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## Olney Medal Address

# A Review of Disperse Dyes

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### ABSTRACT

Disperse dyes have been the chief coloring matter for hydrophobic fibers, beginning with cellulose acetate in the 1920's. The dyes were relatively simple and were required to display only a few fastness properties. Since then, requirements of the trade have demanded higher dye performance. At the same time, the more drastic dyeing conditions and improved methods which developed along with the newer fibers have allowed the use of more complex molecular structures, although many acetate dyes are still used on polyesters and nylon.

Azo, anthraquinone, o-nitrodiphenylamine, methine and quinophthalone chemical classes provide the major commercial disperse dyes. None of these is a new chromophoric system, but intensive investigation and novel elegant synthetic methods have resulted in dyes exhibiting superior properties, especially on the newer fibers. Disperse dyes are also used in the newly popular transfer print process, which requires coloring matters of poor sublimation fastness, a source of trouble in conventional printing.

### KEY TERMS

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Disperse Dyes  
Dyeing  
Hydrophobic Fibers  
Olney Medal Address

THE textile industry, particularly its dye segment, should take great pride in the fact that organic chemistry, with all its later benefits to mankind, was its child. Without the incentive to color our garments and furnishings, the advances in chemistry of aromatics would have been delayed considerably. For centuries man had been dyeing fabrics with vegetable, shellfish and insect derivatives, but their constitutions had not been even guessed at.

Suddenly, in the middle 1800's, chemists began the synthesis and identification of the structures of natural and man-made colors. The skill of those ancient scientists, von Hofmann, Perkin, von Bayer, Griess, Caro, Friedländer, Scholl, and all the rest, never ceases to amaze me. They had no thin layer chromatography, microanalysis, no nuclear magnetic resonance, infrared or mass spectroscopy, yet they came up with accurate structures and reasonable syntheses for some of the most intractable compounds then known. Nor, as far as I have been able to determine, did they have the benefits of job description, skill analysis, five-year plans, or governmentally imposed environmental and safety standards.

The first hydrophobic fiber, cellulose acetate, appeared in the 1920's and was prized for its luster and the drapability and hand of fabrics constructed from it. But the dyes in use for the natural hydrophilic fibers, cotton, wool and silk, had no affinity for the newcomer. These dyes were almost all ionic substances, at least at one stage in their application water soluble, and the new fiber was only slightly stained by any of them. It was not a question of finding new chromophoric systems—these were almost all known.

Several methods of dyeing were ex-

plored and used briefly. Water solubilizing groups which would be removed in the dye bath were attached to the dye molecules. However, release of these groups from different molecules varied greatly, and the pH changes necessary affected the tenacity of the fiber, which could not afford to lose any of this property. Saponification of the fiber in order to utilize cellulosic dyes was tried, but, here again, control proved to be impossible. Hydrophilic groups, such as sulfato, were attached to the dye molecule, but the products were useful in only weak to medium shades. The use of solvents such as methanol to swell the fiber survived much longer than any of the other methods just discussed.

Chemists from several British companies found that grinding the dye with surface active agents (one of the first was sulfuric acid) and the presence of a slightly hydrophilic group such as hydroxyl on the dye molecule was the answer. This system is still in use today. Although not then apparent, it turns out that this combination provided the transitory water solubility necessary to invade the fiber. Many colored substances can be prepared in extremely fine aqueous dispersion but without some water solubility no dyeing occurs. Some may say that to call this process solvent extraction is an oversimplification, but in any case, the product is a solid solution.

In general, commercially successful dyes must possess properties other than color; lightfastness, washfastness, resistance to atmospheric contaminants, changes in dye bath pH, etc. The dyes for man-made fibers also require resistance to sublimation. They have measurable vapor pressures and tend to leave the fiber under conditions of pleating, ironing, heatsetting, etc. A requirement for dyed fibers in gen-

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eral is brightness. Therefore, it becomes somewhat frustrating to the disperse dye chemist to find that someone has paid money to add delusterants to the fibers with which he must deal.

Actually, we should not refer to the fastness of a dye but rather to that of the dye-fiber system. These vary considerably. A dye that is fast to light on polyester is often fugitive on nylon. Dyes that fade rapidly on cellulose acetate when exposed to the oxides of nitrogen show little deterioration on nylon or polyester. These differences are found within even a chemical class. Quite often dyes fast to light on poly(ethylene terephthalate) are unsatisfactory on poly(1,4-cyclohexylenedimethylene terephthalate) and vice versa.

### Accelerated Tests

Much reliance as to actual performance has been placed on accelerated fastness tests. In many cases these are reliable but once in a while an exception appears. About 25 years ago our first director of research made an interesting observation concerning his wife's acetate bathing suit. The fabric was a print, chiefly of C.I. Disperse Red 1 on a white ground. The apparent lightfastness was much better than our Fade-Ometer results indicated. The floral pattern was not a busy one so optical illusion was ruled out. We had no Weather-Ometer then, so we devised all sorts of intermittent wetting schedules on our Fade-Ometer for 15 of our commercial dyes. The result was confusion. Each dye had its own behavioral pattern—there was no apparent correlation with color, structure, water solubility, or any other measurable property. Unfortunately, the need for finding new saleable dyes shelved this project permanently.

During the intense investigation of new polyesters during the 1950's, an economically attractive prospect was discovered. However, lightfast dyes for it were difficult to obtain—especially the blues. C.I. Disperse Blue 27 was the best available, and let me tell you it was terrible—on the Fade-Ometer. Not only did it fade badly, there was a horrible dark reaction. Exposed dyeings after a few months storage disintegrated at the touch of a fingernail. In the meantime, wear test garments dyed in dark brown and navy shades in which C.I. Disperse Blue 27 was the major component had been prepared. On these suits after 10 years of normal wearing not only was there no fabric disintegration but no apparent loss of blue. How many desirable products have we discarded because of misleading results of accelerated test methods?

Obviously, we cannot run a wear test on human beings for every experimental dye-fiber combination. But how can we compensate for the lack of human flesh behind our dyed fabrics? What was the effect of the temperature or chemical content of New York Finger Lake water on the boss's wife's bathing suit? Usually, accelerated tests provide at least a comparative view of actual performance. Why the enormous discrepancy in the case of the C.I. Disperse Blue 27-experimental polyester system?

The first disperse dyes were of rather low molecular weight, because temperatures higher than 80°C affect the textile properties of cellulose acetate, and of basic or phenolic character. They were chemically from the azo, anthraquinone, and *o*-nitrodiphenylamine classes. The last was chiefly responsible for yellow shades; reds and blues came from the other two classes. The major problem was the blues. There was no lightfast, gasfast blue. The azo blues showed poor lightfastness, while the lightfast anthraquinones quickly faded in the presence of the oxides of nitrogen. In the early 1950's, two blues, one from the naphthazarin class (1), and an anthraquinone (2) overcame this difficulty. Actually, these were not completely gasfast, but, since they faded on tone, the change was much less noticeable than that of the earlier compounds which reddened rapidly.

The second hydrophobic and first truly synthetic fiber on which disperse dyes were used was nylon—one of the most versatile fibers yet invented. Actually, acid wool dyes adequately enhance this fiber as far as fastness properties are concerned, but the problem of barré caused by nonuniform conditions in preparation of melt-spun fibers is best covered by some disperse dyes. It may have been this fiber that prompted the saying that the dyehouse is expected to correct everyone else's mistakes. Because of nylon's extraordinary acceptance of most classes of dyes and the fact that the dyebath can be run at the boil, dyes of higher molecular weight and increased negativity can be used. Here again there is a problem with disperse blues. The one most widely used is the ancient and expensive C.I. Disperse Blue 7. There is no lightfast blue that completely withstands "Gulf Coast Fade." This fault varies with the method of texturizing the fiber and can be duplicated by exposure to ozone at high humidity.

### Polyesters

The advent of polyesters, the most important hydrophobic fibers, at least as far as disperse dye use is concerned, both increased the number of and intensified the conditions which the dyes must withstand. Because of the higher dyebath temperatures, dyes must be

less sensitive to hydrolysis. Because the fiber is often heated to temperatures far above those used with the older fibers dyes of extreme resistance to sublimation must be used. Because of the popularity of the durable press process, the dyes must not be sensitive to the acidic metal salts used as catalysts. ("Catalyst" seems to be a strange term for a substance which comprises 15-20% of the total solids in the resin mix.) Because the substance is a polyester/cotton blend, the dyes should not stain cotton since disperse dyes ordinarily have no lightfastness on cellulose. Barré is a substantial problem with polyesters, also.

Polyesters are not very receptive to dyes used in an aqueous bath at atmospheric pressure. For efficient dyeing rates the glass transition temperature of the fiber must be exceeded. Several methods are used to arrive at this condition. The temperature can be increased by dyeing under pressure or the dye dispersion can be padded on and then subjected to dry heat—a very popular method for blends with cotton. Both of these methods require specialized equipment. The other approach is to use a carrier, usually a water-insoluble organic substance, which loosens the molecular structure of the fiber, allowing penetration by the dye molecule. However, many of the most effective carriers are toxic and others affect the lightfastness of the dyeings. All of them are difficult to contain or destroy in the mill so that adherence to air or water pollution codes may be difficult.

### Azo Dyes

The two major classes of disperse dyes are the azos and anthraquinones. The azo dyes are prepared by a simple reaction of nitrous acid with an aromatic amine followed by coupling to a receptive compound—at least it looks simple on paper. This process is very sensitive to temperature, solvent, materials of construction of the reaction vessel, impurities in the starting materials and sometimes methinks the phases of the moon. The overall reaction is a competition between the decomposition of the intermediate diazonium and its coupling to the designated substance. Quite often the coupler itself encourages decomposition of the diazo. While on a 100% basis azo dyes appear to give a high tinctorial yield, the commercial product is often contaminated with decomposition and side reaction products that cause off-colored goods and impaired fastness properties.

Many of the azo dyes are derived from homocyclic diazos. This was true in general of the early members of the series. Lightfast blues were not then to be found, but a recent elegant method of introducing cyano groups into the molecule by replacing halogen

groups by means of copper cyanide—solvent complexes (3) has produced some excellent dyes for polyesters. Some of these dyes were known but no inexpensive synthesis for them was available.

About 1950 serious consideration of the use of heterocyclic diazoles began. Dyes from aminothiazoles (4) gave beautiful blue dyes, and, although the yields were low and the lightfastness poor, their high extinction coefficients and ready dischargeability made them commercially attractive. A few positively substituted benzothiazoles (5) had been in use for dischargeable red to violet shades, but their lightfastness was only mediocre. The use of negatively substituted benzothiazoles (5) considerably improved this property and gave some beautiful reds still in use today. Extension of this investigation to the thiadiazole series has given beautiful bright reds in use on polyamides.

The coupler portion of the azo dye molecule has also received intensive study. In particular, modification of the old 2-alkoxy-5-acetamino-*N,N*-dialkylanilines used in the early days for blues (of medium lightfastness) has resulted in very popular navy blues (6) of adequate lightfastness for polyesters. Heterocyclic couplers, particularly in the pyrazolone series, have given good commercial yellows.

### Anthraquinones

The anthraquinones are usually not as cheaply prepared as the azo dyes and usually have lower tinctorial power. These initial disadvantages may be compensated for by much better fastness properties and often brightness. In many cases this latter effect is due to fluorescence. Although a few disperse azo dyes are fluorescent, none has achieved commercial status. Here again, the written reactions are deceptively simple. Some of our most popular blues are named as homogeneous products, while actually they are mixtures. One of the most popular on cellulose acetate, C.I. Disperse Blue 3, is usually prepared by condensation between two aliphatic amines and 1,4-dihydroxyanthraquinone. Instead of only the three logically expected products, thin layer chromatography showed the presence of 10 to 18 components, depending on the reaction conditions. Here also the purity (or lack thereof) of the starting materials is extremely important.

On cellulose acetate, the mixture just described appears to have better affinity than any of the isolated pure components. This effect holds for many mixes of closely related structures but should not be considered as general for all mixtures. On the contrary, some mixes of differing molecular structure seem to impede dyeability.

The first commercial gasfast anthraquinone blue of practical dyeability on acetate was C.I. Disperse Blue 27 (2). It is a modification of C.I. Disperse Blue 62, an ancient compound (7), which later came into use on polyesters. Although these are also derived from polyfunctional anthraquinones, the reaction is much more easily controlled, but impurities are also possible here.

The higher resistance of polyester to drastic dye bath conditions has allowed the use of dyes of higher molecular weight, particularly with the newer blues. The chemistry of the extremely popular C.I. Disperse Blue 73 has been known (9) for many years. While this dye does not have outstanding fastness properties, its bright shade and good build-up under a variety of conditions make it very attractive. The brightest turquoise shades for polyester are contributed by C.I. Disperse Blue 60 and related types (10). They are prepared by several methods, all of which are outstanding synthetic developments.

Some of the workhorse reds, such as C.I. Disperse Red 60 (8), have long been available. These are 1-amino-2-alkoxy (or aryloxy)-4-hydroxyanthraquinones and provide beautiful, bright, red to pink shades.

From the beginning, yellow dyes from *o*-nitrodiphenylamines have been very useful because of their excellent lightfastness. Examples are C.I. Disperse Yellows 33 and 42, which are also old chemicals (11). In general, these dyes are prepared by condensation of an aromatic amine with an *o*-halonitrobenzene in an inert solvent.

Workhorse yellows such as C.I. Disperse Yellows 54 and 64 for polyesters come from the quinophthalone series (12). These are derived from the ancient Quinoline Yellow, without the sulfonic acid group. Furthermore, the presence of a hydroxy group in the 3' position (on the quinoline moiety) has resulted in much better lightfastness properties.

The methine class of dyes contains some of the brightest and fastest dyes for acetate and polyesters. Their structure gives them a tendency to hydrolyze in the dye bath at pH above about 5.5, but recent structural modifications have increased their affinity for the fiber so they are out of the dye bath before serious hydrolysis can occur. They are readily prepared by condensation of *p*-*N,N*-disubstituted aromatic aldehydes with active methylene compounds such as malononitrile. These are all greenish yellow, and most of them are highly fluorescent.

### Dispersing Agents

The role of dispersing agents is not completely clear. Their primary purpose is to force the dye into the dye bath in a condition favorable for problem-free dyeing. However, there

is no universal dispersing agent. Further, mixing some dyes prepared with different dispersants may cause trouble in dyeing. Agents added to the bath for wetting and other purposes may be detrimental to the desired result. While much has been done privately to solve these antagonisms, much also remains to be done. It is no longer reasonable to let price be the dominant factor in selecting the substances necessary to allow our expensive dyes to penetrate the fiber.

Sometimes a major fault can be converted to an advantage. This has happened in the case of the heat transfer printing process. Disperse dyes of inferior sublimation fastness are printed in a suitable vehicle onto paper. The textile printer then heats the paper in contact with a fabric, usually polyester, to obtain the saleable product. The advantages to the textile printer are the simple machinery required, elimination of expensive skilled labor, excellent register of the finished goods, and reduced contamination of the environment. The more obvious disadvantages are reduced sublimation fastness, the generation of waste paper, and the fact that the conventional printer cannot use his equipment on all classes of fiber.

### Enormous Progress

The years between 1923 and 1977 have seen enormous progress in the textile use of hydrophobic fibers. The robust polyamides and polyesters have penetrated areas not even dreamed of by the frail cellulose acetate. And the simple dye chemistry born in 1923 has grown in stride with every end-use for these fibers.

The blemishes of inadequate resistance to light, poor gasfastness, dullness and sublimation have almost disappeared. Old chemicals, new dyes and improved methods of synthesis have conspired to this end and will continue to do so with each new requirement. ☺

### References

- (1) Sandoz, U.S. Patent 2,553,048 (May 15, 1951).
- (2) Eastman Kodak, U.S. Patent 2,641,602 (June 9, 1953).
- (3) Bayer, U.S. Patent 3,962,209 (June 8, 1976).
- (4) Eastman Kodak, U.S. Patent 2,659,719 (Nov. 17, 1953).
- (5) Eastman Kodak, U.S. Patent 2,785,157 (Mar. 12, 1957).
- (6) Sandoz, U.S. Patent 3,178,405 (Apr. 13, 1965).
- (7) Bayer, German Patent 89,090 (June 1895); Friedländer, Vol. IV, p314.
- (8) *Colour Index*, 3rd Ed., Society of Dyers and Colourists, London, and AATCC, Research Triangle Park, N. C. Vol. 6, 1975, p6402.
- (9) Grasselli Dyestuff, U.S. Patent 1,652,584 (Dec. 13, 1927).
- (10) Du Pont, U.S. Patent 2,628,963 (Feb. 17, 1953); BASF, U.S. Patent 3,137,699 (June 16, 1964).
- (11) Fischer, P., *Berichte der Deutschen Chemischen Gesellschaft*, Vol. 24, 1891, p3794.
- (12) BASF, British Patent 865,308 (Apr. 12, 1961); BASF, German Patent 1,229,663 (Dec. 1, 1966).