Modern Technology of Textile Dyes & Pigments (2nd Revised Edition)
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Dyestuff sector is one of the core chemical industries in India. There are two types of colorants dyes and pigments. Dyes are soluble substances used to pass color to the substrate and find applications primarily in textiles and leather. Pigments are coloring materials, which are water insoluble. Key end-user industries of pigments include wood-coloring, stone, textiles, paints & coatings, food and metals. Pigment are usually manufactured as dry colorants and grounded into fine powder. The dyes market, meanwhile, largely depends upon the fortunes of its principal end-user, textiles, which account for about 70 percent of the total demand. Their importance has grown in almost every area of an economic activity.

In the colorants market, Asia-Pacific accounts for the largest share. This region is one of the key markets for dyes and pigments production. In the Asia-Pacific, India and China are the important countries contributing towards the growth of colorants market. Rising consumer spending will drive increased demand for colorants in textiles. Increases in value demand will reflect the growing importance of expensive, higher value dyes and pigments that meet increasingly stringent performance standards. Growing demand for high-quality value-added pigments is one of the key factors expected to result in a spurt in growth.

This book describes the various formulae, manufacturing processes and photographs of plant & machinery with supplier’s contact details. The major contents of the book are metal pigments, black pigments, inorganic colour pigments, organic colour pigments, extender pigments, white pigments, photocatalytic activity of titanium dioxide pigment, azo pigments, bisazo pyridine pigments, high grade organic pigments, high temperature stable inorganic pigments, anti corrosive pigments, metals and metal ions in pigmentary systems, control of organic pigment dispersion properties, pigments for plastics, rubber & cosmetics, pigments for printing inks, vat dyes, reactive dyes, disperse dyes, direct dyes and sulphur dyes etc.

It will be a standard reference book for professionals, entrepreneurs, those studying and researching in this important area and others interested in the field of textile dyes & pigments.

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CI Vat Brown 1 CAS 2475-33-4
CI Vat Yellow 2 CAS No. 129-09-9
CI Vat Yellow 4 CAS No. 128-66-5
CI Vat Orange 1 CAS No. 1324-11-4
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Sample Chapter:
Metal Pigments

Certainly there is no resemblance or connection between metal pigments and metallic stearates. It was merely a matter of convenience to group these two short subjects together in one chapter.

The principal metal pigments are those made from aluminium, zinc and mixtures of copper and zinc which range from 100% copper to about 70% copper and 30% zinc. Pigments from the copper-zinc alloys are known as “bronze powders.” Metal lead pigments are available and metal silver pigments have specialized uses such as conductive coatings for printed circuits. Similarly, nickel and stainless steel pigments find use where a combination of metallic appearance and alkali resistance is required.

The metal industry produces fine particle size metals in both powder and flake forms which are used in a variety of industries. The paint industry uses chiefly the flake form of aluminium and bronze and zinc in the powder form. Since metal, even as very thin foil, is completely opaque to visible and ultraviolet light, it could be anticipated that metal pigments would have exceptionally good hiding power. However, they have relatively low tinting strength and for some finishes they are coloured with various amounts of colour pigments.

Finely divided metals react with moisture, and hydrogen gas is one of the products. If this reaction occurs in tightly closed containers it may develop sufficient pressure to bulge or rupture the container. Therefore, every effort must be made to store metal pigments under dry conditions and to use paint vehicles which are as nearly anhydrous as possible. In many cases two containers are used to ship metallic paints. One container has the metal pigment and the other contains the remainder of the paint. Shortly before application the metal pigment is mixed into contents of the second container.

Metal pigments fulfill several important functions in coatings. Bronze powders are widely used for decorative coatings. Aluminium pigments also are used for decorative purposes; in addition, they impart heat reflective properties, reduced permeability to moisture, and good durability to coatings. Zinc dust contributes corrosion- inhibitive properties in primers for iron and steel and excellent adhesion in primers for galvanized iron. The many applications for metal pigments and metallic stearates are discussed in later chapters. This chapter outlines the types, method of manufacture, and general properties of the principal metal pigments and metallic stearates available at present.

The lubricant is added to prevent the aluminium particles from being mechanically welded together under impact and also to develop a bright metallic lustre on the flakes. Usually, the lubricant is stearic acid but other fats and oils may be used, such as tallow and olive and rapeseed oils. It is believed that chemical reaction occurs between stearic acid and aluminium during the milling operation to form a
strongly adhering coating of aluminium stearate on the finished flake. This coating makes possible the leafing action of the flakes in a paint film with the resulting brilliant metallic finish. The coating is quite stable under conditions of normal use, but it may be loosened or removed at temperatures above 180°F, also by certain solvents, and by chemical reaction with materials such as lead driers and free acids in vehicles. Further discussion of conditions for proper leafing is given later under physical and chemical properties.

The liquid medium for wet milling usually is mineral spirits, but liquids such as solvent naphtha or certain plasticisers are used for specific applications. The mill is run until test shows the required degree of fineness has been attained; then the paste is washed from the mill with mineral spirits. The batch is filtered and adjusted to the specified solid content either by drying or by addition of liquid medium. The solid content of commercial aluminium pastes usually is 65%, but special grades may be as high as 73.5%. Flake aluminium powders are produces by complete drying of the paste through evaporation of the mineral spirits under vacuum. The foregoing process produces the leafing type of aluminium pigments. These may be treated to convert them into the non-leafing type, or a special lubricant may be used which produces the non-leafing type directly.

An indirect indication of the particle size is obtained from the water-covering test. A weighed amount of powder is dusted on to the surface of a rectangular pan of water as uniformly as possible between two movable baffles. The layer of powder then is manipulated by means of the baffles to produce as extensive an area as possible and still maintain a continuous layer. The area of this layer is measured, and the results are expressed as square centimeters covered per gram of powder. The coverage ranges from about 8000-10,000 sq cm/gm for the coarse grades, 14,000-18,000 sq cm/gm for the lining grades, and 25,000-30,000 sq cm/gm for the extra fine lining grades.

Leafing grades may be distinguished from the non-leafing grades by mixing a small amount of paste or powder with mineral spirits of xylene. The leafing grades produce the familiar metallic surface on the liquid, whereas the non-leafing graders yield a gray suspension. This test does not give satisfactory results with liquids having surface tension values of less than 25. For example, VM&P naphtha does not permit satisfactory leafing because of its low surface tension values. The extent of leafing of aluminium pigments is measured by the spatula immersion test. A polished spatula of standard dimensions is dipped in a specific mixture of pigment and coumarone resin solution, withdrawn rapidly, and allowed to drain in a cylinder for three minutes. The coating then is examined for extent of leafing over the total depth of immersion. The ratio of the depth of the fully leafed portion to the total depth is calculated and expressed as percent leafing. This test may be used to determine possible loss of leafing of an aluminium paint on aging.
Handling and Storage. Aluminium pastes and powders should be stored in closed containers at normal temperatures. Open containers permit loss of volatile liquid from pastes with consequent drying and uncertainty of composition. Free access of pigments to air and moisture should be avoided. Long exposure to air produces oxidation of the metal with a consequent loss of adhesion of the stearate layer and reduction of leafing property. Moisture reacts chemically with finely divided aluminium with a resulting production of hydrogen gas and loss of leafing property. The use of paste eliminate the dust hazard connected with the powder type. In addition, paste has a higher apparent density, therefore it occupies less space and mixes with paint vehicles more easily than powder.

Black Pigments
Charred bones and soot from smoky fires were used as black colouring materials by pre-historic man. Modern man also uses bone black and soot as black pigments for paints and printing inks, but he has wide range of types and grades of black pigments for specific applications. In addition to the blacks composed chiefly of carbon, he used certain inorganic blacks in which good filling properties are more important than depth of colour. The general types of black pigments are listed in Table 1 together with their raw materials and approximate range of composition.

Bone black is obtained by pulverizing carbonized bones. It has good blackness and also low oil absorption and good filling properties. Vegetable black is obtained by carbonizing wood and other plant products. At present it finds-only limited use in coatings, and it is being replaced by blacks having more uniform composition varies with source and type of raw material, and they may be replaced with greater uniformity with mixtures of extender pigments and carbon black.

Mineral black is used in coatings such as freight car paints and metal primers and surfacers. The natural and synthetic black oxides of iron are described. They are used where good filling properties are more important than blackness of colour. Antimony sulfide is used almost exclusively in camouflage paints, since it reflects the same as green foliage when photographed with infrared film. Black toners are organic compounds used in conjunction with carbon black to increase the blackness of specialty finishes. An apparent increase in blackness of finishes made with certain standard carbon blacks may be obtained by addition of up to 25% of in iron blue. The type of iron blue generally used is the toning blue.

In addition to the black pigments listed in Table 1 the paint industry uses a variety of bituminous materials such as pitches, asphalts, and gilsonite in black and dark coloured coatings.

Furnace Black. The furnace process not only give higher yields of
carbon, but also the plant occupies much less space and is free from
the smoke nuisance associated with burner houses. Also, the furnace
process may be adjusted to use either gas or oil as the raw material.
Continued improvements since the furnace process was inaugurated
have produced smaller size particles with better blackness, but it
remains to be seen whether this trend can be continued to produce
colour equal to the better grades of channel black.
In the furnace process the same operations of partial combustion
to produce the necessary temperature and thermal decomposition of
the remainder take place, but a single large flame replaces the large
number of small flames of the channel process. Gas and air are admitted
separately to a firebrick-lined furnace which operates at a temperature
of about 2400°F. Through controlled air supply and the particular
design of the inlet ports, a large portion of the gas is decomposed
instead of being burned completely. The hot gases from the furnace,
carrying the black in suspension, are cooled by water sprays. Then the
products pass through an electrostatic field which agglomerates the
carbon particles so that they may be collected in cyclone collectors,
and the exhaust gases are vented to the atmosphere. From the collectors
the black may be bagged or routed through pelletizing equipment. The
variables in the furnace process are:

**Thermal Black.** Thermal black represents only a small percentage
of carbon black production. Two general types are produced; one is
based on natural gas as the raw material and the other on acetylene.
The black from natural gas has the largest particle size and greyest
colour of the carbon blacks, and the black from acetylene is intermediate
in size and colour between furnace and channel black. Thermal black
is produced by thermal decomposition without simultaneous
combustion.

In the natural gas process the thermal decomposition takes place
in an insulated chamber containing a network of firebrick. First, the
chamber is heated to 1800-2500°F direct combustion of an air-gas
mixture. Then the combustion is stopped, and a charge of “make-gas”
is passed through the heated chamber. The resulting carbon and spent
gases are cooled by water sprays, and the carbon collected in bag
filters. This process gives a high yield of carbon, but the particle size is
large and the colour is quite grey. Somewhat smaller particle size may
be obtained by diluting the make-gas with spent flue gases.
The carbon content of bone black is about 20% that of carbon
black. Since the hiding power and tinting strength depend on the carbon
content, it will be apparent that bone black is much weaker than carbon
black in these respects. However, bone black is much lower in oil
absorption, therefore a greater percentage can be incorporated in a
formulation without developing excessive consistency. This feature is
desirable in the production of low-sheen black finishes or when good
filling properties are required, such as in leather finishing. Its particle
size, relatively large, is expressed as percent retained on a 325-mesh screen. When used with other colours it shows less tendency to float than carbon black because of the larger particle size. Bone black is fairly easy to disperse in coating vehicles and is wetted by water much easier than regular carbon black. For this reason it finds use in tinting calcimine, casein and latex paints, and water base inks. Generally, bone black is considered too abrasive for lithographic inks, but is used in artists colours and many standard coatings.

**Vegetable Black.** Vine black was produced originally from stems and twigs of grape and hop vines and from organic wastes of the wine industry. It is the most important member of the family of “vegetable” blacks which are produced from many kinds of cellulosic materials obtained from plants and trees. Vegetable blacks are made by dry distillation and carbonization of the vegetable material in the absence of air. They range from 30-70% in carbon content, the remainder being a mixture of calcium and potassium carbonates. As may be expected, vegetable blacks show an alkaline reaction. They are somewhat low in colour value and in oil absorption. At present they find very limited application in coatings and have been replaced to a great extent by mixtures of furnace black and black iron oxides.

Mineral blacks are coarse pigments with low oil absorption and good filling properties. They may be used in coatings such as freight car paints and sanding surfacers. In view of the availability at low cost of carefully classified extended pigments described, and of the newer furnace blacks, it would appear that combinations of these materials could be made by paint manufacturers to meet the requirements of mineral blacks with possible improvement in performance.

**Antimony Trisulfide.** Antimony sulfide occurs in nature as the grayblack mineral known as stibnite. It may be pulverized to the required particle size and used as a pigment in camouflage paints. When such paints are photographed with infrared film, the antimony sulfide gives the same reflection characteristics as green foliage. Antimony sulfide may be made by reaction between antimony and sulfur or by precipitation from solution of antimony trichloride with hydrogen sulfide. The natural products range from 64-66% Sb2S3, and the technical grade of precipitated material contains about 94% Sb2S3. Owing to its low colour value, its use in paints is limited almost entirely to the camouflags type.

**Extender Pigments**

**Introduction**

Extender pigments are much lower in price than prime pigments and are used in paints primarily to reduce cost. However, by careful selection of the particular type of extender for specific paints, it is often possible to improve certain properties of the paint or the dry coating. Proper choice of extender may improve properties such as consistency,
leveling, and pigment settling in the paint. Certain extenders reinforce the structure of the dry coating mechanically, while others increase its resistance to the transmission of moisture.

Flat finish and semi-gloss paints are produced by using pigment concentrations high enough to prevent the formation of a layer of clear oil or resin in the surface of the coating which would give it gloss. When pigment particles are in the surface they diffuse the light and prevent specular or glossy reflection. In paints with high pigment concentration sufficient hiding may be obtained by replacing some of the opaque pigment with extender pigment. Since extenders are lower in price than opaque pigments, a reduction in material cost will result. The refractive indexes of extender pigments range from 1.55 to 1.65, and since these values are only slightly different from those for oils and resins, extenders generally do not contribute to the hiding power of paints. In special cases, such as their use in wood fillers and flat varnishes, lack of opacity is desirable to prevent a “muddy” effect in clear furniture finishes. Certain chemically prepared extenders such as Micro-Cel pigments have refractive indexes in the range of those for oils and resins, but in combination with while opaque pigments they contribute slightly to hiding power. The reson for this phenomenon is not clearly understood at characteristics, and the effect of these factors on the scattering of light in the coating. Detailed knowledge of the various types and grades of extenders will enable the paint formulator to produce paints having maximum properties at minimum costs.

**Type of Extenders**

Extender pigment are obtained from two general sources: (1) by pulverization of certain rocks and sedimentary deposits; (2) by chemical precipitation. The two types are referred to as natural and precipitated extenders respectively. The natural deposits such as limestone, quartz, and clay are found in various parts of the country, and the pigments usually are processed at the deposits. The markets are supplied from local deposits whenever possible, because the low price of extender pigments will not permit high freight charges. There may be considerable variation in composition and properties of natural deposits with corresponding differences in extender pigments obtained from them. Therefore paint manufacturers having plants in eastern, central, and western states may have to adjust their formulations containing extenders to accommodate variations in extenders supplied to the different plants.

Extender pigments also may be used to advantage to increase the consistency of paints. Some extenders that have much higher oil absorption values than white pigments may be employed to increase the consistency of white paints without raising the cost. The oil absorption of a particular pigment is directly proportional to its available surface; therefore the grade having finer particle size usually has higher oil absorption. Since oil absorption also is affected by the
nature of the pigment surface, the oil absorption values vary among
the different type of extender pigments because their different surface characteristics as discussed before.
Extender pigments are marketed as white powders, but because of their low refractive indexes they do not contribute whiteness or high reflectance to oleoresinous paints. However, some grades of natural extenders contain traces of metallic oxides, such as iron oxide, which cause slight discolouration or reduction in reflectance of white paints. Such grades should not be used for flat or semi-gloss white finishes but would be entirely satisfactory for coloured finishes or in metal primers and surfacers.
Extender pigments may vary considerably in characteristics such as reactivity with components of paint vehicles, sensitivity to and solubility in water, and in the pH of water slurries. Their reactivity is due in part to variations in origin and methods of processing, but some of the reactivity is inherent in the particular extenders. For example, barytes is very inert chemically and not sensitive to moisture adsorption, whereas calcium carbonate is more readily affected by acidic conditions. Calcium sulfate may adsorb sufficient moisture in humid weather to change the consistency characteristics of a paint. The pH and specific resistance of water slurries of extenders are important if these pigments are to be used in water-dispersed paints; they should be checked carefully. Some extenders have sufficient solubility in water to liberate enough cations to affect the stability of latex or other types of emulsion paints.

**Calcium Carbonate Extenders.** Calcium carbonate extender pigments are very widely used and are frequently referred to as whiting. They are available as both natural and precipitated types and in a wide range of particle size. The very coarse grades are preferred for putty and glazing compounds, the intermediate sizes for oleoresinous flat and semi-gloss finishes and caulking compounds, and ultrafine precipitated grades are available for gloss finished and printing inks. Natural whiting is obtained from two main sources: limestone and chalk. Limestone is widely distributed throughout the world and is found in most of the states of the United States. Limestone and the related rocks, marble and calcite, are crystalline and were formed in the earth’s crust by reactions between calcium salts and water containing carbon dioxide. When magnesium salts were present, a mixture of magnesium and calcium carbonates were precipitated which is known as dolomite limestone. Chalk is an oolitic variety of calcium carbonate and was formed by deposition of shells and marine animals. Natural whittings are made by quarrying the rock, crushing and grinding it, and then classifying the powdered material for particle size requirement. The grinding process may be either dry or wet. In dry grinding the screened crushed rock is powdered with a hammer or roller mill and classified for particle size by the air-flotation process. A
stream of compressed air passes through the mill and carries out the particles which are small enough to “float” on it; the larger particles drop back into the mill. The rate of air flow is a factor in the particle size obtained in the product.

High Temperature Stable Inorganic Pigments
The pottery industry has, for several thousand years, been using high temperature stable inorganic pigments, which do not fade or discolor even at the high temperatures (between 400o and 1400oC) required for the maturing of enamels and glazes. Moreover, there are many examples of beautiful color and decoration work from as early as the Shang dynasty in China (1500 B.C.), which have come down to our period without much change in the shade or brightness of the colors. While it is true, that the glaze substrate in which these pigments are embodied, provides substantial protection from contact with air, water, chemicals and other destructive elements, it is nevertheless also true that the light-fastness of these pigments must be something fantastic for them to have remained unchanged for periods of 3000 years and more.

While the tinting power of many inorganic colors tends to the rather less than that of organic pigments, inorganic pigments tend to have greater opacity, hiding power, bleed resistance, and of course light-fastness. They are more resistant to heat, and, being mostly ionic bonded, are usually less reactive with the organic vehicles, which are usually covalent bonded.

High temperature stable inorganic pigments can also be used for normal temperature applications such as the pigmentation of rubbers, plastics, paints, cements, etc. Almost any color and shade, including those shown in IS:5-1978 and many more not shown in the I.S. charts, are obtainable with high temperature stable pigments.

High temperature stable pigments are mostly oxides, sulphides or silicates of various metals.

Shades of red, yellow, pink and violet are also obtainable from compounds of tin, copper and gold. Such compounds are, naturally, quite expensive, but produce very attractive, long lasting shades. Blues and violets are produced from compounds of vanadium, titanium, uranium, copper and cobalt. Cobalt colors are, of course, fairly expensive, but have excellent light-fastness and binding power. They come mostly in the spinel crystalline form, which are stable up to 1600oC., and inert to acids and alkalis.

Because of chemical stability, light-fastness, resistance to dilute acids and alkalis, dispersability and compatibility with other organic and inorganic pigments, high temperature stable pigments make excellent colors for.

Preparation of Iron Oxide Pigment from Industrial Waste
Paint is used for decoration, protection of metals and functional applications. The constituents of a paint are vehicle, pigment, solvent
and additives. Pigments are mainly used for giving body to the paint, protection and for specialised functions. These are finely divided solids of different shades used in the paint to give colour, hiding, consistency, durability, build, etc. These particles are substantially insoluble in water. Pigments may be classified as natural and synthetic, depending on their origin.

Iron oxides are extensively used as inert pigments in the paint industry. A dye intermediate manufacturing industry in the country was faced with the problem of accumulation of huge volumes of sludge in their factory during the iron and acid reduction process. Efforts have been made elsewhere to convert the sludge into useful pigment. These results of the preliminary studies made in this direction are reported in this paper.

**Preparation of the pigment**
The sample supplied by the firm contained total iron as Fe₂O₃-90.5% and ferrous iron as FeO 3%. The colour of the product was black. The sludge was washed first with water to remove the soluble impurities such as chlorides, etc. This washed product was subsequently subjected to the treatments as shown in Table 1 and visual observations were made.

A water wash was given to remove the chloride present in the sludge. It may be seen from the above table that the sludge heated to 500°C at the end of one hour only showed some slight change in the colour. The temperature was gradually increased from 150°C and the colour change was observed at 500°C only. The time of heating also determined by increasing the duration from 30 minutes onwards and changes could be seen only at the end of 60 minutes. Further heating did not show any change. No change could be observed when the sludge was treated with different treatments as indicated in Sl. Nos. 2 to 6. When the chloride-free sludge was treated with 10% iron oxide or pigment grade synthetic iron oxide, the colour of the sludge changed to that of the pigment grade red oxide at 500°C itself. But the product was heated to 700°C and maintained there for three hours for the transformation to be completed. Thus the waste product was converted into a pigment grade iron oxide.

The water extract of the waste as well as the treated products were analysed for pH and chloride. It was found that the pH was neutral i.e. 6.5-7.0 in all the cases except the sludge which was slightly acidic (<6). The chloride content in the water extract was determined. It was found that the sludge contained 30 mg of chloride/100 ml of the extract, whereas it was negligible for others.

The oil uptake value for the pigment grade iron oxide with the commercial grade LSO was 20 and the oil uptake value of the converted product by both the methods viz. Sl. Nos. 7 and 8 of Table 1 was 18-22. It shows that the oil uptake of the converted pigment from waste is on par with the pigment grade iron oxide. This again shows that the
fineness of the pigment got from the waste is more or less similar to that of the pigment grade iron oxide.

**An Overview of Aluminium Pigment Technologies**

Through the use of aluminum pigments in coatings and inks, a wide and varied set of aesthetics is achievable. With the ever-changing aluminum pigment technologies, the opportunities for applications in these areas in the nineties are indeed exciting.

An overview is provided, covering a general introduction to aluminium pigments, along with those physical properties which make them particularly appealing in the automotive; general industrial; and ink markets. Along with the physical properties of aluminium pigments, formulation parameters including - pigment grades; resins; solvents; and additives, typically used by the coatings formulator, are detailed. Water-based and high solids systems suggesting starting points for the nineties are exhibited. Application procedures along with key clay; handling; and storage procedures are also presented.

At the close of the last decade, the Automotive Industry, worldwide, produced over forty-four million automobiles and trucks, totaling approximately five hundred and sixty billion dollars in sales. An analysis from a geographical standpoint shows that the United States produced 37.7% of these units, followed closely by Japan, with 29.6%. The European community was led by West Germany with 9.5%, followed closely by France, with 8.8%; then Italy, with 5.4%; Sweden, with 1.3%; Britain, with 1.1%; and finally, the Soviet Union, with 3%.

The Far East has Korea as a rapidly growing producer of automobiles with 3% market share.

One of the fastest growing markets is in Asia. It is estimated that automobile sales in Asia, excluding Japan, Australia and New Zealand, grew from 3.2% of global unit sales in 1980 to 4.7% in 1987 and had increased to 8.7% in 1995. While the number of units on a global basis are not large in this area, the growth potential is enormous.

Aluminium pigments, used in metallic automotive top coats in North America, accounted for nearly 50% of the cars produced. In Europe, the figure is slightly higher, while in Japan the figure is lower, but rapidly catching up.

The use of aluminium pigments in automotive coatings is a relatively recent invention. Up until the 1930's all automotive top coat finishes were solid colours, with black being the most popular. The introduction of aluminium pigments in automotive finishes, by Chrysler in 1934, signaled their rise to today's level of popularity. By the close of the 1940's, approximately 20% of American automobiles utilized metallic finishes. By the close of the 1950's, brighter metallic finishes were seen in the market place, utilizing coarser controlled grades. Prior to the 60's, the grade typically used were the non-leafing, non-acid resistant types. With the advent of the '60's, newer, innovative, acid resistant grades of aluminium pigment were introduced to the
marketplace, which in addition, offered greater control over particle size distribution. The culmination of these improvements was the introduction of Sparkle Silver type aluminium flake pigments in the 1970’s. The Sparkle Silver grades offer exceptional brilliance, sparkle, and whiteness in a wide range of grades from very coarse to very fine particle size. During the ’80’s, the Coating Industry experienced environmental limitations being placed on coatings, in terms of VOC (volatile organic compound) emissions allowed into the atmosphere. The legislation forced the Industry into developing higher solids coatings, which presented the formulator with many problems. The most significant one is the development of aesthetically pleasing metallic finishes. Along with the advent of high solids, research and development work in the area of waterborne unicoat and base coat/clear coat systems was ongoing. During this time, the need also arose for more degradation resistant pigments, as well as more aesthetically pleasing pigments to maximize the styling changes going on in the Industry. With the automobile stylists developing more rounded, softer looking body styles to lower air drag and increase fuel efficiency, the stylist was faced with the responsibility of accentuating these body designs. New developments in the base coat/clear coat grades were offered, by providing whiter, finer Sparkle Silver grades with deeper flop than previously available in the marketplace. Whiter grades were developed for higher solids finishes, while Tufflake grades were introduced to solve the problems of colour change, during coating application in the automotive plants. Along with these challenges, aluminium pigment grades for use in waterborne systems were introduced.

Generally, to overcome this type of phenomenon, a coarser grade is required. Coarser grades being brighter enables one to achieve approximately the same colour with the high solids system as you would have had in the conventional system, with a finer particle size aluminium flake.

In automotive OEM coatings, it is interesting to note that normally high solids solvent borne base coat/clear coat systems tend to have difficulty in achieving high gloss and smoothness on vertical surfaces, when compared to horizontal surfaces. The VOC restrictions for the high solids systems does hamper the flow and leveling on vertical surfaces. The use of waterborne base coats, coupled with higher solids clear coats, marries the two types of technology, yielding improved aesthetics in the Automobile Industry today.

Within the Ink Industry, similar environmental restrictions are being faced. The ink formulator faces ever-increasing pressure to develop waterborne inks, which meet the performance and application characteristics of their solvent-based counterparts. For acrylic emulsion ink, finding the best resin is just the start of the quest to develop a suitable ink. The formulator also must select and evaluate defoamers,
dispersion agents, surface tension modifiers, flow control agents, coalescents, and co-solvents before a final formulation is developed and fully tested on line.

In meeting the needs of this Industry, Siliberline offers a wide variety of products: standard aluminum pastes (mineral spirits); Silvex; Silvet granules; Isopropyl Alcohol (IPA) based. Summarized in Figure 6 is a matrix illustrating which class of products is applicable to Letterpress and Litho-Offset; flexo and gravure, screen and UV ink systems.

Recent laboratory efforts have been focused in developing new grades, with (IPA) as the solvent carrier, which find application in aqueous, liquid, flexo and/or gravure inks.

In summary, Silberline continues to support research activity for the present and future needs of their industries, worldwide.

**Reactive Dyes**

A reactive dye, according to a useful definition by Rys and Zollinger, is a coloured compound which has a suitable group enable of forming a covalent bond between a carbon atom of a hydroxy, an amino or a mercapto group respectively of the substrate. They point out that this definition excludes mordant dyes and 1:1 chromium azo dye complexes, which are used in dyeing protein fibres, may form covalent bonds between metal ion and nucleophilic groups of the fibre.

The idea that the establishment of a covalent bond between dye and substrate would result in improved wash fastness compared with that of ordinary dye-substrate systems where weaker forces were operative is an old one. The invention consisted in the synthesis of dyes containing a reactive group, the 2,4,6-dichlorotriazinylamino group which has two labile chlorine atoms activated by the electron-withdrawing action of the three N atoms, and the Devising of dyebath conditions, which, while bringing about the formation of a covalent bond, were mild enough to avoid serious damage to the fibre.

The chlorotriazinyl reactive dyes are by far the most important class and have proved a serious rival to the vat dyes as regards washfastness and in other ways. The main chromogens employed are azo, metal-azo, anthraquinone and phthalocyanine systems. The question of cotton substantivity is an important one. It should be high enough to ensure a high 'fixation-yield' but at the same time a substantivity of the unfixed, hydrolysed dye should be low enough to permit easy removal by soaping and rinsing to ensure maximum fastness to wet treatments in the finished dyeing. Structural modifications to the molecule, which (a) inhibit coplanarity or (b) increase the watersolubility, tend to reduce substantivity.

Since their introduction reactive dyes have been the subject of a very large number of patents comparable only with the numbers granted for inventions in the disperse dye field and in that of synthetic
organic pigments. Most dye manufacturers have invested heavily in research programmes concerning new reactive systems and variations of molecular structure to achieve optimum fastness and other properties. Attention has naturally turned to reactive dyes for substrates other than cellulose and dyes have been developed which are suitable for wool and polyamides. Water-insoluble disperse dyes having reactive groups (Procynyl dyes, ICI) have been introduced principally for the dyeing of polyamide fibres on which they show improved washing and heat fastness. Reactive systems may be divided into two main types:

- Those involving nucleophilic substitution
- Those involving nucleophilic addition

**Nucleophilic Substitution Systems**

The monochloro and dichlorotriazinyl dyes, of which early examples have already been given, account for 50% of all reactive dyes used in commerce.

**Evidence for Chemical Combination Cellulose**

Stamm, Zollinger and co-workers have endeavoured to obtain experimental evidence of the formation of a covalent link and to demonstrate its position in the D-glucose unit of cellulose. Cotton dyed with a Remazol dye was subjected to microbiological hydrolysis, a mixture of oligomers being formed. Further degradation, with dilute sulphuric acid, gave a glucose derivative in which one hydroxyl group was blocked by a dye molecule. Methylation of this under very mild conditions, followed by alkaline treatment to remove the dye molecule, and then acid hydrolysis to remove the glucosidic methyl group gave finally a known trimethylglucose. Stamm later showed that a glucoside is normally formed by Remazol dyes acting on cellulose and concluded that the earlier findings were ambiguous. Cellulose dyed with a chlorotriazinyl reactive dye however will not dissolve in cuprammonium solution, whereas cellulose dyes with direct dyes will dissolve.

**Direct Dyes**

The direct dyes, also known as the substantive colours, differ from the basic and acid dyes because cellulosic fibres have a strong affinity for them. Many of them will also dye the protein fibres and, as was explained in the previous chapter, the majority is sulphonated azo compounds very similar to the acid dyes in constitution, there being no clear demarcation between the two classes. Selected substantive dyes can be used to give solid shades on wool and cotton mixtures. This was the first direct dye, and its discovery was quickly followed by the preparation of many similar colours, opening a new era in cotton dyeing. Before 1884 cellulosic fibres could only be dyed on a mordant or by means of indigo and a limited number of other
naturally occurring vat dyes. Both of these methods were troublesome and expensive. Cotton was made in large quantities in the last century for markets where cheapness was a most important consideration. The direct dyes were inexpensive and easy to apply and, although of indifferent wet-fastness, their use spread with great rapidity because they fulfilled an outstanding demand. New members with improved fastness are still being added to this class.

CLASSIFICATION ACCORDING TO DYEING BEHAVIOUR

It was appreciated by earlier workers that the behaviour of individual direct dyes varied considerably. This necessitated special care in selection, particularly in mixture, in order to achieve optimum results and to prevent the occurrence of faults, such as uneven or insufficiently penetrated dyeings on all types of materials and listing or ending with jig-dyed fabrics. As a result attention was given to devising suitable laboratory test methods to characterise the dyeing behaviour of individual direct dyes and thereby enable the best selection to be made for a particular dyeing method, highlighting the parameters to be observed in controlling the dyeing cycle.

In the UK pioneer work in this area by C M Whittaker, John Boulton and their colleagues at Courtaulds in the 1940s was concerned with the dyeing of viscose. A characteristic of individual direct dyes, described as the time of half dyeing (i.e. the time taken to reach 50% of the equilibrium absorption under specified conditions), is an indication of the rate at which a direct dye is absorbed by the fibre. In the direct dye range it varies from 0.72 to 280 min. Arising from this work, it was suggested that dyes exhibiting a similar time of half dyeing would be the preferred choice in mixtures. It was found later, however, that measurements of the so-called rate of dyeing, related to time of half dyeing, were inadequate to obtain a full understanding of the compatibility of direct dyes. Subsequently it was confirmed that rate of dyeing alone is insufficient to predict compatibility and that rate of migration and salt controllability are of greater importance.

As a result of a detailed study of the subject by the Society of Dyers and Colourists' Committee on the Dyeing Properties of Direct Cotton Dyes it was concluded that determination of four parameters was necessary, i.e., migration (or leveling power), salt controllability and the influence of temperature and of liquor ratio on exhaustion. Tests are prescribed for migration and salt controllability whilst a statement covers the influence of temperature and liquor ratio, no tests being prescribed. The aforementioned SDC committee recommended that direct dyes be classified as follows.

Temperature-ranges tests are useful for determining the behaviour of individual dyes at various temperatures of dyeing and are of particular value in the selection of compatible dyes for mixtures. The percentage absorption of dye under standard conditions of electrolyte concentration, liquor ratio and time of dyeing at a variety of
temperatures is estimated visually or colorimetrically and the results are given in the form of graphs. The selection of compatible dyes for padding and jig dyeing processes is not wholly covered by the SDC ABC classification and related tests. This can be done, however, by carrying out simple dip or strike tests in which fabric or yarn samples are dyed for short periods, e.g. for 1-2 min, removed from the dyebaths, replaced by fresh samples and the procedure repeated several times; the patterns are mounted in series and assessed visually for change of hue and depth. Marked changes of hue indicate incompatibility.

The various tests described are simple to perform, required the minimum of apparatus and skill, and the results obtained are easy to interpret. They provide valuable information on the performance of individual direct dyes, either alone or mixtures.

**Sulphur Dyes**

**Introduction**

These constitute a group of dyes of unknown constitution which can be applied to fibres when reduced with sodium sulphide. Most of them are insoluble in water before reduction. After reduction they are soluble and can be absorbed by fibres by fibres and than oxidised to an insoluble form with air. These dyes are popular because of their heavy shades, such as blue, green, black, brown, etc. of reasonable fastness to light and ordinary washing at a low cost. These dyes are second to the azo dyes in quantity produced.

Although structures cannot be written for the sulphur dyes, the methods for reproducing individual types are well established. These are manufactured by treating aromatic amines, phenols, ammo-phenols, with sulphur and or sodium polysulphide at 150-200°C. Some important sulphur dyes are described as follows:

(i) Sulphur black I is manufactured by heating //i-dinitrophenol with sodium polysulphide. The fused mass is dissolved in water and blown with air until all the dye has separated. It is then filtered, washed and dried.

(ii) Brown sulphur dyes are obtained by fusing m-diamines (e.g. m-toluenediamine) with sulphur. During this preparation, hydrogen sulphide gas is evolved.

(iii) Red shades are obtained by fusing sulphur with derivatives of azine, such as the compound below which produces sulphur red 6.

**Properties of Sulphur Dyes**

From the name it is clear that these dyes contain little amount of sulphuric acid. The fibers those can be dyed by these dyes are Viscous, Staple fibers. Yarn, any materials which give a resin finish, silk etc.

- These dyes have an excellent light fastness properties.
- Dyeing temperature: 80-95 degree C (Optimum) but sometimes at cold temperature also.
• It is a good soluble in Na2S.
• It has a good exhaustion.
• Its dyeing rate is moderate.
• It is a soluble in water.
• Make rapid black on cellulose materials.
• Sometimes create direct prints on cellulose.

Since so little is known of their structures, sulphur dyes are usually classified according to the chemistry of their starting materials. The manufacturing processes are chiefly of three types:

1. A dry mixture of the organic starting material (or material) with sulphur is heated (the temperature usually exceeding 200°C).
2. As 1, but using sodium polysulphide instead, sulphur. The baking temperature varies widely.
3. The starting material is heated with aqueous sodium polysulphide, either under reflux or in a closed vessel under pressure. Some or all of the water may be replaced by butanol.

The shade and properties of the resulting dyes may vary considerably with the reaction temperature and duration of heating. In all cases hydrogen sulphide is evolved during reaction and it is absorbed in aqueous caustic soda. The dyes are usually isolated from alkaline solution by air oxidation. Many of them are subject to deterioration during prolonged storage.

The properties of sulphur dyes are intermediate between those of direct dyes and vat dyes. As already stated, reds are poorly represented, only dull Bordeaux shades being available. Other hues are plentiful, but almost all sulphur dyes are somewhat dull. Wet fastness properties are usually good, but resistance to bleaching is poor. With some notable exceptions, as in sulphur black T and its equivalents, light-fastness is only fair or moderate. The great demand for sulphur dyes is due to their moderately good properties and low cost.

They are applied almost exclusively to cellulosic fibres, the alkaline batch required being unsuitable for wool and silk. The process consists in dissolving the dye in a solution of sodium sulphide, whereby it is reduced to a leuco compound with affinity for the fibre, carrying out dyeing just below the boil, then exposing the dyed material to air so that oxidation and development of the shade take place. Sometimes the dyeings are aftertreated with a mixture of a dichromate and copper sulphate for improvement in fastness to light and wet treatments, but this is liable to result in tendering of the fibre by slow liberating of sulphuric acid. Cotton dyed with sulphur colours acquires affinity for basic dyes, and there are sometimes applied as ‘topping’ colours in order to brighten the shades. Sulphur blacks can also be topped with aniline Black to give very deep black shades with increased fastness to milling.
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