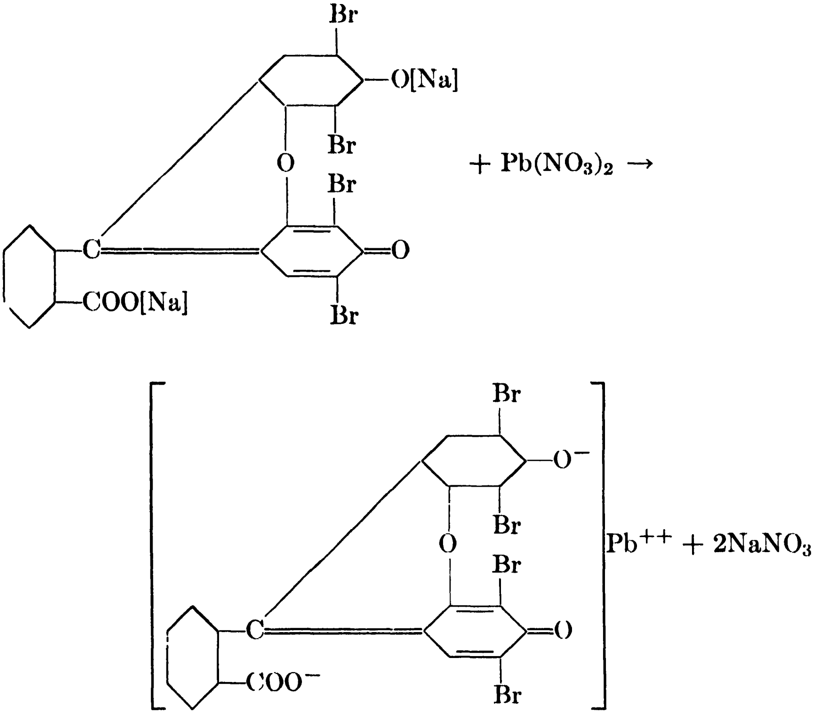
Bromination is conducted in either alcoholic or aqueous solution, and in actual practice sodium chlorate is added to oxidize the hydrobromic acid formed, regenerating free bromine, thus achieving a more economical operation.

The acid of Eosin is generally known as Bromo acid.

Lakes and Toners. Eosin, in spite of its extreme lack of permanency to light and its poor resistance to alkalinity, is used in very large volume in the preparation of lakes and toners, the latter being known as Phlox or Phloxin toners. The use of the term "Phloxin" toners is confusing since they are not derived from the dyestuff phloxin, which is a di- or tetrachlorotetrabromfluorescein. It is probable that the term has its real derivation, rather, in the older use of the name "Phlox" toner in which the pigment was named for the phlox flower.

The precipitation is usually accomplished with soluble salts of lead, although other salts such as aluminum salts are sometimes used.

Lakes may be prepared by precipitation of the pigment on various bases such as alumina hydrate, blanc fixe, gloss white, and others, since no absorption of color by the base is necessary. The reaction may be indicated as follows:

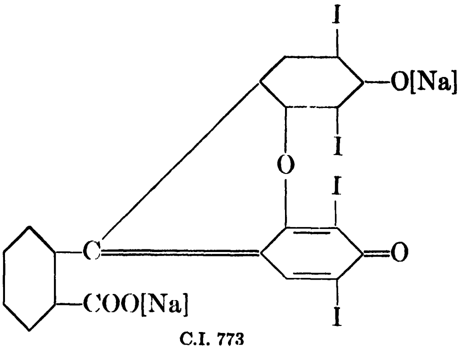


The pigment is sufficiently insoluble that a very slight excess of lead salt is required.

This pigment represents another case in which the physical condition of the product is of great importance. With no change in the amounts or identity of the reacting materials, it is possible to bring about very wide variations in the tinctorial properties of the product by modifications in the conditions of preparation. Changes in temperature, concentration, rates of treatment, and agitation are all capable of effecting wide variations in color characteristics, and are used as means of control in practical manufacture.

Other dyestuffs of importance in this group include:

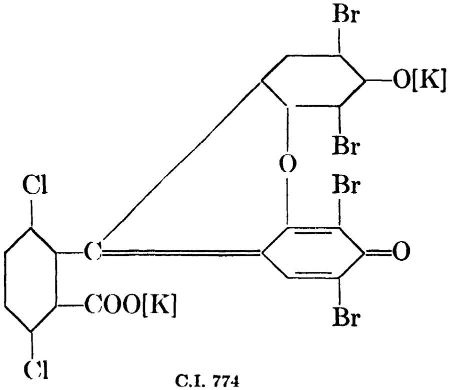
Erythrosin 3B



C.I. 773
Sch. No. 592

Obtained by complete iodination of Fluorescein.

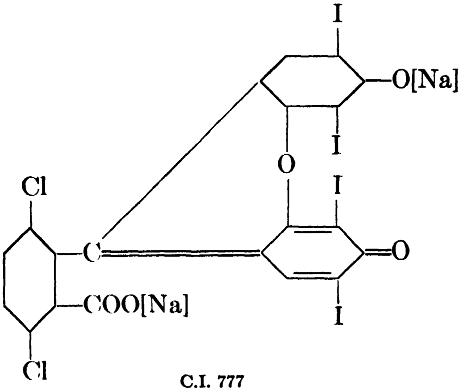
Phloxin



C.I. 774
Sch. No. 593

Obtained by bromination of Dichlorofluorescein.

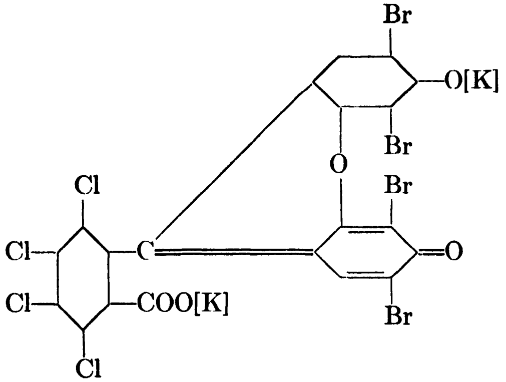
Rose Bengal



C.I. 777
Sch. No. 595

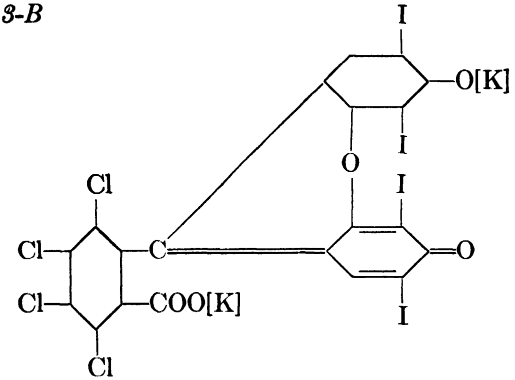
Obtained by iodination of Dichlorofluorescein.

Phloxin B



C.I. 778
Sch. No. 596

Rose Bengal 3-B



C.I. 779
Sch. No. 597

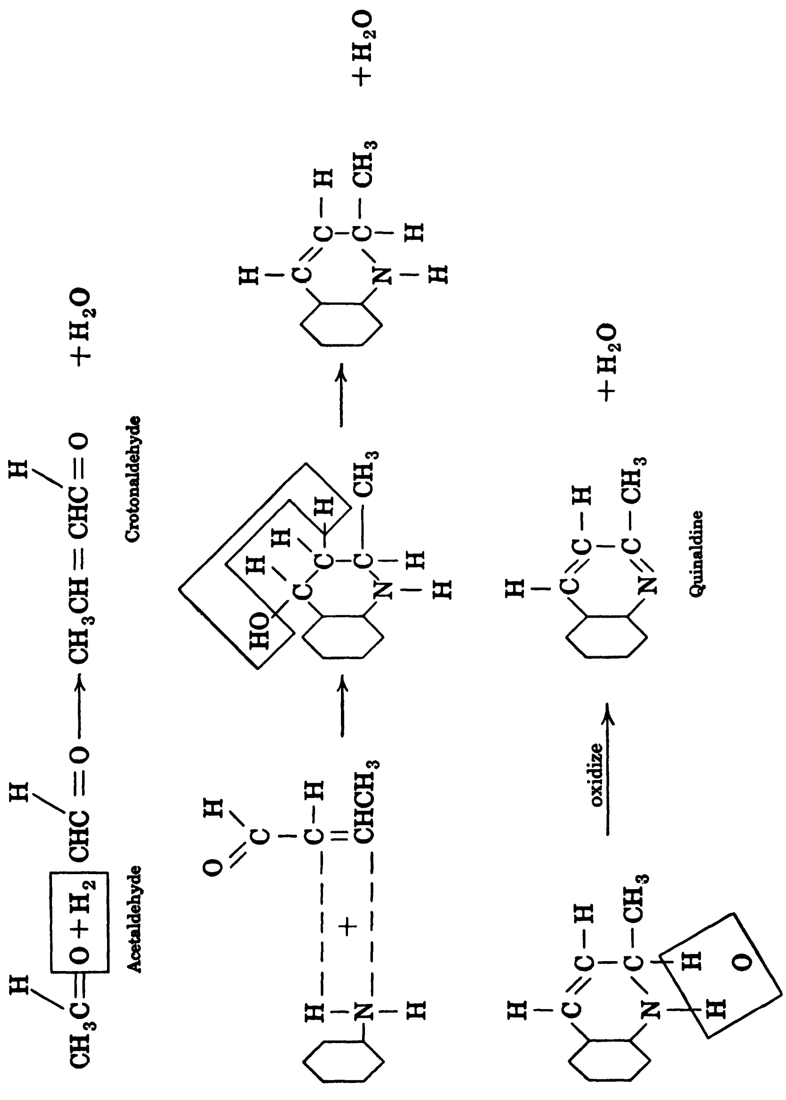
The Quinoline Group

The quinoline coloring matters, although relatively few in number, have been of considerable value in the sensitizing of photographic emulsions. Only one, Quinoline Yellow, also known as Chinoline Yellow, has found extensive use in the pigment field.

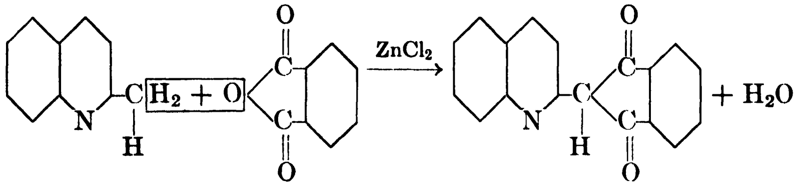
In the past, Quinoline Yellow was favored in the group of yellow lakes because of its extremely clean greenish tone, even though its tinctorial power and resistance to light were decidedly low. Equally important also was its use in a series of widely used green lakes prepared by precipitating the Quinoline Yellow, with Acid Green on alumina hydrate or gloss white bases. These greens were exceptionally brilliant but were very fugitive to light as both the Quinoline Yellow and the Acid Green are fugitive colors, and high dispersion in the formation of the lakes greatly intensified this defect.

Quinoline Yellow is prepared from quinaldine, which is made from aniline and paraldehyde in the presence of hydrochloric acid (36).

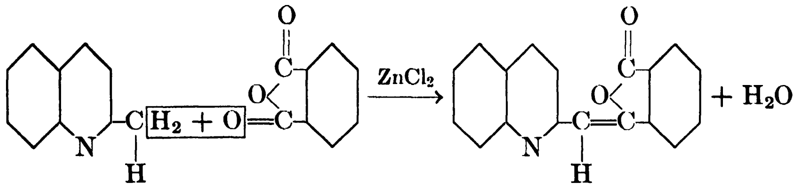
The synthesis of quinaldine may be represented in the following series: formation of crotonaldehyde by elimination of water from two molecules of acetaldehyde, direct addition of aniline, loss of water, and, finally, oxidation.



Owing to the activity of the methyl hydrogens, in this position, quinaldine can be condensed with phthalic anhydride to yield quinophthalone and isoquinophthalone (73).



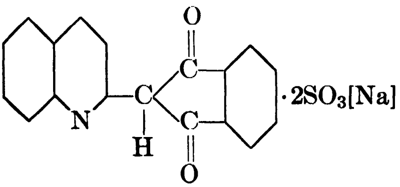
Quinophthalone



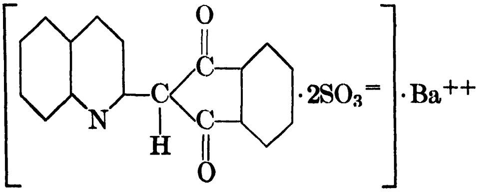
Isoquinophthalone

At higher temperatures, the first represents the major reaction, and the mixed product is the commercial Spirit Soluble Quinoline Yellow which has been used as an alcohol and fat-soluble color.

Soluble Quinoline Yellow, which is the form found useful in pigment preparation, is the sodium salt of the mixed mono- and disulfonic acid derivatives of this spirit-soluble type. The sulfonic acid groups are evidently in the quinaldine residue as phthalic acid is the chief product of oxidation. Its structure may be represented, therefore, as follows:



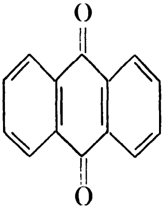
and the barium lake, disregarding the alumina hydrate base, as



Within recent years a dyestuff has become available known as Canary Lake Yellow PL,* which is a very close tinctorial match for Quinoline Yellow. This dyestuff, however, yields a pigment very much more resistant to light than that from Quinoline Yellow and has, therefore, been used advantageously in the form of both yellow and green lakes of improved stability.

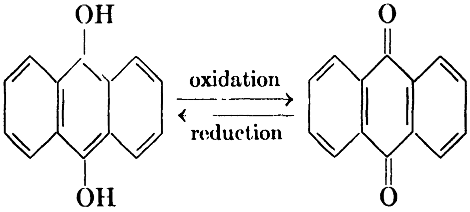
ANTHRAQUINONE PIGMENTS

The anthraquinone group is based on the chromogen



which is anthraquinone. It is the parent substance of an extensive and most interesting and valuable group of dyestuffs that have found use in a variety of fields, in textiles, primarily, up to the present time, but also, to some extent, in pigments.

Anthraquinone itself was made by the oxidation of anthracene with nitric acid as early as 1840, by Laurent, and has been more recently manufactured with sodium bichromate and sulfuric acid as the oxidizing agent. It consists of yellow crystals, melting at 284 to 285°, which are reduced with zinc dust and alkali to anthrahydroquinone. This is readily oxidized by air back to anthraquinone.



Anthraquinone, on treatment with sulfuric acid, readily yields mono- and disulfonated products. It is interesting that control of the position of substitution in sulfonation is obtained, to a considerable extent, by

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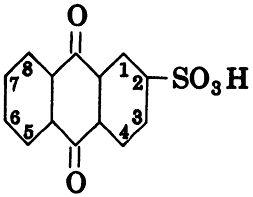
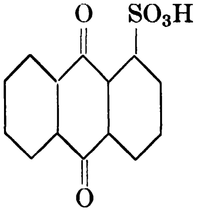
* National Aniline and Chemical Company, New York, N. Y.

the presence, or absence, of mercury as a catalyst during the reaction.

Direct sulfonation gives primarily the β- or 2-sulfonic acid



whereas, in the presence of mercury, the chief product is the α- or 1-sulfonic acid.



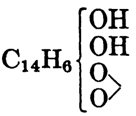
Disulfonation products formed in the presence of mercury are primarily the 1.5 and 1.8 isomers, whereas, in the absence of mercury, the 1.6, 1.7, 2.6, and 2.7 isomers are formed. These products are of value in the formation of further anthraquinone derivatives (75).

The sulfonation products of anthraquinone have been especially valuable in the introduction of hydroxyl (OH) groups into the molecule, making possible the synthesis of anthraquinone derivatives which have been of tremendous interest and great commercial value.

Hydroxyanthraquinones

Dihydroxyanthraquinones. Alizarin Dyestuffs (24). Alizarin is one of the oldest of the natural dyestuffs, being known to the Egyptians, Persians, and Indians. It was prepared, originally, from the madder root (*Rubia tinctorum* L.), (hence the term madder lake) in which it occurs in the form of a glucoside, ruberythric acid, which can be converted into a sugar and alizarin on boiling with dilute acids.

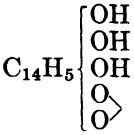
In 1868 Graebe and Liebermann (60) made the important discovery that the chief madder dyestuff, alizarin, is a derivative of anthracene, since it could be converted into this hydrocarbon by distillation with zinc dust, a method which had been discovered shortly before by Baeyer (9). In the same way Graebe and Liebermann also found that the dyestuff purpurin, which accompanies alizarin in madder, gave anthracene on distillation with zinc dust. These and other researches led Graebe and Liebermann to assume that alizarin is a dihydroxyanthraquinone and purpurin a trihydroxyanthraquinone.



$$C_{14}H_6\begin{cases}OH\\OH\\O\rangle\\O\rangle\end{cases}$$

Alizarin

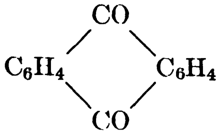
and



$$C_{14}H_5\begin{cases}OH\\OH\\OH\\O\rangle\\O\rangle\end{cases}$$

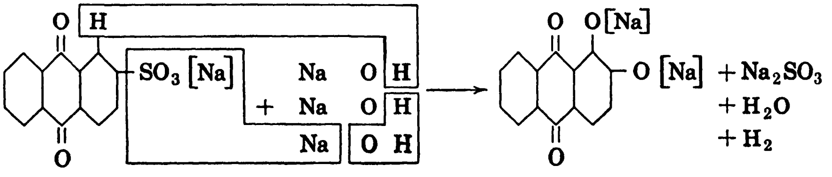
Purpurin

Zincke and Fitting later established the fact that anthraquinone is a diketone of the formula



Continuing their investigations, Graebe and Liebermann found that the compound previously prepared by Laurent, by the direct oxidation of anthracene, is identical with anthraquinone. In order to convert this into a dihydroxy derivative, they transformed it first into the dibromo derivative, and then, by fusing with potash, produced a dihydroxyanthraquinone identical with the alizarin from madder root. This synthesis started a new epoch, as it represented the first artificial preparation of a natural dyestuff.

It was soon discovered that alizarin can be more readily prepared from 2-anthraquinonesulfonic acid by fusion with caustic soda. The probable equation representing the formation is:



Sodium Alizarate

C.I. 1027
Sch. No. 778

In modern practice oxidizing agents such as sodium chlorate or sodium nitrate are added, in the fusion, to oxidize the hydrogen which previously had been responsible for low yields of alizarin.

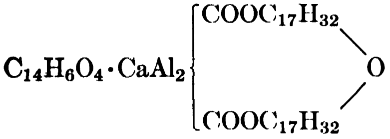
The color of the alizarin dyestuff itself is weak, but its solution with sodium hydroxide is a strong purplish violet, and the lakes, which the dye forms with metallic salts, are intensely colored.

As alizarin is a polygenetic dyestuff, the color of the lake varies with the metallic salt used as a mordant or precipitant:

Magnesium	violet
Calcium	purple-red
Barium	purple-red
Aluminum	rose-red
Iron (ferric)	brown-black
Lead	purple-red
Tin (stannous)	red

Although the toner, or full-strength metallic salt of alizarin, can be prepared, it does not possess desirable tinctorial or working properties and therefore has not been of interest in the pigment field. On the other hand, the lakes have been of great value and interest, representing one of the few instances in which the material of ancient times appears to have been of a quality commensurate with the tinctorial requirements of the present day.

The preparation of madder lakes involves, typically, the precipitation of a complex made up of the dyestuff, a metal, usually calcium, and a fatty acid such as Turkey Red oil on an alumina hydrate base. Although the reactions involved do not appear to be simple and cannot be definitely represented by the usual chemical equations, the following empirical formula by Kornfeld (83):



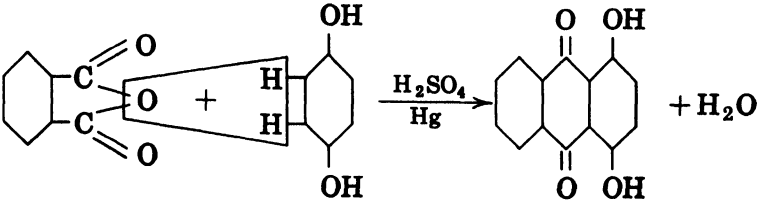
$$C_{14}H_6O_4\cdot CaAl_2\left\{\begin{array}{l} COOC_{17}H_{32}\diagdown \\ \qquad\qquad\qquad O \\ COOC_{17}H_{32}\diagup \end{array}\right.$$

gives the probable constitution of a good commercial lake containing a fatty acid complex.

Although the methods for the preparation of alizarin lakes may vary greatly in detail according to Harrison (63), the combination is always brought about by boiling the alizarin with alumina hydrate in the presence of Turkey Red oil and a salt of calcium, the suspension being neutral or slightly acid. Phosphates of aluminum or calcium are usually incorporated, and they considerably improve the resulting lakes.

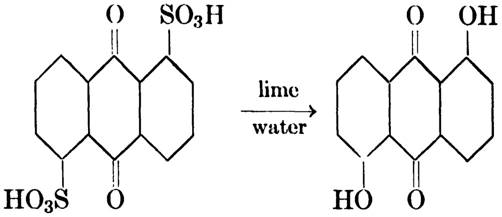
Two other dihydroxyanthraquinones are of interest since they are isomers of alizarin.

Quinizarin is formed in the oxidation of anthraquinone, particularly in the presence of mercury, and it is also formed in the condensation of phthalic anhydride and hydroquinone, which quite definitely establishes its structure:



Phthalic Anhydride **Hydroquinone** **Quinizarin**

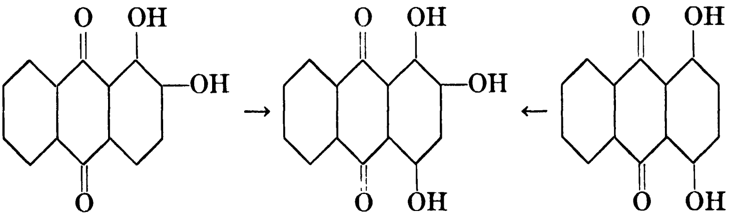
Anthrarufin is formed in the treatment of anthraquinone-1,5-disulfonic acid with alkali, and it is therefore the 1,5-dihydroxy derivative:



Anthrarufin

As these last two dihydroxy derivatives are not mordant dyestuffs, because the hydroxyl groups are not adjacent to each other, they are not used directly in the field of either dyes or pigments. They do serve, however, as intermediates in the formation of other dyestuffs.

Trihydroxyanthraquinones. One trihydroxyanthraquinone is of great interest as it is a normal constituent of natural madder lake. It is purpurin, which is formed, synthetically, by the oxidation of either alizarin or quinizarin:

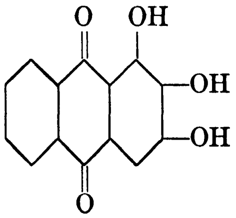


Alizarin **Purpurin** **Quinizarin**

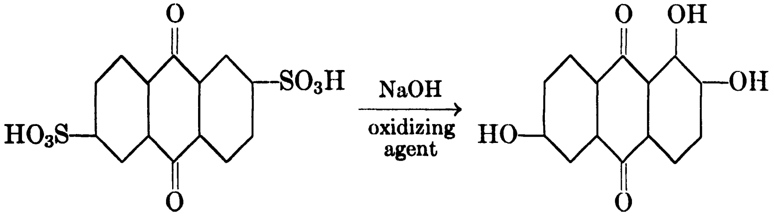
Its structure is, therefore, quite definitely established as shown above.

The lake is very similar to, but slightly yellower than, that from alizarin, which accounts for the fact that natural madder lake is usually slightly yellower than that made from synthetic alizarin.

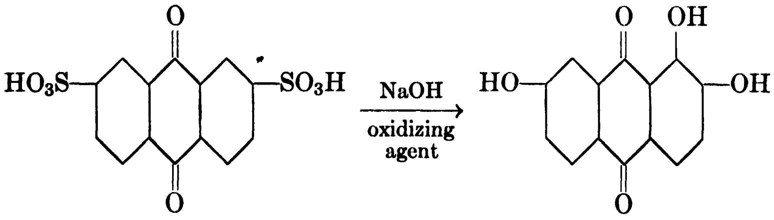
Other trihydroxy derivatives include three important materials: Anthragallol is formed from benzoic and gallic acids by heating with sulfuric acid:



Flavopurpurin is made by fusing anthraquinone 2,6-disulfonic acid with caustic soda:

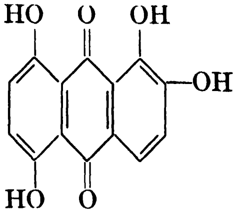


Anthrapurpurin is prepared by the caustic fusion of anthraquinone 2,7-disulfonic acid:



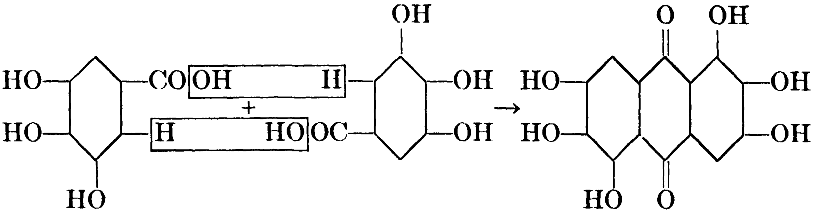
These materials are primarily of value as intermediates rather than directly as dyestuffs and have not yet proved important in pigment work.

Polyhydroxyanthraquinones. Still more complex hydroxyanthraquinone derivatives are known and, in a few cases, are of importance in the pigment field. Thus Alizarin Bordeaux is produced in the oxidation of alizarin with fuming sulfuric acid.



This dye gives a brownish violet chromium lake and a bordeaux aluminum lake.

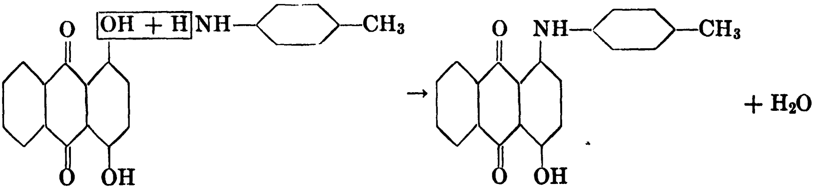
Rufigallic acid is formed in the heating of gallic acid with concentrated sulfuric acid.



This dyestuff forms red aluminum lakes, violet iron lakes, and brown chromium lakes.

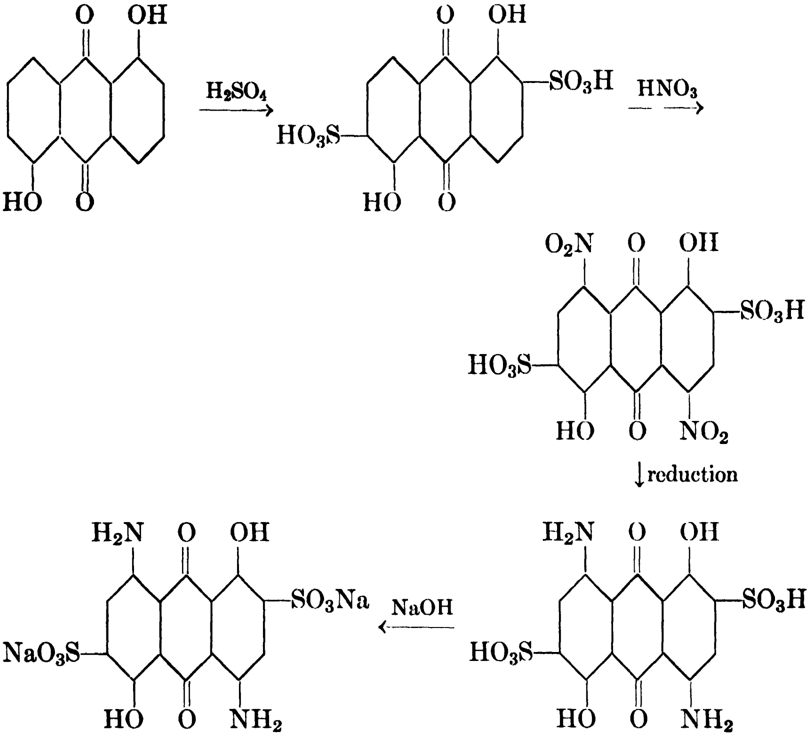
Derivatives of Hydroxyanthraquinones. Various derivatives of the hydroxyanthraquinones have been developed which have proved useful in the pigment as well as the textile field. These derivatives involve, as a rule, the introduction of the amino or substituted amino groups, nitro and sulfonic acid groups.

An hydroxyl group, for example, may be replaced by heating with a primary aromatic amine in the presence of a condensing agent.



A nitro or sulfonic acid group may be introduced by direct nitration or sulfonation, and an amino group by reduction of a nitro group.

These may all be illustrated in the formation of Alizarine Saphirol (24).



Alizarin Saphirol

C.I. 1054
Sch. No. 858

These materials at the present time are not of real importance in the pigment field. In the future, however, it is entirely possible that improvements in the means of controlling the physical characteristics, and the suitable employment of modifiers, may make available the highly desirable tinctorial properties of these materials.

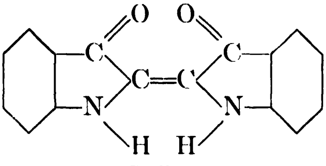
VAT COLOR PIGMENTS

The vat colors, so-called because they are normally reduced to the leuco form in a special vat or reducing solution, consisting of an alkaline solution of sodium hydrosulfite or other suitable reducing agent, prior to application to textile fibers, are, as a rule, typical pigments, since they are completely insoluble in water and highly resistant to chemical attack. In their usual form, however, vat colors are of little value as pigments owing possibly to their low degree of dispersion, as they are quite lacking in brilliance and also exhibit a very low tinctorial power.

In the normal methods of using vat colors in textile dyeing and printing, they are brought into a soluble condition by reduction, which is usually accomplished by treating the insoluble dyestuff, in a caustic solution, with sodium hydrosulfite $Na_2S_2O_4 \cdot 2H_2O$ or the formaldehyde-sulfoxylate $CH_2OH \cdot OSONa \cdot 2H_2O$, also known as Rongalite. Other reducing agents are also used under certain conditions. In this reduced condition the color has an affinity for the cotton fiber, which, therefore, takes it up and the full color is then developed by oxidation, frequently simply air oxidation.

In textile work the vat colors are generally not dried but are used in the form of 10 to 20 per cent suspensions. If the materials are dried in air, the products are hard in texture and of little value as pigments.

The vat colors are to be found in two main groups, the indigoid, which are derivatives of indigo:



Cis Form

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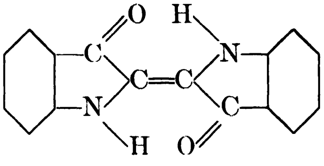
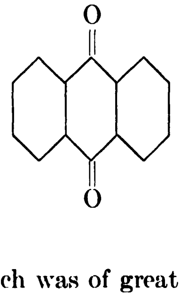


Trans Form

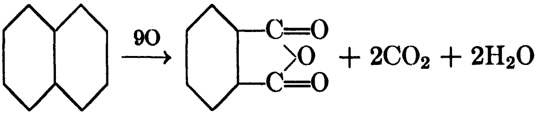
and the anthraquinone group, which are derivatives of anthraquinone:



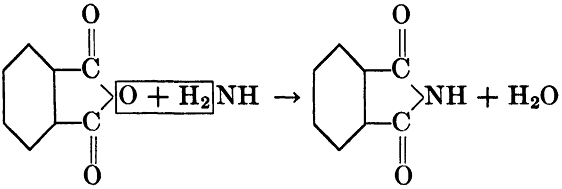
The Indigoid Group

The dyestuff indigo, which was of great importance when obtained entirely from natural sources, has maintained its position since the synthetic product has replaced the natural, and today is used in very large amounts in the dyeing of cotton goods. It is the parent substance for quite a large number of derivatives, some of which have excellent physical and tinctorial properties for pigments.

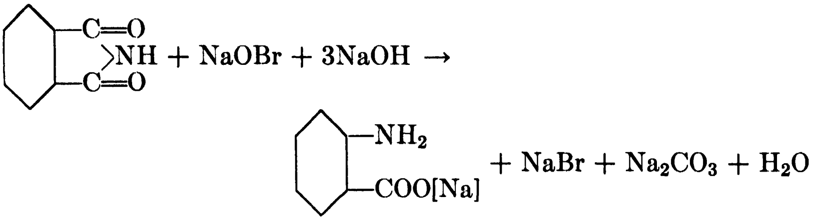
The complete synthesis of indigo from naphthalene (108) by one of the most practical among the several procedures which have been developed may be indicated in the following reactions. Naphthalene is oxidized to phthalic anhydride by the catalytic vapor-phase method of Gibbs and Conover (55).



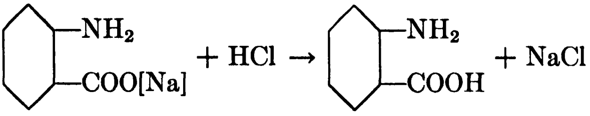
Phthalic anhydride is converted into phthalimide by heating with ammonium carbonate or ammonia at about 225° C.



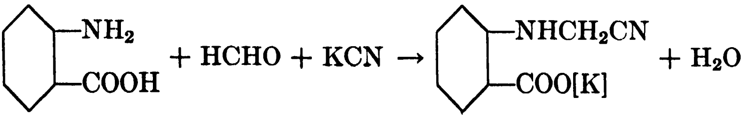
Phthalimide is then converted to sodium anthranilate, using an alkaline solution of sodium bromate:



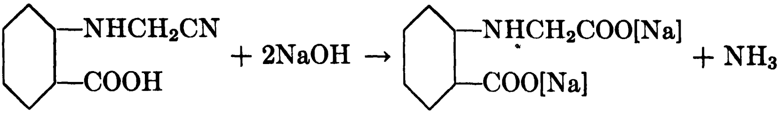
The free anthranilic acid is then precipitated with hydrochloric acid:



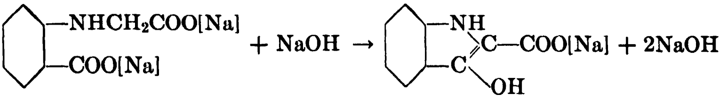
Cyanomethylanthranilic acid is made by treating the anthranilic acid in benzene solution with potassium cyanide and formaldehyde:



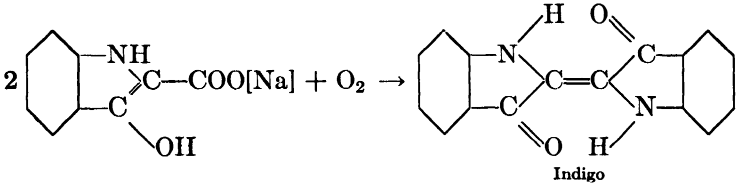
This nitrile is then hydrolyzed in alkaline solution to sodium phenylglycine-*o*-carboxylate.



Sodium indoxylate is then formed by fusing the sodium salt with caustic soda at about 250 to 270° C in paraffin:



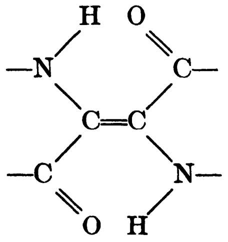
The homogeneous paste is cooled and boiled with water in the absence of air or in the presence of small amounts of sodium hyposulfite (hydrosulfite). The aqueous solution is filtered from the paraffin, oxidized by passing in air, and indigo is precipitated:



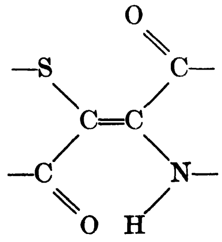
The Colour Index shows this dye as the cis isomer, but the stable trans form is the one now more generally accepted (125).

Indigo itself is not a satisfactory pigment because of its inferior brilliance, low strength, and lack of covering power. Certain derivatives, on the other hand, have been found useful in spite of their rather high cost.

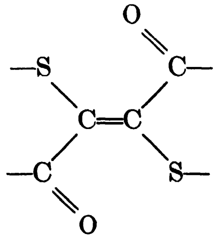
From the standpoint of structure and composition the indigo group of colors is of great interest. Bohn (15) has classified the types as follows, including three symmetrical and three unsymmetrical forms, all containing the chromophore (—CO—C=C—CO—). The six chromogens are shown with the names of the typical dyestuffs:



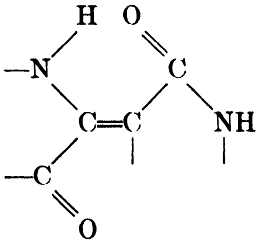
Indigo



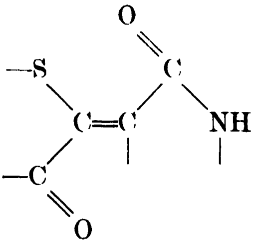
Ciba Violet



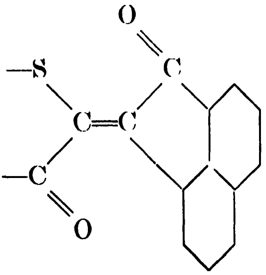
Thioindigo B



Indirubine

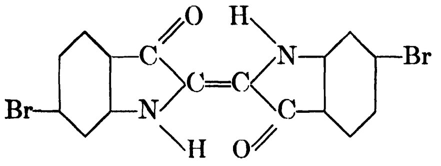


Thioindigo Scarlet



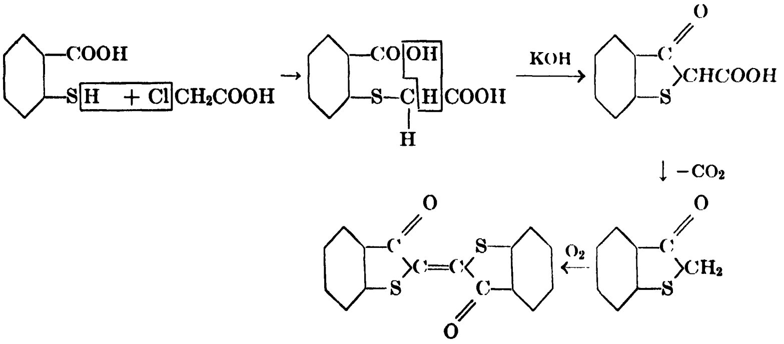
Ciba Scarlet G

One derivative of indigo is of special interest as it appears to be identical with the natural dye known as "Purple of the Ancients." It is the 6,6-dibromoindigo:



The thioindigos have proved to be the most desirable of the indigo derivatives up to this time. These materials were developed in the work of Friedländer in which he tried to replace the —NH Groups with sulfur.

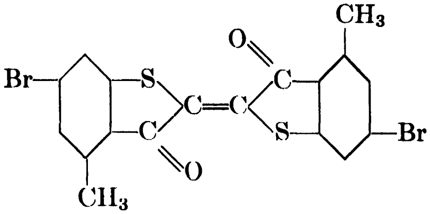
One way in which this replacement was accomplished was by starting with thiosalicylic acid:



Thioindigo Red B

C.I. 1207
Sch. N. 912

This product, which was the first red vat color of satisfactory tinctorial properties, shows the same stability and fastness to light as indigo. A derivative known as Thioindigo Pink has found some use in the pigment field:



Trans Form

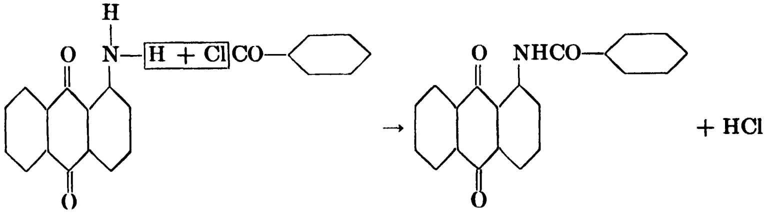
C.I. 1211
Sch. No. 910

In order to improve the tinctorial characteristics of the indigoid colors, they have been reduced to the leuco forms under a variety of conditions and then reoxidized to the stable-colored form again. In general some improvement results, but the products are in many cases still deficient as pigments. Further improvement in some cases has been obtained by treatment of the reoxidized material with wetting, dispersing, or other modifying agents. The problem of bringing these vat colors into an entirely satisfactory condition for broad pigment use, however, is still to be worked out.

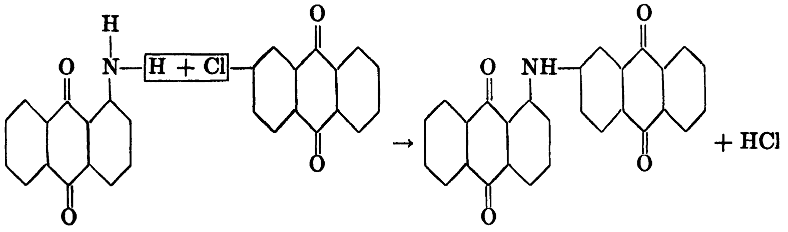
The Anthraquinone Group

The anthraquinone derivatives that are to be classed with the vat colors are known as complex ring quinones, and in many instances consist of two molecules of anthraquinone or anthraquinone derivatives, linked together through nitrogen or carbon. In other cases, however, the structures are very complex.

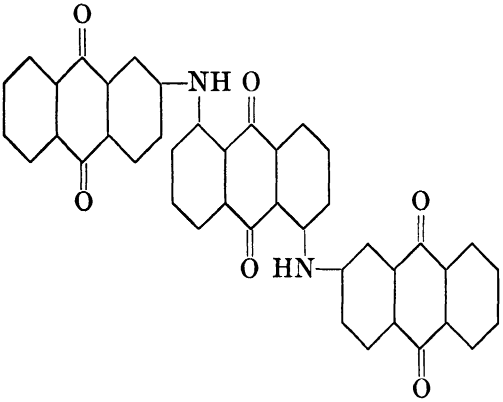
The simplest vat colors of this group are of the type of Algol Yellow that is the benzoyl derivative of α-aminoanthraquinone, prepared by heating the amino compound with benzoylchloride in an inert solvent.



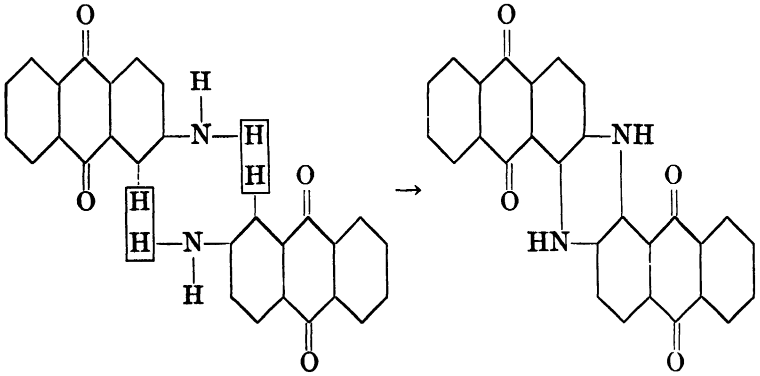
A somewhat more complex type is Indanthrene Orange, formed by the condensation of α-aminoanthraquinone and β-chloroanthraquinone:



In a further extension of this type of product two molecules of the amino derivatives are condensed with one molecule of the dichloranthraquinone, as in the case of Indanthrene Bordeaux.



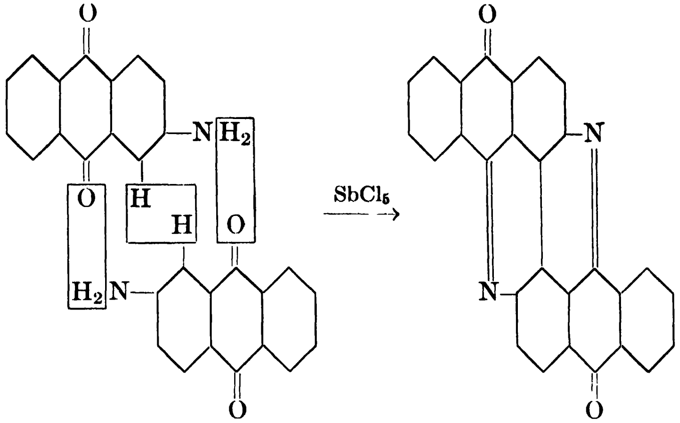
The first ring complex appears in the indanthrene blue group, which is prepared by heating β-aminoanthraquinone or its derivatives with caustic potash:



Indanthrene Blue

C.I. 1106
Sch. No. 837

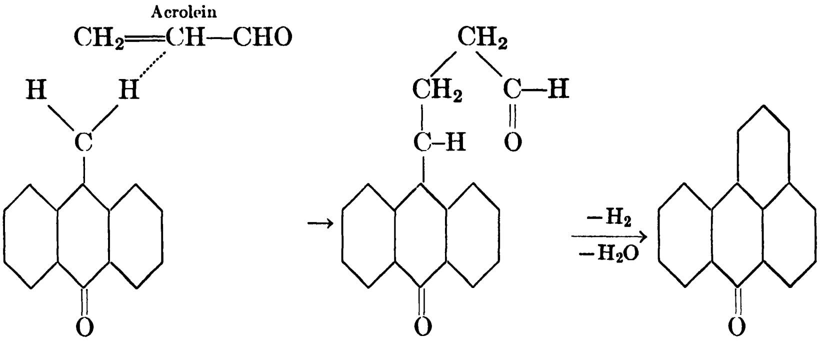
In the flavanthrene group the linkage takes place through the formation of a double ring bridge:



Flavanthrene

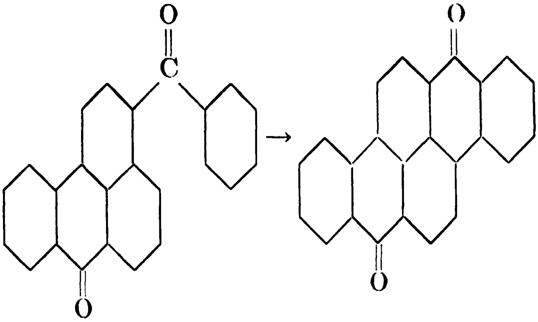
Still more complicated structures are to be found in the benzanthrone group, which is based on the formation of derivatives of benzanthrone by heating anthranol and anthraquinone or their derivatives with glycerol and sulfuric acid.

According to Cain and Thorpe (24), part of the anthraquinone is reduced to anthrone, which combines with acrolein, formed from glycerol and sulfuric acid, to form an aldol:

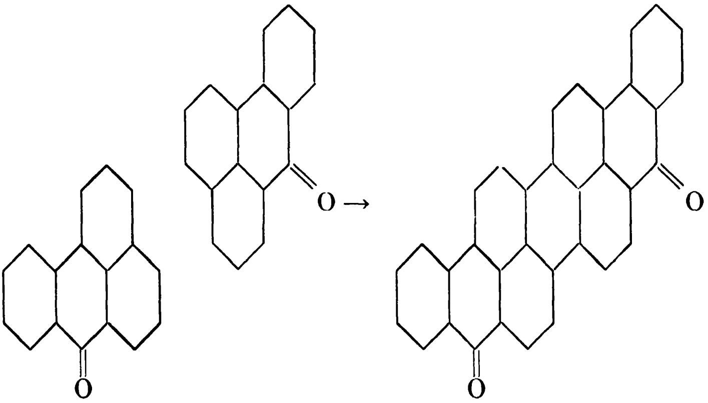


Anthrone **Benzanthrone**

The benzoyl derivative of benzanthrone, on being heated with aluminum chloride, gives dibenzpyrenequinone, of which a chloro derivative is Indanthrene Golden Yellow:



Another complex structure is illustrated by Indanthrene Dark Blue. In the fusion of benzanthrone with potash, two molecules condense, with the elimination of hydrogen:



Indanthrene Dark Blue

These few typical structures, although far from giving a broad view of the large number of individual vat colors that are of value in textile work and might under certain conditions be of interest in the pigment field, do give a fair idea of the nature of the compounds formed. It is apparent that they represent, in general, compounds that are chemically quite inert and contain no groups that have a tendency to confer on them water solubility or the ability to form salts with either acidic or alkaline reagents. These are characteristics of value in the pigment field, but in the present instance they are not associated with other characteristics that are also essential to high-grade pigments, namely, brilliance and high tinctorial power.

For many years the possible value of these materials in the pigment field has been recognized, and many attempts have been made to eliminate their usual deficiencies. One of the first methods tried involved reduction to the leuco form and subsequent reoxidation, under a variety of conditions, to the color in a more highly dispersed form. A certain amount of improvement attended the use of this method, but, with a few exceptions, the products were still deficient in both brilliance and strength.

Another method that has given some improvement in certain instances is the so-called acid-pasting procedure. It involves solution of the dyestuff in an acid such as sulfuric or phosphoric and then precipitation of the color in a finely divided condition by running the acid solution into cold water under efficient agitation. In this method the efficiency of dispersion can be modified in many ways, such as by controlling the concentration of color in the acid, the strength of the acid, the temperature of the solution, the relative volume of the drowning liquor, the rate of drowning, the type of feed, temperature of the drowning liquor, the efficiency of agitation, the heat treatment during and following precipitation, time of holding in the final liquor, presence of salts during and after precipitation, presence of modifiers during and after precipitation, type of filtration, and degree of washing, drying, and grinding. In some cases this procedure has given results even better than those obtained by the reduction-oxidation method, but the technique is not sufficiently effective in all cases to remove the deficiencies in the products of this type.

Another process offering some promise is the conditioning method of O'Neal (101), in which an anthraquinone color is first mixed with a liquid aromatic amine having the aniline nucleus and then the amine is removed, preferably by forming a water-soluble amine salt and washing it out of the mixture with water, or by other means such as steam distillation. The process is said to give high tinctorial strength, improved masstone, clarity of hue, and softness of particle, thus enabling these pigments to be employed to new advantage in paints, enamels, lacquers, inks, plastics, and in other general and well-known uses.

Further improvements in the tinctorial and working properties of vat colors may be the result of studies involving the use of modifiers or assistants, either by themselves in normal manufacturing operations or in conjunction with the above or other methods of special treatment.

Within recent years a great number of modifiers, such as wetting, dispersing, penetrating and other agents, of both anionic and cationic types, have been brought on the market, many of them designed primarily for use in the processing and finishing of textile products.

They have been broadly studied in their application to the manufacture of pigments of special properties, and in many instances valuable results have been obtained. The rosin soap lakes (4), discussed in this chapter under lithols (page 127), represent one important group of products which has been developed in line with this study.

In its application to vat colors this study may also bring about marked improvements in the tinctorial properties of the vat-type colors. If this result should appear, it is probable that a great increase may be expected in the use of vat colors in this field.

THE PHTHALOCYANINES

Within the past few years a new type of colored compound has been discovered which represents a truly startling innovation in the field of synthetic organic pigments. In the preparation of phthalimide it was found that part of the material was dark in color, owing to the presence of what de Diesbach and von der Weid (38) found to be an insoluble blue substance, which they identified as complex metallic salts of aromatic dinitriles with copper and pyridine. Using cuprous cyanide, *o*-dibromobenzene, and pyridine, they prepared an insoluble blue compound for which they suggested the formula:

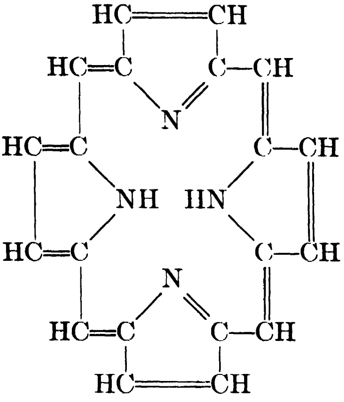
$$[C_6H_4(CN)_2 + C_5H_5N]_2\,Cu$$

In 1928 Danbridge, Drescher, and Thomas (35) applied for a patent in Great Britain covering new insoluble colored organic compounds obtained by reaction between phthalic anhydride, phthalamide, or phthalimide with ammonia in the presence of metals.

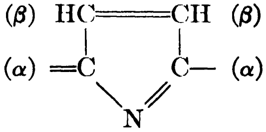
Further investigation of these interesting and useful materials was undertaken by Linstead and his coworkers of the Imperial Institute of Science and Technology, London, and their basic structure was established. In the first report on this work, in which the name phthalocyanines was suggested, they stated (4): "Analysis shows them to contain the units ($C_8H_4N_2$) combined in their simplest form with a divalent metal or with hydrogen in the manner: $(C_8H_4N_2)_4H_2$ or $(C_8H_4N_2)_4$ metal. The mode of synthesis and the reaction of these compounds indicate that they contain a system of iso-indole rings linked by nitrogen atoms and forming a large ring with the metal held in the center by primary and secondary valencies."

The phthalocyanines appear to be based structurally on porphin, which is also the basis of the natural coloring matters of the chlorophyll and hemin types.

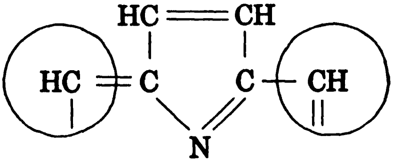
Porphin is represented as:



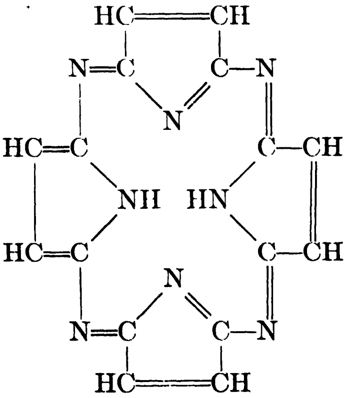
This structure consists of four pyrrol nuclei:



joined in all the alpha positions by methine groups:



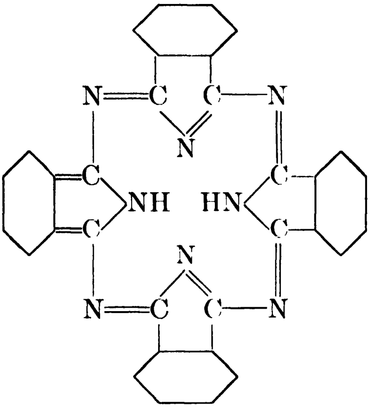
Replacement of these methine (≡CH) groups by nitrogen atoms yields a structure referred to as porphyrazine, which has not yet been synthesized (91):



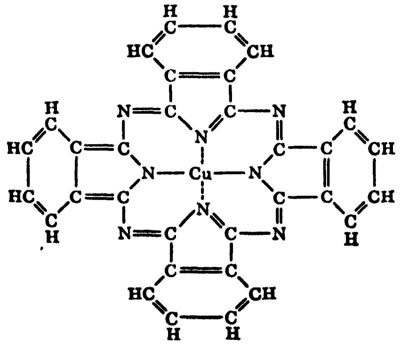
A compound, however, has been prepared in which the eight outside hydrogen atoms have been replaced by phenyl groups and the two inside hydrogen atoms by metals such as magnesium, tin, lead, and copper. These are the metal derivatives of tetraphenylporphyrazine. The tetra-*p*-nitrophenylporphyrazine derivatives have also been made.

It is evident, also, that the pairs of hydrogen atoms on the pyrrol nuclei might be replaced by cyclic structures, and such compounds appear to represent the new phthalocyanines.

The tetrabenzo derivative is shown below:



And this material in the form of the copper complex (replacing the two central hydrogen atoms attached to nitrogen) is the commercial pigment, Monastral Blue or Copper Phthalocyanine:

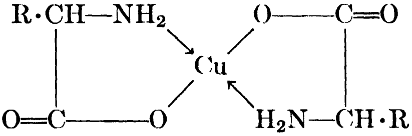


In this structure the copper is shown as a coordination complex, linkages being indicated to each of the four central nitrogen atoms.

It may also be regarded as a chelate structure. That it differs intrinsically from an ordinary metal salt is shown by its stability and its retention of copper when dissolved in concentrated sulfuric acid and reprecipitated in water. Certain other metal salts such as sodium, magnesium, lead, and stannous tin, under similar treatment, yield the metal-free phthalocyanine.

Metals with a valency higher than two, according to Sander (117), such as Al(3) Fe(3), and Sn(4), when acting as the central atom in the above type of complex, can firmly hold halogens and certain other negative groups.

This type of compound is similar in principle to those mentioned by Sidgwick, Taylor, and Baker (125), which are formed by boiling amino acids, such as glycine, with freshly precipitated copper oxide. The blue products are not true salts of copper. Their solutions have only a very small conductivity and do not show the characteristic reactions of the cupric ion. They are coordination complexes of the structure:

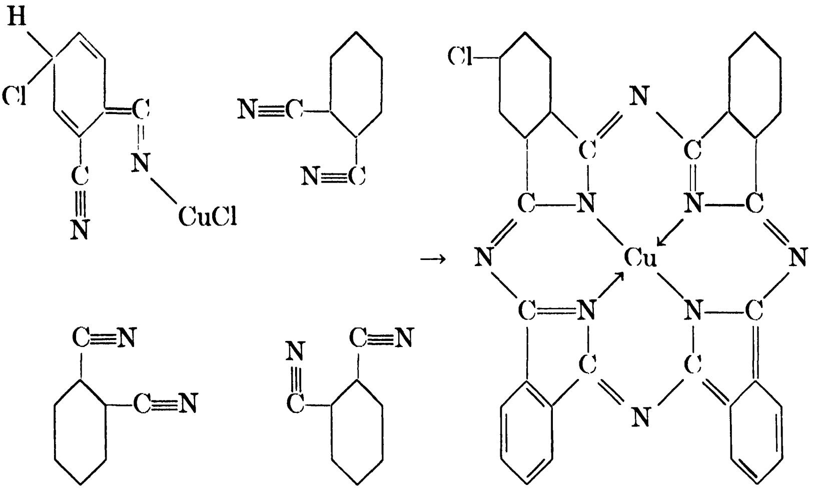


The outside hydrogen atoms, attached to carbon, are found to be replaceable by halogens, sulfonic acid groups, amino and substituted amino groups, phenyl, nitro, and azo groups. The two inside hydrogens, attached to nitrogen, have been replaced by such metals as lithium, sodium, potassium, beryllium, magnesium, calcium, barium, zinc, cadmium, nickel, manganese, cobalt, chromium, lead, copper, mercury, stannous tin, and ferrous iron.

In certain cases, such as halogenation, the dye may be substituted directly. In other cases it is necessary to employ intermediates containing the desired substituting elements or groups. For example, direct chlorination of the metal phthalocyanine may introduce fourteen to sixteen chlorine atoms and yield a green pigment of considerable interest. On the other hand, phthalocyanines, in which the outside hydrogens are replaced with methyl, ethyl, or propyl groups, have been prepared by treating the intermediate phthalonitrile with the corresponding Grignard reagents (17).

It is very difficult if not impossible at the present time to account fully for the mechanisms of the reactions entering into the formation of the phthalocyanine structures, even though the possibility of addition reactions with the cyanide or nitrile compounds is well recognized.

Without attempting a complete picture of the reaction mechanisms involved, Sander (117) has presented an arrangement which is very interesting:



The indicated formation of a halogen derivative when using a metal halide, such as CuCl, with the ortho dinitrile, was for some time an objection to the use of such halides. The amount of halogenation was reduced by using metallic copper with the cuprous chloride in forming copper phthalocyanine. Lacey (86) was able to produce the halogen-free material by conducting the reaction of the *o*-dinitrile and cupric halide in the presence of an inert diluent and anhydrous or substantially anhydrous ammonia.

Copper phthalocyanine is quite readily sulfonated by dissolving in concentrated sulfuric acid and heating or by using the stronger sulfonating acids. It is possible to introduce sulfonic acid groups in all four of the benzene rings of a phthalocyanine, but the disulfonate has been found most useful. This product is soluble in water and can be readily precipitated with alkaline earth salts. In this way the color can be thrown down on white bases such as alumina hydrate or blanc fixe to yield very clean and quite light-fast lakes.

The phthalocyanine pigments, therefore, include four important types:

1. Metal phthalocyanines.
2. Metal-free phthalocyanines.
3. Halogenated metal phthalocyanines.
4. Sulfonated metal phthalocyanines.

Properties of the Phthalocyanines

Phthalocyanine pigments (4) as a class vary from blue to green and are brilliant tinctorially. They are insoluble in water and substantially insoluble in the vehicles and solvents used commercially in the pigment-consuming industries.

They are extremely stable to heat and to the majority of chemical actions, but somewhat sensitive to acid-oxidizing agents, which yield phthalimide and ammonium salts. At temperatures of about 500° C, copper phthalocyanine and the metal-free phthalocyanine sublime without appreciable decomposition. Strong acids, such as sulfuric, phosphoric, and trichloracetic, give stable solutions, in some cases with gentle heating, which reprecipitate the original color on drowning in water, whereas heating with fuming sulfuric acid yields the water-soluble sulfonic acids. The halogens, chlorine and bromine, react readily with the phthalocyanines at ordinary temperatures; at higher temperatures, substitution is much more complete.

When used as a pigment, in certain vehicles, there appears to be an action, similar to crystal growth, which steadily changes the nature of the pigment particle, causing some difficulty in its use. The change is accompanied by progressive loss of tinctorial strength as well as alteration in hue and brilliance.

Copper Phthalocyanine

The most important of the phthalocyanine pigments, up to the present time, has been the copper derivative, known commercially as Monastral Blue, Heliogen Blue, or Syan Blue. One reason for its early and enthusiastic reception was the fact that its tinctorial characteristics supplied a long-felt need for a brilliant blue of excellent permanency toward light and resistance to chemical influences. Another reason was the possibility of obtaining greens of satisfactory properties by blending the phthalocyanine blue with highly permanent pigments such as hansa, benzidine, and zinc yellows.

The manufacture of copper phthalocyanine may be carried out according to three modifications of the type process (4):

1. Phthalonitrile + copper → copper phthalocyanine
2. Phthalonitrile + cuprous chloride → copper phthalocyanine + monochlorocopper phthalocyanine
3. Phthalic anhydride + urea + cupric chloride catalysts → copper phthalocyanine

The mechanism and the optimum conditions of these synthetic reactions are not so well known, the third method especially being poorly understood. Although this reaction, resulting in the synthesis of the highly complex molecule, is effected with surprising ease, numerous difficulties are involved in actual manufacture, such as choice of materials for equipment and the control of a highly exothermic reaction.

After completion of the direct synthesis, the task of supplying a marketable pigment is only partially finished. The product when prepared as outlined above is essentially useless as a pigment because of its hard gritty nature and otherwise undesirable properties, as well as its low tinctorial strength. These very serious shortcomings may, apparently, be ascribed to unfavorable crystal structure. Favorable alteration of this property is accomplished by dissolving the crude pigment in concentrated sulfuric acid, whereupon the green sulfate is formed, then drowning in a very large volume of water, under agitation, which results in the regeneration, through hydrolysis, of free copper phthalocyanine in a completely altered physical form. The conditions for this acid-pasting operation can be varied over a wide range, and, by proper choice of conditions, a product is obtained in the much more intensely colored form in which it is known in the pigment industry.

The ability of the copper compound to pass through this acid-pasting process, without liberation of the copper, is an excellent illustration of the fact that this metal is united in the organic molecule much more firmly than by a salt-like union. If this water paste is dried out by orthodox procedures, the pigment is still hard and gritty and yields its full color value with extreme reluctance in typical commercial grinding procedures. In connection with this operation noteworthy progress has been made in conducting the drying so that the fine dispersion is retained, producing a pigment of acceptable texture. Full-strength or "toner" products, therefore, are finding worthwhile industrial use.

A much larger amount of the present output finds its way to the consuming trade through the medium of products modified in various ways. For instance, the water wet paste is supplied to the pigment-manufacturing trade, where it is converted into products extended on barytes, blanc fixe, gloss white, alkaline earth resinates, et cetera. The water paste may also be converted into a so-called water dispersible or colloidal form by proper mixing into suitable organic media, after which it may be dried and ground to a powder showing, when placed in water, a dispersion suggesting that of a true solution. These products are used in wallpaper and cold water paints, usually after further processing by means of suitable diluents such as barytes, clay and talc.

The full-strength pigment is deep blue, with a strong bronze reflection. The extended products, including the water-dispersible type, are brilliant blue powders largely lacking in this surface bronziness. The shade is exceptionally pure, showing an almost complete absorption in the red and yellow portions of the spectrum. Copper phthalocyanine is insoluble in all ordinary solvents with the exception of concentrated sulfuric, phosphoric, chlorsulfonic, ethylsulfuric, and trichloroacetic acids. It is also resistant, even at high temperature, to organic solvents such as hydrocarbons, esters, alcohols, and ketones. It is unusually stable to heat, subliming unchanged at about 500° C and is little affected by ordinary oxidizing and reducing agents.

Copper phthalocyanine is high in tinting strength, being approximately twice as strong as iron blues and twenty or more times as strong as ultramarine. These values hold in medium and light tints; in deep shades the pigment suffers from the fact that its high strength does not make it possible to obtain the desired "bulk." Like iron blue, it gives full-strength finishes that sometimes show a troublesome bronze.

Because of the above properties, copper phthalocyanine is already finding very wide use in the formulation of various types of colored finishes, where it is used not only to obtain desirable types of blue shades but also in combination with yellow pigments, particularly zinc yellow, to give permanent greens. It is also finding a wide use in the printing ink field, where there is a considerable demand for blues of this shade with good resistance to light and chemical agents. Its other uses include the various applications of colored pigments, namely, artists' colors, water paints, coated textiles, paper, linoleum, rubber, and plastics.

The satisfactory use of copper phthalocyanine as a rubber pigment is further evidence of the unusual chemical linkage. It was pointed out by Dahlen (34) that, although it contains copper, and traces of copper ions accelerate deterioration, copper phthalocyanine has no harmful action on rubber. This indicates the unusually strong nitrogen-to-copper bond.

Chlorinated Copper Phthalocyanine

The unusual properties of copper phthalocyanine resulted in attempts to determine the effect of introducing substituents into the molecule, and these studies led to the discovery that the introduction of chlorine gave a brilliant green possessing the same outstanding fastness properties as the parent blue pigment. It was found that, as the degree of chlorination was increased, a gradual greening of the blue shade resulted, and that when twelve or more chlorine atoms were introduced into the benzene nuclei, the product was a definite green. A number of technical difficulties had to be solved in preparing the material commercially but there are now several methods which have been found to be practicable. As in the case of the blue, it is extremely important to give attention to the physical conditioning of the pigment in order to obtain satisfactory working properties, particularly texture and ease of dispersion. The same general methods which are used in the manufacture of the blue pigment are likewise applicable to the green.

The chlorine enters the molecule by substituting for the external or benzo hydrogen atoms. The commercial chlorinated copper phthalocyanine pigment contains approximately fourteen chlorine atoms per phthalocyanine unit, whereas sixteen are required for saturation. The product is a very deep bluish-green, which is almost black, with a strong bronze reflection in full or masstone shades. Lakes, including the dry dispersible type, vary from deep to light greens, depending upon the type of substratum and dilution. Resistance to chemical agents is much the same as in the case of the blue, and all evidence points to the fact that the halogen substituents are very tightly bound in the compound.

The pigment has not been commercially available for so long a period as the blue, but present indications are that it can be used for the same purpose where a brilliant bluish-green shade combined with extreme fastness is required. In such cases it has been successfully used in formulations to replace chrome greens, various lakes of basic colors, Pigment Green B, and chromium tetrahydroxide or Guignet's green. Like the unchlorinated derivative, it is high in tinting strength, being, under certain conditions of use, almost twenty times that of the last-named of the above pigments.

Metal-Free Phthalocyanine

It is of interest to note that this simplest member of the series did not receive commercial attention until the copper derivative had been developed, partly because of synthetic difficulties but chiefly because the copper pigment was discovered first. Although the metal-free product may be prepared by those synthetic processes which avoid the presence of metals, the commercial processes employ the indirect method, that is, certain metallic derivatives are first synthesized, e.g., magnesium, lead, stannous tin, or sodium, and then the metal eliminated by acid treatment.

Proper physical conditioning is achieved by the acid-pasting process already described. However, because of the ease of sulfonation, some care must be observed in carrying out this operation.

Metal-free phthalocyanine is similar in appearance to copper phthalocyanine but extends with white to a distinctly greener shade of blue more nearly approaching that of the Peacock Blue used in the printing ink industry. Its shade can be approximated by mixing copper phthalocyanine with chlorinated copper phthalocyanine, but the brilliancy of the mixture is somewhat reduced.

The fields of application are the same as those of the other types except where the greenish-blue shade is required.

Sulfonated Copper Phthalocyanine

In the work on the preparation of new derivatives, efforts have been directed toward preparing a sulfonated product, chiefly from the angle of utilizing the dye in a soluble form for the dyeing of textiles and other materials. The reaction can be carried out by the usual sulfonation procedures, and it is possible to introduce sulfonic acid groups by replacement of hydrogen in any or all of the four benzene nuclei of copper phthalocyanine. As might be expected, the solubility in water, particularly that of the alkali-metal salts of the sulfonic acid, increases as the degree of sulfonation is increased. For most purposes the disulfonic acid is the most suitable product.

Sulfonated copper phthalocyanine is a brilliant greenish-blue dye of moderate solubility and can be converted to insoluble toners and lakes by precipitation with alkaline earth salts. It has been investigated in only a preliminary way in the finishes field, and there is some doubt that it will reach the importance of the types discussed above since it is somewhat lacking in extreme fastness to light.

Comparisons with Other Pigments

It is evident that phthalocyanine derivatives represent definite chemical novelties in the pigment industry, neither more nor less complicated than many existing commercial materials used by this trade. It is not surprising that their physical properties are likewise quite different from those of existing materials and present many problems to the pigment-manufacturing and pigment-consuming trades. This statement applies not only to texture as touched upon above but also to the larger and possibly more intangible problems of hiding power, bronzing on weathering, can stability in shelf goods, gloss of enamels, oil absorption, et cetera, all of which are very incompletely understood as properties of this group of pigments but which will probably be explored gradually in future activities. It is emphasized at this point that in attacking these problems a new class of products is being dealt with and too much dependence should not be placed on methods of approach that have been effective in orthodox materials.

Because of this very decided difference between phthalocyanine derivatives and existing products, estimates of the relationships in the field of usages are likely to prove extremely erratic and have been avoided in this review. Comparisons of copper phthalocyanine with iron blue and with ultramarine blue in certain properties and of chlorinated copper phthalocyanine with Guignet's green are recorded, however, for what suggestive value they may contain.

For instance, iron blue of the paint and lacquer type gives a deep blue-black masstone in full shades and very pleasing blue shades of good permanence and durability with 10 to 25 per cent of zinc oxide or other extending whites. As the extension increases, a point is reached where the color stability fails, and this shortcoming of iron blues is quite generally recognized. If copper phthalocyanine is formulated in finishes in full shades, it gives dirty greenish-black tones of a high and objectionable bronze which increases on weathering. As the white is increased, the pleasing shade of blue results and bronziness disappears. These light-blue shades are more brilliant and durable than those prepared in an analogous manner from iron blue and white. Two important practical problems confront the producer of finishes in connection with the formulation of this "ladder": (1) the determination of the points at which bronziness is eliminated, the resultant of the balance of a number of factors other than concentration of colored pigment, e.g., the vehicle and type of extender, and (2) the study of the influence of varying concentrations and types of white extenders with respect to chalking.

As compared with ultramarine blue, copper phthalocyanine is greener, less brilliant, and very much stronger. It shows a better degree of durability, however, under most conditions; hence there will be some encroachment in the field of these finishes where durability is paramount. Agencies and factors such as these have been widely studied by paint chemists and technicians in connection with the orthodox pigments, and, as their behavior in connection with this new class of pigments is better understood, the usage of these new colors can be expected to expand.

Likewise phthalocyanine green shows a somewhat similar relationship to orthodox pigments. It is unsatisfactory in full shades, but, just as in the case of the blue, desirable shades may be obtained by proper formulation. Thus by proper choice of vehicles and of white extenders, brilliant bluish-green shades are obtained; and here again the possibility of tints of acceptable durability is suggested. The shade is more nearly that of chromium hydrate or Guignet's green than of any of the established pigments. Because of its greater brilliancy and much higher strength, its market price will not prevent it from invading this field to some extent.

These relationships may be taken as illustrative of the problems associated with the determination of the industrial place for this new class of pigments. Exact statements relative to the degree of replacement of orthodox products cannot be made, but the position of the new products will be worked out as a result of persistent and continued research. As suggested above, there will be some invasions of the field of iron blues, ultramarine, and chromium hydrate. Nevertheless, it is believed that their greatest consumption will be in fields of their own which they will gradually establish. Now that the synthetic and manufacturing phases of this important development have proceeded to a point where the products described above are widely available commercially, the most active field of research for the more immediate future is likely to be concerned with usage problems.

Chapter IX

Testing of Pigments

GENERAL CONSIDERATIONS

The artistic or commercial value of a pigment is dependent to a negligible degree on the physical, chemical, or tinctorial properties of the material in straight pigment form, but to a very high degree on these same properties when incorporated into various media. Thus a pigment too hard to be dispersed in a very finely divided form in a given medium, whether it be an oil, varnish, or rubber, is of little value, whereas a soft pigment of the same general tinctorial properties may be useful in many commercial fields. This simple example illustrates the necessity of developing methods that are able to establish accurately, in specific instances, the suitability of a given material as a pigment, and, in addition, to reveal the type of use to which the product is best adapted.

It is customary, therefore, to employ a great variety of tests, not, as a rule, to determine whether a product is suitable for use as a pigment but in order to control the desirable qualities of the material in either experimental development or manufacture. Previous chapters have indicated the sensitivity of many pigments in the various steps of normal synthesis and the control methods employed to eliminate, as completely as possible, variable factors in those operations. It is essential to be able to determine quickly and definitely the results of unavoidable variations that appear.

Many tests are based on the special use to which the product is to be put, involving perhaps the use of a special formulation in which may appear an unusual vehicle. Other tests are designed to give information of a more general nature, applying, possibly to the use of the pigment in a variety of color-consuming industries.

As a rule, the physical factors are noted first, the fineness, softness, and freedom from excessive moisture. A more critical examination follows, including actual determination of moisture content, analysis for water-soluble materials, estimation of fineness by screen test, determination of specific gravity and oil absorption, and a measurement of softness of texture by grinding in a suitable vehicle.

Beyond preliminary and control tests, many procedures are available for establishing the suitability of a pigment for use in such different fields as paint, varnish, lacquer, enamel, printing ink, rubber, linoleum, leather, wax, plastics of various types, paper, wallpaper, casein, and other aqueous paints, surface coating formulations, cements, and ceramics. It would not be feasible, however, to cover a great number of these tests in detail in this book, as other books, such as Gardner's (51), make such information quite complete and readily available. Only a few of the more usual and important tests will be discussed. They may be arranged in three major groups: physical tests; chemical tests; formulation tests.

PHYSICAL TESTS

Physical tests are those observations and measurements that are made upon the straight pigment in paste, lump, or powder form. They include the following:

Physical appearance
Fineness
Texture or hardness
Moisture
Specific gravity
Bulking value
Water-soluble matter

Physical Appearance Test

The physical appearance test is purely an observational test of special value in comparing different batches or lots of the same product. In some cases variations in quality are reflected in significant differences in appearance that may be due either to physical or to chemical fluctuations from the normal. Errors in conditions of formation, washing, drying, or grinding may cause notable alterations in the physical appearance of the final lump and ground product.

This observation may be of special interest in connection with certain types of reduced pigments, such as crayon colors, for example, which contain a high percentage of clay or other inert white material. A simple mixture of the full-strength color with the clay and other colorless ingredients would probably appear to be a very weak chalky powder, showing definite white and colored streaks if pressed or rubbed with a spatula. A wet mixture of the same composition, dried and ground, would have a much fuller richer color and be nearly free from streaking tendencies when tested as before. The latter product would make a far stronger appeal to the good judgment of the buyer.

Hardness or softness of a pigment may be quite definitely reflected in the physical appearance, the soft product appearing more fluffy and the harder product more dense and sandy. Occasionally a variation of as much as 160 per cent will be observed in the apparent density of products which have been thrown into a condition of extreme hardness by errors in manufacture.

Physical appearance is of the greatest value to the manufacturer at the time the product is discharged from the dryer in lump form. At that point observations of great significance can be made bearing on the efficiency of washing and drying and, frequently, indicating the hardness or texture and uniformity of final product.

This is a test of broad significance and great value.

Fineness Test

The fineness test is a measure of considerable value as it indicates whether the disintegration of the dry lump product has been conducted under normal conditions. It may also serve to detect accidental holes in the grinder screen which permit the passage of incompletely ground particles. It is influenced to some extent by the hardness or texture of the dry pigment, but should not be confused with it. Further grinding has a definite and marked effect on fineness, but none on hardness.

Fineness is conveniently determined by passing a weighed sample of the powder through a nest of calibrated screens of possibly 80, 100, and 200 mesh, and weighing the material retained on each.

Another common test is made by washing a weighed sample of powder, thoroughly wet with water, through a 325-mesh screen and weighing the dried residue on the screen.

Fineness is generally a more important consideration in a pigment that is hard in texture, as it favors a more ready incorporation of the product in the vehicle or medium to be used. In soft pigments fineness is much less essential.

Texture Test

The term *texture* has a variety of meanings in the field of pigment colors. One definition is based on the incorporation of the pigment in a varnish and a rating of the ease with which a smooth ink is obtained upon grinding on a roller, or other type, mill. This is frequently referred to also as *ease of grinding*, and more properly so, inasmuch as the interpretation of texture is dependent on the grinding efficiency, which is a distinctly variable factor, and also on the strength of the sample, which may give variable effects at different points in a progressive grinding operation.

The so-called finger test for texture of the dry powder is not so well understood as it should be. As frequently used, it is hardly more than an indication of fineness, while, if properly used, it is entirely independent of that factor. Those who use this test properly, prefer to use it on lump or unground materials, as it is then somewhat easier to disregard the factor of fineness.

The test should be made by placing the pigment upon a somewhat rough type of paper and then feeling the material with a fingertip, using a variable pressure. Relatively small differences in hardness become immediately evident. The distinction between a product of a soft talcy feel and one with a slight "tooth" is very sharp, and some of the really soft pigments give a characteristic "squeak" when the finger is drawn slowly over them with a fairly strong pressure. The wide departures from mere considerations of hardness and softness, encountered in practical use, make this test, when properly handled, the only reliable test available for evaluating the texture of the straight dry pigment.

Gardner (51) recognizes the sharp distinction between texture of the dry pigment and that of the ink or paint in which it may be incorporated. He says:*

> With respect to pigments, texture is the hardness and possibly the shape of the individual particles rather than the degree of subdivision. A pigment may be finely divided and hard or soft: may be finely divided and flaky or needle shaped, etc. With respect to the film of paint or enamel, the texture may be rough or smooth and at the same time hard or soft. A hard finely divided pigment may produce paints of good (smooth) or poor (rough) texture. Texture is a factor in grinding. Hard pigments may cause great wear on grinding mills, but their paints may have a smooth texture. Soft pigments may sometimes result in paint of rough texture. Pigments may first disperse satisfactorily in a vehicle to produce a paint of good texture, but, on aging of the paint, may gradually flocculate into hard aggregates and convert the paint into one of poor texture. Generally speaking, however, a pigment of soft texture disperses more readily, has less tendency to settle and harden, and grinds more easily, produces a smoother finish, makes a better flowing and spreading paint than one of the hard texture.

These two conceptions of texture, pigment texture and ink or paint texture, should be recognized as distinct and examined individually, as each is capable of contributing information of real value in the development and control, as well as in the use, of commercial products.

Moisture Test

Organic pigments, considered as a class, are exceedingly variable in their retention of moisture under normal drying conditions. Certain types appear to retain no water in either combined or loosely combined

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form. Others, such as the alumina hydrate lakes, retain a considerable amount of water, part of it loosely combined, that is, removable by drying in an oven at 120 to 180° F, and part more tightly bound and removable only at higher temperatures.

In another type of pigment, of which the sodium Red Lake C is an example, moisture appears to be retained as actual water of crystallization. The color values and working characteristics of the pigment are dependent directly on the amount of water in combination.

With these variable types of material it is evident that the method of moisture determination must be adapted to the individual pigments. For example, the first type mentioned above may be dried in an air oven for two or three hours or more at 110° C, depending upon the size of sample, with excellent results. Pigments of the alumina hydrate lake type should be dried in an oven for several (4-8) hours at 140° F in order to eliminate more than the normal amount of moisture. The lakes will dry to very nearly constant weight at this temperature; at higher temperatures more water is progressively lost.

In hydrated colors, like sodium Red Lake C, it may be of primary interest to know the total amount of moisture present, and not simply the excess above a normal amount. This may be accomplished by drying to constant weight at 150° C.

Distillation Method. A method of moisture determination quite commonly used for pigments is distillation with organic liquid such as toluene. The sample of pigment is placed in a flask with toluene, which has been boiled free of moisture. The toluene is then distilled, carrying the moisture over into a condenser that retains the condensed water and returns the toluene to the flask. When no more water comes over, it is measured volumetrically. This method is very useful.

Specific Gravity Test

The specific gravity, or density, determination is of comparatively little value as a test in ordinary pigment work, but it has real significance in connection with formulations using vehicles, in cases where one material is replaced with another. In such cases it is important that the volume relations of pigment to vehicle should be but little changed, and the densities of the two materials are used to maintain fairly constant proportions. Of course the specific gravity could be used to differentiate between certain types of pigments, but as a rule more rapid and significant tests are available.

Specific gravity is generally determined by introducing a weighed amount of pigment powder into a pycnometer, wetting thoroughly with an organic solvent, such as a petroleum distillate, which has no tendency to dissolve the pigment, filling to the mark with solvent, centrifuging to eliminate air, refilling to the mark, and weighing. The specific gravity is then calculated as follows:

$$\text{Sp. G.} = \frac{A \times B}{A + (C + D) - (C + D + A)}$$

in which A = weight of pigment,
B = specific gravity of solvent,
C = weight of pycnometer,
D = weight of solvent.

Bulking Value Test

Bulking value, or what is sometimes called *apparent density,* is determined by sifting the powder carefully through a Scott volumeter into a carefully calibrated container, usually of 3 cubic inches capacity. When the container is filled to overflowing, the excess is scraped off carefully with a spatula held perpendicular to the container top, and then weighed.

The bulking value is expressed as the weight of product per cubic inch in grams. It is useful in the handling of formulations.

Water-Soluble Matter Test

In organic pigments, water-soluble matter may consist entirely of inorganic salts, such as sodium chloride or sodium sulfate, or it may contain material of organic composition such as coloring matters, rosin or fatty acid soaps, or sulfonates of aromatic compounds.

Two methods in common use for determination of water-soluble matter are (1) extraction with water followed by evaporation or (2) measurement of the conductivity of the aqueous extract.

Extraction with Water. Extraction with water, followed by evaporation, is the more reliable method as it gives directly the entire material actually removed from the pigment in the extraction. The question of technique to be followed, however, is important. Pigments that have no tendency to dissolve in water, or to hydrolyze, may be extracted by a prolonged digestion with a considerable volume of water, and possibly at elevated temperature. In this way a very complete removal of soluble matter will be accomplished.

Other pigments, such as reduced lakes of soluble dyestuffs, have a tendency to hydrolyze and develop a "bleed" in water. This tendency is increased by larger volumes of water, longer time of digestion, and by higher temperatures, so that it becomes necessary in such cases to establish conditions that result in removal of a great portion of the water-soluble materials without causing too much hydrolysis. These details may be different for each type of pigment, and it must be recognized that the value obtained is an approximation.

Conductivity Method. In the conductivity method, a given weight of pigment is digested for a definite length of time in a measured volume of water, sometimes with the addition of a wetting agent, at a definite temperature. The aqueous extract is filtered off, placed in the conductivity cell, and the resistance to passage of an electric current measured. The result is calculated in terms of the known resistance of a salt solution such as sodium chloride or sodium sulfate.

The method is particularly useful in control of established operations, such as washing, in which the actual value is of less importance than the relative value from one operation to another. However, when the water-soluble matter is known to be a definite salt, such as NaCl, the accuracy may be very high.

BLEED TESTS (40)

Water Bleed

In this test 0.3 gram of color is vigorously shaken with 15 cc of water in a test tube for one minute, then filtered through two thicknesses of filter paper. Filtration is repeated until no suspended material remains in the filtrate. The filtrate is then compared for discoloration with an equal quantity of water and rated accordingly.

Oil Bleed

In testing for the bleeding in oil, the color is rubbed in the customary ratio to give a thoroughly ground paste. To this is added enough additional oil to give a very thin ink that will drop off the tip of a spatula. The thinned paste is spotted on porous filter paper and the "ring" observed. The ratings given are based on a comparison with a spot of oil alone. If the colors are very finely divided, a very fine dispersion may result, which should not be confused with a true bleed.

Lacquer Bleed

A typical lacquer thinner consisting of approximately 40 per cent esters and alcohols, 50 per cent coal tars, and 10 per cent naphtha is used. In this test 0.3 gram of color is vigorously shaken with 15 cc of the thinner in a test tube for one minute, then filtered through filter paper. Filtration is repeated until the filtrate is free of suspended material. The filtrate is then compared for discoloration with an equal quantity of clean thinner and rated accordingly.

Synthetic Bleed

This test is made similarly to the lacquer bleed test except that pure coal tar thinners are used in place of lacquer thinners.

TESTS DEPENDING ON ELECTROMAGNETIC WAVES

Among the most useful physical tests which make it possible to gain an insight into the nature of the pigment particle are those depending upon the various types of radiant energy composing the electromagnetic spectrum. One portion of this spectrum is known as light, or the visible spectrum, but this portion is only a very small part, estimated as one so-called octave, of the spectrum as a whole. Beyond the red in the visible spectrum lies the longer wavelength infrared region, which extends over a range of about seven octaves. On the other side, beyond the violet of the visible spectrum, lies the shorter wavelength ultraviolet region, which extends over a range of only two or three octaves. Still farther out in the same direction lies the X-ray region, which covers a range of about five octaves. This entire useful range covers about twenty octaves.

In order that records may be made in the invisible regions of the spectrum it is necessary to have some means of detecting and recording the energy corresponding to those wavelengths. It is a fortunate circumstance that the photographic film is sensitive to all twenty octaves of the electromagnetic spectrum involved in these tests so that the instruments that have been devised for measurements of this sort depend largely upon photographic records.

The Spectrograph

The instrument that has been of greatest value in the field of pigments in the past, and will continue to be of very great value in the future, is the spectrograph (18). In this instrument, light or electromagnetic waves are passed through a series of slits, lenses, and prisms as shown in Fig. 26 in such a way that the light is dispersed into a band of wavelengths, the shorter wavelengths being dispersed to the greatest degree.

There are two fundamentally different types of spectrograph, one designed to record the bright line spectrum of a material placed in the electric arc and completely burned. This instrument is used primarily in the identification and quantitative estimation of metallic constituents as indicated in the section on spectrographic analysis (page 254). The other type, the spectrophotometer, is used to record the existence and nature of absorption when light of continuously changing wavelength is transmitted through or reflected from a given material.

The adaptability of this basic instrument to a wide variety of uses has extended its field tremendously. For example, in order to extend the recording of absorption spectra into the infrared region it was necessary to employ prisms of rock salt or sodium chloride, whereas in order to record absorption in the ultraviolet region it was necessary to employ prisms and lenses of quartz. With these instruments it has been possible to study the problems of absorption over a wide range of the electromagnetic spectrum.

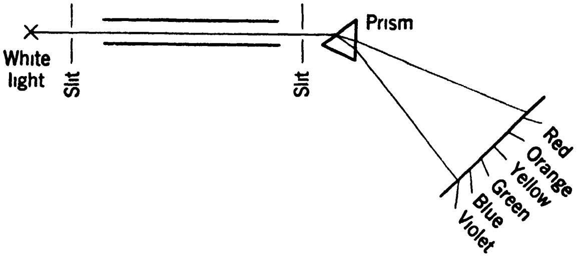

FIG. 26. Path of Light Rays in Spectrograph.

The use of the spectrograph in analyzing pigments for their metallic and non-metallic constituents is covered more fully in the section on chemical analysis (page 254). Its use in the recording of absorption characteristics in pigments and dyestuffs brings it into the group of physical tests used particularly in identification work, and for this reason it will be discussed more fully in the section on color curves in Chapter X (page 299).

Microscopes

The microscope, in principle, is an instrument provided with lenses so arranged that a very minute object may be enlarged to a degree that will permit it to be seen with the eye, or photographed. Photography is of special value in this field since the photographic film is sensitive to the entire twenty octaves of the electromagnetic spectrum, and records of permanent value can therefore be made in the regions in which the eye is of no assistance.

The Light Microscope. The light microscope has been used quite extensively in the study of organic pigments not only in the finished pigment form but also in connection with the investigation and control of intermediate stages in manufacture.

In certain azo type pigments, intermediate compounds are in a solid crystalline condition and the microscope makes it possible to detect and record changes in physical condition which are highly significant. For example, in the lithol red operations, Tobias acid, 2-aminonaphthalene-1-sulfonic acid, is precipitated in the form of the free insoluble acid. Very interesting and significant changes are revealed by microscopical examination and may be recorded photographically. When the Tobias acid is diazotized, the diazonium salt is also insoluble and precipitates in the form of crystals which undergo rapid and important changes in crystal form and size. These changes can also be closely followed and recorded. Such records are shown in Chapter VIII under lithol reds (page 116), as made by the Research Laboratories of the Imperial Paper and Color Corporation. Low magnification, of 200 to 500 diameters, is suitable for these studies.

The final pigments, whether in the form of the wet suspension or the dry powder, exhibit a very small particle size, and a much higher degree of magnification is required. The photomicrographs of toluidine red shown in Chapter VIII are made at a magnification of 1750.

The factor of particle size, as revealed by the microscope, is rather indefinite. As a rule the particles shown on a photomicrograph are not uniform but cover a wide range in shape and size. For this reason the significant value in such an estimation is the size distribution curve which appears to be of considerable significance.

The samples for microscopic examination may be taken or prepared in a variety of ways. The aqueous suspensions used in manufacture can be employed to advantage in many cases, and this is particularly fortunate in studies made to follow and record rapid changes in the particle. A drop of the suspension is simply placed on a microscope slide and pressed out to a fairly thin layer under a cover glass.

In the case of the final dry pigment, the powder can be incorporated into a suitable vehicle, such as an oil or a varnish or even a nitrocellulose lacquer, by means of a method of grinding or breaking down of the solid aggregate which will not fracture the fine crystal particles too severely. The resulting ink is placed between a microscope slide and the cover glass and pressed to a thin film.

The results of microscopic examination of final pigment particles are, in some instances, less striking than may have been anticipated. For example, it may be of interest to check the changes in particle size, shape, and uniformity which occur when a change in procedure results in a marked alteration in color values. Frequently no appreciable change is detected in either the size or shape of the visible particles. A simple examination of the actual physical conditions existing in the two cases may reveal why the change is not more evident. There may be, perhaps, a change of 10 per cent in the strength of the product. This may be related to a change of 10 per cent, possibly, in either the surface area or the cross-section area of the particles. In either case the actual change is not in the size of the medium particles, as their average remains essentially the same, but almost entirely in the large number of very fine particles that are much less conspicuous and may in many cases be practically disregarded. Those are the particles that contribute toward crystal growth by going into solution and redepositing on the larger crystals, or by attaching to the larger crystals and

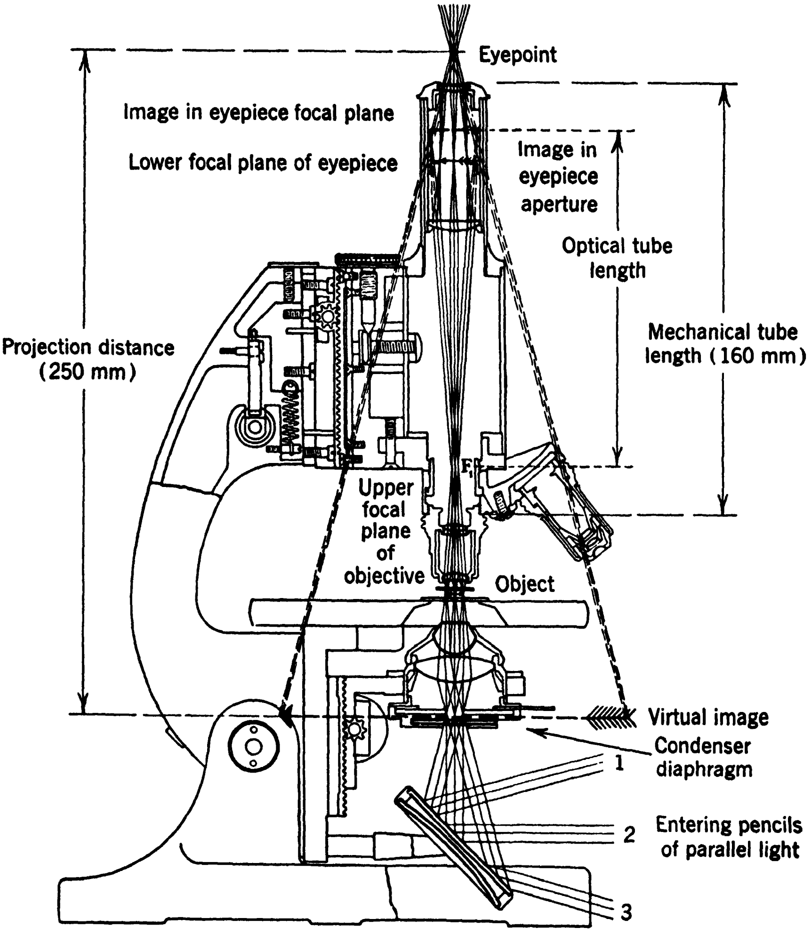

FIG. 27. Light Microscope. (*Courtesy of Bausch and Lomb Optical Co.*)

becoming firmly united with them, but their disappearance may not be recorded.

If, for example, a suspension consisting of uniformly graded particles, from large to extremely small, should undergo a change whereby all increased in size by 10 per cent, to all appearances the gradation would be as before. The only evident changes would be in the 10 per cent increase in the size of the few very large particles and the disappearance of a considerable number of the extremely fine particles, but this change should be recorded in an accurate size distribution curve.

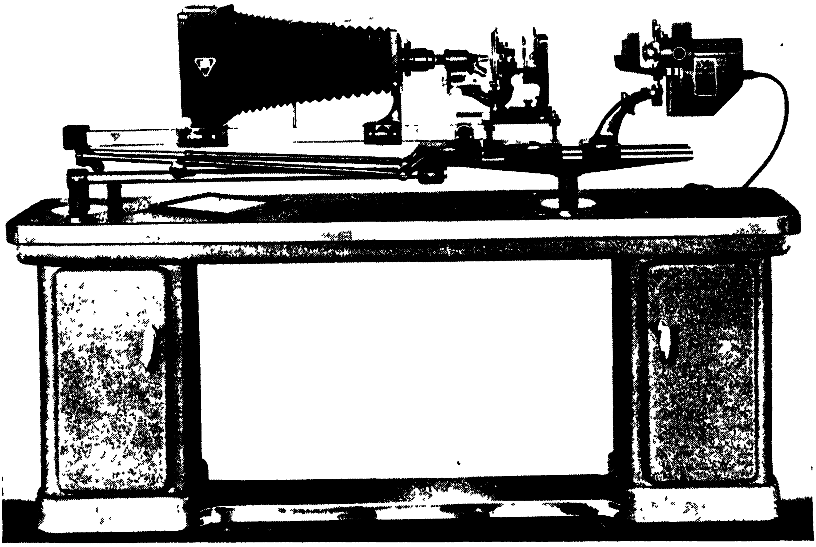

Fig. 28. Research Microscope on the Photomicrographic Equipment. (*Courtesy of Bausch and Lomb Optical Co.*)

Although the microscope is one of the oldest types of scientific instruments, marked improvements have been made in the past few years. The modern research microscope is an exceedingly interesting and useful tool in the hands of the investigator. Figure 27 is a chart of the mechanical construction and the path of light of one of the new research instruments, made available through the courtesy of the Bausch and Lomb Optical Company. It is of special interest for comparison with the schematic diagram of the electron microscope shown in the next section.

These instruments are adapted not only for direct visual examination but also for enlargement by projection. The set-up for photomicrographic work is shown in Fig. 28.

The Ultraviolet Microscope. The ordinary light microscope is limited in its usefulness by the fact that it employs relatively long light or electromagnetic waves, in the region of 400 to 700 mμ. Observation of particles of dimensions in this range, however, is unsatisfactory and observation of smaller particles is impossible. When the dimensions of a particle approach one half the wavelength of the light being used, the object cannot be clearly observed.

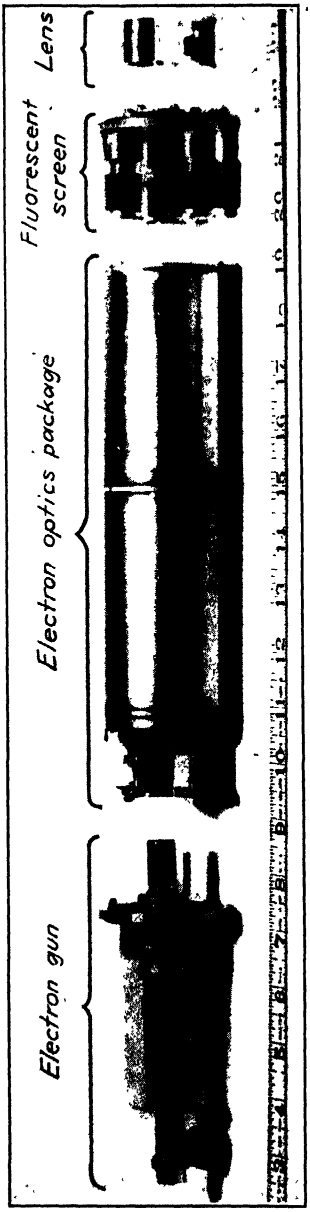

FIG. 29. Electron Microscope Units. (Courtesy of General Electric Co.)

It has, however, been possible (121) to extend the application appreciably unto the range of smaller particles by using the shorter wavelength ultraviolet light instead of visible light. This is accomplished by using quartz lenses in the microscope, as quartz is transparent to ultraviolet rays while the usual glass lenses are opaque to the shorter wavelengths. The technique has proved useful in many cases when combined with microphotography.

The Electron Microscope. In the attempt to observe very fine particles, a further step was taken in the development of the electron microscope, which originally appeared as a very expensive and cumbersome instrument. It is now being built and used as a relatively portable type of equipment. The principle of the electron microscope is based on the fact that streams of electrons, in a high vacuum, when passed through an electrical helix, can be focused just as light is focused by glass lenses in the light microscope.

Figure 29 shows the assembly of the units in the new type of electron microscope and Fig. 30 a parallel diagram of the path of the electrons through the system. The power of the instrument depends upon the voltage impressed upon the beams of electrons, accelerating their velocity.

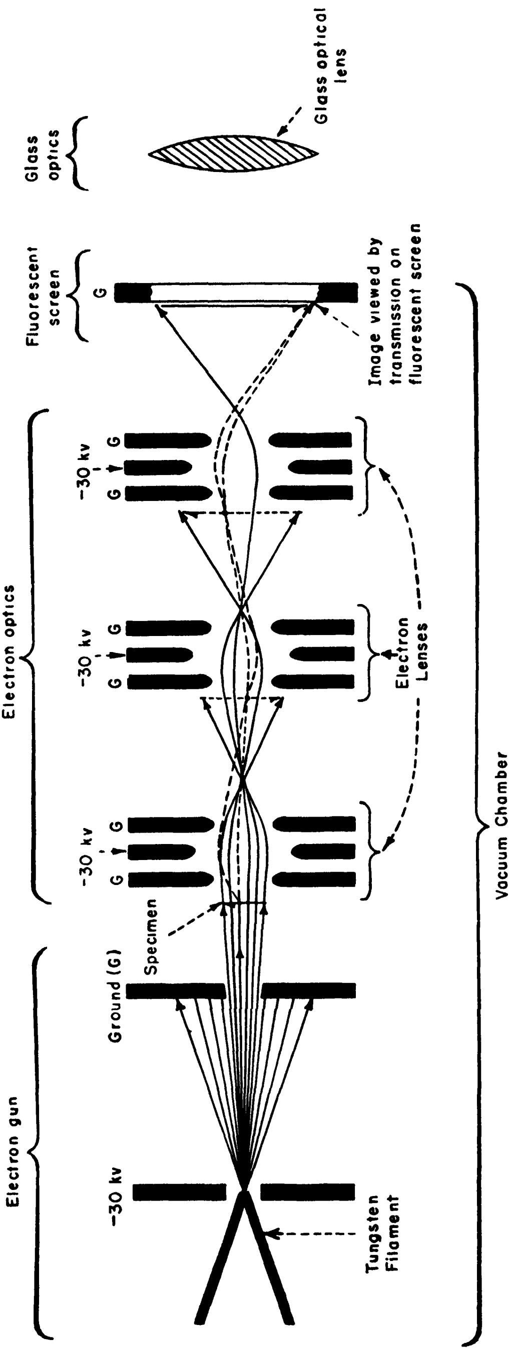

FIG. 30. Path of Electrons in Electron Microscope. (*Courtesy of General Electric Co.*)

Since most solid materials are nearly opaque to the electron streams, the particles are generally shown in silhouette, and magnification may reach 100,000 or even more. As a rule, electron micrographs of organic pigments are made at magnifications of 5000 to 20,000.

The practical limits of these various types of microscope, in comparison with the average human eye, are indicated by Gans (50), in terms of the distance between two minute particles which can be just distinguished as separate.

Human eye	50 microns
Light microscope	0.200 micron
Ultraviolet microscope	0.100 micron
Electron microscope	0.001 micron

1 micron (μ) = 0.001 millimeter = 10,000 Å (Angstrom Units)

According to Sawyer (121):*

> In electron microscopy, the specimen is carried on a fine screen (200 to 325 mesh). Anderson (6) discusses the technique of specimen preparation in considerable detail. Many specimens can be dusted or fumed directly on the support. . . . When more support than this is required, a thin film of nitrocellulose is cast on water and transferred to the screen. Wiegand used films of 150 Å for this purpose. He prepared the pigment within the film by predispersing the pigment in nitrocellulose solution before casting. He also dusted the dry pigment on the mounted nitrocellulose film.
>
> Extremely thin films are required to permit sufficient electron penetration. The fragility of the specimen support prohibits mounting techniques used in regular microscopy. The preparation of a specimen mount of proper dispersion and thickness is a matter of skill and requires considerable variation in technique from sample to sample. It is usually more convenient to disperse the specimen on, rather than in, the supporting film. This can frequently be done by dispersing the pigment in a volatile liquid. The liquid is evaporated from the supporting film after a drop has been placed on it.

Brubaker (19) has indicated the relation between particle size determinations made with the light and the electron microscopes. The light microscope has a very definite limitation, particularly in the observation of particles of very small size, owing to the "limit set on the resolving power by diffraction effects and the small depth of field." He writes:†

> The limit set on the resolving power of light microscopes by diffraction is about 0.11 micron for an ultraviolet microscope using light of 2500 Å wavelength and 0.16 micron for a glass lens microscope using light of 3650 Å wavelength. The diffraction effects which limit the resolving power cause the images formed of such particles to be inaccurate, the departure from the truth being greater the smaller

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* Reprinted with permission from "Microscopy in the Paint and Varnish Industry," Chapter 9 of *Protective and Decorative Coatings*, Vol. IV, edited by J. J. Mattiello and published by John Wiley and Sons.

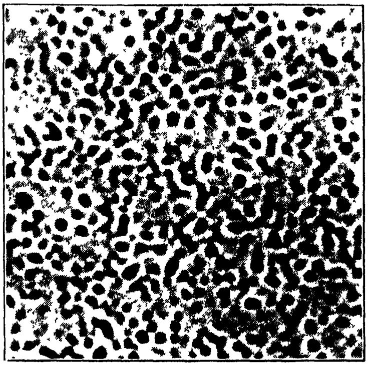
† Reprinted with permission from "Light and Electron Microscopy of Pigments, Resolution and Depth of Field," published in *Industrial and Engineering Chemistry*, Vol. 17, 1945.

the particle. Particles of size below the resolving power of the instrument with which they are viewed all appear the same size regardless of the actual size. Two small particles close together may appear as one. The contours of all images are somewhat diffused. Sharp corners appear rounded.

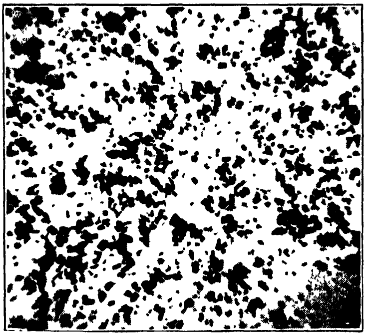
The effects of the small depth of field which is the inevitable result of the high numerical aperture of a high-power light microscope may be just as serious as low resolving power in obscuring the true shapes and sizes of particles and sometimes in producing a fictitious distribution in size. The depth of field of a high-power light microscope used photographically is only 0.1 micron or less. As a result particles, or features of particles which are more than 0.05 micron from the object plane, will not appear in focus in the microscope. Since the majority of pigment particles are larger than this, it is a practical impossibility to obtain a light micrograph of a pigment in which the outlines of all particles are in focus.

Because of the low numerical apertures which are used, the depth of field of electron microscopes as used at present is of the order of several microns. In an electron micrograph properly made, all parts of the outlines of all but the very largest particles, in any field of view, will be in satisfactory focus.

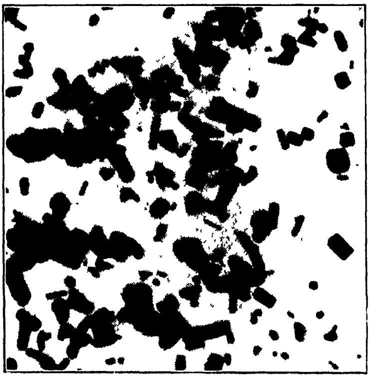
These conditions are illustrated in the three micrographs in Fig. 31. *A* is a light micrograph 3855 ×. *B* is an electron micrograph, 4000 ×, and *C* is an electron micrograph, 16,000 ×. These were all made from a specimen of small particle size zinc oxide in a thin nitrocellulose film mounted on a thin brass disk 3 mm in diameter and having a hole through its center about 0.1 mm in diameter. It is apparent that *B* gives a much cleaner indication of particle size, shape, and distribution than *A*. With reference to organic pigments, the extreme degree of disintegration used in the



A. Light micrograph, ×3855



B. Electron micrograph, ×4000



C. Electron micrograph, ×16,000

Fig. 31. Light and Electron Micrographs of Small Particle Size Zinc Oxide. (*Courtesy of the New Jersey Zinc Co.*)

earlier electron microscopic technique may interfere very definitely with obtaining the most valuable results. If penetration of the electron rays, or the transparency of suitable supporting media to the rays, can be improved, it may be feasible to operate at lower magnification, in which ranges results of greater significance may appear.

The electron microscope clearly promises to open up new vistas in pigment research. Studies of size and shape can be made without the handicap of resolving power which sorely restricts the use of the visible microscope. The next important developments in pigment microscopy almost certainly will be with the electron microscope.

X-ray and Electron Diffraction

In his book, *Applied X-rays*, Clark (30) * indicates that "knowledge of the crystalline state of matter was decidedly limited prior to the discovery, by Laue and the Braggs, that X-rays could be applied to the analysis of the internal structure of crystals. The great and relatively aged science of crystallography had been built up to the conclusion, from careful observations with microscopes and optical goniometers, that apparently almost all true solids were really crystals, either single entities with pairs of parallel bounding surfaces disposed in definite geometric fashion, at angles which could be measured, or aggregates of these single crystals."

In solids, great complications arise because the atoms and molecules are bound together tightly by their mutual forces. It is evident that the exercise of these forces should tend to produce regularity of arrangement. X-ray analysis has shown that a regularity does exist in practically every solid substance.

Assuming that such a condition of regularity requires that the large crystal should consist of smaller units of similar nature, "it follows that planes of three sets in the principal directions will enclose a small unit cell—the smallest possible subdivision which has the properties of the visible macrocrystal and which by repetition or translation of itself in all directions actually builds the crystal."

In discussing X-ray diffraction apparatus, the North American Philips Company, Inc., gives the following interesting information: †

> Every substance has a different and distinct atomic arrangement which determines its properties. Among these properties is the diffractive effect produced on X-radiation. A substance intercepting a fine beam of X-rays will produce a series

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* Reprinted with permission from *Applied X-rays*, 3d Ed., McGraw-Hill Book Co.

† Pamphlet of North American Philips Company, Inc., New York, N. Y.

of emergent beams whose separations and intensities are characteristic of the material. This phenomenon has been utilized as the basis of diffraction analysis.

By employing radiographic film, a record is obtained of both locations and intensities of diffracted beams. These form a unique pattern which in many cases serves to identify or classify the substance. In effect, the patterns provide a "finger printing" system inasmuch as no two substances have been found to produce identical patterns. In consequence, a powerful medium of comparison and identification is available.

The most extensive application for X-ray diffraction is to investigate materials that are crystalline in nature, but it has been found that valuable information regarding physical or chemical states may be obtained even from non-crystalline, or amorphous, substances.

Of recent interest to industry is the utilization of X-ray scattering to determine minute particle size and particle distribution.

Up to the present time the study of organic pigments by X-ray diffraction methods has not been extensive, but it is becoming apparent that this is a field in which results of great value may be expected. The method is now capable of giving significant information on several different phases of crystal characteristics, including the following (30):

1. Crystalline or non-crystalline nature.
2. Crystallographic system, unit cell dimensions, space group, parameters of atoms or molecules.
3. Deduction of crystal unit (atom, ion, molecule), of size of unit, of type of building, and of general properties of solid to be expected.
4. Chemical identity, chemical and crystallographic changes and stability.
5. Allotropic modifications.
6. Single crystal or aggregate.
7. Crystallographic orientation of single crystal or of grains in aggregate.
8. Random or fibered aggregate and relative degree of preferred orientation in intermediate stages.
9. Grain size in an aggregate (particularly in colloidal range).
10. Differentiation between surface and interior structure, and film structure.

It should also be realized that, in addition to the above information applying to the product itself, similar information can be gained relative to foreign materials or impurities which may exist with the product. It should be possible, therefore, to gain a much clearer picture of a given pigment, from all points of view, than has been possible in the past.

Three general methods have been used in the recording of X-ray diffraction. They are shown in Figs. 32, 33, and 34 through the courtesy of General Electric X-ray Corporation.

1. Transmission, or Laue technique.
2. Back reflection technique.
3. Hull-Debye-Sherrer Powder Camera.

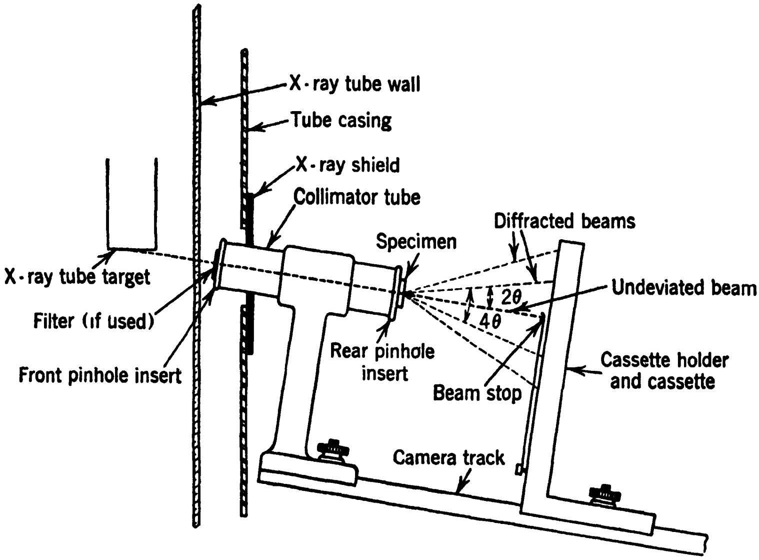

FIG. 32. X-ray Diffraction. Transmission or Laue Technique. (*Courtesy of General Electric Co.*)

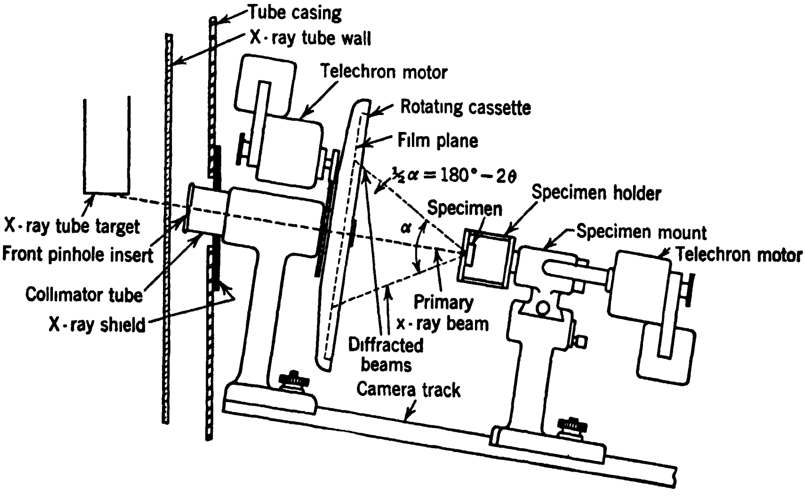

FIG. 33. X-ray Diffraction. Back Reflection Technique. (*Courtesy of General Electric Co.*)

In each case the X-ray is brought in a fine beam to the specimen. In 1 the beam passes through the specimen and the rays are diffracted at specific angles to fall on the photographic film in the cassette or film holder. The direct ray is smothered by the beam stop. In 2 the beam strikes the specimen and is reflected at specific angles back to the cassette bearing the photographic film. In 3 the specimen is placed at the center of a circular camera, which bears a photographic film around the circumference. The fine X-ray beam strikes the specimen and part is reflected to give the reflectance diffraction angles while part is transmitted to give the direct diffraction angles. In this type the primary beam is smothered after passing through the specimen.

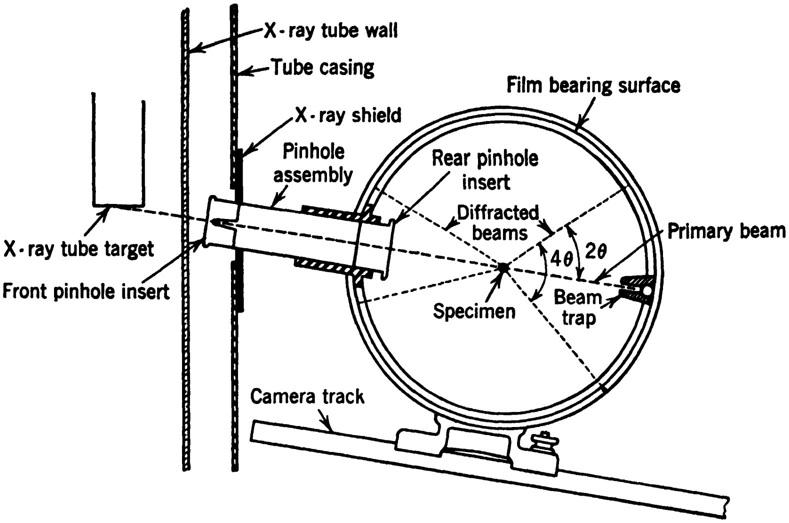

FIG. 34. X-ray Diffraction. Hull-Debye-Sherrer Powder Camera. (*Courtesy of General Electric Co.*)

A typical result obtained by the General Electric X-ray Corporation is shown in Figs. 35 and 36. Figure 35*A* is an example of the transmission or Laue technique applied to a sample of toluidine red pigment; Fig. 36 is a similar picture of a sample of toluidine red pigment recrystallized from chloroform.

The clean-cut rings formed by the diffracted rays upon the photographic film (Fig. 35*A*) indicate the fine crystalline nature of the sample, the crystals being of the order of 10^{-5} in crystal diameter. The rough, spotty rings in Fig. 36 are an indication of the crystalline

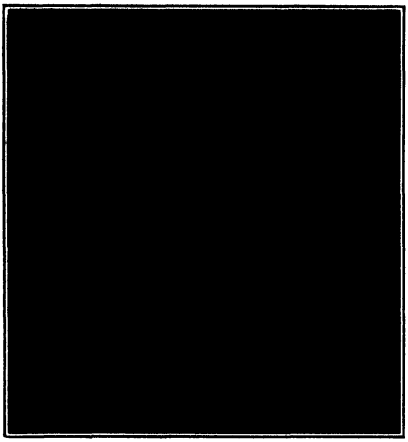

FIG. 35*A*. Toluidine Red Pigment.

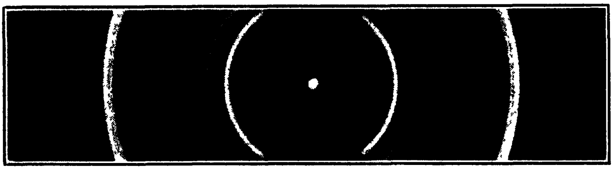

FIG. 35*B*. Toluidine Red Pigment. Transmission Portion of Record from the Hull-Debye-Sherrer Powder Camera.

(*Photographs courtesy of General Electric Co.*)

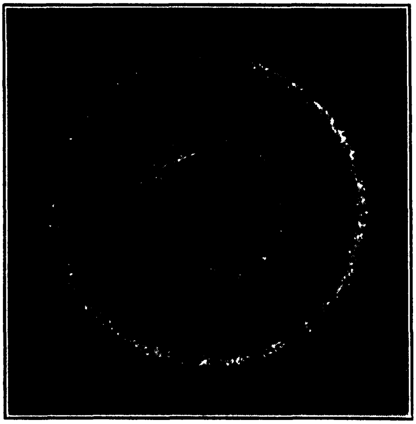

FIG. 36. Toluidine Red Pigment. Crystallized from Chloroform. (*Photograph courtesy of General Electric Co.*)

condition of the sample but also indicate that the crystals in the sample of Fig. 36 are about a thousand times as large as those in the sample of Fig. 35*A*. The similarity of the rings in the two samples indicates that the crystal forms are the same. Figure 35*B* is similar to Fig. 35*A* except that it is the transmission portion of the record made in the Hull-Debye-Sherrer Powder Camera (Fig. 34).

Another type of X-ray diffraction technique that gives valuable results, particularly in connection with indications of fine particle size or structure, is the so-called low angle scattering. In this method the rays that are deflected to only a slight extent, in some cases as little as 5 degrees of angle, are recorded photographically. A special camera (Fig. 37) known as the low angle scatter camera* is used in this work and it will undoubtedly have valuable application to the study of organic pigments.

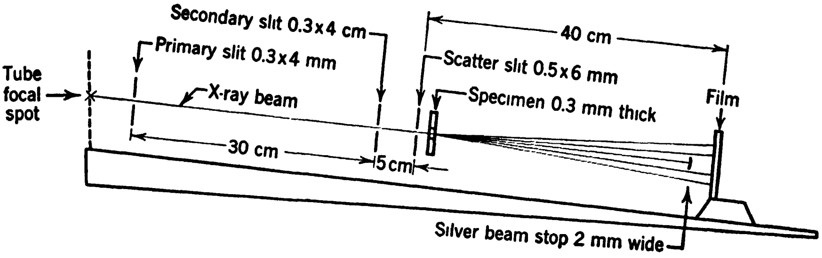

FIG. 37. X-ray Diffraction. Low-Angle Scatter Camera. (*Courtesy of North American Philips Co., Inc.*)

It is probable that the results will be of special value in the study of the surface of pigment particles, their structure, and possibly the presence of foreign materials.

CHEMICAL TESTS

The organic pigments, representing a great number of chemical types, respond to a wide variety of chemical tests, some of which are dependent upon the nature of the pigment itself, and others upon the presence or absence of impurities, inorganic salts, or excess of reagents used in the pigment preparation. Some of these tests are especially adapted for use in the identification of new or unknown pigments; others are of particular value in the control of quality in manufacture.

The chemical tests range from simple "spot tests" to complex analytical procedures and spectroscopic examination and from the

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* North American Philips Company, Inc., New York, N. Y.

detection and identification of soluble salts to the decomposition of the pigment, separation and identification of the dyestuff, or even decomposition of the color molecule with separation and identification of the intermediates from which it was prepared. The chemical tests will be discussed under the following general divisions:

Spot tests.
Chromatographic analysis.
Capillary separation tests.
Dyeing tests.
Chemical analysis.

Spot Tests

Spot tests, many of which have been popular for years as quick, simple, and, in many cases, highly accurate and reliable means of establishing the presence or absence of certain materials or conditions, have been more recently greatly extended and brought into a rather complete systematic arrangement by Feigl (45). All "test-paper" methods, such as those for acidity and alkalinity, or *p*H determination, starch-iodide tests for free nitrous acid or free halogens, and lead acetate paper tests for hydrogen sulfide, are spot tests.

A simple spot test that has been widely used in the pigment field is the alcoholic KOH test for para reds. This is carried out by applying a drop of alcoholic KOH to a so-called print of the pigment made by dispersing the color in varnish and drawing the ink in a thin film on paper. If para red is present, a purple spot appears. This test has been very useful even though it is not entirely specific.

The type of test more commonly referred to as a spot test is that in which the colors, appearing in a sulfuric acid solution of the product, are observed.

Sulfuric Acid Test (108). To a few drops of C.P. sulfuric acid, in one of the hollows on a porcelain spot plate, add a tiny particle of the pigment. Without stirring, observe the colors that appear, particularly in the zones of varying intensity, radiating out into the acid from the solid material. Then stir the mixture thoroughly to a uniform color. Finally, remove a drop on the end of a glass rod and introduce into a few drops of water in another hollow. This may result in a sharp change of color, separation of a colored solid material, or simply in dilution of the original.

Parallel tests made with pigments, or in some cases dyes, of known dyestuff content permit a very significant and conclusive comparison, and frequently a satisfactory identification, to be made.

This test may, or may not, reveal the presence of more than one dyestuff, but the technique of allowing the particle of pigment to go into solution in the acid without stirring, in the early stage, greatly improves the possibility of such detection.

A useful series of spot tests may be made on the dried prints of the pigments in varnish by applying various reagents with a glass rod and noting the *immediate* results. Table XV (144) shows a series of tests that may be applied quickly. They include spot tests, bleeding tests, baking stability tests, and resistance-to-light tests. The bleeding tests may be applied either to the dry pigments or to strips of the print, but the more delicate tests are obtained when applied to the dry pigments.

Chromatographic Adsorption Analysis

The basis for chromatographic analysis is the adsorption, and removal from solution, of colored substances. This may be accomplished by passing the colored solution through a layer or column of some material such as alumina hydrate, calcium carbonate, clay, paper pulp, active carbon, and so on, which will hold the coloring matter while allowing the solvent to pass through. In this way it is possible to eliminate undesirable substances or even separate different coloring matters.

It is also possible in many cases to adsorb two or more coloring materials, such as dyes, on the adsorbing column and then separate them by continuing to pass further quantities of the solvent through the column. Migration of the different colored substances usually occurs at different rates, and, when this is the case, continued passage of the solvent may bring about complete separation. It is then possible to examine the individual colored materials and identify them by means of spot tests and other methods.

Strain (129) in his book *Chromatographic Adsorption Analysis* discusses the application of this method to separations among the dyestuffs and particularly among the basic colors. It is possible to absorb these dyestuffs from aqueous solution on columns of either alumina hydrate or calcium carbonate, but there is a distinct variation in the ease of adsorption. His list indicates the order in which certain dyestuffs are adsorbed:

Victoria Blue B
Methylene Blue D, Patent Phosphine G
Crystal Violet 5BO, Fuchsin G, Safranine OO
Brilliant Green, Malachite Green
Auramine

TABLE

IDENTIFICATION AND PROPERTIES

Common Name of Color	Spot Tests		
	Conc. Sulfuric Acid	Conc. Nitric Acid	Conc. Caustic Soda
Lithol Toner Red	Deep blue-purple	Deep blue-purple	No change
Para Toner Red	Deep red	No change	Purple with alcoholic KOH
Toluidine Toner Red	Reddish purple	No change	No change
Red for Lake C	No change	Rich red-purple	Color partly bleached
Madder Lake	Light brown	Golden brown	No change
Permanent Rhodamine *	Light yellow-brown	Light golden brown	No change
Malachite Green Lake	Light golden brown	Bright orange	Slightly dull and darker
Methyl Violet Lake	Light golden brown	Yellowish green	Gray and brown
Perm. Violet Toner *	Light golden brown	Light golden brown	Slightly darker and gray
Perm. Blue Toner *	Yellowish green	Green-blue to brown	Grayer and blacker
Reflex Alkali Blue	Color turns brown	Color turns green	Bronze destroy
Peacock Blue Lake	Light gray-green	Greenish yellow	Greener and grayer
Perm. Peacock Blue *	Greenish yellow	Greenish yellow	Greener and grayer

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* Phosphotungstic, phosphomolybdic, or mixed toners. Other items are included

XV

OF ORGANIC PIGMENTS

Bleeding Tests			Properties		
Hot-Water Bleed	Den. Alco. Bleed	Acetic Acid Bleed	Waxed Paper Test	Bake 20 min at 270° F	Light Resistance
Does not bleed	Red bleed	Does not bleed	Does not bleed	Turns slightly brown	Fair when conc.
Slight red bleed	Slight red bleed	Dirty yellow bleed	Red bleed	Turns slightly brown	Very good
Very slight bleed	Very slight bleed	Slight orange-yellow bleed	Slight red bleed	Very poorly	Excellent if conc.
Does not bleed	Does not bleed	Orange-yellow bleed	Does not bleed	Barium lake OK. Na poor	Fair when conc.
Does not bleed	Does not bleed	Does not bleed	Does not bleed	Very poorly	Excellent
Very slight bleed	Red bleed	Pink opalescent bleed	Does not bleed	No change	Fair
Green bleed	Green bleed	Green bleed	Does not bleed	Bakes fairly well	Very fugitive
Very slight bleed	Purple bleed	Red-violet bleed	Does not bleed	Bakes fairly well	Poor
Does not bleed	Violet bleed	Violet bleed	Does not bleed	Bakes fairly well	Fair
Does not bleed	Blue bleed	Blue bleed	Does not bleed	Bakes fairly well	Excellent permanent
Does not bleed	Blue bleed	Blue bleed	Does not bleed	Bakes fairly well	Fair
Blue bleed	Blue bleed	Blue bleed	Does not bleed	Turns slightly redder	Very fugitive
Blue bleed	Blue bleed	Blue bleed	Does not bleed	Bakes very well	Fair

for comparison.

It was found that, out of thirty-six mixtures containing two of these nine dyes, all but four were resolved by adsorption. The four inseparable mixtures were:

Auramine and Malachite Green
Brilliant Green and Malachite Green
Patent Phosphine and Methylene Blue and
Fuchsin G and Safranine

A similar series was found in the substituted phthalein dyes. They were found to be contaminated with other members of the series which could be removed by adsorption methods. The dyes themselves were adsorbed in the following order, each dye containing the number of halogens indicated in the parentheses:

Rose Bengal (4I, 2Cl)
Erythrosin (4I), Phloxin (4Br, 4Cl)
Eosin (4Br), Spirit Eosin (4Br)
Fluorescein

Capillary Separation Test

A very simple example of the chromatographic adsorption method, which has been used extensively in both dye and pigment work, has been referred to (108) as the capillary separation test. To carry out this test the dyestuff must be brought into a soluble condition, so it must be clear that different types of pigments will require different methods of treatment to accomplish this result, and in certain cases it may not be a feasible procedure.

In dealing with pigments of the basic dyestuffs, as the phosphotungstic type, for example, solution can be brought about by boiling a small amount (0.1 gram) of the pigment with about 10 cc of 5 per cent Na_2CO_3 for 10 minutes. Addition of sufficient $BaCl_2$ solution to precipitate all soluble carbonates, phosphates, tungstates, and molybdates, followed by acidification with acetic acid, gives a satisfactory solution of the dyestuff.

To a strip of filter paper 2 inches wide and 6 inches long apply a line of dye solution about 1 inch from one end. Suspend the paper so that the lower end, near the line of dye, is just immersed in water. As the water rises, by capillary attraction, in the paper, the dye is carried upward; and if more than one dyestuff is present in the pigment, it will be evident, owing to the difference in rate of migration of the dye lines. It is frequently possible to separate the colors completely in this manner. Spot and other tests with various reagents can then be made on the paper dyeings to establish the identity of the dyestuffs very satisfactorily.

In similar study of lakes and toners from soluble acid type dyestuffs it is frequently only necessary to boil the pigment with sodium carbonate or caustic soda solution and spot the resulting dye solution directly on filter paper. Capillary separation is then made as in the case of the basic dyestuffs.

With other pigments, such as the para reds and toluidines, which are insoluble in aqueous solutions it is probable that similar action may be obtained using organic solvents.

There are still other pigments, not included in the above groups, which are appreciably soluble only in materials such as sulfuric acid which would make tests of this nature difficult. It is entirely probable, however, that a similar technique using sulfuric acid as the solvent in connection with a suitable porous material, and protecting the system from atmospheric moisture, would give results of a similar nature.

The principle of chromatographic separation and analysis is of very broad application, which can be only briefly suggested in the above discussion.

Dyeing Tests

Many colored materials, particularly dyestuffs, have the ability under certain rather definite conditions of acidity or alkalinity, and temperature, to dye certain specific fibers as wool, silk, or cotton. It is, therefore, possible to obtain excellent confirmatory identifications, in some cases, by applying the dyestuffs, which have been isolated as individuals by the above methods, to the appropriate fibers by suitable methods.

The results may be checked by comparison with dyestuffs of known composition, and rather definite conclusions drawn, in many cases, regarding the nature, and possibly the identity, of the unknown coloring matters.

Chemical Analysis

The chemical analysis of organic pigments may be undertaken for a variety of reasons, to establish identity, to determine concentration or purity and to detect the presence of foreign or unusual materials. It is comparatively seldom, however, that complete chemical analysis is resorted to, partially on account of the difficulties encountered but more generally due to the simple and quite satisfactory methods available for establishing the identity and concentrations of unknown products.

Certain types of pigments of completely organic nature, including the para reds, toluidine reds, Permaton Orange, hansa and benzidine yellows, the Naphthol AS colors, vat colors, and others, may be handled by the usual methods of complete organic analysis, whereas others, such as the metal toners and lakes, are partially, and in some cases largely, inorganic in nature and are therefore subject to treatment for determination of the inorganic constituents and groups, as well. The above use of the term "complete organic analysis" is not restricted to the determination of C, H, N, O, S, and other essentially inorganic constituents, but also includes those methods which permit the determination of significant molecular groupings.

Spectrographic Analysis

The spectrograph is by far the most sensitive means available for the detection of metallic constituents of organic pigments. It has also proved especially valuable in the examination and control of raw materials, making it possible to detect minor contents of foreign substances which may cause trouble in the manufacturing operations.

In the usual types of spectroscope, spectrograph, or spectrophotometer, the light from an incandescent source, such as an electric arc, is passed through a narrow slit, a prism, and a series of lenses, and then focused on an eyepiece, a photographic plate, or an instrument to record the receipt of electromagnetic energy.

As a rule the determinations are carried out by introducing a known amount of pigment, or the ash of a pigment, diluted in some cases with a salt of known spectral characteristics, in the hollow tip of an electrode, and then using the electrode in setting up an arc source of light in the spectrograph.

In analytical work the spectrographic type of equipment is employed and the spectrum is recorded photographically. When properly made the spectrum is composed of a series of lines which occupy positions definitely related to the wavelengths of the light reaching the photographic plate. Each metallic element gives a characteristic spectrum made up of lines of fixed wavelengths and a wide range of intensity. Positive identification of any one of these lines is proof of the presence of that particular element in the sample. Thus an element may give both weak and strong lines in the same spectrum. Also some elements give spectra of high intensity when present in insignificant amount; others give spectra of relatively low intensity even when the sample contains a considerable percentage.

The extreme sensitivity of the instrument from a qualitative point of view and the very satisfactory accuracy of its quantitative application which does, however, require the expenditure of considerable more time in the setting up of suitable standards for comparison have made possible the adoption of three types of analysis of very great value.

The Survey Analysis. The survey analysis is made by producing a spectrum record of suitable intensity to permit the identification of as many lines as may be recognized and identified with particular elements. All elements identified are then reported.

The Quantitative Estimate. The quantitative estimate is made by producing a spectrum record of suitable intensity so that by rough comparison with another spectrum, or by visual estimation, the approximate content of a particular element may be determined. The contents reported may be accurate within 10 to 100 per cent.

The Quantitative Analysis. The quantitative analysis is made by comparing a spectrum line with a similar line produced in another standard spectrum under, as nearly as possible, identical conditions of exposure. In the older method the standard and the sample spectra were made adjacent to each other on the film, and this made it possible to determine the relative intensities quite accurately visually. More recently, sensitive recording instruments have been devised with which the intensities of the spectrum lines can be much more accurately measured, and this has improved the reliability of the final values obtained.

It was found, however, that errors appeared in the intensities of the various spectra, even though they were made under carefully standardized conditions, owing, among other things, to traveling of the arc over the area of the electrode tips and consequent variations in the light entering the spectrograph slit.

The present procedure is to employ what is referred to by Sawyer (120) as an "internal standard." It may be a selected line of convenient intensity from one of the normal major constituents, or from a definite known amount of a selected element added to the sample being analyzed to give a convenient line for reference with a line of similar intensity for the element sought. The two lines chosen should be of about equal intensity and near together. "Their relative intensities are determined by some photometric procedure and plotted as a function of concentration. The resulting graph serves as a basis for the determination of the concentration of any unknown sample. If the two variables are plotted on logarithmic scales the resulting analytical curve, over a considerable range, is usually very close to a straight line."

The new technique, under best conditions, brings the quantitative analysis an accuracy within 1 per cent of the actual content. In addition to its extreme sensitivity in detection, and highly satisfactory accuracy in quantitative determination, spectrographic analysis possesses a tremendous advantage in speed.

This method of examination has been very useful in the pigment field in the examination of unknown pigments and in the detection of both known and suspected impurities in raw materials and finished products.

The spectra shown in Figs. 38, 39, and 40 were made by H. S. Read * and illustrate quite clearly the two primary uses for spectrographic analyses, the detection of elements and their quantitative estimation.

The spectra represent the following pigment samples.

1. Lithol red	containing	Ba
2. Lithol red	containing	Ba, Pb
3. Lithol red	containing	Ba, Pb, Ca, Sr
4. Peacock blue	containing	Ba, Al
5. Peacock blue	containing	0.1 per cent iron blue, Ba, Al, Fe
6. Peacock blue	containing	1.0 per cent iron blue, Ba, Al, Fe
7. Maroon toner	containing	Ca
8. Maroon toner	containing	Ca, Mn
9. Maroon toner	containing	Ca, Mn, Cd

The following are quantitative relations of interest in checking the spectral indications:

No. 3 contains one-half as much Ba as 1 and 2.
No. 3 contains one-half as much Pb as 2.
No. 6 contains ten times as much Fe as 5.
No. 8 contains approximately as much Mn as 9.

Points of special interest are found at the marked wavelengths.

At wavelength 4554 Å samples 1 to 6 inclusive show very intense barium lines, all too strong to permit of accurate quantitative estimation.

At wavelength 4607 Å sample 3 shows a strong strontium line. Sample 2 also shows a decided test.

At wavelength 2873 Å samples 2 and 3 show distinct lead lines and 2 is noticeably stronger than 3.

At wavelengths 3082 and 3093 Å samples 4, 5, and 6 show strong aluminum lines.

At wavelength 3021 Å samples 5 and 6 show strong iron lines and 6 is much stronger than 5, although all the samples show distinct tests.

At wavelengths 2940 and 2949 Å samples 8 and 9 show strong manganese lines.

At wavelength 3261 Å sample 9 shows a strong cadmium line.

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* H. S. Read, Ph. D. physicist, Harry S. Read Company, Westfield, N. J.

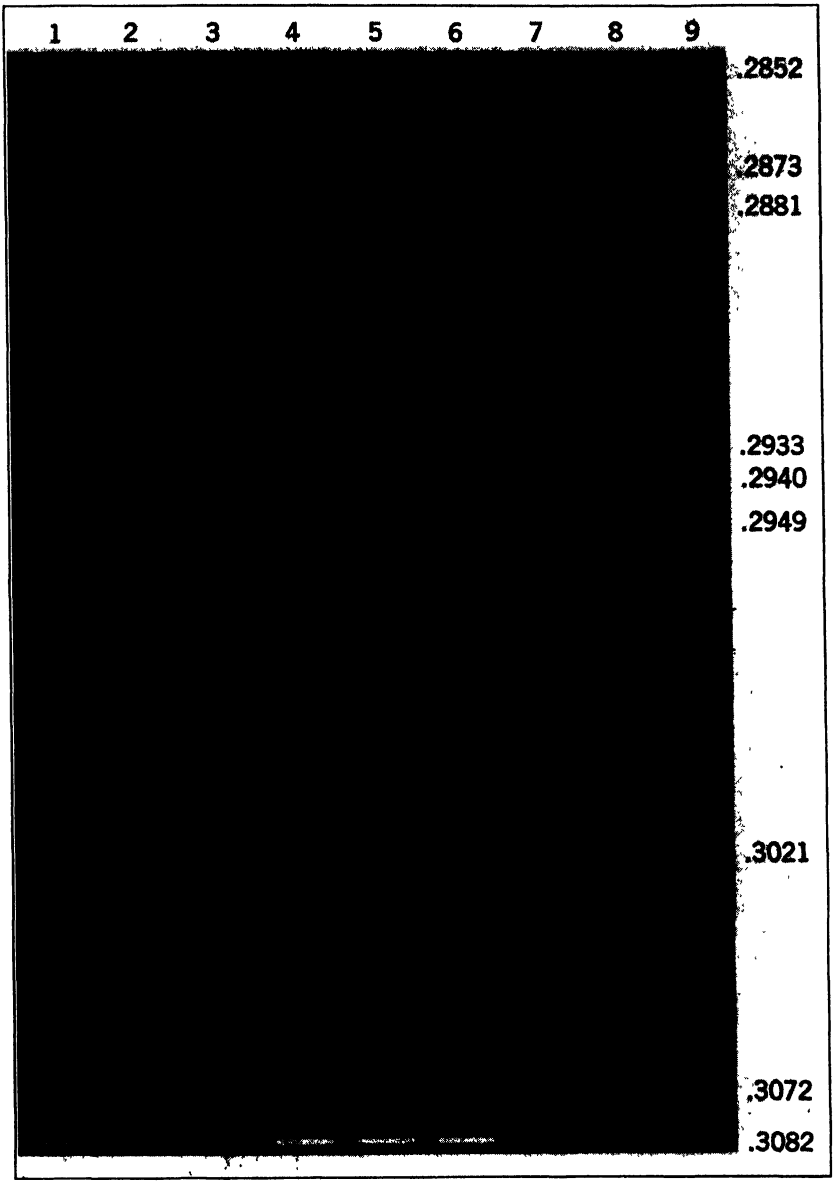


Fig. 38.

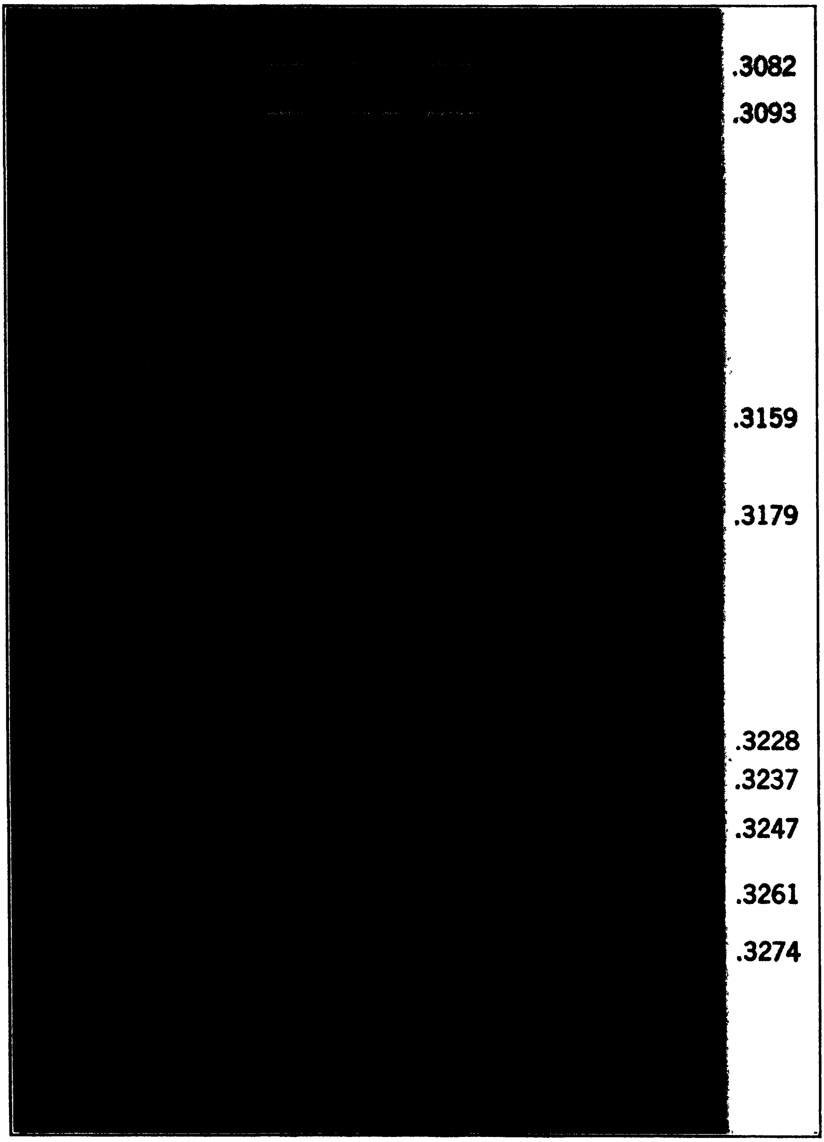


Fig. 39.

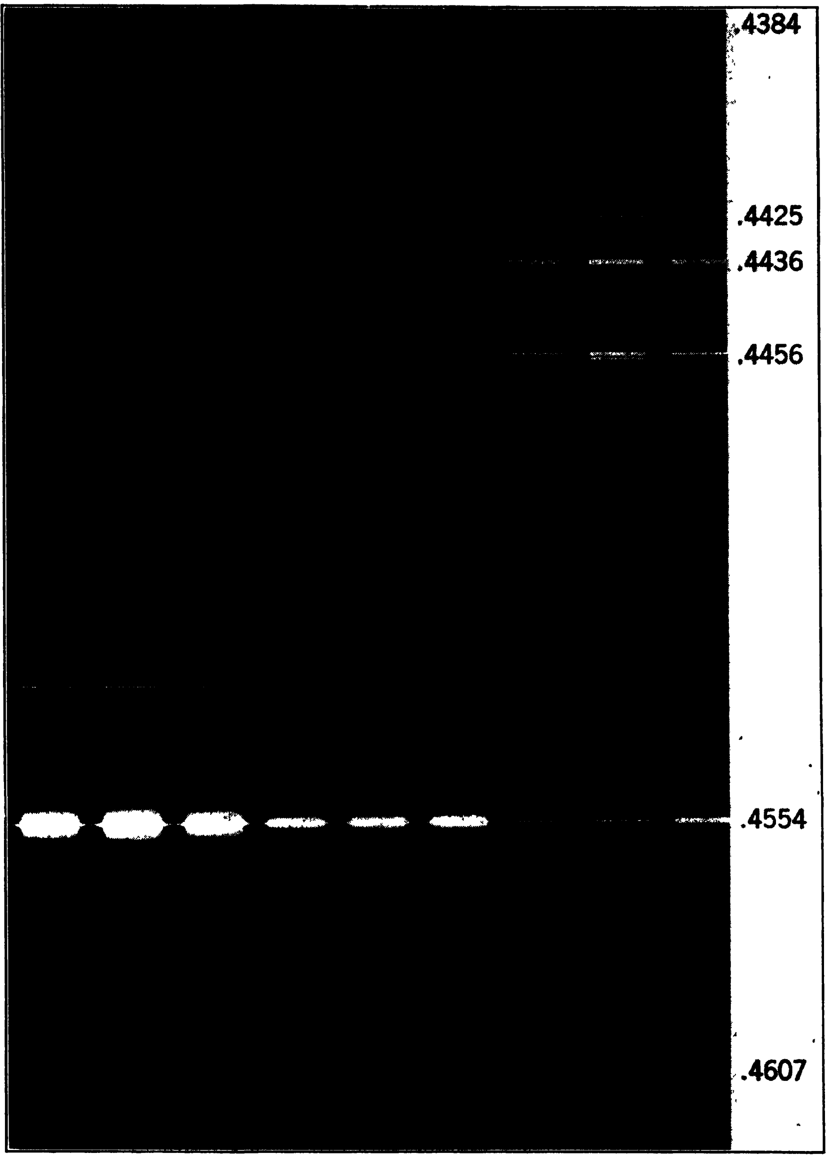


Fig. 40.

In highly accurate quantitative determinations it is customary to run standards of known content along with the test spectrum. In this way comparatively slight differences can be noted.

Owing to the extreme sensitivity of the spectrographic method many elements are shown in the spectra which represent insignificant or casual impurities. For example, at wavelength 2881 Å all samples show the definite presence of silicon; and at wavelengths 3247 and 3274 Å all samples show distinct tests for copper. Both these materials are casual impurities in these samples and entirely lacking in practical significance.

A revolutionary improvement in spectrographic technique has been made by Saunderson, Caldecourt, and Peterson (119) which combines great speed, simplicity of operation, and exceptionally good analytical results.

A simplified description of the method is given in Fig. 41. Two sample electrodes are held in specially designed clamps for sparking. Light from the spark passes through the entrance slit of the spectrometer and falls upon a concave grating which separates the light according to wavelength or color. An exit slit for each element allows only light from that element to reach the special photo-multiplier tubes. During the 20-second sparking period, with the switches *S* closed in the vertical direction, the phototubes receive light from the various elements in the sample and produce an electrical current which is stored in the condensers C_0, C_1, C_2, etc. At the end of the sparking period, a measurement of the charges stored in the condensers tells how much of the various elements is present in the original sample.

The charges in the condensers are measured indirectly by recording the time required to discharge each condenser from its initial voltage down to a small known voltage. A set of special amplifiers performs this function automatically. The measurement period begins when the switches *S* close in the horizontal position, thus connecting the condensers to the discharge resistors R_0, R_1, R_2, etc. At the same instant the recorder, carrying a strip of electrical marking paper, is set in motion. The amplifiers follow the decreasing voltages on the condensers and operate the relays S_0, S_1, S_2, etc., when these voltages become about one volt. The system is arranged so that the relay S_0 operates later than the relays S_1, S_2, etc. By this scheme, marks are recorded on the chart of varying lengths, beginning with the closing of relays S_1, S_2, etc., and all ending with the opening of relay S_0. It can be shown that each mark on the chart is a measure of the intensity of the light from one of the unknown elements in the sample, relative to the light from the element magnesium. That is, relative light intensities rather than absolute intensities are used for calibration with the actual percentages of the unknown elements.

Before the analysis of unknown samples is undertaken, calibration curves for each element are established by running a group of samples or standards containing known amounts of the various elements. For example, when the lengths of the mark for aluminium on the record is plotted against the concentration of aluminium in the standard samples, a calibration curve is obtained. Such a curve makes an analysis possible, since one can measure the length of the mark for an unknown sample and find directly from the curve the unknown concentration. For convenience in routine operation, the calibration curves for the various elements are projected onto calibration scales. A set of such scales, one for each element to be determined, then allows the operator to read the desired concentrations directly from the record obtained on an unknown sample.

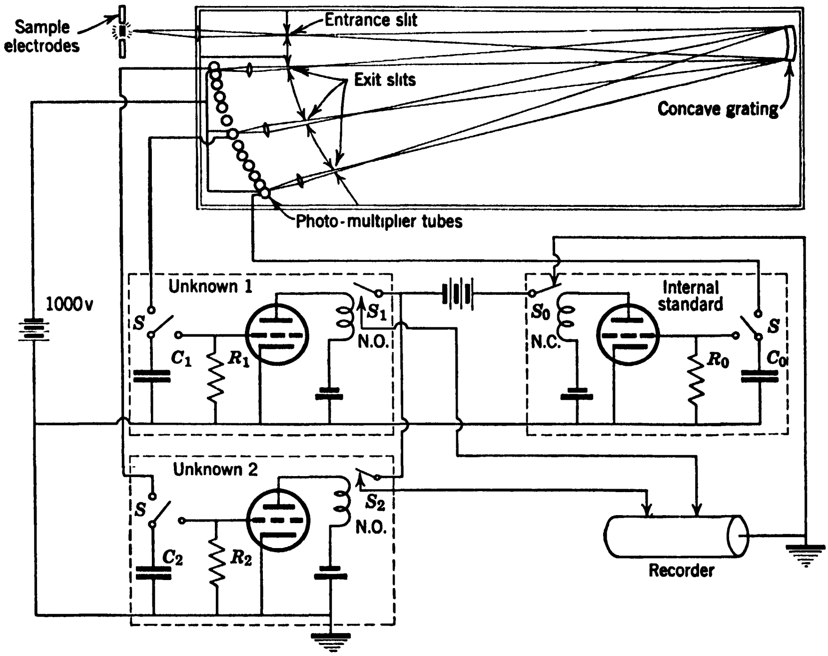
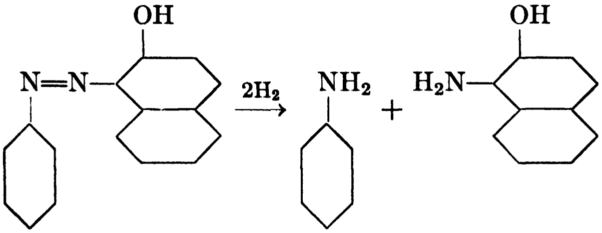


FIG. 41. Direct-Reading Spectrometer. (*Courtesy of the Dow Chemical Co.*)

With this instrument, which, in practice, is equipped with eleven exit slits and electron multipliers, phototubes, samples are being analyzed at the rate of about 4000 per month, representing roughly 20,000 quantitative determinations.

Reduction

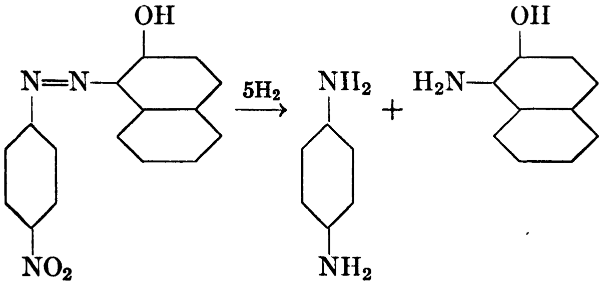
Reduction of Azo Pigments. Amino compounds, formed by reduction of azo compounds, may be separated and identified. A typical illustration might be



Azo Pigment Aniline 1-Amino-2-naphthol

In this instance the original amino compound is recovered unchanged, but the original β-naphthol is recovered as the amino derivative.

It is clear that the results obtained must be interpreted with considerable care. For example, a nitro group, in the original intermediates and in the pigment, is also changed to an amino group in the reduction.



Para Red p-Phenylenediamine 1-Amino-2-naphthol

In many cases separation of the mixture of amino compounds is difficult, and it is necessary to form salts or condensation products which can be more easily purified. From identification of these amino derivatives it is possible to gain valuable information bearing on the structure of the original pigment.

There are many ways in which the reduction may be conducted, such as with

1. Tin and hydrochloric acid.
2. Stannous chloride.
3. Zinc and hydrochloric acid.
4. Sodium hydrosulfite in alkaline solution, hot.

The sodium hydrosulfite ($Na_2S_2O_7$) reduction is particularly useful in the testing of unknown pigments, as restoration of the original color, by oxidation, often by simple exposure to the air, indicates that the pigment is not an azo compound but possibly a vat type.

When using the metal reductions it is frequently desirable to eliminate the metal from solution, by means of hydrogen sulfide, before proceeding with the separation or purification of the reduction products. The purified amino compounds are usually identified by melting point as well as by other characteristic tests.

Chen and Cross (29) have shown that, although with few exceptions aromatic sulfonic acids have no definite melting points, they do yield, with aromatic bases, well-defined crystal salts which in numerous instances possess sharp melting points. In general the arylamine salts are prepared by adding the base, dissolved in a slight excess of dilute hydrochloric acid, to a boiling aqueous solution of an equivalent quantity of the sodium salt of the sulfonic acid, when the arylamine salt separates from the boiling solution, or on cooling, or after concentrating and cooling. They conducted experimental work on the identification of sulfonic acid reduction products of azo dyes, and it is entirely probable that extension of the study to pigments would be equally successful.

Reduction with Titanium Trichloride. The Knecht volumetric method of reduction (82), using a hot acid solution of titanium trichloride, carefully protected from air contact by an atmosphere of nitrogen or carbon dioxide, has been found very useful, not only in the quantitative analysis of pigments but particularly in the control analysis of dyestuffs to be used in the manufacture of pigments. This applies not alone to azo dyestuffs (82) but to basic and acid (116) triphenylmethane (26) and vat dyestuffs, as well as to nitro (27) compounds in general.

It is quite essential, in the use of this method, to establish for each individual dyestuff or intermediate, the hydrogen equivalent required for complete reduction. Once this is determined on carefully purified material, the method affords results of a high degree of accuracy.

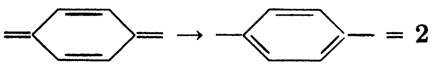
In practice the titanous chloride stock solution is generally held under an atmosphere of hydrogen to avoid contact with oxygen of the air, whereas the solution in the reaction flask during an actual titration is generally protected with an atmosphere of carbon dioxide or nitrogen.

In the analysis of a soluble dyestuff, the dyestuff may serve well as the indicator for the completion of reduction. In other cases it is customary to employ an excess of titanous chloride ($TiCl_3$) at the beginning, boil for 2 to 3 minutes to complete the reduction, and then, after cooling, back-titrate with a standard solution of iron-alum until a drop, removed from the flask, just shows a red color when tested against potassium thiocyanate solution.

Calculation of analytical results may be referred to either hydrogen or iron equivalent, and this should be established, if possible, for the pure material. The equation $TiCl_3 + HCl \rightarrow TiCl_4 + H$ indicates that the hydrogen equivalent of certain common groups is as follows:

$$—N{=}N— \rightarrow —NH_2 + H_2N— = 4$$

$$—NO_2 \rightarrow —NH_2 + 2H_2O = 6$$

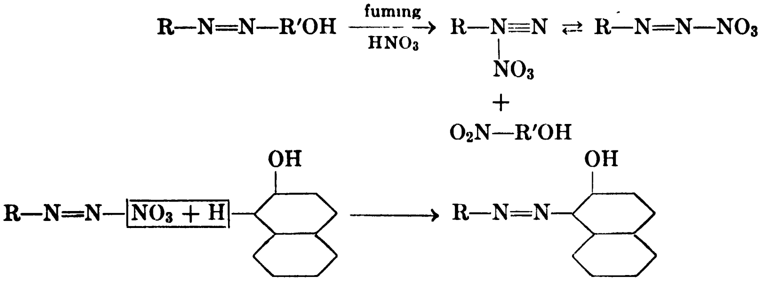


or the azo group requires four molecules of $TiCl_3$ for complete reduction, the nitro group six and the quinone group two.

Fuming Nitric Acid

The test with fuming nitric acid has been employed to some extent in pigment work to determine in certain cases the identity of the original amino compounds used in preparation of the pigment.

The test is based on the reaction of the azo compound with nitric acid to give the diazonium nitrate of the original amino compound and the nitrated derivative of the second component. The diazonium compound in solution is then filtered and coupled with a known second component, such as β-naphthol or Naphthol AS, and the product identified, possibly by melting point, to establish the identity of the amino compound.



Azo Dye

Ash

Determination of the ash of an organic pigment, by slow and complete combustion of the organic matter and resulting carbon, gives very significant information of the type of pigment under examination. It may be used in the identification of an unknown pigment, or in controlling the quality of regular production. For example, in the latter case a high ash may indicate incomplete or insufficient washing.

The ash value of an unknown pigment may place it very definitely in certain classes of products. Pigments such as para reds, toluidine reds, hansa and benzidine yellows, and Naphthol AS colors have no salt-forming groups and theoretically should have no ash. Yet all commercial pigments of this type do carry a small amount of inorganic salt due to incomplete washing and possibly occlusion, and this may be found in an ash value of less than 1.0 per cent as a rule.

Products which include the metal toners of both soluble and insoluble dyestuffs, such as the lithol reds, reds for lake C, and so on, show a considerably higher ash, varying from 25 to 35 per cent.

Another group of toners, or full-strength pigments, which include most of the phosphotungstic, phosphomolybdic, and phosphotungstomolybdic toners of the basic dyestuffs, show ash values in the region of 50 per cent. In this particular group the ashing operation should be conducted with gentle heating, owing to the volatile nature of the molybdenum oxide and danger of partial or even complete loss.

The ash of most of these pigments supplies suitable material for further inorganic analysis.

The ash values of reduced pigments or lakes are of no great significance as a rule, but in many cases the ashing step is carried out to supply suitable material for further inorganic analysis.

Total and Combined Sulfur, Nitrogen, and Halogens

These analyses are carried out by essentially standard methods of procedure.

Phosphotungstic and Phosphomolybdic Pigments

Direct analysis of the phosphotungstic and phosphomolybdic pigments is a very difficult procedure. It is practically essential to accomplish a complete separation of the dyestuff in soluble form from the inorganic complex. This operation is by no means simple, and, even if it were successfully accomplished, the subsequent analyses of the dye and the inorganic residue are both difficult and the accuracy open to question.

The contents of tungsten and molybdenum can be fairly accurately determined if the pigment is very carefully ignited to destroy the organic matter and burn off the resulting carbon, but loss of molybdenum due to volatilization of the oxide is difficult to avoid and may in some cases be complete. Determination of phosphorus, or the oxide, is particularly inaccurate, owing to the extremely small amount contained in the compound and to the fact that there is almost invariably a loss during ignition.

The following methods may serve as a basis for analytical studies which are quite essential in establishing a satisfactory analytical technique.

Separation of Tungsten from Molybdenum (123),* Hommel's Process. The moist oxides of tungsten and molybdenum are digested with concentrated sulfuric acid and a few drops of dilute nitric acid in a porcelain dish over a free flame for about half an hour. About three times its volume of water is added to the cooled solution, the residue, WO_3, filtered off and washed with dilute sulfuric acid (1:20), followed by three washings with alcohol. The residue is ignited separately from the paper and weighed with the ash of paper as WO_3.

Molybdenum is in the filtrate and may be precipitated in a pressure flask with H_2S.

Precipitation of Molybdenum as Molybdenum Sulfide (131).† The precipitation of molybdenum as sulfide can take place in two ways: Either the acid solution may be precipitated by hydrogen sulfide gas or the solution of ammonium thiomolybdate may be acidified with dilute acid.

A. Precipitation from Acid Solutions. Place the molybdenum solution, slightly acid with sulfuric acid, in a small pressure flask and saturate with hydrogen sulfide. Close the flask and heat on the water bath until the precipitate has completely settled, and filter after it has become cold. Wash the precipitate with very dilute sulfuric acid and finally with alcohol until the acid has been completely removed. Place the moist filter in a large porcelain crucible and dry upon the water bath. Cover the crucible and heat very carefully over a small flame until no more hydrocarbons are expelled. Remove the cover, burn off the carbon from the sides of the crucible at as low a temperature as possible, and, by raising the temperature gradually, change the sulfide to oxide. The operation is finished when no more sulfur dioxide is formed. After cooling, add a little mercuric oxide suspended in water to the contents of the crucible, stir the mixture well, evaporate to dryness on the water bath, remove the mercuric oxide by gentle ignition, and weigh the residue of MoO_3. The mercuric oxide helps to remove particles of unburned carbon.

B. Precipitation from Alkaline Solution. To the molybdenum solution add an excess of ammonium hydroxide and saturate the solution

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* Based closely on Scott's *Standard Methods of Chemical Analysis*, 4th Ed., published by D. Van Nostrand Co. Adapted with permission.

† Based closely on Treadwell and Hall's *Analytical Chemistry*, Vol. I, 7th Ed., published by John Wiley and Sons. Adapted with permission.

with hydrogen sulfide until it assumes a bright red color. Make acid with sulfuric acid and treat the precipitate as described under *A*.

Colorimetric methods (126) are available that are of special value in the estimation of very small amounts of molybdenum and tungsten (65).

FORMULATION TESTS

Formulation tests include those which are based on the incorporation of the pigment into suitable vehicle in order approximately to duplicate practical commercial products such as printing ink, paint, varnish, lacquer, enamel, rubber, linoleum, wax, and various types of plastic compositions. These products require a great variety of raw materials, including oils, solvents, resins, waxes, soaps, inerts, and others, so that a great many different tests are essential even in each separate field.

Fundamentally each test involves the dispersion of the pigment in an oil or some suitable vehicle by grinding or mixing, the means employed depending on the nature of the vehicle.

Mixing

Such vehicles as rubber and linoleum do not readily lend themselves to fine grinding of the pigment being introduced, owing to their extremely heavy body. It is, therefore, general practice to add the pigment to these formulations under conditions of powerful mixing. It is readily understood that, under these conditions, it is essential that the pigment should be soft and of a texture which will permit easy breakdown of the pigment particle and ready wetting by the vehicle.

Grinding

In the grinding of a pigment into a vehicle such as an oil or varnish the two are usually well mixed before actual grinding, in order to avoid excessive dusting and loss of pigment. On a large scale this is frequently accomplished in a so-called pony mixer which is, in principle, a rotating can with an eccentric four-blade stirrer and a scraper to prevent the wall from building up an accumulation of either ingredient. When well mixed, the material is transferred to a mill, which may be one of several types.

Roll Mill. The roll mill, which may consist of three, five, or more rolls, is made up of carefully turned and polished metal (usually steel) cylinders or rods that rotate in direct contact with each other at different speeds, thus causing a shearing action on an oil film passing between the contact surfaces.

The mixture mentioned above is placed between the slowest and the next slowest rolls. The pasty mix is carried between the cylinders, and two actions take place. The coarser particles of pigment are crushed, and the finer ones pulled apart by the shear set up in the oil film between the rolls. The partially ground film on the second roll is carried between the second and third rolls, where the process is repeated. It is obvious that in each succeeding passage between adjacent rolls the effective grinding by shearing action is rapidly increasing and the crushing action is progressively eliminated. It is desirable that the crushing action is minimized as far as possible throughout the grinding as it results in condensing the pigment in a form not readily dispersed in the later shearing stages of the operation.

From the last roll the finished ink is removed by a scraper or doctor blade. Practical manufacture may require several passes through the mill to obtain an ink or paint of suitable characteristics.

Burr-Stone Mill. Another mill which has been extensively used, especially in the manufacture of paints, is the burr-stone mill. It consists of two circular stones, the upper stationary and the lower rotating on a vertical shaft, which are brought into contact by suitable adjustments. The stones are polished and in close contact near the periphery, but cut in various designs which tend to work outward any material being introduced near the center. The upper stone has a large hole in the center, through which the above mix can be fed to the grinding area.

This mill also gives a combination of crushing and shearing action and requires several passes to accomplish a high degree of dispersion.

The Ball Mill. The ball mill is a closed cylinder or vessel, rotating on a horizontal shaft and partially filled with either flint pebbles or steel balls. This type of mill can be fed with the above mix of oil and pigment, or the ingredients may be placed in the mill without previous mixing.

The efficiency of this mill is based largely on a crushing action, but owing to the small size of the balls or pebbles and the low pressure exerted on the coarse pigment particles, there appears to be very little if any condensing action to interfere with strength development.

The degree of dispersion is controlled by the time of rotation, which may be 24 to 72 or more hours.

Laboratory Procedures. Small models of all these types of grinding equipment are used in the laboratory in normal testing and afford a wide variety of methods for duplication of conditions met with in commercial practice.

Hand Mulling. For many years the great proportion of laboratory testing has been done by the hand mulling or hand rubbing procedure.

In this procedure the required amount of pigment and a vehicle, such as O Varnish, are weighed and mixed thoroughly with a spatula on a ground glass slab until all the larger lumps and particles are broken down and wet with the vehicle. Then the paste is rubbed with a glass muller having a ground glass face, using strokes to confine the ink to a strip about 8 to 10 inches long.

The ink should be scraped up with a spatula after each 25 strokes, well mixed, and the mulling continued for 50 to 200 strokes, depending on the nature of the pigment, its hardness, and its wetting characteristics. The product of this operation is the full-tone ink.

The tint is made by weighing a small amount (20 mg perhaps) of the full-tone ink and 1.0 gram of white ink (zinc oxide ground in a similar vehicle) and mixing them very thoroughly on a smooth glass slab. This gives a 50 to 1 tint.

Comparisons can now be made with ink and tint prepared in a similar manner from the standard pigment. Comparisons are conveniently made on small sheets of a good grade of bond paper and on sheet tin or glass. In special tests different grades of paper are employed to bring out the ink characteristics on some particular paper, but even then the essential principles are the same.

Paper Tests. In making the test on paper, small portions of each ink are placed on the paper in crescents quite close together. A broad spatula blade is then drawn lightly down over the two crescents in such a way as to cause the inks to meet in the center and follow down the paper about one inch. The spatula is then brought into a more upright position, considerable pressure is applied, and the spatula edge drawn downward to the edge of the paper.

The tints are applied to paper in a similar manner except that the light pressure is used completely to the edge of the paper.

The following observations can be made:

Masstone—the heavy upper portion of the ink on the full-tone paper test.
Overtone—the lighter lower portion of the ink on the full-tone paper test examined directly.
Undertone—the overtone portion examined by transmitted light.
Tint—the reduced ink drawn down lightly.

Masstone. Comparison of the two adjacent masstones gives information on the following: depth or lightness, brilliance or cleanness, dirtiness or flatness, presence or absence of bronze, oil absorption or consistency, texture or hardness, and degree of dispersion.

Observation of the back of the paper reveals the tendency toward penetration.

Overtone. Overtone comparisons give information of special value on the cleanness and brilliance of the printing qualities, freedom from bronziness, finish, consistency, and general tone quality.

Undertone. Undertone comparisons are of value particularly for detecting slight differences in hue and variations in intensity which may be related directly to strength and inversely to consistency.

Tint. Tint comparisons reveal most sharply slight differences in hue and cleanness, and indicate directly the relations in strength.

With slight differences in hue the estimation of strength relations may be appreciably more difficult; with marked difference, the estimation may be exceedingly unreliable. In such a case the accuracy may be greatly improved by making 200 to 1 or even 400 to 1 tints, in which cases the tone or hue differences are much less disturbing.

Permanency or Fastness to Light. All the above forms of exhibit are employed in determinations of the resistance of the pigment to the destructive action of light rays, usually in the Fadometer * or in direct sunlight.

Masstone exposures usually show only a darkening or lightening of tone and require a long exposure. Overtone exposures show more marked changes and generally result in definite fading. The tint exposure gives the best measure of actual fastness to light, as the strength can, and should be, accurately adjusted before exposure. In many cases a difference in strength of only 5 per cent will give an appreciably better light-fastness. An error is sometimes made in interpreting a light exposure, of a tint exhibit, which may have been accurately adjusted for strength, but which in further drying under the heat of the arc has flooded slightly to disturb the original accurate strength adjustment. The result in this case is the same as though the original adjustment had been made in the same direction. It is difficult to correct these changes, but not particularly difficult to recognize and evaluate them properly.

This series of tests makes it possible to examine quickly a new or unknown pigment, comparing it with known pigments of somewhat similar color values to establish any advantage or deficiency it may possess and gain information which may determine the special field of use for which it shows desirable properties.

Resistance to Heat (40). The color to be tested for resistance to heat is rubbed in O Litho Varnish and drier in the usual ratio. This paste is then applied to small tin panels, making certain to get a uniform amount on the tin. Four tins are prepared. One is allowed to air-dry

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* Atlas Electric Devices Company.

to get a basis for color comparison. The others are subjected, respectively, to temperatures of 165° F, 230° F, and 320° F, in electric ovens. The baking times used are 5 hours at 165° F, 4 hours at 230° F, and 1½ hours at 320° F. This amount of time is necessary to give complete dryness to the panels. By using a baking type vehicle containing volatile, much shorter periods than these would normally be required for the temperatures at which these tests are run.

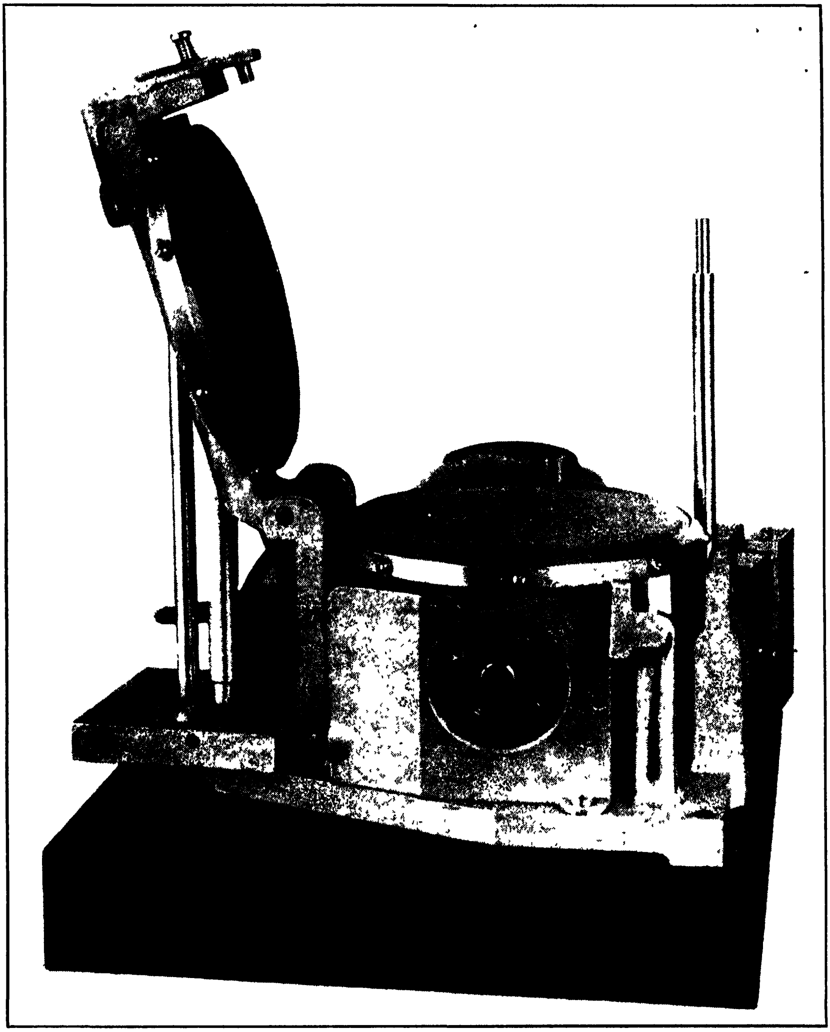

FIG. 42. Automatic Muller. (*Courtesy of C. E. Hoover, Colors, New York.*)

The panels are then compared with the air-dried panel for color change. The maximum temperature at which no color change took place is regarded as the baking temperature which that particular color will stand.

Resistance to Acid. A thoroughly dried drawdown is suspended in 5 per cent hydrochloric acid solution for 10 minutes and examined at the end of that time.

Resistance to Alkali. A thoroughly dried drawdown of the color is used for test. The drawdown is suspended in 1 per cent sodium hydroxide solution for 15 minutes and the condition of the drawdown and the solution examined. The rating for resistance to alkali is then made on the basis of the condition noted.

The Hoover Automatic Muller.* Within the past few years a machine has been perfected which will conveniently handle the type of laboratory testing formerly done by hand, as well as provide a close duplication of the three-roll mill results. This is the Hoover Automatic Muller, shown in Fig. 42. The principle of this machine is somewhat similar to that of the burr-stone mill in that one ground glass disk is rigid while the other rotates, but the grinding is at the center rather than at the edge. The pressure on the plates can be accurately adjusted and a counter is built in to give a close control on the number of rotations employed. After each twenty-five or fifty rotations, the machine should be opened and the ink carefully collected with a spatula, mixed, and redistributed.

This machine has proved its value, particularly during the period of wartime labor shortage, and will certainly become a permanent type of equipment for laboratory testing in the field of pigments.

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* C. E. Hoover, Colors, 1250 Sixth Avenue, Rockefeller Center, New York, N. Y.

Chapter X

Identification of Organic Pigments

Identification of unknown organic pigments is a problem frequently met in industrial work. This is due, partially, to the practice of selling new products under trade names which are not significant chemically, or under codes. Examination of an unknown pigment therefore involves the use of simple physical and chemical tests which will yield information on the nature of the product.

MELTING POINT

The most simple and direct method of identification of a pigment color is to determine its melting point, but this procedure is feasible only with those pigments which are entirely organic in composition and show a well-defined melting point.

Theoretically this method is applicable to such pigments as the para reds, toluidine reds, permanent oranges, couplings of the Naphthol AS derivatives which contain no salt-forming groups, hansa yellows, and dichlorobenzidine yellows, but owing to the high temperatures involved in many cases, and tendencies to carbonize rather than melt in others, the method is employed rather infrequently.

It is quite essential to purify the pigment by crystallization from a suitable solvent, in order to eliminate such materials as resins, which might interfere with melting at the correct point. It is then possible to compare with a suspected known pigment and to confirm the identity by testing mixtures of the unknown and known materials.

SPOT TESTS

One of the most commonly used tests in identifications incorporates the pigment in an ink vehicle, such as varnish, in the same manner as that indicated in Chapter IX, under "hand mulling" (page 268). The full-tone ink, placed on a white paper and drawn down to a thin film with a knife or spatula edge, gives a film which can be readily observed and tested to establish the type of pigment in question.

Spotting of this film with reagents such as caustic alkalies, mineral and organic acids, stannous chloride, sodium hydrosulfite, alcohol, toluene, chloroform, potassium permanganate, etc., particularly in direct comparison with known pigments handled in a similar manner, gives in most cases a fairly definite identification of the unknown material.

SULFURIC ACID TESTS AND CAPILLARY SEPARATION TESTS

Sulfuric acid tests and capillary separation tests, as outlined and discussed in Chapter IX, are used primarily in the identification of unknown pigments. Owing to the simplicity of the tests and their reliability, much information may be readily gained by setting up comparisons with unknown pigments and in many cases with unknown dyestuffs. In addition, these tests frequently reveal the presence of mixtures and make possible the separation and identification of the components.

Table XV shows a useful series of tests which may be quickly applied (108). The spot tests are made by applying a drop of the various reagents to the dried prints of the pigments by means of a glass rod and noting the immediate results.

The bleeding tests may be applied either to the dry pigments or to strips of the print, but the most delicate tests are obtained when applied to the dry pigments.

SYSTEMATIC IDENTIFICATION

A systematic identification of organic pigments has been presented by Weisberg and Smith (137) which is based on the use of a minimum of reagents. The authors indicate that it has very definite restrictions which should be clearly recognized. It is intended to apply only to pure pigments, but many of the testing methods offer the possibility of distinguishing the components of mixtures. It is designed primarily to handle dry colors, but has been used successfully with a drop of printing ink, paint, or enamel, or a small piece of printed matter or chip of dry surface coating. It attempts to cover only those pigments listed. It is anticipated that as pigments are encountered which do not fall within the scope of the scheme as written, their properties will be studied with a view to incorporating them in the method. In the pages following immediately (pages 275–284) the Weisberg-Smith system has been reproduced with modifications.

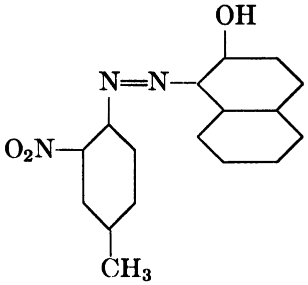
In the case of mixtures, new pigments, or finished products involving vehicles, the success achieved in positive identification will naturally be measured by the ingenuity of the operator plus his knowledge of the properties of the pigments.

Obviously, the first step in the identification of a pigment is its visual classification into a color group. Because of fundamental differences, the color groups themselves may be subdivided into two subgroups, each of which may then be further subdivided as indicated in the following outline:

I. Yellows, Oranges, Reds, Maroons
  A. Pigment dyestuffs
  B. Salt-type pigments
    1. Metal salts of acid dyes
      a. Of acid azo dyes
      b. Of other acid dyes
    2. Heteropolyacid and simple acid salts of basic dyes

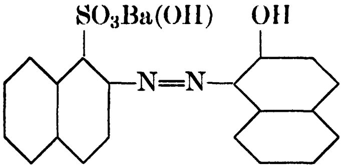
II. Blues, Violets, Greens
  A. Metal salts of acid dyes
  B. Acid salts of basic dyes
    1. Heteropolyacid salts
    2. Other acid salts
  C. Others

The *pigment dyestuffs* are those dyestuffs which happen coincidentally to possess pigment properties, but lack free acid groups or basic groups and, hence, are incapable of forming salts with metal ions or acid ions. A well-known example of this type pigment is toluidine red. Its structure is

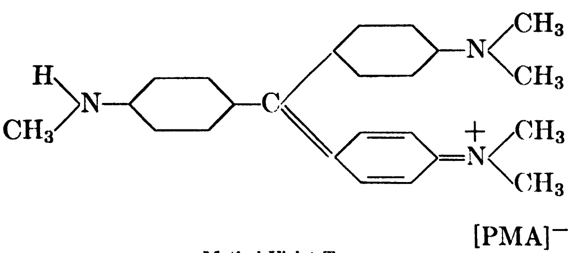


The only free groups on the molecule are methyl, nitro, and hydroxyl, none of which, in this case, is capable of salt formation.

Pigment dyestuffs may be contrasted with the salt-type pigments by referring to the structures shown for lithol red, an example of a metal salt of an acid azo dye, and for a phosphomolybdated purple toner, which is an example of a heteropolyacid salt of a basic dyestuff.



Barium Lithol Toner



Methyl Violet Toner

In the former case, the free sulfonic acid group readily forms insoluble salts with many metals, such as barium or calcium; in the latter instance the substituted amino group is basic and forms insoluble salts with complex acids of high molecular weight, such as phosphotungstic and phosphomolybdic acids, and also with more simple acids such as silicic and arsenic.

Because of the fundamental differences between these two types of pigments, their distinction, one from the other, is a fairly simple matter. Within the groups, however, individual distinctions are somewhat more difficult to make since, in many cases, similarity in chemical structure gives similar responses to most reagents. The following is a list of more or less general properties that have been kept in mind during the evolution of the systematic identification:

1. Pigment dyestuffs in general are soluble in dioxane in contradistinction to all other pigments that are insoluble or at most slightly soluble.

2. Aromatic nitro compounds in general give colored solutions when treated with strong alkali, the color varying in intensity and in hue, depending upon the extent of nitration and the relative positions of the nitro group, or groups, and other substituents.

3. The concentrated sulfuric acid solutions of most organic pigments are intensely colored and, in some cases, it is possible to use the hue of color developed to place a given pigment in a small group.

4. All azo dyes are reduced in acid solution by stannous chloride to colorless or nearly colorless solutions, depending upon the acidity and concentration of reductant, and some basic dyes and anthraquinone dyes are also decolorized by this treatment. A distinction can be made, however, between azo dyes whose solutions after reduction remain essentially colorless upon treatment with hydrogen peroxide and all other cases in which either the original color is restored or at least some color is developed in the solution.

5. All acid dyestuffs show a distinct solubility in hot dilute aqueous caustic alkali.

6. All basic dyestuffs show a distinct solubility in methyl alcoholic hydrochloric acid.

Table XVI shows the distribution of the most commonly encountered organic pigments according to the method of classification described above.

It should be emphasized that the following applies to a dry color assumed to be a single pigment. Results at variance with those anticipated in the directions may be interpreted as indicating mixtures, and the specific result obtained is often indicative of the composition of the mixture.

Between 5 and 10 mg of dry color should be used for each test requiring a fresh sample, and the test tubes should be dry to assure as little pigment as possible adhering to the walls and to avoid dilution of other solvents used. A test, proving a certain color, identifies only the organic portion of the structure. Thus if a test identifies a pigment as lithol red, this will mean any of the various metal salts used, such as sodium, barium, calcium, etc., or any of these reduced with white bases.

If the shade and strength are insufficient evidence upon which to choose the proper salt, or determine the amount of extender present, recourse must be had to methods of inorganic analysis. Likewise, in the case of basic dyes, no hint is given here as to the nature of the acid radical used to precipitate them. Separate inorganic analyses may be made for tungstate, molybdate, phosphate, arsenate, silicate, or other precipitating anion.

YELLOWS

1. Hansa Yellow
2. Benzidine Yellow
3. Tartrazine Yellow
4. Naphthol Yellow
5. Quinoline Yellow

I. To a sample of the pigment contained in a dry test tube, add 2 cc of dioxane, heat to the boiling point, add 2 cc of water and 2 drops of

TABLE XVI

Distribution of Organic Pigments

	Yellows	Oranges	Reds	Maroons	Greens	Blues	Purples
Pigment Dyestuffs	Hansa Benzidine	Dinitroaniline *o*-Nitroaniline	Toluidine Para Ocpna Pcona Brilliant Red	Toluidine Indanthrene			
Salt-Type Pigments **Metal Salts of Azo Dyes**	Tartrazine	Sodium Lithol Sodium Red Lake C Persian Orange	Lithol Red Lake C Red Lake D Lithol Rubine Lithosol 2B Pigment Scarlet Acid Scarlet	Helio Bordeaux Acid Bordeaux Azo Bordeaux B.O.N. Maroon Lithol Maroon			
Salt-Type Pigments **Metal Salts of Other Acid Dyes**	Naphthol Quinoline		Phloxin Madder	Helio Fast Rubine	Acid Green	Peacock Alkali Blue	Acid Violet
Acid Salts of the Indicated Basic Dyes			Rhodamine B Rhodamine 6G		Malachite Brilliant Thioflavin * Auramine *	Peacock Victoria	Methyl Violet
Others					Phthalocyanine Green †	Phthalocyanine Blue †	

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* Thioflavin and auramine, although yellow dyestuffs, are classified under "Greens" since these find almost their sole use in combination with the bluer-shade green dyestuffs.

† Phthalocyanine pigments are listed separately since they are not precisely analogous to either the pigment dyestuff or the salt-type pigments. They are really very high molecular weight pigment dyestuffs or the metal coordination complexes of these molecules. Their size, in addition to other specific molecular properties, gives them a stability both to solvent action and to ordinary chemical reagents which merits a separate classification. *Code:* Ocpna = Ortho-chloro-para-nitroaniline. Pcona = Para-chloro-ortho-nitroaniline.

20 per cent NaOH. A deep orange-red coloration proves hansa yellow. If the solution remains yellow, this proves the absence of hansa yellow and indicates 2, 3, 4, or 5, as outlined above. Proceed as follows:

II. Add to the above solution 4 cc of water, 5 drops of concentrated HCl, heat to the boiling point, and filter one-half of the suspension. (See Note 1.) A colorless or very faintly yellow filtrate proves benzidine yellow. A distinctly yellow filtrate indicates 3, 4, or 5. Proceed as follows:

III. To the remaining half of the suspension (or to one-half of the solution, provided that it was clear and no filtration was necessary) add 3 cc of 4 *N* stannous chloride solution, heat to the boiling point, and boil gently for 3 to 5 minutes. The solution may:

A. Become colorless or very nearly so. This indicates 3 or 4. Add hydrogen peroxide solution dropwise until an excess is present (indicated by bubbles).

1. If the solution remains colorless, this proves tartrazine yellow.
2. If the solution turns a light reddish orange, this proves naphthol yellow.
3. If the solution retains its yellow color, this indicates 5. To confirm this test, dissolve a fresh sample of the pigment in 20 drops of concentrated sulfuric acid (cold). Add 5 drops of concentrated nitric acid and shake gently. If the solution decolorizes completely and almost immediately, this proves quinoline yellow. (See Note 2.)

Notes

1. In some cases a clear yellow solution will result at this point. It is not necessary to filter, obviously, but simply to proceed as directed, using one-half of the solution.

2. If the solution does not decolorize completely and at once, this indicates the possibility that insufficient stannous chloride was used in the test preceding. In that case, repeat the stannous chloride test, using smaller amounts of the pigment or more of the reagent to insure complete reduction.

ORANGES

1. Dinitroaniline Orange
2. *o*-Nitroaniline Orange
3. Sodium Red for Lake C
4. Sodium Lithol
5. Persian Orange

I. To a sample of the pigment contained in a dry test tube add 2 cc of dioxane, heat to boil, and add 2 cc of water and 2 drops of 20 per cent NaOH. A deep blue color proves dinitroaniline orange. All the others turn a deep orange-red color. In this case, proceed as follows.

II. To the above solution, add 4 cc of water, 5 drops of concentrated HCl, and shake the tube vigorously for a minute or so. A light yellow-orange flocculent precipitate which separates toward the surface of the solution proves *o*-nitroaniline orange. Instead of this result, a brown-red or purple-red flocculent precipitate or an orange solution may be obtained. This indicates 3, 4, or 5. Proceed as follows.

III. Dissolve a fresh sample of the pigment in 20 drops of cold concentrated sulfuric acid by shaking 2 or 3 minutes. Add 5 cc of water and shake vigorously. Three results are possible. (See note below.)

A. A dirty orange-red suspension results (looking through the tube at daylight), from which a brown-red flocculent precipitate separates rapidly to the surface. This proves sodium red for Lake C.

B. A purplish-red suspension results (looking through the tube at daylight), from which a dark brown flocculent precipitate separates slowly toward the surface. This proves sodium lithol.

C. An orange solution results. This proves Persian orange.

Note. The results of this test are quite definite once the operator has seen them. It is recommended that it be performed on known samples so that the actual colors may be carefully noted.

REDS

1. Toluidine Red
2. *p*-Nitroaniline Red
3. *o*-Chloro-*p*-nitroaniline Red
4. *p*-Chloro-*o*-nitroaniline Red
5. Brilliant Red (*p*-Nitro-*o*-toluidine-naphthol AS)
6. Lithol Red Salts
7. Red for Lake C Salts
8. Red for Lake D Salts
9. Lithol Rubine
10. Lithosol Red 2B
11. Pigment Scarlet 3B Lakes
12. Acid Scarlet 2R Lakes
13. Rhodamine B Toners
14. Rhodamine 6G Toners
15. Phloxins
16. Madder Lake

I. To a sample of the pigment, add 5 cc of dioxane, shake 2 to 3 minutes, filter and refilter to make sure no fine solid pigment particles have gone through. Four conditions of the filtrate may be noted:

A. It is a definite orange or orange-red color. This indicates 1, 2, 3, 4, or 5. In this case, add an equal volume of water and shake vigorously. The appearance of a light flocculent precipitation of pigment, or a cloudiness, is further indicative of numbers 1 to 5, inclusive. Now heat to the boiling point and add 5 drops of 20 per cent NaOH. Three color changes may be noted which serve to distinguish each member of this subdivision from all others. (See Note 1.)

1. If the solution acquires a deep wine or deep cherry red color, this proves toluidine red or *p*-chloro-*o*-nitroaniline red. These can be distinguished by shade since the latter is definitely orange compared to the former.
2. If the solution turns a deep purple color, this proves *p*-nitroaniline red or *o*-chloro-*p*-nitroaniline red. These may also be distinguished one from the other on basis of shade.
3. If the solution turns a light brown or brownish orange, this proves brilliant red.

B. It is a blue-red color typical of Rhodamine B solutions and exhibits a slight fluorescence which is not dispersed by acidification or making alkaline. The color becomes bluer on dilution with an equal volume of water. This proves Rhodamine B.

C. It exhibits a yellowish fluorescence, which indicates Rhodamine 6G or phloxin. To a fresh sample, add 1 cc of 20 per cent NaOH.

1. The color dissolves to a yellow-red fluorescent solution. This proves phloxin.
2. The solution is not colored. This proves Rhodamine 6G.

D. It shows a *very slight* pink or orange tint. This indicates 6, 7, 8, 9, 10, 11, 12, and 16. Proceed as follows: To a fresh sample of 2 or 3 mg in a dry test tube, add 2 cc of concentrated sulfuric acid and shake for about a minute.

1. A yellowish red solution indicates Pigment Scarlet 3B, Acid Scarlet 2R, or Madder Lake. Add 3 drops of concentrated nitric acid and shake 1 to 2 minutes.
   - *a.* If the solution retains a definite red color, this proves Acid Scarlet 2R.
   - *b.* If the solution turns pale yellow, this indicates Pigment Scarlet 3B or Madder Lake. To a fresh sample, add 5 cc of water, 5 drops of concentrated HCl, and heat to boiling. Add 5 cc of 20 per cent NaOH.
     - (1) The formation of an intense violet color proves Madder Lake.
     - (2) A pale yellowish orange solution proves Pigment Scarlet 3B.
2. A deep purplish or magenta-red solution indicates 6, 7, 8, 9, or 10. Proceed as follows:
   - *a.* To a fresh sample of the dry pigment in a dry test tube, add 5 cc of glacial acetic acid and heat to boil. A bright yellow-orange suspension proves Red Lake D. (See Note 2.)

b. To a fresh sample (10 mg or less), add 3 cc of water and 4 drops of stannous chloride solution. Heat to boil and boil 2 to 3 minutes. Complete reduction of the pigment, leaving no unreduced particles (except rosin) and a colorless solution, proves lithol rubine. (See Note 3.) If some of the pigment remains unreduced (see Note 4), this indicates 6, 7, or 10. Proceed as follows. Dissolve a fresh sample in ice-cold concentrated sulfuric acid in a dry test tube by shaking 2 to 3 minutes and then add 5 cc of water. Shake vigorously. If:

(1) A dirty orange-red suspension results (looking through the tube at daylight), from which a brown-red flocculent precipitate separates rapidly to the surface. This proves red for lake C.

(2) A purplish red suspension results (looking through the tube at daylight), from which a dark brown flocculent precipitate separates slowly toward the surface. This proves lithol.

(3) The pigment comes out of solution as bright red flocs approximating its original appearance. This proves Lithosol Red 2B.

Notes

1. It will be observed that: Both toluidine red and *p*-chloro-*o*-nitroaniline red have a nitro group ortho to the azo linkage and give similar colors with alkali. Both *p*-nitroaniline red and the chlorinated derivative, as well as dinitroaniline orange (*vide supra*), have a nitro group para to the azo linkage and give blue or purplish colors with alkali, the shade differences being due to other substituents. Brilliant red has a nitro group meta to the azo linkage and gives a color with alkali quite different from the others.

2. At this point a yellowish red clear solution is an indication of lithol rubine toner, a similar solution containing a residual cloudiness is indicative of reduced lithol rubine toner, whereas a blue-red solution or cloudy solution indicates Lithosol Red 2B.

3. During the 2 to 3 minutes boiling period, any pigment particles which adhere to the walls of the test tube should be returned to the solution by means of a stirring rod equipped with a policeman.

4. If there is doubt that particles remaining are color particles, they may be filtered off and smudged on filter paper with the finger tip.

MAROONS

1. Toluidine Maroon
2. Indanthrene Maroon
3. Helio Fast Rubine 4BL
4. Helio Bordeaux
5. Azo-Bordeaux or Acid Bordeaux
6. Tobias Acid β-Oxy Naphthoic Acid Maroon
7. Lithol Maroon

To a sample of the pigment contained in a dry test tube, add 5 cc of dioxane, heat to the boiling point, boil 1 minute, and filter one-half the suspension. The filtrate may be:

A. Colored an intense orange-red. Add an equal volume of water and 2 drops of 20 per cent NaOH. If the color intensifies, this proves Toluidine Maroon.

B. Colored an intense blue-violet. This proves Indanthrene Maroon.

C. Colorless or faintly colored. This indicates 3, 4, 5, 6, or 7. Proceed as follows. To a fresh sample, add 10 cc of water, 5 drops of 20 per cent NaOH, and shake vigorously.

1. A blue color proves Helio Fast Rubine. (See Note 1.)
2. A red solution or suspension indicates 4, 5, 6, or 7. Filter the suspension.
   - *a*. An intense red filtrate indicates 4 or 5. Proceed as follows. To a fresh sample, add 5 cc of methanol, shake vigorously for 1 minute, and filter.
     - (1) An intense red filtrate proves Helio Bordeaux.
     - (2) A very pale red filtrate proves Azo-Bordeaux or Acid Bordeaux.
   - *b*. A colorless or very pale filtrate indicates 6 or 7. Proceed as follows. To a fresh sample, add 5 cc of glacial acetic acid and 5 drops of concentrated nitric acid. Heat to boil and boil 30 seconds. (See Note 2.)
     - (1) If the suspension retains a very definite red color, this proves Tobias acid-β-oxynaphthoic acid maroon.
     - (2) If the suspension turns light yellow or yellow-orange, this proves lithol maroon.

Notes

1. This test will be positive with any alizarin maroon. Helio Fast Rubine was used as an example.
2. The conditions of this test must be strictly adhered to since higher concentration of reagents or longer boiling may lead to contradictory results.

BLUES

1. Peacock Blue (acid dye)
2. Peacock Blue (basic dye)
3. Alkali Blue Pigments
4. Victoria Blue Pigments
5. Phthalocyanine Pigments

To a sample of the pigment, add 5 cc of water, 5 drops of 20 per cent NaOH, boil, and filter.

A. A distinct blue filtrate proves Acid Peacock Blue or Alkali Blue, which are distinguishable by shade.

B. A colorless filtrate indicates 2, 4, or 5. Proceed as follows. To a fresh sample, add 5 cc of methanol. Shake a minute or two and filter.

1. A deep blue filtrate turning green on addition of a few drops of concentrated HCl proves Victoria Blue or Victoria Pure Blue.
2. A pale peacock blue filtrate proves Basic Peacock.
3. A colorless filtrate proves Phthalocyanine Blue.

GREENS

1. Acid Greens
2. Basic Greens (Malachite Green, Brilliant Green, or this in admixture with Thioflavin or Auramine yellows)
3. Phthalocyanine Green

To a sample of the pigment, add 5 cc of water and 5 drops of 20 per cent NaOH. Heat to boiling, boil half a minute, and filter.

A. A distinctly green filtrate proves Acid Green. A colorless filtrate indicates 2 or 3. Proceed as follows:

B. To a fresh sample, add 5 cc of methanol, 10 drops of concentrated HCl, boil, and filter.

1. A blue-green, yellow-green, or yellow filtrate proves basic green. (See Note.)
2. A colorless filtrate proves phthalocyanine green.

Note. Under the conditions of this test, Malachite Green pigments will give a blue-green, Brilliant Green pigment a yellowish solution. Yellow-shade greens made in part with Thioflavin or Auramine will give correspondingly yellower filtrates.

PURPLES

1. Acid Violet
2. Methyl Violet (basic)

To a sample of the pigment, add 5 cc of water, 5 drops of 20 per cent NaOH, boil, and filter.

A. An intense violet color proves Acid Violet.

B. A colorless filtrate proves Methyl Violet. This can be confirmed by observing the violet filtrate resulting on treating the pigment with methanol.

THE MICROSCOPIC IDENTIFICATION OF AZO-DYES AND ORGANIC PIGMENTS

Vesce has carried out some very interesting and valuable experimental work in the past few years in which he has demonstrated through the medium of excellent photomicrographic exhibits that the individual organic pigments and dyestuffs crystallize from strong sulfuric acid in characteristic crystal forms.

Historical Review (132) *

Among the many qualitative tests which can be applied to the identification of organic coloring matter, the oldest, simplest, and most useful is the well-known concentrated sulfuric acid reaction test. The characteristic color changes which are developed by concentrated sulfuric acid frequently serve as an excellent means of identification. The action of this reagent upon dyes and pigments is almost instantaneous and quite specific. Further confirmatory changes of hues are also observed when the above test mixture is diluted with water.

In the year 1880, Nietzki [100] observed in his investigations of Biebrich Scarlet dye that concentrated sulfuric acid dissolved the material to a dark-green solution and that it separated unchanged upon the addition of water. This is the earliest reference found on the use of sulfuric acid as applied toward the study of the properties of organic coal-tar coloring matter.

In 1886 Otto N. Witt [143] described the action of various reagents on coal-tar dyes and made extensive use of the color reaction produced by the action of concentrated sulfuric acid on these dyes.

On the basis of Witt's work, Weingaertner [136] in 1887 published a method for differentiating azo dyes by means of their color reaction with concentrated sulfuric acid. The technique employed was to place water-white sulfuric acid in a clean white porcelain dish and to sprinkle carefully several grains of dyestuff on its surface. In this way, it was stated, owing to the sensitivity of the reaction, the individual constituents in mixtures of azo dyes could be easily recognized.

Bamberger and Bordt [12] suggested a valuable confirmatory analytical procedure for the analysis of various dyes, the measurement of the wavelength of greatest absorption of the dye dissolved in water. Absorption spectra data were given directly in terms of wavelength; this work was done chiefly in aqueous solution, and no mention was made of the concentrated sulfuric acid reaction. However, Vogel [134] in 1889, while working on the identification of various dyes, observed that the absorption spectra lines of some azo dyes are sharper when made in concentrated sulfuric acid and consequently are more easily analyzed than when the dyes were dissolved in alcohol or water.

Graebe [59] in 1892 extended the work of Vogel in an investigation covering more than one hundred selected dyes. He studied, for the most part, the absorption spectra of dyes in concentrated sulfuric acid and the effect upon them of addition of alcohol, ice, water, and other diluents.

There are cases, however, where several coloring materials of different chemical constitution produce color reactions so similar to each other that further tests are required to identify each with certainty, and the test must be supplemented by a more detailed analysis.

New Microscopic Method

Researches carried out in the author's [Vesce's] laboratory [132] have demonstrated the complete applicability of microcrystallization techniques to the problem of identification of dyestuffs. If the concentrated sulfuric acid test mixture is allowed to stand, and then examined under the microscope, most organic coal-tar pigments or dyes are seen to deposit crystals of highly specific and characteristic appearance. No two organic pigments of different chemical structure are found

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to yield the same crystals. These crystals are deposited after the reaction mixture is allowed to stand for some time, and first appear around the edges of the cover glass. The test is performed on a microscopic slide, and observed under the microscope using low-power objectives, the magnification generally being between 150 and 200 diameters.

Among the dyes and pigments tested there were many which comprised metallic precipitations of azo dyestuffs. The nature of the metal in these precipitated dyestuffs did not in any way interfere with the kind of crystals produced, thereby proving that it is the organic portion of the molecule that is essentially responsible for the individual habit of the crystal. Thus, it was found that the pigment comprising the barium salt of lithol toner produced crystals identical with those from the calcium salt of lithol toner.

The exact mechanism of these crystal formations is not as yet clearly understood. Three possibilities exist.

1. The free acid of the dye which occurs during solution in the concentrated acid at the outset, upon standing, absorbs atmospheric moisture, with deposition of crystals of the water-insoluble free acid dye molecule.
2. The sulfuric acid attaches itself directly to the chromophore group of the color to form an additive compound which crystallizes out upon standing.
3. The additive sulfuric acid compound postulated above is formed through the auxochrome or chromogen groups of the dye.

It is realized that the majority of the crystals formed by action of concentrated sulfuric acid upon pigments and dyes are decidedly dendritic in character, and, unless the conditions for producing these crystals are strictly standardized and uniform, they may be subject to such erratic variations that possibly erroneous conclusions may be drawn. A dendritic deposit is known generally as a labile shower and is characterized by a profusion of needle-like crystals, which show none of the external characteristics of well-developed macrocrystals. Although dendritic crystals are considered useless for crystallographic studies, in this case the crystals are prepared by a strictly standardized procedure (described later) so that they can be easily reproduced at will. The size and shape of the particular formation is peculiar to the particular azo dye. From a qualitative standpoint, it has been possible to recognize, identify, and reproduce the characteristic dendritic growths from most coal-tar pigments or dyes.

It was found that the strength of the sulfuric acid reagent employed is a factor in the speed with which these crystal growths appeared. Very often the size and general character of the crystals were also affected by the strength of the acid used. As a general rule, it was found that 93 per cent sulfuric acid produced the most uniform and easily reproducible results. The action was accelerated as a rule by using sulfuric acid of higher concentration, such as 98.5 per cent strength, but the growths were occasionally unstable. The amount of dye mixed with the sulfuric acid was also found to be an important factor which influenced the speed with which the crystals appeared. Some pigments or dyes seem to require higher concentrations than others to produce rapid crystal formation.

In every case the tests were conducted at ordinary room temperature, 27° C., and the temperature of the acid was also carefully maintained at this temperature.

Technique

After numerous experiments the following standard technique was adopted:

On the center of a large, clean, dry microscopic slide, 2 inches × 3 inches, is placed a drop of concentrated sulfuric acid of 93 per cent strength (drop measured approximately 4 mm. in diameter). Then a small, loose mass of powdered pigment, measuring approximately 2 mm., is stirred into the drop of acid by using a fine glass rod or platinum spatula. A round cover glass is placed over the mixture and carefully pressed down to exclude as many air bubbles as possible. The slide is then examined under the microscope, and usually after several minutes definite beginning of crystal formation is observed, the growth occurring first around the edges of the cover glass. These quickly grow in size and number of deposits. The slide is examined periodically to note any changes which may have occurred since the initial formation of crystals formed and of formation of different or secondary crystals.

An alternative procedure is to take a small amount of loose powdered pigment, measuring approximately 2 mm. in diameter, and place it on a large microscopic slide. After placing a cover glass over the dry mass, it is gently rubbed with a circular motion until the powder is spread out uniformly beneath the cover glass. The slide preparation is then placed under a microscope and properly focused. Then a small drop of concentrated sulfuric acid is dropped on the extreme edge of the cover glass and through capillarity the liquid quickly spreads and the action of the liquid upon the powder can be directly observed under the microscope. By examining a field near the edges, crystal growth will soon be observed.

While in most cases the first-mentioned technique works very well, it may sometimes be necessary to employ the latter method in order to determine the best procedure for the particular pigment examined.

On azo pigments substantially soluble in solvents, such as benzol, it is sometimes well to recrystallize the pigments from benzol or toluene in order to obtain a better crystal growth when making the test described above. In this way impurities are removed in the pigment that might interfere with an easy crystal formation.

Procedure for Making Photomicrographs

In making the photomicrographs which appear at the end of this chapter [Figs. 43–76] the illumination was furnished by a carbon arc, the objective used was a Zeiss 12× apochromat, and the photographic eyepiece employed is known as Homal I. The bellows extension was adjusted to a previously standardized magnification of 200 diameters. Koehler's method of critical illumination was provided, and the negatives were Wratten M plates, which were developed to low contrast in D76C in order to preserve detail. The paper employed in printing was Eastman's azo glossy No. 3 contrast, which was developed in D-72 as usual.

While the pigments herein reported represent only a relatively small percentage of all pigments, preliminary observations on many others indicate that nearly all the azo type pigments, as well as others, will yield crystals that can serve for qualitative identification.

Crystal formations resulting from mixtures of pigments have not yet been studied. It is hoped that the observations and photographs presented herewith will serve as a basis for future work along these lines.

No attempt was made to study the chemical composition of the crystals. Most of the colors studied comprised coloring matter possessing the azo group as the chromophore. No attempt has been made to measure or collect any crystallographic data, such as refractive indices, etc., which would contribute further toward the exact identification of some of these materials. It might be mentioned, however, that with polarized light under crossed nicols, most of these crystals were anisotropic in character.

Fig. 43. Scarlet 3B Pigment.

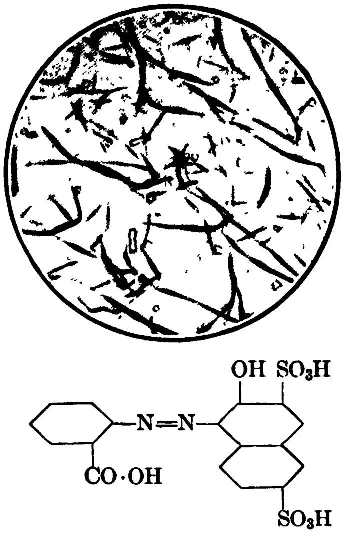


Fig. 44. B.O.N. Maroon Pigment.

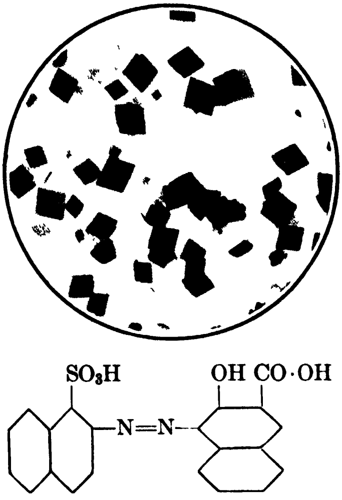


Fig. 45. B.O.N. Maroon Pigment.

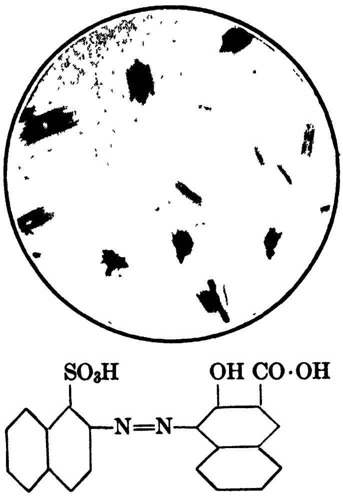


Fig. 46. B.O.N. Maroon Pigment.

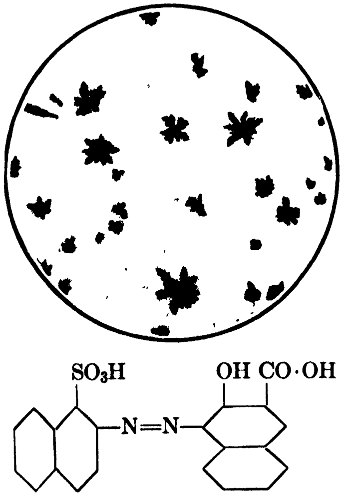


Fig. 47. Red Pigment Rubine 3G.

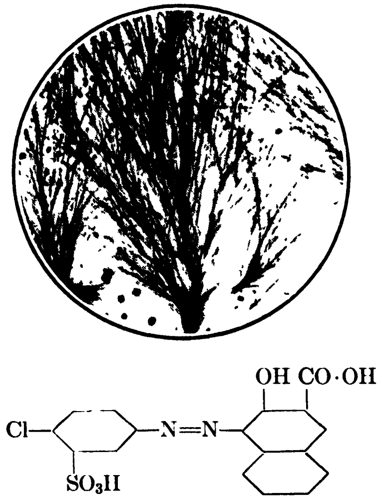


Fig. 48. Red Pigment from Anthosine B Dye.

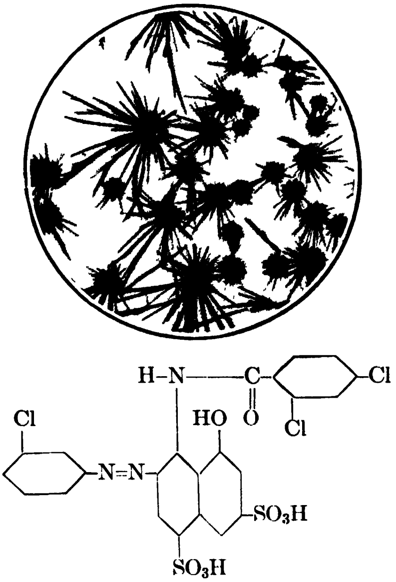


Fig. 49. Red Pigment from Anthosine B Dye.

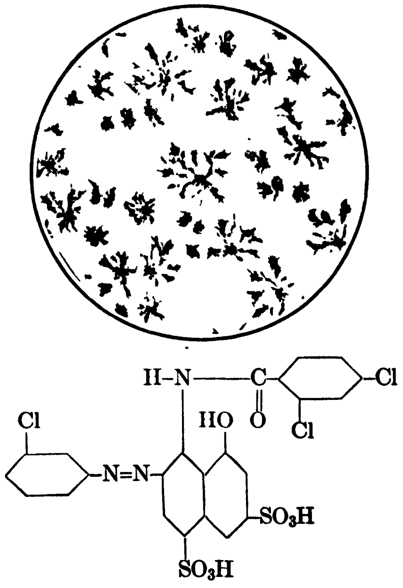


Fig. 50. Maroon Pigment.

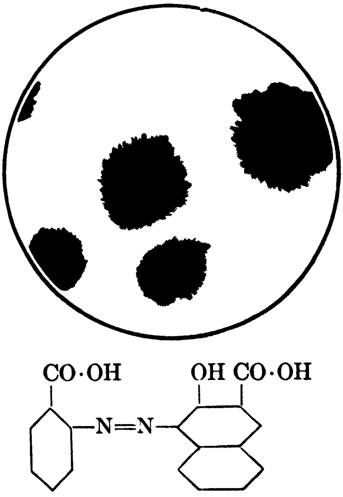


FIG. 51. MAROON PIGMENT.

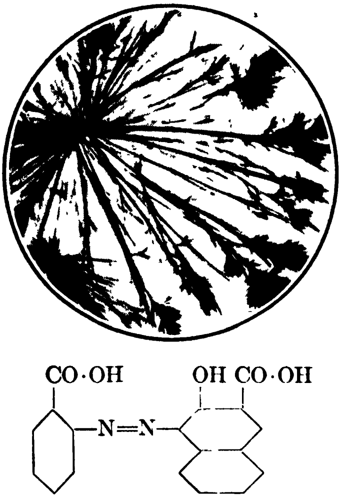


FIG. 52. ORANGE PIGMENT.

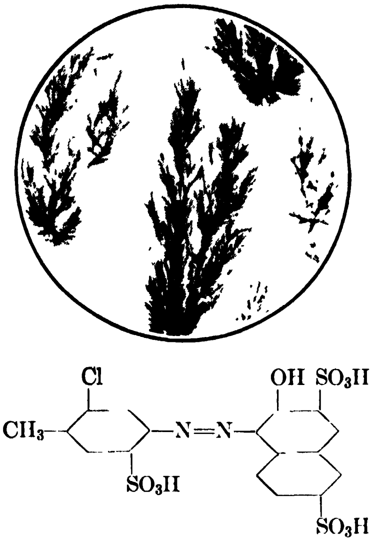


FIG. 53. RED PIGMENT.

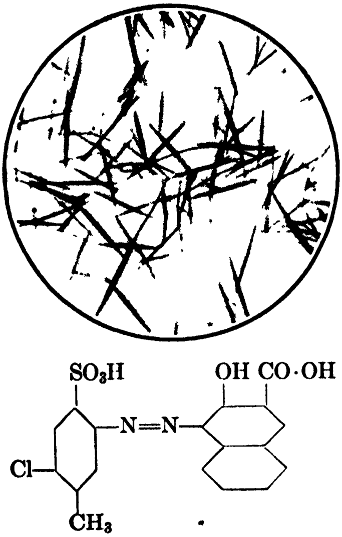


FIG. 54. RED PIGMENT.

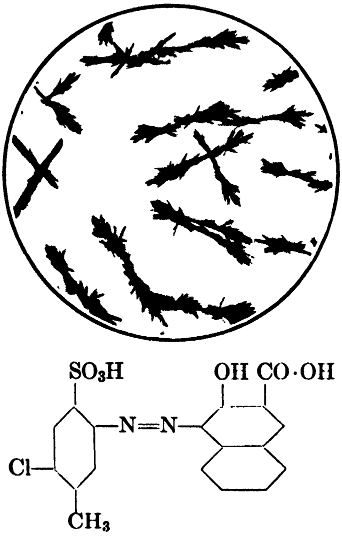
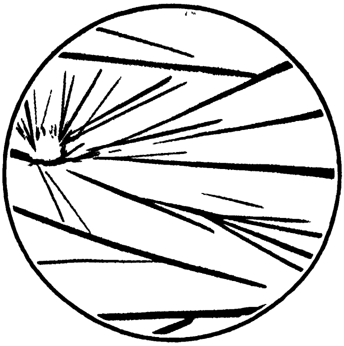


Fig. 55. Copper Phthalocyanine.



See page 216.

Fig. 56. Copper Phthalocyanine.

See page 216.

Fig 57. Lithol Red Pigment.

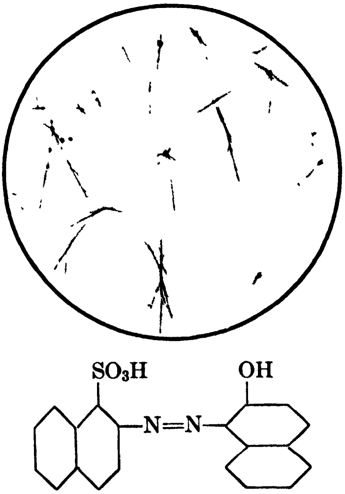


Fig. 58. Persian Orange Lake Pigment.

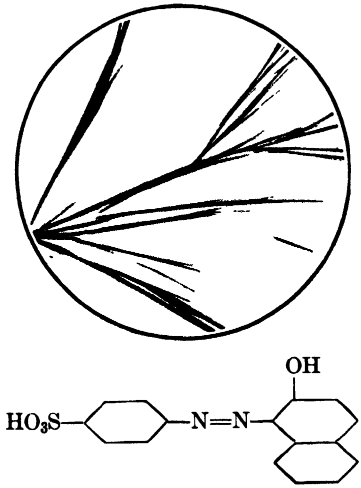


Fig. 59. Red Lake C Pigment.

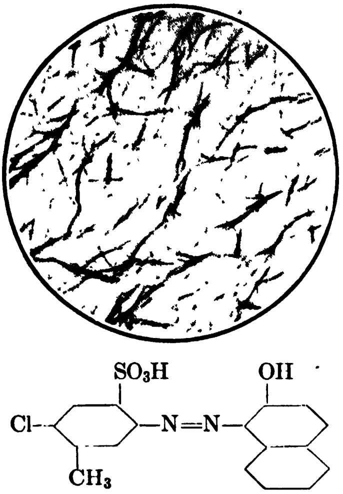


Fig. 60. Red Lake R Pigment.

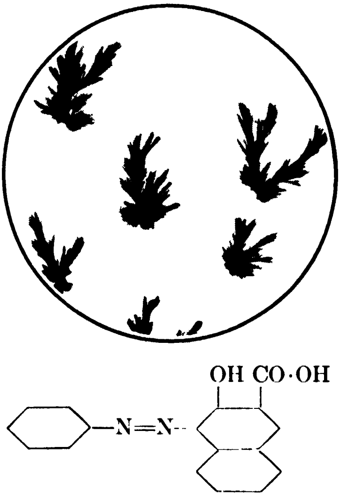


Fig. 61. Red Lake D Pigment.

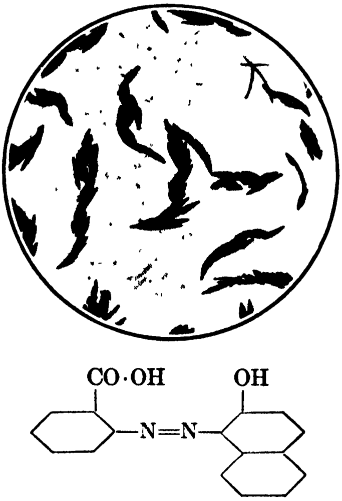
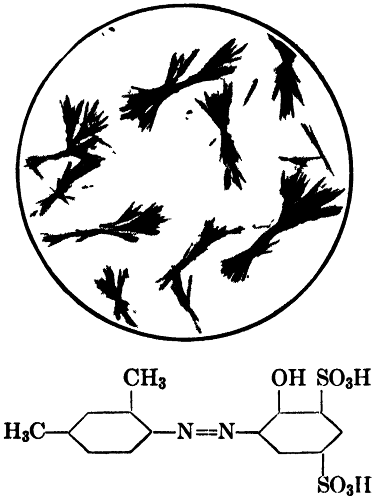


Fig. 62. Scarlet Lake Pigment.



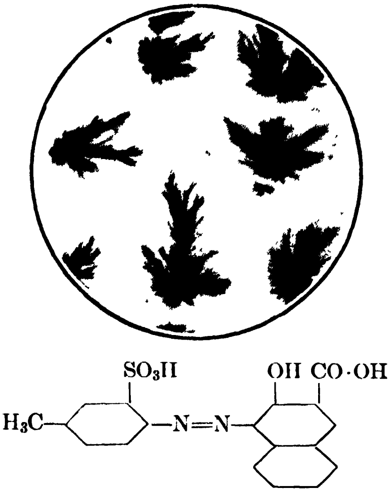


FIG. 63. LITHOL RUBINE RED PIGMENT.

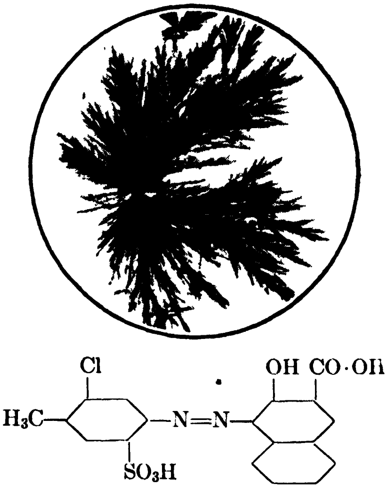


FIG. 64. RED PIGMENT.

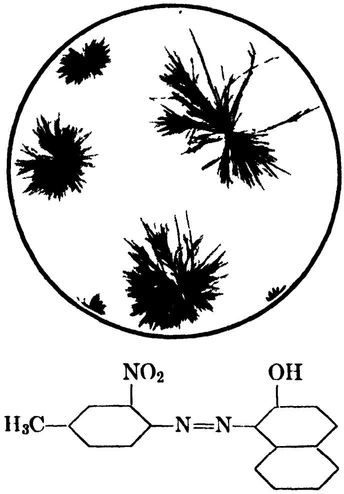


FIG. 65. TOLUIDINE RED PIGMENT.

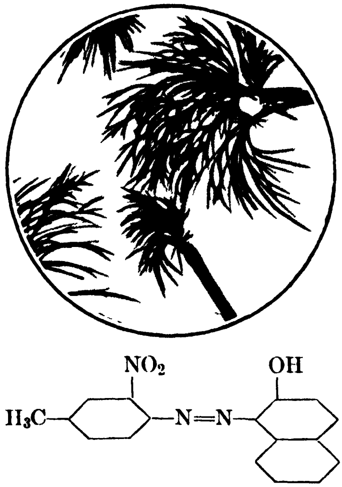


FIG. 66. TOLUIDINE RED PIGMENT.

Fig. 67. Para Red Pigment.

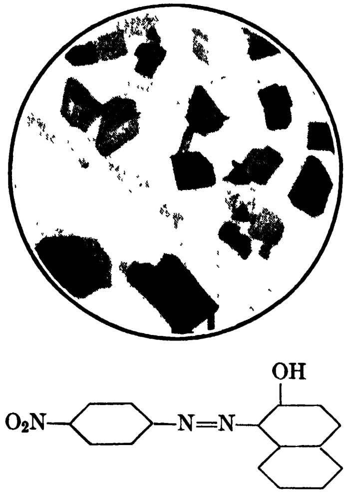


Fig. 68. Para Red Pigment.

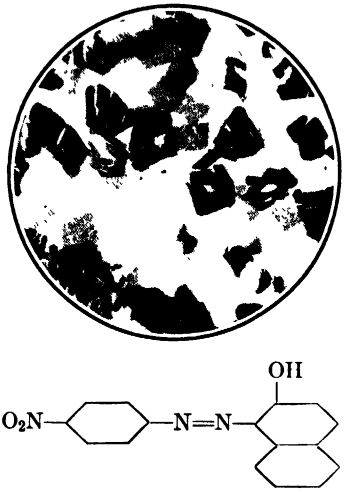


Fig. 69. Red Pigment.

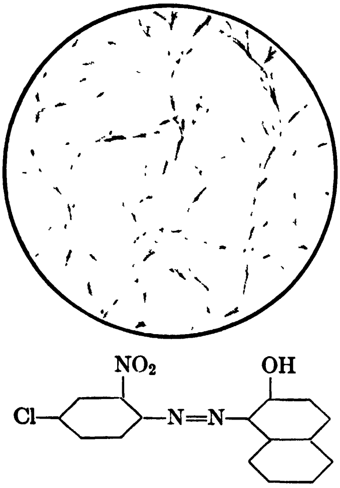


Fig. 70. Red Pigment.

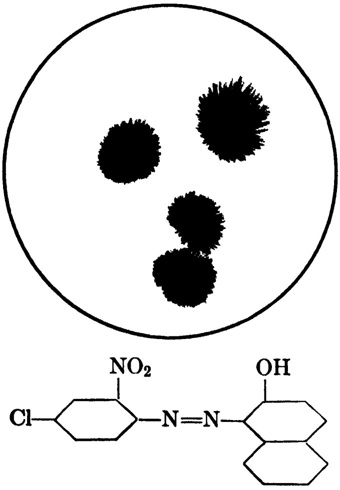


FIG. 71. RED PIGMENT.

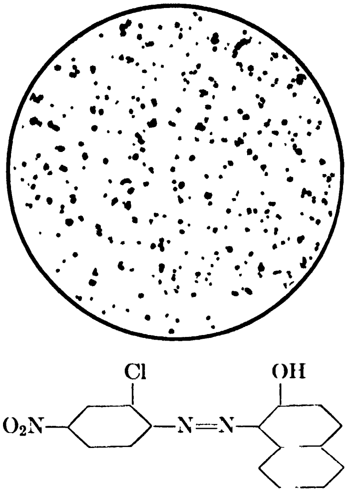


FIG. 72. NITRO TOLUIDINE RED PIGMENT.

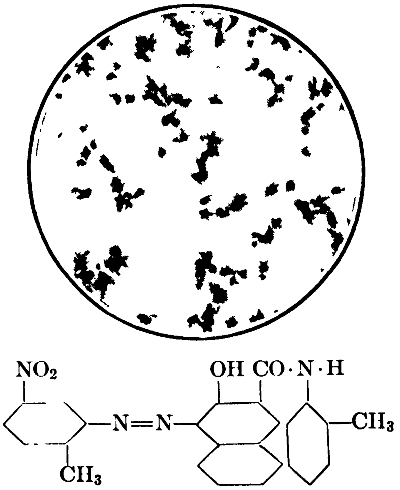


FIG. 73. CHLOR TOLUIDINE RED PIGMENT.

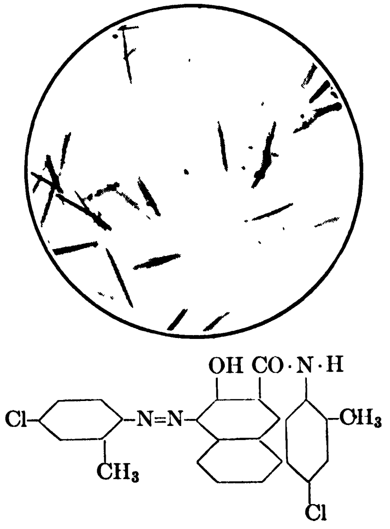


FIG. 74. NITRO ANISIDINE RED PIGMENT.

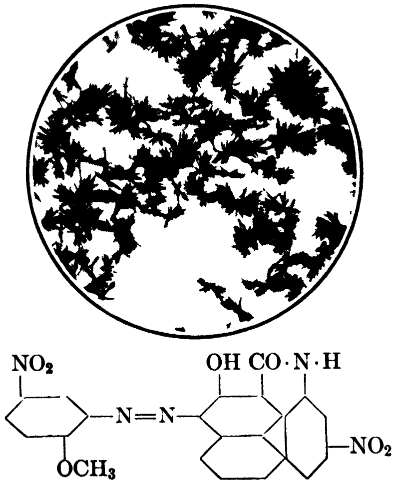


FIG. 75. ORANGE PIGMENT.

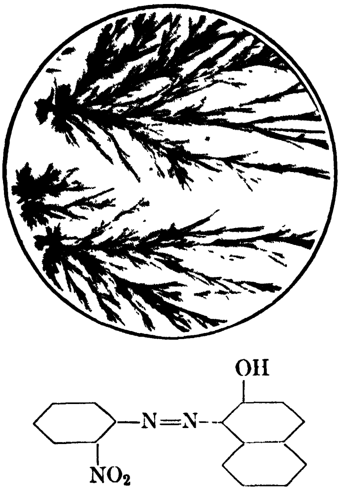
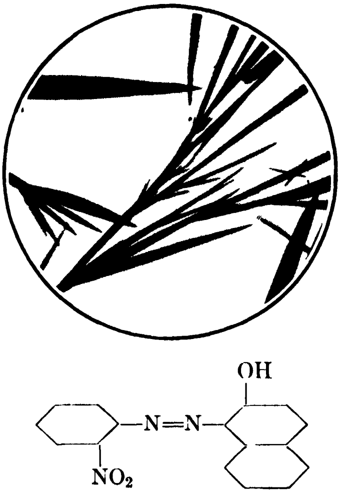


FIG. 76. ORANGE PIGMENT.



INDEX FOR FIGURES 43-76

FIGURE 43. SCARLET 3B PIGMENT

1-(*o*-Carboxyphenylazo)-2-naphthol-3,6-disulfonic acid. Light golden brown crystals form in about 30 minutes. Initially very small crystals start in about 5 minutes. They appear ribbon-like in character.

FIGURE 44. B.O.N. MAROON PIGMENT

1-Sulfo-2-naphthaleneazo-2-hydroxy-3-naphthoic acid. Initial small rhombic plates appearing in about 5 minutes and growing larger upon standing. They are brownish in color. See also Figs. 45 and 46.

FIGURE 45. B.O.N. MAROON PIGMENT

1-Sulfo-2-naphthaleneazo-2-hydroxy-3-naphthoic acid. Transitory formation occurring from crystals shown in Fig. 44. See also Fig. 46.

FIGURE 46. B.O.N. MAROON PIGMENT

1-Sulfo-2-naphthaleneazo-2-hydroxy-3-naphthoic acid. Feathery crystals also appearing together with the rhombic plates shown in Fig. 44. Possibly the result of action occurring in Fig. 45.

FIGURE 47. RED PIGMENT RUBINE 3G

Fine brownish hair-like crystals appearing in 15 minutes. Eventually they disperse and later produce large, massive, black crystals which grow on standing.

FIGURE 48. RED PIGMENT FROM ANTHOSINE B DYE

1-Chloro-3-benzeneazo-2,4-dichlorobenzoyl-K-acid. Yellowish brown crystals forming in 10 minutes. Groups of crystals starting with center nucleus with needles spreading out in all directions. See also Fig. 49.

FIGURE 49. RED PIGMENT FROM ANTHOSINE B DYE

1-Chloro-3-benzeneazo-2,4-dichlorobenzoyl-K-acid. Final form of crystals produced from those shown in Fig. 48.

FIGURE 50. MAROON PIGMENT

1-Carboxy-2-benzeneazo-2-hydroxy-3-naphthoic acid. Small bluish red ball-like dendrites appear in about 8 minutes. Upon standing, they grow to very large size. See also Fig. 51.

FIGURE 51. MAROON PIGMENT

1-Carboxy-2-benzeneazo-2-hydroxy-3-naphthoic acid. Final form of crystals from those shown in Fig. 56.

FIGURE 52. ORANGE PIGMENT

1-Methyl-2-chloro-5-sulfo-4-benzeneazo-2-naphthol-3,6-disulfonic acid R. Dark orange to brown dendritic branches form in 2 minutes. They appear to keep this form very well.

FIGURE 53. RED PIGMENT

1-Methyl-2-chloro-4-sulfo-5-benzeneazo-2-hydroxy-3-naphthoic acid. Initial form —thick irregular needles forming in about 10 minutes. They are brownish red in color. After standing about 15 minutes, they change to those shown in Fig. 54.

FIGURE 54. RED PIGMENT.

1-Methyl-2-chloro-4-sulfo-5-benzeneazo-2-hydroxy-3-naphthoic acid. Final form of crystal from those shown in Fig. 53.

FIGURE 55. COPPER PHTHALOCYANINE

"Monastral" and "Heliogen" Blues. Grass-like blades, green crystals. One of the two types which appear in about 5 minutes. For other type, see Fig. 56.

FIGURE 56. COPPER PHTHALOCYANINE

Crystals also formed cubic in type and are disintegrated, from which small fine branches appear.

FIGURE 57. LITHOL RED PIGMENT

1-Sulfo-2-naphthaleneazo-2-naphthol. Fine, needle-like crystals forming in about 6 minutes. They are bluish red in color and continue to branch out on growing.

FIGURE 58. PERSIAN ORANGE LAKE PIGMENT

1-Sulfo-4-benzeneazo-2-naphthol. Large branch-like long crystals forming in about 10 minutes. They are yellowish red or brown in color and continue to branch out on growing.

FIGURE 59. RED LAKE C PIGMENT

1-Methyl-2-chloro-4-sulfo-5-benzeneazo-2-naphthol. Wavy mass of delicate, fine, hair-like crystals. They are purple in color and begin to form in about 10 minutes.

FIGURE 60. RED LAKE R PIGMENT

Benzeneazo-2-hydroxy-3-naphthoic acid. Feathery, dark, bluish red crystals which do not grow very much larger. They form in about 10 minutes and carbonize on standing.

FIGURE 61. RED LAKE D PIGMENT

1-Carboxy-2-benzeneazo-2-naphthol. Initial crystals form in about 5 minutes, resembling claws of a boiled lobster. They do not keep well on standing because they disintegrate.

FIGURE 62. SCARLET LAKE PIGMENT

1,3-Dimethyl-4-benzeneazo-2-naphthol-3,6-disulfonic acid R. Crystals start to form in about 10 minutes and resemble bundles of straw in both color and appearance. They do not grow very much larger and keep very well.

FIGURE 63. LITHOL RUBINE RED PIGMENT

1-Methyl-3-sulfo-4-benzeneazo-2-hydroxy-3-naphthoic acid. Small crystals appear to form in about 5 minutes. They are brown in color and feathery in character. They seem to keep fairly well.

FIGURE 64. RED PIGMENT

1-Methyl-2-chloro-5-sulfo-4-benzeneazo-2-hydroxy-3-naphthoic acid. Crystals appear in about one-half hour and become gray in color. They keep very well on standing.

FIGURE 65. TOLUIDINE RED PIGMENT

2-Nitro-*p*-tolueneazo-2-naphthol. One of the two types of crystals which appear except when pigment and acid concentrations are very low. These delicate crystals are purple in color. For other crystals, see Fig. 66.

FIGURE 66. TOLUIDINE RED PIGMENT

2-Nitro-*p*-tolueneazo-2-naphthol. Above crystals also formed and are brownish in color.

FIGURE 67. PARA RED PIGMENT

p-Nitrobenzeneazo-2-naphthol. Crystals begin to appear in about 10 minutes. They are red and after some time break up, as shown in Fig. 68.

FIGURE 68. PARA RED PIGMENT

p-Nitrobenzeneazo-2-naphthol. Final form of crystals produced from those shown in Fig. 67.

FIGURE 69. RED PIGMENT

o-Nitro-*p*-chlorobenzeneazo-2-naphthol. One of the two types of crystals appearing in about 10 minutes. The above vine-like crystals appear when pigment is low in relation to the amount of acid used; they are grayish brown in color. For other type of crystals, see Fig. 70.

FIGURE 70. RED PIGMENT

o-Nitro-*p*-chlorobenzeneazo-2-naphthol. Together with crystals shown in Fig. 69, this type of crystal also was produced. The crystals are durable and quite characteristic.

FIGURE 71. RED PIGMENT

o-Chloro-*p*-nitrobenzeneazo-2-naphthol. Very fine hexagonal plates, deep red color, forming in about 5 minutes.

FIGURE 72. NITRO TOLUIDINE RED PIGMENT

5-Nitro-2-methyl-1-benzeneazo-*o*-toluidide of 2-hydroxy-3-naphthoic acid. Very pale, transparent pink crystals begin to form in about 5 to 7 minutes. They are delicate and quite characteristic.

FIGURE 73. CHLOR TOLUIDINE RED PIGMENT

4-Chloro-2-methyl-1-benzeneazo-2-hydroxynaphthoic-chlorotoluidide. Small yellowish brown crystals form all over the slide in about 4 minutes. Larger crystals develop on standing.

FIGURE 74. NITRO ANISIDINE RED PIGMENT

5-Nitro-2-methoxyl-1-benzeneazo-*m*-nitranilide of 2-hydroxy-3-naphthoic acid. Formation of small needles occur at edges of the slide in about 7 minutes, developing gradually into larger branched purplish red crystals. These crystals are relatively stable even 36 hours after they have formed.

FIGURE 75. ORANGE PIGMENT

o-Nitrobenzeneazo-2-naphthol. One of the two types of crystals appearing when the pigment is low with respect to the amount of acid used. The large feathery crystals are brown in color and attain very large proportions. For other type of crystals, see Fig. 76.

FIGURE 76. ORANGE PIGMENT

o-Nitrobenzeneazo-2-naphthol. Crystals form in about 5 minutes, sword-like in character, reddish brown in color.

COLOR CURVE ANALYSIS

The tinctorial properties of a pigment are dependent on the action which takes place when it is exposed to electromagnetic vibrations including, as a rule, those of the visible spectrum. In the case of a so-called colored material it is evident that some portion of the incident radiation has disappeared owing to what is generally termed absorption, an effect caused by a state of resonance between the light ray and the colored molecule.

Experience has confirmed the very reasonable assumption that each molecule of a definite structure will be thrown into resonance with certain specific wavelengths and therefore absorb those wavelengths from the incident light. The absorption will therefore be characteristic of that particular molecule or pigment. At the present time means are available for measuring with a high degree of accuracy both the position and the degree of such an energy absorption. The equipment which is in general use for this purpose is the spectrophotometer.

According to Barnes (14): *

From the standpoint of measuring and classifying an infinite number of colors in a way which permits each to retain its individuality, the spectrophotometric method offers an accurate and objective specification of color.

The basic instrument for color measurement by this method is the recording photoelectric spectrophotometer, developed by Hardy [62] and produced by the General Electric Company. A commercial design of such an instrument is shown in Fig. 77, and a schematic diagram showing its operation in Fig. 78. The analysis of the color of a pigment consists in determining the percentage of light reflected, or transmitted in the case of solutions, by the object at each wave-length in the visible spectrum. Thus the sample to be measured is illuminated with spectrum light of substantially a single color, and the light reflected or transmitted by the sample, relative to a standard color, is automatically plotted against the wave-length of the incident light.

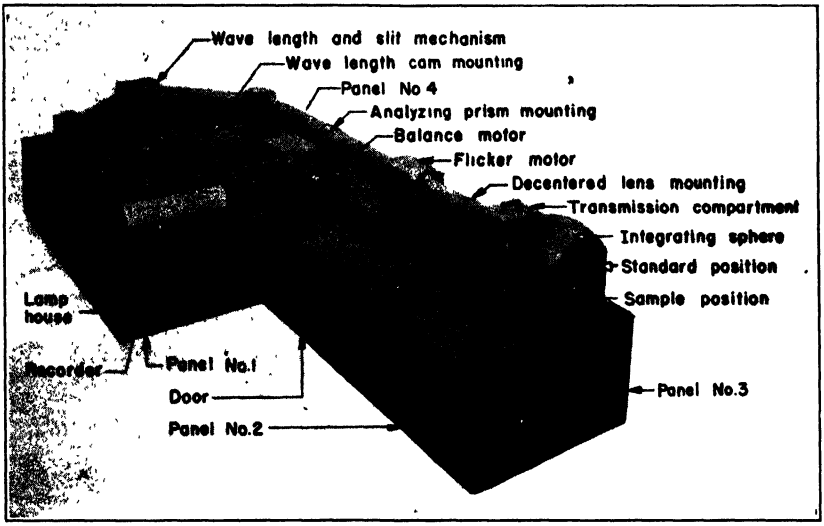


FIG. 77. G-E Recording Photoelectric Spectrophotometer. (*Courtesy of General Electric Co.*)

This standard color—white—which forms a basis for color comparison, is a freshly smoked magnesium-oxide surface, chosen because of its uniform reflectance of practically all the incident light in the visible spectrum. This white color has further been accepted internationally as the standard for color measurements.

In the form of the spectrophotometric curve a permanent record of the transmission or reflectance of each sample is obtained, and there is no need to depend further upon the original sample. When the color is recorded in this way—as an inherent property of the material—the objective specification gives results that are free from the numerous subjective errors of the human eye.

The applications of spectrophotometry have grown at such a rapid pace that the spectrophotometer has become a powerful analytical tool, both in the academic

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and industrial fields. The measurements may be divided into two groups, transmission and reflection.

In the former group, the spectrophotometric curve gives the per cent of light transmitted by the material as a continuous function of the wave-length of the light in the visible spectrum. This data can be used directly, or it can be used to give additional information about the sample. For example, if one has a series of colored, homogeneous solutions, differing only in the concentration of the coloring material, the values of the various concentrations can be calculated directly from the transmission values. Thus a new and sensitive method of quantitative analysis is available to the investigator which is particularly adapted to the analysis of dye and pigment solutions. A qualitative means of identifying a material, either as the sample itself or as an impurity, or as one of the component parts in a mixture, is often possible through the mere inspection of the shape and position of the absorption bands characteristic of that particular color.

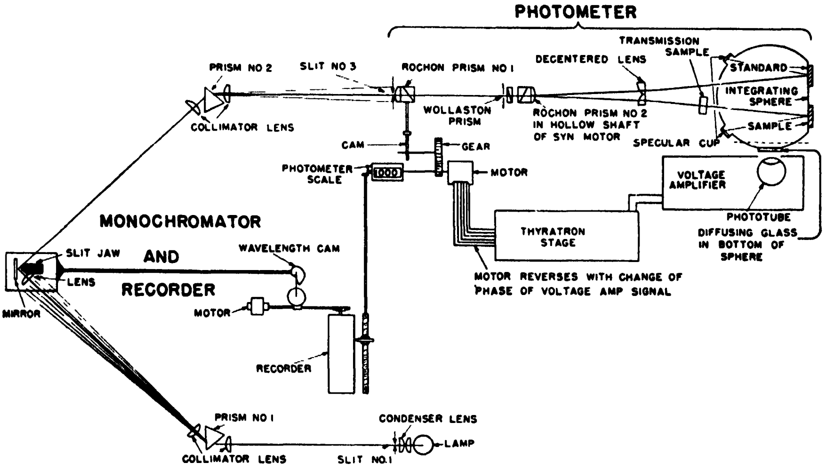

FIG. 78. Schematic Diagram Showing Operation of the Recording Photoelectric Spectrophotometer. (*Courtesy of General Electric Co.*)

Spectrophotometric qualitative and quantitative analytical methods apply equally well in the field of reflection measurements. An additional factor involved in this field is the physical nature of the reflecting surface. If this surface reflects light as a mirror does, the reflected light is referred to as being specularly reflected. On the other hand, if the surface scatters the reflected light in all directions, the light is said to be diffusely reflected. Most materials have their surface characteristics between these two extremes, and it therefore becomes necessary to interpret the reflection values in terms of surface characteristics.

Abbott and Stearns (1)* have outlined the procedure which may be followed in identification of an unknown pigment or in some cases the identification of the components of a mixture of pigments.

* Courtesy of Calco Chemical Division, American Cyanamid Company.

The following media were chosen.

- Pyridine
- Ortho-dichlor-benzene
- Sulfuric acid
- Zinc oxide pull-down

Solubilities of the order of 10 parts per million are adequate for identification by curve shape provided the entire sample is dissolved.

The curve of the unknown, dissolved in pyridine, falls into one of the following four classes.

Class I—sharp single absorption maximum
- Bromo Toner
- Rhodamine BX Lake

Class II—broad double absorption maximum
- Naphthosol
- Toluidine Red

Class III—broad single absorption maximum
- Lithol Red
- Lake Red C
- Para Red
- Permaton Orange

Class IV—Insoluble
- Lithol Rubine

Figure 79 shows the curve shapes of typical members of each class. The classification has been found to be quite distinct except perhaps for Toluidine Red and Permaton Orange. The Toluidine Reds have only a moderate double maximum in pyridine solution but to make certain of its identity, the sample may be dissolved in ortho-dichlor-benzene in which solvent the double peak is more pronounced. If the Permaton Orange should be erroneously placed in Class II, it would be readily apparent in the zinc oxide reduction discriminatory test to which the Class II members are subjected.

The members of Class I may be distinguished one from the other directly from the pyridine curves as shown in Fig. 80 since the Bromo absorption maximum falls at 546 mμ and the Rhodamine maximum falls at 562 mμ.

The members of Class II may be distinguished one from the other by the zinc oxide reductions. Figure 81 shows how the Naphthosols tend to retain their double peak while Toluidine Red loses it. Figure 81 also shows the characteristic curve of Permaton Orange which might have been thrown into this group erroneously by the pyridine test.

The members of Class III are first divided into group (*a*) or group (*b*). Group (*a*) is the "bluer" group with the absorption maximum falling at a longer wavelength (above 500 mμ) while group (*b*) is the "yellower" group having absorption maxima at a shorter wavelength (below 490 mμ). Groups (*a*) and (*b*) are also radically different in sulfuric acid solution. Group (*a*) consists of Lithol Red and Lake Red C which may be distinguished by zinc oxide reductions as shown in Fig. 82. Group (*b*) consists of Para Red and Permaton Orange which may be distinguished by zinc oxide reductions as shown in Fig. 83.

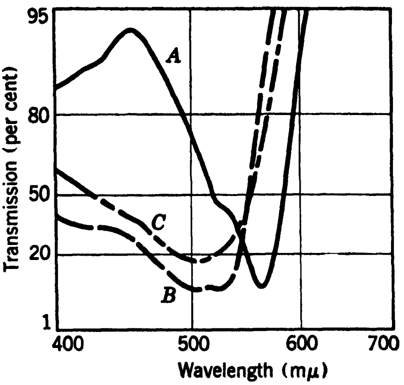

Fig. 79. Identification of Class by Curve Shape in Pyridine Solution: *A*. Class I. *B*. Class II. *C*. Class III.

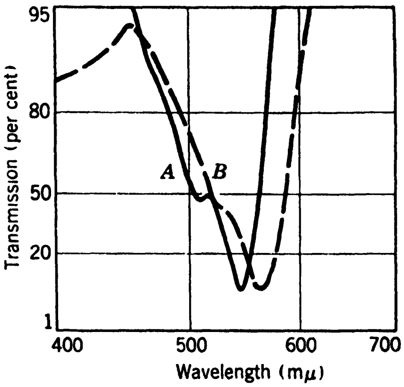

Fig. 80. Identification of Members of Class I by Curve Shape in Pyridine Solution: *A*. Bromo Toner. *B*. Rhodamine BX Lake.

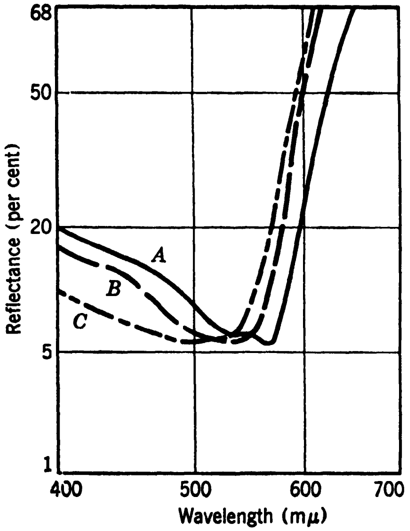

Fig. 81. Identification of Members of Class II by Reflectance Curves of Zinc Oxide Reductions: *A*. Naphthosol. *B*. Toluidine Red. *C*. Permaton Orange.

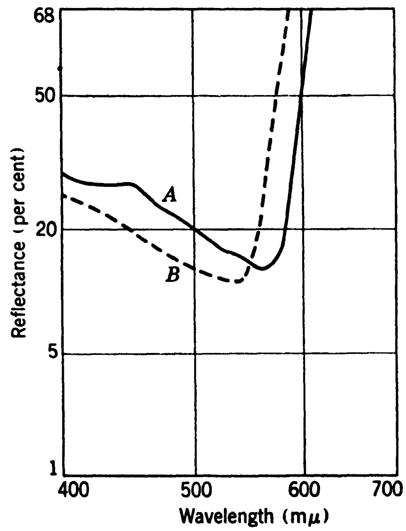

Fig. 82. Identification of Members of Class III(*a*) by Reflectance Curves of Zinc Oxide Reductions: *A*. Lithol Red. *B*. Lake Red C.

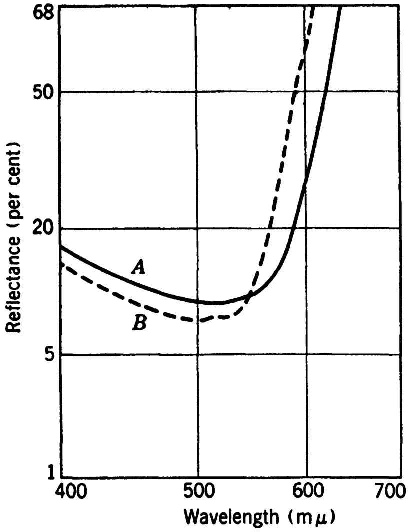

FIG. 83. Identification of Members of Class III(*b*) by Reflectance Curves of Zinc Oxide Reductions: *A*. Para Red. *B*. Permaton Orange.

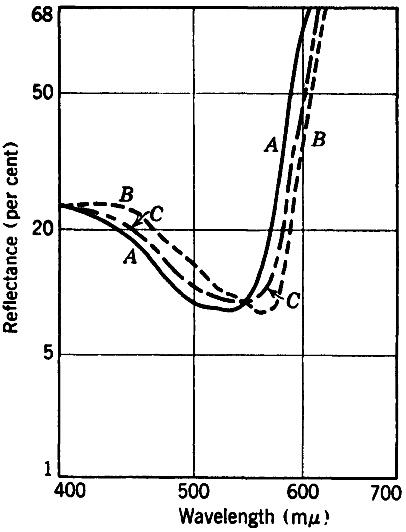

FIG. 84. Analysis of Mixture of Members of Class III(*a*) by Reflectance Curves of Zinc Oxide Reductions: *A*. Lake C. *B*. Lithol Red. *C*. 50–50 Mixture.

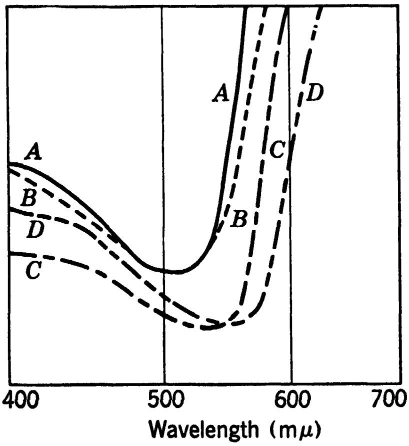

FIG. 85. Pyridine Curves (*A* and *B*) Indicate Identity as Lithols. Zinc Oxide Reductions Curves (*C* and *D*) Show Differentiation of the Two Metallic Salts. Sodium and Calcium Lithols: *A* and *C*. Sodium Lithol. *B* and *D*. Calcium Lithol.

The insoluble Lithol Rubine of Class IV has a characteristic zinc oxide reduction curve somewhat like the Bromo of Class I.

The ordinates of the spectrophotometric curves should, of course, be chosen so as to give curve shapes independent of concentration. This requires plots of $\log \frac{\log 1}{T}$ for transmission data and $\log \frac{(1 - R)^2}{R}$ for reflectance data (where T = transmission, R = body reflectance).

Mixtures of pigments of different chemical natures can often be analyzed. For instance, Fig. 84 shows a 50-50 mixture of Lake Red C and Lithol Red analyzed graphically for percentage composition according to methods applicable if the correct ordinate plot is chosen.

Slight physical differences which result in the light, medium and deep shades of the toners have little effect on the solution curve shape of the product. Similarly neither acid nor alkaline couplings nor toning colors, present in only small amounts, result in curve shape changes which seriously interfere with identification. Thus minor differences do not invalidate these identifications. For instance, the Sodium and Calcium Lithols are widely different in color and as would be expected have different reflectance curves as zinc oxide reductions but, dissolved in pyridine, the metallic salts are apparently broken up since the same curve shape results, indicating a fundamental chemical identity as a Lithol. (See Fig. 85.)

When an unknown sample is received, it is recommended that it be made up in a routine manner in all 4 media. Agreement with standard curves of a known compound in all media is very strong evidence of correct identification. In addition to broad classifications, smaller specific differences may be ascertained.

In general the advantages of this method are that it is quicker than a complete chemical analysis, it works well for mixtures provided the curves of the individual components are available, very small amounts of sample are needed, and some information can be obtained regardless of the form of the sample.

The following reflectance curves (Figs. 86 to 103), made particularly for this publication by Abbott and Stearns (1), are representative of individual pigments taken from 50 to 1 zinc oxide reductions in lithographic varnish. They include some of the more important present-day organic pigments.

Figure 103 shows the variations which appear when a certain pigment, in this case Permaton Orange, is measured for its transmission curves in different solvents, pyridine, acetone, and sulfuric acid. The differences shown illustrate rather clearly that the absorption of energy is not an independent function or characteristic of the molecule, but that variations in environment exert a very decided influence on the tone of resonance. Consequently it is hardly surprising that absorption appears to be markedly affected by differences in physical condition, such as variations in particle size and shape, and the environment, as illustrated bv crystal form and size, may be of even greater influence on absorption than environment as illustrated by a vehicle or solvent.

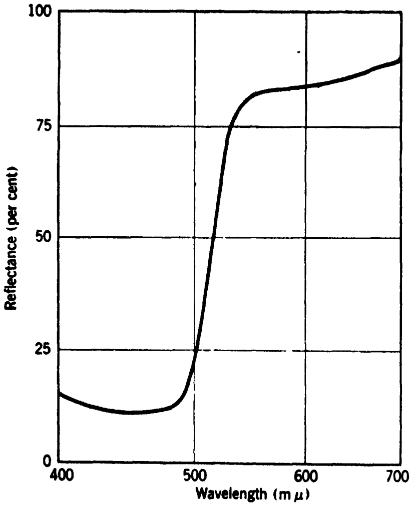

FIG. 86. Hansa Yellow G.

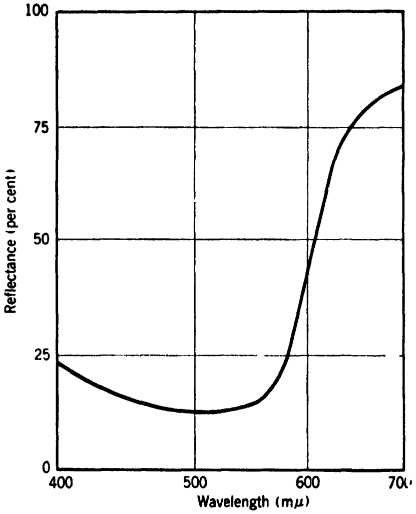

FIG. 87. Para Red Y.

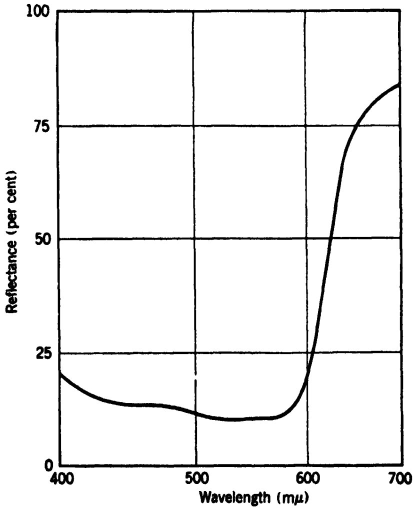

FIG. 88. Para Red B.

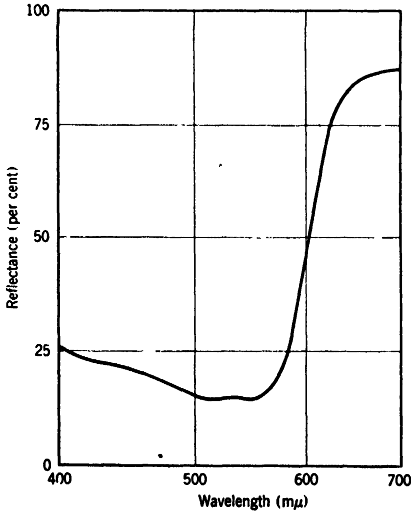

FIG. 89. Toluidine Red Light.

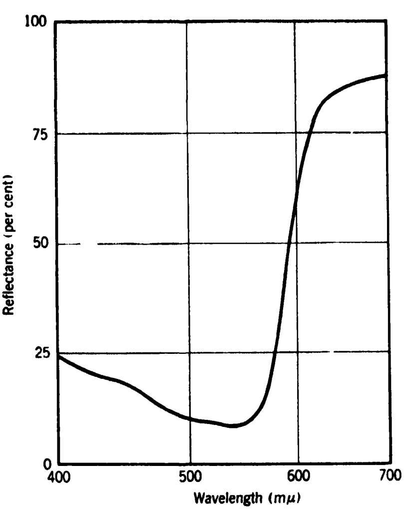

Fig. 90. Red Lake C. (Barium).

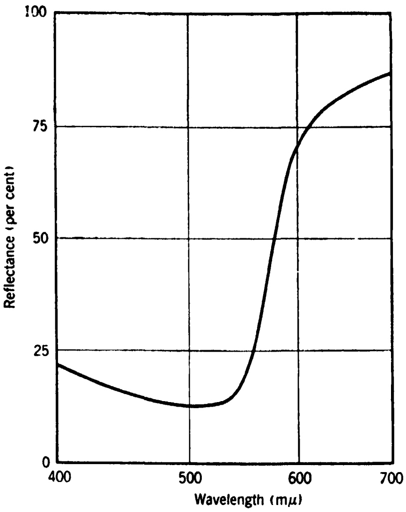

Fig. 91. Permaton Orange.

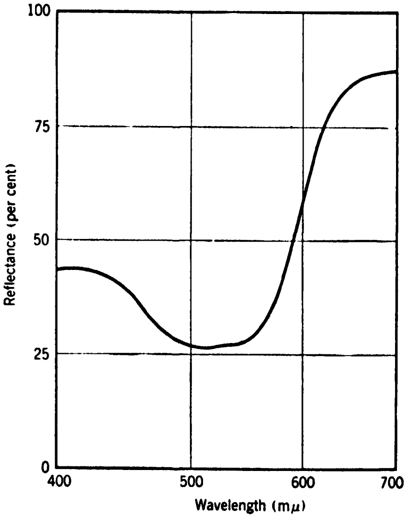

Fig. 92. Scarlet Lake.

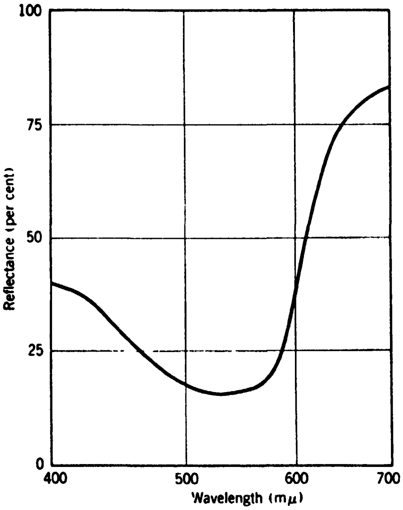

Fig. 93. Madder Lake.

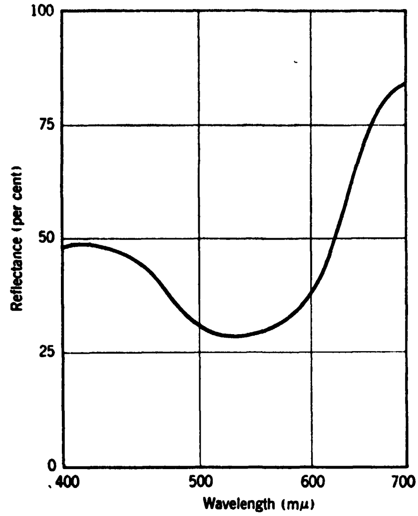

FIG. 94. Bordeaux Lake.

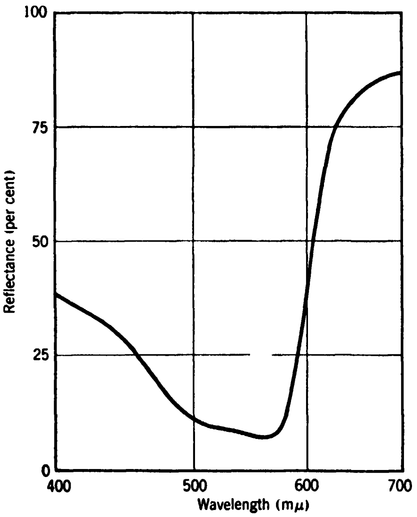

FIG. 95. Phloxin Toner.

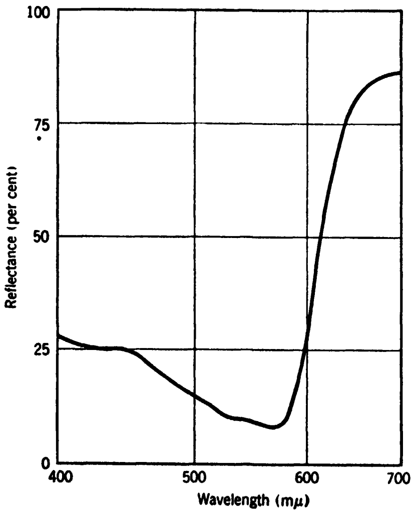

FIG. 96. Lithol Rubine.

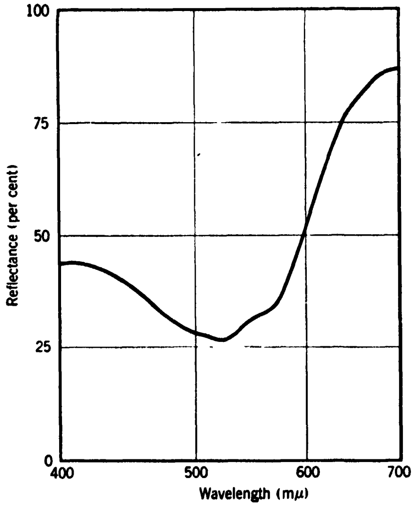

FIG. 97. Toluidine Maroon.

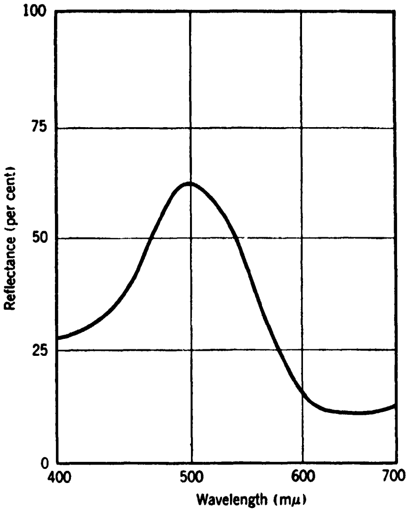

FIG. 98. Phthalocyanine Green.

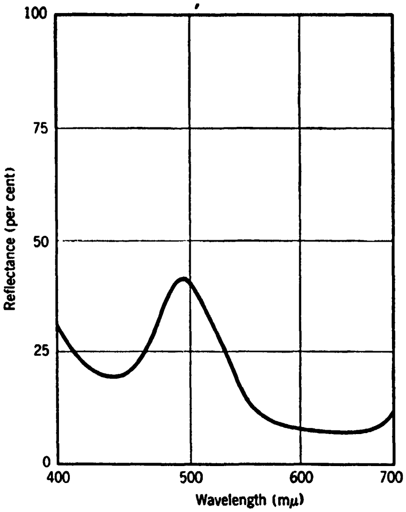

FIG. 99. Permanent Green. Malachite Green.

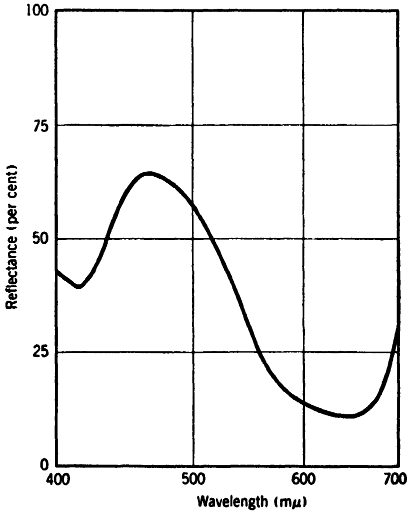

FIG. 100. Peacock Blue Lake.

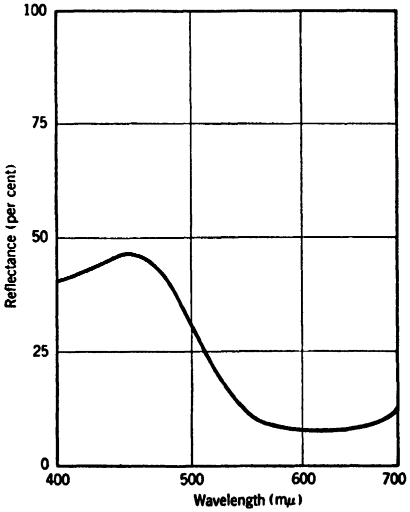

FIG. 101. Alkali Blue.

With these circumstances in mind it will be appreciated that a faithful record of the absorption curve of a given substance may not check rigidly the record of a different quality of the same material. For example, two samples of toluidine red which are identical in chemical composition but differ in particle size owing to differences in dispersion and crystal growth, and therefore differ in color values, may show distinct differences in their reflectance absorption curves. On the other hand, their transmission absorption curves, measured in pyridine, acetone, or sulfuric acid solutions, which eliminates the particle size and shape environment, should be essentially identical. For purposes of identification, therefore, it may be advisable to register absorption curves by reflectance as well as by transmission in more than one solvent, in order to gain the most complete information concerning the sample under test.

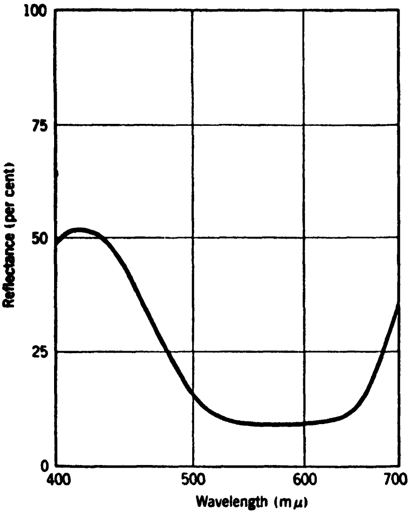

FIG. 102. Permanent Violet.

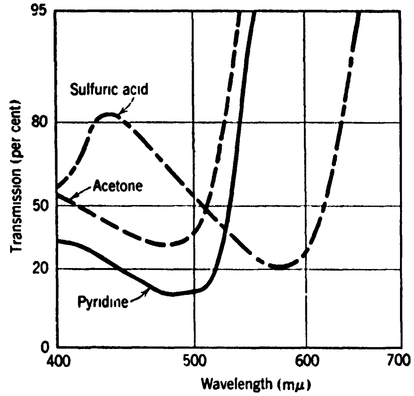

FIG. 103. Permaton Orange.

The information to be gained from absorption curves has found useful application in several directions: for example, (1) the analysis for strength and for purity of dye solutions, (2) determination of the strength and color values of pigments, (3) recording the tinctorial characteristics of standard pigments for future reference and duplication, and (4) identification of unknown pigments and constituents of mixtures of pigments.

Chapter XI

Pigment Types and Properties

The organic pigments might be casually regarded as possessing only the chemical and physical characteristics generally associated with organic materials, and this view would be quite correct in certain instances. The products referred to as of the pigment type, including the para reds, toluidine reds, permaton reds and oranges, hansa and benzidine yellows, and others containing no salt-forming groups, are typically organic in nature, as is evidenced by solubility in organic solvents and in many cases by well-defined melting points.

In other groups, however, the actual conditions are quite definitely at variance with this view. In certain types, such as the lithols, C-reds, pigment scarlets, and rubines, the pigment is a metal or alkali-metal salt of an organic acid, or sulfonic acid, which gives it partial inorganic or hydrophyllic characteristics. In other types, such as the basic color phosphotungstates and phosphomolybdates and many of the lake colors, the inorganic complex acid residue, or inorganic base, represents a large part of the entire substance, even as high as 80 to 90 per cent. These and other attendant characteristics, including color values, texture, solubility, fineness, stability, reactivity, and working properties, determine to a large degree the field in which a given product will find its greatest usefulness. For example, a material with an appreciable solubility in alcohol or other organic solvents would be of little value in the lacquer field; products of hard texture are of but slight value in rubber; those which are fugitive to light are not suitable for outside use in paints, lacquers, and enamels; those possessing poor working characteristics, including wetting, consistency, and flow, are undesirable for use in printing inks; and many lakes which are highly reactive are unsuited to uses in which they will be frequently exposed to acid or alkaline conditions and water.

It is therefore possible to establish the nature of each individual pigment by a series of rather generally accepted tests and assign it to some particular field of use to which it is adapted.

Table XVII, rearranged from a tabulation by Doty (40), is made up of a selected series of tests applied to representatives of practically all the common groups of organic pigments, which bear particularly

TABLE

PIGMENT TYPES

Pigments	Resistance to Light		Resistance to		
	Full Shade	Tint	Heat °F	Acid	Alkali
RED TONERS					
Para Red Light	good	poor	230	good	good
Para Red Dark	good	poor	230	good	good
Toluidine Red	excellent	good	320	good	good
Red Lake C-Barium	excellent	good	250	good	fair
Barium Lithol	fair	poor	165	good	good
Calcium Lithol	fair	poor	230	good	good
o-Chloro-*p*-nitroaniline Red	excellent	fair	165	good	good
p-Chloro-*o*-nitroaniline Red	excellent	fair	165	good	good
Lithol Rubine	excellent	good	320	good	good
Solfast Red Y	excellent	very good	230	good	good
Solfast Red B	excellent	very good	230	poor	poor
Solfast Pink 3Y	excellent	excellent	230	fair	fair
Solfast Pink 3B	excellent	excellent	230	fair	fair
Tungstated Rhodamine Y	excellent	very good	320	good	poor
Tungstated Rhodamine B	excellent	good	320	good	poor
RED LAKES					
Scarlet 2R Lake	fair	poor	230	poor	poor
Pigment Scarlet Lake	good	fair	230	poor	poor
MAROON TONERS					
Lithol Maroon	good	fair	230	good	good
Tobias Acid-β-oxynaphthoic Acid	good	fair	320	good	good
Toluidine Maroon	excellent	good	320	good	good
Helio Bordeaux BL	good	fair	230	good	good
MAROON LAKES					
Madder Lake	excellent	good	230	good	excellent
Alizarine Cyclamine Lake	excellent	fair	230	good	excellent
Helio Fast Rubine 4BL Lake	excellent	good	230	good	excellent
Amaranth Lake	fair	poor	230	poor	poor
Bordeaux Lake	fair	poor	230	fair	fair
YELLOW TONERS					
Hansa Yellow G (Lemon)	excellent	good	320	good	good
Hansa Yellow 10G (Primrose)	excellent	good	230	good	good
YELLOW LAKES					
Quinoline Yellow Lake	fair	poor	230	poor	poor
Naphthol Yellow Lake	fair	poor	230	poor	poor
Tartrazine Yellow Lake	fair	poor	230	good	poor
ORANGE TONERS					
o-Nitroaniline Orange	excellent	poor	230	good	good
2,4-Dinitroaniline Orange	very good	excellent	230	good	good
ORANGE LAKE					
Persian Orange Lake	fair	poor	230	poor	poor
GREEN TONERS					
Brilliant Green—Thioflavin } Phosphotungstic	very good	fair	320	good	fair
Brilliant Green	very good	fair	320	good	fair
Malachite Green	very good	fair	320	good	good
Pigment Green B	excellent	good	230	good	very good
BLUE TONERS					
Victoria Blue } Phosphotungstic	good	fair	230	good	good
Peacock Blue	good	fair	320	good	fair
Monastral Blue	excellent	excellent	320	excellent	excellent
BLUE LAKES					
Peacock Blue (Erioglaucine)	poor	poor	230	poor	poor
VIOLET TONERS					
Methyl Violet—Phosphotungstic	fair	poor	230	good	good
VIOLET LAKES					
Methyl Violet—Tannate	poor	poor	230	poor	poor
Helio Fast Violet AL	good	fair	230	poor	poor

XVII

AND PROPERTIES

Bleeding in				Specific Gravity	Bulking Value	Oil Absorption	Fineness Residue on 325-Mesh	Covering Sq ft per lb	Ease of Grinding
Water	Oil	Lacquer	Synthetic						
							%		
slight	yes	yes	yes	1.49	.08058	36.1–53.9	.15–.75	270–300	good
slight	yes	yes	yes	1.49	.08058	32.0–50.2	.08–.30	285–325	fair
no	no	yes	yes	1.40	.08576	34.6–37.2	.04–.12	205–260	excellent
no	no	no	no	1.70	.07120	39.0–44.0	. .	. . .	good
no	no	yes	slight	1.74	.06901	40.0	.30	145–225	good
no	no	no	slight	1.65	.07278	34.0	.24	100–145	good
no	no	no	yes	1.56	.07698	27.9	.10	225	excellent
no	no	no	yes	1.60	.07550	32.7	.10	157	excellent
no	no	no	slight	1.61	.07457	43.0	.68	144	fair
no	no	no	slight	1.92	.06254	33 5	.30	......	fair
no	no	no	slight	1.73	.06940	37.2	.12	162	fair
no	no	no	slight	1.93	.06219	41.9	.04	183	fair
no	no	no	slight	1 77	.06784	41.0	.05	190	fair
no	no	yes	slight	2.63	.04583	40.9	.10	195	good
no	no	yes	slight	2.52	.04764	44.0	.40	303	good
no	no	no	no	2.82	.04257	36.0	.60	37	good
no	no	no	no	2.54	.04726	60.0	.30	55	good
no	no	no	slight	1.20	.1000	37 0	.07	140–145	fair
no	no	no	slight	1.62–1.81	.07413–.06631	42.0–32.0	.65–.31	109–158	fair
no	no	slight	slight	1.58	.07599	37.8	2.48	172	fair
no	no	no	slight	1.58	.07599	41.1	.42	395	good
no	no	no	no	1.76	.06821	33.6	7.4	...	good
no	no	no	no	1.67	.07189	37.2	.10	115	good
no	no	no	no	1.91	.06285	54.0	.50	117	good
no	no	no	no	2 95	.04070	31.7	6.9	52	good
no	no	no	no	2.88	.04168	32.5	.40	69	good
no	no	slight	yes	1.46	.08224	33.5	.10	89	good
no	no	slight	yes	1.58	.07599	45.0	.11	83	good
slight	no	no	no	1.63	.07364	50.0	.12	. .	good
slight	no	no	no	1.94	.06188	40.0	.10	.. ....	good
slight	no	no	no	2.60	.04617	53.9	.10	. . . .	good
slight	yes	yes	yes	1.46	.08224	39.1	.08	145	excellent
no	no	no	no	1.45	.08278	32.0	.11	165	excellent
slight	no	no	no	1.80	.06671	45.0	.10	. . .	good
no	no	yes	slight	2.63	.04564	40.9	.10	509	good
no	no	yes	slight	2.41	.04980	58.6	.10	568	good
no	no	no	slight	2.63	.04564	38.2	.08	910	good
no	no	no	slight	1.47	.08163	37.2	.02	1794	good
no	no	slight	slight	1.99	.06031	41.0	.03	301	fair
no	no	slight	no	2.66	.04513	44.0	.10	636	good
no	no	no	no	1.64	.07321	25.0	.10	465	fair
slight	no	slight	slight	2.02	.05942	57.2	.10	71.5	good
no	no	slight	slight	2.24	.05359	37.0	.04	646	fair
no	no	no	no	1.37	.08764	94.6	.10	1000	fair
no	no	yes	no	1.97	.06094	68.5	.10	479	fair

on the use of the respective products in the paint field. These tests, however, are of very general significance and application and indicate also the value of the various materials in the printing ink field.

Even in the fields of paint and printing inks many unusual tests are required in connection with the use of special formulations, and this variation in methods of testing is expanded to a great extent in other color-consuming industries such as rubber, linoleum, wax, plastics, textile, and metal printing and camouflage, in which the vehicles and methods of incorporation and application are widely different from those used in paints and printing inks. It is quite impossible to discuss this phase of the subject broadly in this book, but the data in the attached table illustrate very clearly the variations which occur in commercial pigments.

With these factors in mind it can readily be appreciated that the physical condition of a pigment, with regard particularly to the size, shape, uniformity, and aggregation of the ultimate particles, may exert a very strong influence on its tinctorial properties and its value in different industries. It is quite generally recognized, for example, that in many organic pigments an increased degree of dispersion, whether gained by mechanical means, by dilution, by variations in speed of reaction, or by using dispersing agents, yields pigments which on incorporation in oil vehicles show deeper masstones, greater strength, improved brilliance, higher body or consistency, and generally a harder texture.

On the other hand, the reverse of this condition, a lower degree of dispersion, gained by mechanical means, by concentration, by variations in speed of reaction, by avoiding the presence of dispersing agents, and more particularly by employing conditions such as heat to favor crystal growth or what is frequently called "development" of the product, yields pigments which, on incorporation into oil vehicles, show lower strength, lighter masstones, decreased brilliance, lower body or consistency, and generally a softer texture. These relatively small variations in tinctorial properties are sought, usually, in the development of products showing improved values for special purposes, and their recognition and control are of fundamental importance in this field.

It is frequently possible to upset these rather systematically arranged results by the use of special procedures and by the introduction of materials into the reactions which have a strong tendency to change the degree of dispersion or to alter the nature of the product by combining with it either chemically or physically.

Chapter XII

Conclusion

In selecting and preparing material for incorporation in this book it has been impossible to attempt a complete review or survey of all existing literature and patents related to the field of organic pigments. Special attention, however, has been given to deriving the essential material from a wide range of sources in order that reference to the original literature may serve to present to the reader a truly representative cross section of experience and opinion which has influenced developments in this most interesting branch of industrial science.

An effort has been made to bring out clearly the fact that in this field the physical factors assume a position of fully equal importance with the chemical. An attempt is made also to establish a definite recognized relation between tinctorial characteristics and physical structure, which is regarded as supplementary to the basic conception of a relation between color and chemical or molecular structure. With a more comprehensive review of the chemical, physical, and practical background readily available, it is anticipated that new workers in the field will be able to approach more effectively the intricate requirements of the future and contribute further to the fundamental principles on which the formation and control of pigment characteristics depend.

This book is not regarded as the last word in organic pigment chemistry, but rather as a guide to future work, as, perhaps, a consolidation of the gains already made to serve as an inspiration to a broader attack on the real fundamentals, and to more careful survey of the known facts to reach conclusions which may build the foundation of a firmly established science.

The future in this field is wide open to the reception of new pigments, new methods of use, new qualities, and other interesting and valuable developments. No close approach has yet been made to the creation of a perfect pigment, even from the point of view of any single branch of the industry, but many improvements have been made in the past, and the technique of introducing modifications has been placed on a progressively more rational basis. In the future, the recognition of principles which have been established in the past should accelerate tremendously the rate of acquisition of new knowledge, its assimilation, and its application to the problems of industry.

Since the future of the organic pigment industries is dependent on the use of color, it is most interesting to note the indications of new methods of application and new purposes to be accomplished. Within the last few years several methods have been employed to achieve more rapid printing of papers, magazines, posters, and books, which involves, primarily, more rapid drying of the inks after impression. By using vehicles which volatilize very rapidly under the influence of heat, or are set to a non-tacky condition by cooling or by vapor or water contact, it is now possible to print, not only in black, but also in full color, at a very much higher rate than formerly. Progress in this direction is in its early stages. Similar methods are also being applied to the direct printing of textile fabrics, with pigments in suitable vehicles. This phase of color use should reach extensive proportions in the years to come.

Increased use of pigment colors in the shading and dyeing of paper, in the coloring of both natural and the various new synthetic rubbers, and particularly in the great variety of new synthetic resins which are certain to find a tremendous variety of new and valuable uses is sure to reflect a steadily increasing importance in the development of new and improved products.

In addition to these specific items, which promise an ever-increasing importance to the organic pigment industry, a movement has recently assumed impressive proportions which may result in an eventual marked increase in pigment use. For a number of years, scattered efforts have been made to improve the lighting in manufacturing plants, schools, and homes as a result of recognition of the fact that failure to see clearly results in inefficient work, physical discomfort, and, in many cases, danger of injury. These efforts have finally crystallized into what has already become almost a science of color use and is referred to as "Color Dynamics" (107). As the name implies, this is a positive or dynamic use of color to accomplish very definite ends. The earliest studies were in connection with the use of colors in hospitals to create a healthy atmosphere and psychological effects favorable to relaxation and recovery, both physical and mental. The results were exceedingly favorable.

In industry, particularly in the great modern war plants, in which efficiency was of the highest importance, color has been employed to relieve eye strain by bringing out a clear contrast between the machine and the material upon which work is being carried out. The machine has been given an overall color particularly restful to the eyes, and the surrounding walls, ceilings, and floors are painted in colors that improve the general distribution of light, relieve eye strain, create cheerful working conditions, and therefore achieve readily measurable improvement in efficiency and production.

The success already met with in the application of these principles assures their broad extension in industries, hospitals, schools, and homes. They constitute one of the brightest prospects for increased use of pigment colors. It appears, therefore, that the future of the organic pigment industry is sufficiently bright to justify employment of the devotion and skill of capable scientists in the solution of its basic as well as its current problems.

The author prefers to regard this book not as the end but as the beginning of a fruitful chapter in the history of the organic pigments.

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