

Chapter 6: Azoic Combinations: Chemical Principles

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Few people know that about half of all organic textile colorants made today use reactions first discovered in the laboratories of a large brewery, around 1862, just six years after Perkin's discovery of the first synthetic dye. The conjunction seems appropriate inasmuch as organic chemistry was in a state of ferment and chemists were intoxicated by the prospects for the chemical industry. The brewery was British, the chemist (Peter Griess) was German, and the reactions are called diazotization and coupling. In conjunction, these reactions are used in the synthesis of the very important azo group of color chemicals.

Azo colors, dyes or pigments, soluble or insoluble in water, contain one or more azo chromophores, written $-N=N-$, which take their name from the French word for nitrogen, *azote*.

To appreciate the reactions involved with azoic combinations, it is first necessary to look at those related to azo colors in general.

Azo Colors

Except in special cases the synthesis of an azo chromophore always requires the interaction, or combination, of two components. One carries the nitrogen which will eventually participate in the azo group.

ABSTRACT

The differences between azo and azoic colors are explained as is the general chemistry of diazotization and coupling. This is followed by an account of the introduction into dyehouses of azoic combinations, in the form of azoic couplers and azoic diazo components, as fast color bases and salts.

KEY TERMS

Azo
Azoic
Azoic Combinations
Batch Application
Continuous Application
Coupling
Coupling Components
Diazo Components
Diazotization
Fast Bases
Fast Salts
Naphthols

This is called the diazo component. The other component, called the coupling component, or coupler, carries an electron-rich (electronegative) carbon atom to which the first component will become attached. The reaction of attachment is called coupling, and it involves bridging the gap between the two components with a new azo group, $-N=N-$.

Diazo Components

The term diazo component can refer to any one of several interrelated chemicals in different stages of readiness for reaction with the coupling component.

The diazo component can be a base, an aromatic primary amine, which can be written in chemical shorthand, $ArNH_2$, although it is sometimes the corresponding hydrochloride, written $ArNH_3^+ \cdot Cl^-$ or $ArNH_2 \cdot HCl$. Here, $-NH_2$ represents the primary amino group and Ar is any suitable derivative of benzene, naphthalene or other carbon-containing ring structure, with alternating double and single bonds between atoms. The aromatic group may or may not have additional water solubilizing anionic or cationic substituents. The base is one step away from being ready for coupling.

Alternatively, the diazo component can be in the form of a diazonium salt, which is a derivative of the original primary aromatic amine, or base, and which is ready to undergo coupling.

The diazonium salt is made from the base by the reaction known as diazotization, in which the single nitrogen atom of the primary amino group has a second one added to it. This is effected by reaction with a nitrosation carrier, such as nitrous acid, HNO_2 , formed by the combination of sodium nitrite and hydrochloric acid. The reaction is complex, but is well understood (1).

The product is the diazonium cation, written $Ar-N_2^+$ or $Ar-N^+ \equiv N$, which in conjunction with an anion forms a diazonium salt. The diazonium cation is the reactive species, and is one of the most powerfully electrophilic (electron loving) species known. Diazonium salts can be unstable and they are usually prepared at low temperatures, which often requires cooling with ice.

Coupling Components

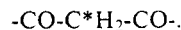
Coupling components are compounds which contain at least one electronegative

carbon atom, and can be of three different types, all of which may contain water solubilizing substituents:

- Aromatic Amines. It is not necessary that they are primary amines, for the nitrogen can be substituted in a variety of ways, provided the substituents do not withdraw too much electronegativity (electrons) from the aromatic ring. They can be written: $Ar-N \equiv R_1R_2$, where R_1 , and R_2 may be different, and are normally either hydrogen or alkyl derivatives.

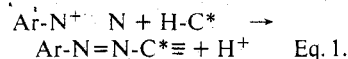
- Aromatic hydroxy compounds, such as substituted phenols and naphthols, which can be written: $Ar-OH$.

- There are a few important compounds which have reactive methylene groups, $-CH_2-$, in which the carbon atom (*) is made more electronegative by an adjacent carbonyl group, $-CO-$, or groups; e.g.,



Coupling

The formation of the azo group occurs when both diazo and coupling components are present, in combination, under the appropriate conditions of pH and temperature, and the reaction can be written:



Here, C^* is the electronegative carbon to which the diazonium ion is attracted. Hydrogen ion is released in the reaction, and, in the absence of a buffering system, would lower the pH. *Note:* The carbon atom (*) has three bonds which may be the double and single bonds of an aromatic or benzene ring, or may be attached to a hydrogen and two carbons.

Now that the general background chemistry of the azo colors has been introduced, it is easier to understand some of the terminology used when talking about azoic combinations—a color application category.

Azoic Combinations

The author has deliberately selected this form of words as a preferred way to describe the particular color application category, which at first may seem a less positive name than, for example, direct dyes. However, the reasons for the choice will be much clearer after the next few sections have described the development and chemistry of azoic diazo components, azoic coupling components and the azo

pigments formed when they react. Under the heading NOMENCLATURE, other name options will be discussed.

Development

Already by 1880 the opportunity to synthesize a few azo pigments within the cellulosic fiber had been grasped by Read, Holliday and Sons in the U.K. But, as new color development continued at a frantic pace into the twentieth century, there was still a great incentive to develop a new, wider range of colors for cotton goods, to fill the need for bright and heavy shades of scarlet, red and bordeaux, with favorable economics as well as good lightfastness and wetfastness, and which were easy to apply.

There were brilliant basic dyes available, which could be applied to mordanted cotton, but the fastness properties of their dyeings were poor. There were no existing vat dyes nor sulfur dyes which could give such shades, and they are still missing, even today. Iizarin, originally extracted from the roots of the Madder plant, but by then readily synthesized, could produce a range of heavy scarlet through bordeaux shades on a variety of different metallic salt mordants, but application processes could literally take weeks. Direct dyes were not, and still are not, capable of producing dyeings of very good wetfastness in this shade area. Even with the advent of fiber reactive dyes in 1956, this need was not entirely eliminated, for while the range of desired shades can be produced the economics are not favorable for the heavier shades.

There was also an economic incentive to take dye synthesis out of the hands of the dye manufacturers and into the dyehouse, and that step was taken as azoic diazo components and coupling components became available to the dyers. Processes were developed for application of alkaline solutions of couplers, derived mainly from naphthol derivatives, to cellulosic fibers, followed by removal of the excess solution and treatment of the coupler-impregnated fibers with diazonium salt solutions so that insoluble azo colors were formed within the fibers.

Perhaps the single most important early development was the introduction, in 1911, of the 2-hydroxy-3-naphthoic acid anilide (a derivative of the well known beta-naphthol) as a coupling component, see Fig. 1d). The principle advantage this product had over its predecessors was that the anion, formed when the product was dissolved in alkali (Fig. 1f), had some substantivity for cellulose, which could be improved to give an exhaustion of approximately 30% when salt was added. Although this is low substantivity compared with that of many coupling components in use today, and certainly when compared with direct, leuco-vat and leuco-sulfur dye anions, it was the discovery that first made

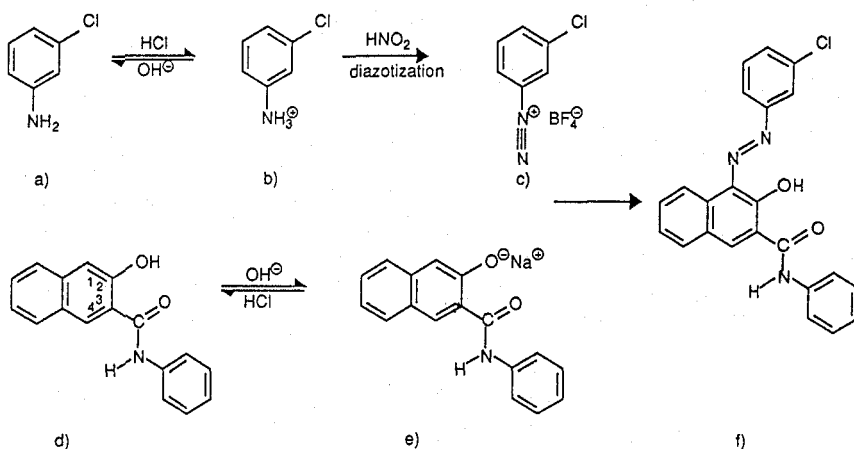


Fig. 1.—Typical Azoic Combination Chemistry: (a) Aromatic base: liquid, immiscible in water; (b) Fast Color Base: soluble colorless solid, (hydrochloride), C.I. Diazo Component 2; (c) Fast Color Salt: soluble colorless solid, (fluoroborate), C.I. Diazo Component 2; (d) Naphthol: insoluble colorless solid, C.I. Coupling Component 2; (e) Substantive yellow anion formed from (d) in alkaline solution; (f) Azo pigment from reaction of (c) and (e), C.I. Pigment Orange 24.

batchwise application of coupling components practicable.

Azoic Diazo Components: Fast Bases and Salts

Azoic simply means "of the azo variety," so these azoic components are a sub-group of the primary aromatic amines, or bases, and their corresponding diazonium salts mentioned earlier under the heading azo-colors.

The aromatic portion is almost always a relatively simple, substituted derivative of benzene and, although the substituents may themselves contain one or two additional benzene rings, and in some cases (for blacks) even an azo group, there is no call for naphthalene derivatives. Apart from the functional amino or diazonium substituents, they contain no ionic or potentially water solubilizing groups. These components are sold under two generic names:

- Fast Color Bases. These are normally free amines in powder form, Ar-NH_2 , Fig.

1a), but some of the lower melting amines are sold as the corresponding salts of hydrochloric acid, $\text{Ar-NH}_3^+ \cdot \text{Cl}^-$, or amine hydrochlorides, Fig. 1b). Either way, they are still referred to as Fast (Color) Bases. The word fast is a holdover from the early years, when azoic dyeings were noted for their good fastness, and the word color is optional.

- Fast Color Salts: The diazonium cations as sold are usually in the form of powders, stabilized by interacting them with carefully selected anionic compounds to give salts. Such anions can be fluoroborates (or borofluorides), BF_4^- , naphthalene or substituted benzene sulfonates, Ar-SO_3^- , and particularly the zinc chloride double salts, ZnCl_4^{2-} , for which it takes two diazonium cations to neutralize the divalent, tetrachlorozincate ion.

A less common method of stabilizing the diazonium cations is to react them with an aliphatic amino compound containing a water solubilizing group. The products are stable and soluble in alkaline solutions but liberate the diazonium cation on acidification. This makes it possible to apply such products at the same time as applying the alkaline solution of the azoic coupling components.

Azoic Coupling Components: Naphthols

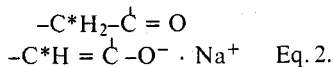
Naphthols are sub-set of the azo couplers mentioned earlier. Probably 75% or more of the coupling components in use today are variously substituted anilides of substituted or unsubstituted 2-hydroxy-3-naphthoic acid. For this reason and for the convenience of having a simpler name, azoic coupling components are often referred to as *naphthols*. They all dissolve to some extent in alkaline solutions, to give solutions of their corresponding naphtholate anions (cf. Fig. 1e).

The remaining 25% are diazo coupling components derived from chemicals with

About This Series

THIS is the tenth installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December), vat dyes (January and February), sulfur dyes (March and April) and reactive dyes (May and June). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

reactive methylene groups and carbonyl groups (nothing to do with naphthoic anilides) which also dissolve in alkaline solutions to give water soluble anions, as shown below. They, too, are called naphthols for convenience.



There are no other solubilizing groups in azoic coupling components, and there are no azoic coupling components which depend on an amino group to activate an adjacent carbon atom for coupling. Both these features contrast strongly with the coupling components used in large numbers of azo dyes.

Sorption of Naphtholate Anions

The sorption of organic aromatic anions by cellulose in the presence of salts has already been discussed. There is no reason to believe that those derived from diazo coupling components should be sorbed by any other mechanism than that applicable to leuco-vat, leuco-sulfur and direct dye anions. But, although it is generally accepted that this is the case, little fundamental work has been carried out to confirm or deny it (1).

The main differences to be expected between azoic coupler anions (naphtholates) and those of the other dye application categories is the relatively small size of the molecules, which results in their considerably reduced substantivity. This small molecular size should, and does, allow the anions to diffuse much more rapidly from the surface into the fibers than, for example, direct dye anions.

Permutations and Combinations

For the last several years the AATCC BUYER'S GUIDE (2) has listed about 25 C.I. Azoic Coupling Components and a similar number of C.I. Diazo Components, and between them they boast about 150 products from six suppliers. The versatility of azo chemistry is illustrated by the number of different azo pigments which can be formed from combining each of the 25

diazo components with all 25 coupling components in turn. The result is that 625 pigments (25 × 25) can be made from only 50 (25 + 25) intermediates. Furthermore, they are formed in close to theoretical yield. However, not all combinations yield commercially desirable products.

The essence of the azoic reactions is shown in Fig. 1 with a specific example in which even the final azo pigment has a C.I. Name, Fig. 1f. *Note:* In these naphthol derivatives, coupling takes place at the 1 position; i.e., at the carbon atom with no apparent substituent, adjacent to the carbon atom bearing the hydroxy or hydroxylate group.

Nomenclature

It should now be evident that *azoic* means *azo*, but in a restricted sense only. It relates to just those coupling agents which are soluble in alkali, can be applied to cellulosic fibers from alkaline solutions, and which yield pigments within the fiber after suitable diazonium salts (or derivatives) are also applied. One should qualify this by adding "under the correct conditions," and these will be discussed later.

In other words, the color application process requires the use and combination of two organic intermediates, whose characteristics are well defined. For this reason the author prefers to call the whole subject "Azoic Combinations and Their Application."

The same subject has been widely described as *dyeing*, even though no dye is involved. The problem lies with the use of the word *dye*. Some use *dye* to distinguish between dyes and pigments, or solubility and insolubility. Some use it to denote colored products within fibers (not on the surface) which got there as a result of an application process known broadly as *dyeing*. There is plenty of food for thought here. For example, when should vat colors be referred to as dyes, and when as pigments? Why are the terms *mass pigmentation*, *dope dyeing* and *producer coloration* used synonymously? Which is the better term? All refer to incorporating

pigments into polymers, either molten or in solution.

From the following list of titles, pick out the one which describes the present subject most clearly and correctly:

- Dyeing with Azoic Dyes
- Dyeing with Azoic Colors
- Dyeing with Azoic Combinations
- Dyeing with Naphthol Dyes
- Application of Azoic Combinations

There is no winner and no loser, so long as the reader comes to appreciate the problem in the use of the words. Nobody is perfect. Even the COLOUR INDEX uses the oxymoron *insoluble azo dyes* in defining azoic coloring matters (3). An easy way out is to refer to the whole application category simply as *azoics* and let it go at that.

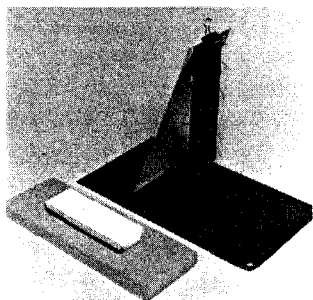
Review

Azoic combinations, or azoics, can give heavy orange, scarlet, red and bordeaux shades on cellulose which are still unbeatable for economy. Navy blue and black shades are also widely used.

The color application category is the one in which the chemistry of dye synthesis and dyeing overlap the farthest. Historically, it required a commitment by the dyer to practice some of the skills of the chemist, in exchange for economic benefits. Nowadays, the need for chemical skills has largely been replaced by excellent technical literature from the major manufacturers of the azoics—naphthols, fast bases and fast salts—which can reduce their application to an ability to follow a procedure. However, it is never harmful to understand the reasons for a procedure, or the consequences of making procedural changes. ☺

References

- (1) *The Theory of Coloration of Textiles*, Second Edition, Edited by A. Johnson, Society of Dyers and Colourists, 1989, Chapter 7.
- (2) *Buyer's Guide for the Textile Wet Processing Industry*, published each year as the July issue of *Textile Chemist and Colorist*.
- (3) *Colour Index*, AATCC and the Society of Dyers and Colourists, Vol. 4, Third Edition, 1971.



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