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AZO DYES

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Abstract: In this general text on azo dyestuffs, a historical survey of the development of azo dye technology is followed by a discussion of the chemical reactions and mechanisms underlying synthetic dye derivation. Specific descriptions, methods of derivation and applications of dyes, soluble and insoluble in water and organic compounds, are given. The structures of all the important dyes discussed are pictured throughout the text and in tables.

NOTICE

206

B. A. Poray-Koshits

AZO DYES

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Table of Contents

This book is one of the last works of an outstanding Soviet specialist in the field of organic dyes and intermediate products. It is devoted to the methods of deriving, classifying and characterizing azo dyes, which are the most extensive of all of the classes of synthetic organic dyestuffs. The diazotization reactions of aromatic amines, and the structure and properties of diazo compounds are described, and the mechanism of the diazotization reaction is worked out.

From among the individual representatives of azo dyes, the water soluble azo dyes with colored anions (lacquer, complexing, mordant, acidic) and the azo dyes which are difficultly soluble and insoluble in water and have colored cations, are considered in detail.

The book is intended for scientific workers, teachers, students and graduate students of the higher chemical institutes who are specializing in the field of dye derivation, research and application.

FOREWORD

Boris Aleksandrovich Poray-Koshits, who died prematurely in 1969, was one of the leading specialists in the field of the chemistry and technology of dyes and intermediate products. In successfully carrying on the tradition of academician A. E. Poray-Koshits, the founder of the Leningrad School for Aniline Dyes, Boris Aleksandrovich enriched a number of branches of the chemistry and technology of compounds or the aromatic and heterocyclic series with valuable results.

Throughout almost all of his scientific career, B. A. Poray-Koshits devoted particular attention to the class of diazo compounds, which are of theoretical and practical interest as initial products for the derivation of azo dyes.

In this monograph, B. A. Poray-Koshits provides the reader with an exposition of the contemporary representations of the structure and reaction mechanisms of diazo compounds, as well as a description of the methods for deriving and the technical properties of the most interesting groups of azo dyes.

The present publication of such a book is extremely timely, since the last monograph on this subject ("Khimiya Azokrasiteley" of G. Tsollinger) was published in Russian more than ten years ago.

This book will promote both further efforts in this field as well as provide for a proper evaluation of the contribution of a great and original scientist who gave so much to the development of the chemistry of diazo compounds.

Academician N. N. Vorozhtsov

INTRODUCTION

The class of azo dyes which are characterized by the presence in their molecule of one or several of the —N=N— azo groups, which bond predominantly aromatic radicals, are the most extensive of all of the classes of synthetic organic dyeing substances. At the present time several thousand industrially interesting azo dyes of the most diverse colors and properties are known. The diversity in their physical and chemical properties and the relative simplicity of industrial derivation and application accounts for the the extensive development of this class of dyes from a large assortment of raw materials.

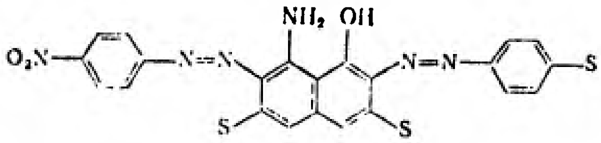
Although it is possible to obtain azo dyes in several ways (and many of them are employed from time to time in industry), the basic means of deriving them is a nitrogen coupling reaction, the interaction between an aromatic diazo compound and a so-called azo component, which most often belongs to the group of aromatic or hetereocyclic amino or hydroxy compounds. The reaction is usually carried out in water solutions, runs its course quickly and leads to a high output of the final azo dye.

The multiplicity of representatives has also made it possible to create dyes which belong to almost all categories of technical classification. Included among them are forward, acidic, basic, cationic, those obtained in the fiber, those containing metal or strengthening metallic salts, dispersed, active, dyes for the food industry, for coloring leather, fur, oxidized metals and even stones. Even representatives of vat dyes are included among the azo dyes, although it is true they have not found wide application.

Writing the fully expanded formulas of azo dyes is often very complex and not always necessary. There are many proposals in the literature [1] which make it possible to partially avoid fully writing out the formulas. In those places where it is possible, we will take recourse to a quite convenient method in which the source amine (diazo component) used to derive the diazo compound is connected by an arrow with the name of the azo component. For example, in order to use this method to depict the dye obtained by combination of the diazotized n-nitroaniline with 2-naphthol, it is necessary to write:

n-nitroaniline → 2-naphthol

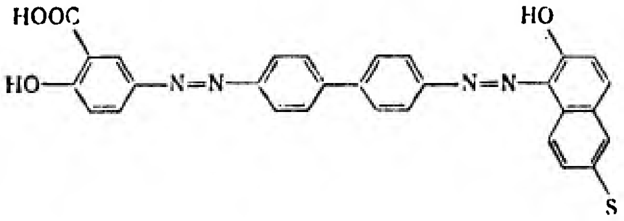
If, as will be apparent from what follows, it is possible to obtain different dyes when using the same azo component in acid or alkaline media, then (a) and (al) respectively are written above the arrow. Finally, if the order of nitrogen coupling is, as is often the case, of substantial significance, then the numbers 1, 2, 3, etc. corresponding to the order of occurrence of the nitrogen coupling reaction, are placed above the arrow along with these letters. By way of example we shall show a diazo dye obtained from H-acid by serial combination with diazotized n-nitroaniline in an acid medium and with diazotized sulfanilic acid in an alkaline medium. Such a dye having the formula[1]



can be written in the following simplified form:

n-nitroaniline $\xrightarrow{1\ (a)}$ H-acid $\xleftarrow{2\ (al)}$ sulfanilic acid

The dye obtained by combining bisdiazotized benzidine with salicin acid and Schaffer's acid, which has the structure:



should be written thus:

salicin acid $\xleftarrow{1}$ benzidine $\xrightarrow{2}$ Schaffer's acid

The history of the creation of the class of azo dyes begins with the remarkable discovery of aromatic diazo compounds by Peter Griess in 1858. Having successfully used picramic acid for a reaction with nitrogen oxides [2], he obtained a new substance which proved to be a diazo compound, in fact one of the most stable. He was successful in extending this reaction to a large number of amines. Assuming that two atoms were replacing two hydrogen atoms in the benzene ring, Griess called this class of compounds the diazo compounds [3]. His extensive study of the new class of compounds unwittingly eclipsed the work

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[1] S here and from now on stands for the sulfo group, combined with the aromatic ring.

of Mene [4] which was published in 1861 and in which, independently of Griess, he describes the derivation of diazo compounds. Griess's method, the passing of nitrogen oxides obtained from the reduction of nitric acid by starch, through an alcohol solution of an amine salt, was soon replaced by the simpler action of sodium nitrate in an acidic medium. The honor of discovering diazo-amine compounds belongs to Mene. He obtained diazo-amine benzol and the first azo dye from it, amino-azo benzol (aniline yellow), though without separating the diazotization and nitrogen coupling phases. The derivation of the first azo dye in two stages was achieved by Caro and White in 1875. In 1879, Nitskiy obtained the first diazo dye (Biebrich scarlet). In 1894 Boettiger synthesized a dye (Congo red) capable of dyeing cotton without any preliminary treatment (substantive or direct dyeing). In 1911 the azotols (AS naphthols) were synthesized, because of which so-called cold or ice dyeing (obtaining the azo pigments in the fiber) began to develop rapidly.

Somewhat earlier the chromizing dyes were discovered (now called "chrome"), which in the ortho position contain hydroxy groups on the azo group. This approach was developed and led to the discovery of azo dyes in 1912 - 1914 capable of complexing with copper salts, which significantly increased their durability and made it possible in a number of cases to dye protein fiber from a neutral bath.

In 1921 Kavel in Switzerland discovered the group of difficultly soluble dyes given the designation dispersed, and capable of dyeing acetate silk.

It is impossible to overestimate the importance of the creation of dyes in 1952 - 1956 containing a residue of cyanur chloride or another similar to it, leading to the synthesis of active dyes formed when coloring the covalent bond with the substrate — with a plant, protein or artificial and synthetic fiber [6]. These dyes possess exceptional durability and brilliance of hue. Along with the new methods, the old continued to develop, for example the ice coloring processes, and preparations were created which were mixtures of the diazo compounds and azo components prepared beforehand which facilitate the work of the dye chemist.

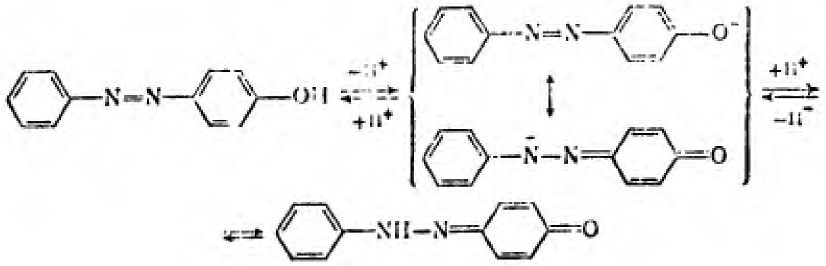
* * *

The structure of azo dyes, in spite of the apparent simplicity, caused at that time [7] and sometimes even now some discussion. The fact is that the same azo dye can sometimes be derived in various ways. Thus, Zincke showed [8] that the combination of diazotized aniline with 1-naphthol can yield hydrazone just as the action of phenyl hydrazine on 1,4-naphthoquinone. However, if we work solely from the structure of the raw materials and base the final product structure on it — a method which is very productive and widely used in organic chemistry — it should be expected that we will obtain two products, and not one as is observed in reality. The attempt was made to establish its structure by purely chemical means. Thus, methyl esters were obtained from the action of methylating media, which confirmed the azo structure of the product. However, during the action of 2,4 dinitrophenylhydrazine or semicarbazide, typical derivative ketones were obtained which confirmed the hydrazone structure of the substance being studied.

Paskal [9] first advanced the idea of equilibrium between the two forms. Later, Hantzsch and his co-workers [10] formulated the position on the azo-quinohydrazone tautomer of the hydroxy azo dyes with a rapidly established equilibrium.

In order to study this indicated tautomer equilibrium, the absorption spectra of benzolazonaphthol [11, 12] and other compounds [13], which were compared with the spectra of fixed forms (with alkylated or acylated derivatives of azo and hydrazo-compounds) were employed. This comparison showed the dependence of the position of tautomer equilibrium on the nature of the solvent: thus, in pyridine and alcohol equilibrium shifts to the side of the azo form, and in nitrobenzol, to the side of the quinohydrazone form. Additionally, the absorption spectra of para-hydroxy azo dyes were compared with the meta-hydroxy derivatives, for which the formation of the quinohydrazone form is structurally impossible. These latter were obtained in an indirect manner. As was to be expected, the meta-isomers possessed absorption spectra similar to the spectra of azo dyes in alcohol or pyridine [13, 14] solutions.

Para-hydroxy azo dyes dissociate in alkaline media with the formation of an ion having balanced bonds common for both tautomers:



The structure of the ortho-azo dyes is more complex than their para-isomers, and some reactions in this series occur in a unique fashion. Thus, the acidic characteristics of these dyes are greatly reduced. Their absorption spectra have an expressed similarity with the corresponding fixed form of quinohydrazone [15].

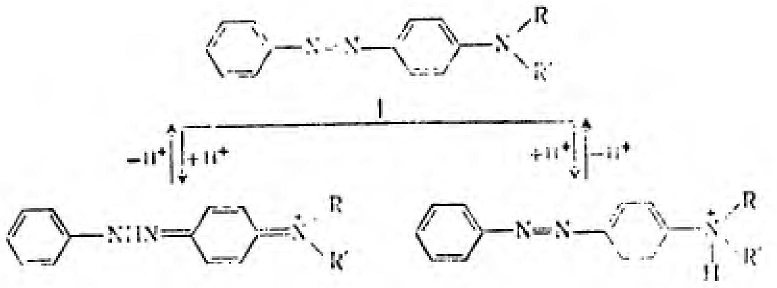
As early as 1900, Bamberger discovered [16] that ortho-hydroxy azo dyes form complex compounds with copper salts capable of dissolving in non-polar solvents, and yielding brightly colored melts, typical of complex compounds.

This property of ortho-hydroxy azo compounds was later widely employed in industry to derive durable metal-containing dyes.

All of these features forced the positing of the presence of a hydrogen bond in ortho-hydroxy azo dyes. At the same time, just as the para-isomers they were capable of realizing the tautomer. Thus, spectral investigations of 2-phenylazophenol [12] and sulfonated o-phenylazonaphthols [17] indicated that the azo compounds are first, and the quinohydrazone second. Both this and other isomers have sharply pronounced hydrogen bonds which determine their reduced acidity, the characteristics of the fusion temperatures and other properties (in particular, the absence of the characteristic hydroxy group frequencies in the infrared region of the spectrum). The difficulty, and sometimes even the impossibility of chemically separating the tautomers is likewise explained by the presence of a hydrogen bond.

As far as the structure of amino-azo dyes is concerned, in the opinion of Martinoff [18] they always exist in the azideform, although to deny the possibility of an azo-quinonehydrazone tautomer for them is hardly possible.

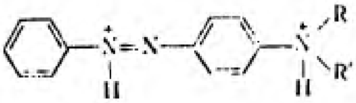
The para-amino-azo dyes during interaction with acids are capable of attaching a proton to nitrogen of the amino or azo group, forming two tautomers, for example:



I

II

Tautomer (I) is more deeply colored (the absorption lies around 520 nm) than tautomer (II) (320 nm) and the original proton-less dye (450 nm) [19]. The application of similar dyes as indicators is based on the depth of dyeing during proton attachment. The attachment of a second proton to the proton-less nitrogen atom leads to the formation of a doubly charged ion



colored approximately the same as the original dye (440–460 nm).

The question of the spatial structure of the azo dye molecules was likewise subjected to comprehensive experimental study. Hartley [20] in studying the solubility of azobenzol discovered its second modification. The second modification has a dipole moment [21] and for this reason a cis-isomer structure is attributed to it. Later, the cis-configuration of azobenzene was demonstrated by crystallographic analysis [22]. Success has likewise been met in revealing cis-isomers for several substituted azobenzenes and azonaphthalenes [23].

In the majority of commercial azo dyes which are predominantly derivatives of the ortho series, the trans-configuration is fixed by a hydrogen bond and the detection of a second isomer is not possible. For dispersion dyes, derivatives of 4-aminoazobenzene, the phenomenon of phototropism following dyeing of an acetate fiber is well known. This is probably connected with the transformation of the trans-isomer into an unstable cis-isomer [24]. The original color of the fiber quickly returns when the sample is placed in the dark (the dark effect) [25].

DIAZO COMPOUNDS

DIAZOTIZATION

Aromatic Amines

The reaction for the diazotization of amines is one of the most complex in organic chemistry. Owing to instability, the resulting diazo compounds are separable only with difficulty. Even if this is successfully done, the ease of various transformations which the diazo compounds are capable of, does not permit any certainty in the fact that the separated substance has the same structure as the product formed during diazotization.

The method usually employed for diazotization consists of treating an amine dissolved in an aqueous mineral acid, with nitrates of alkaline metals at low temperatures. The amount of mineral acid, in accordance with the general equation for diazotization

$$ArNH_2 + NaNO_2 + 2HCl \longrightarrow ArN_2Cl + NaCl + 2H_2O$$

should be equal to two equivalents. However, for a smooth reaction an excess of 0.2 – 1 equivalent is necessary, depending on the concentration, in order that at the end of the reaction the magnitude of the pH of the reaction mass does not exceed 0.5 – 1.5. In the absence of pH meters, the acidity of the reaction mass is controlled using Congo paper (a clear-cut reaction should be observed). This condition is necessary so that the ammonia $\rightleftharpoons$ amine ion equilibrium is not displaced to the side of the free amine (although as we will see below, just it and not its salt has the capability of diazotization) because of its lower solubility in water. Additionally, the lowering of the pH values has a beneficial influence on the formation of the most active particles taking part in the reaction with amine (see below). Finally, the acid medium clearly does not permit the resulting diazo compound to react with the remaining amine in the reaction mass and form side products — diazo amino compounds or amino azo compounds. However, there are no general rules for the concentration and quantity of mineral acid used for the diazotization reaction. During the diazotization of weakly basic amines, taking into account the equilibrium between aryl ammonia and free amine greater quantities of mineral acid are required than for the diazotization of strongly basic amines for the reasons given above. For example, during the diazotization of n-nitroaniline (a very weak base) an increased concentration of hydrochloric acid is recommended in order to avoid severe hydrolysis of the amine salt.

As far as the nitrates of alkaline metals are concerned, they are used in strictly controlled amounts. Both an excess and a deficiency of nitrous acid has a quite detrimental effect on the stability of the resultant diazo compound. For this reason, it is carefully regulated during diazotization and as soon as it is revealed that it is present in the solution, the feed of the aqueous nitrate solution is shut off.

Control is accomplished using either iodine starch paper or with special indicators -- metanil yellow or a sulfone reagent [26] which yields weakly colored solutions with nitrous acid. For continuous content control of the free nitrous acid in the reaction mass both in industry and in the laboratory, it is convenient to measure the oxidation - reduction potential of the system using a platinum indicating electrode paired with a calomel (or chlorine silver) comparison electrode. Changes in the potential of the medium are determined by a redox meter and make it possible to come to a conclusion concerning the presence of absence of nitrous acid in the reaction mass [27].

If a small excess of nitrous acid remains in the reaction solution following diazotization, it is destroyed by introducing a substance into the solution which reacts easily with nitrous acid. Such substances are urea, or better, sulfamic acid (the acid amide of sulfuric acid) [28]. The low reaction temperature (0° C and below) is usually maintained by the addition of ice to the reaction mass, or with a cooling brine through the jacket of the apparatus.

The method described above which was proposed by Martins was termed direct. As is apparent from the preceding, the diazotization conditions depend to a significant extent on the solubility of the amines in an acid solution, which is related to the basic properties of the latter.

For amine salts which are poorly soluble in water, for example, for sulfanilic, naphthionic, and aminobenzoic acids, as well as for some other weakly basic amines, the so-called indirect method is employed, in which a mixture of alkaline salts of nitrous acid and the aminosulfo acid or aminocarboxylic acid to be azotized is poured into well cooled mineral acid. The latter is displaced from nitrous acid nitrites which diazotize the free amine found in the solution (in equilibrium with the salt). For effecting diazotization of poorly soluble amines, the use of dispergators from the class of cation active booster agents is recommended, in particular SN Sapamine [30], occurring as the oleate of acylated asymmetrical diethylethylenediamine:

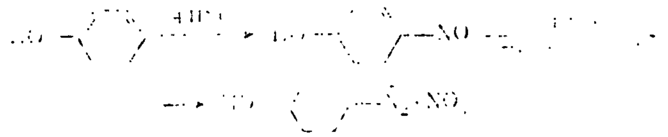
$$C_{17}H_{33}CONHCH_2CH_2N(C_2H_5)_2 \cdot HCl$$

Amines which oxidize easily under normal conditions are diazotized in a weakly acid medium with the addition of copper or zinc salts [31]. The ions of the metals in forming complex compounds with the original compounds (for example, with the aminonaphthols), protect the amine from the oxidizing action of nitrous acid and in this way promote a smooth course for the diazotization reaction.

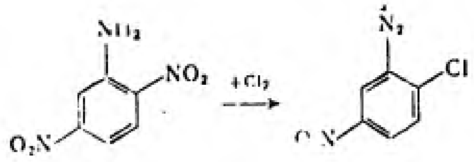
With a reduction in the basicity of the diazo components, it becomes more difficult to carry out diazotization in aqueous solutions. During the diazotization of very weakly basic amines, it is recommended that the reaction be conducted in concentrated acids, utilizing them as solvents. Concentrated sulfuric or acetic acid is used more frequently than the others. A 90 - 95% concentration of sulfuric acid appears to be optimum for the dissolution of sodium nitrite without a noticeable generation of nitrogen oxides [32]. In a solution prepared in this fashion, the amine to be diazotized is introduced slowly while mixing well, and during which the temperature increases to 30 - 40° C. Nitrosylsulfuric acid is employed in a number of cases for diazotization [33, 34, 35].

Griess's method noted above was modified by Knoevenagel [36], who used alkyl nitrites instead of "gaseous nitrous acid." This method is used even to this day in laboratory practice if precipitate salts of the diazo compounds are desired. Hantzsch determined that the alcohol used as a solvent in this case can be replaced by iced acetic acid [37].

Such are the primary methods of diazotizing the aromatic amines. Besides the diazotization of amines, some other means of forming diazo groups are also described. When phenol or phenolsulfo acids are treated with an excess of nitrous acid, the nitrate of hydroxyphenyldiazonium is formed, for example:



Bergstrom and Buehler [39] observed the formation of benzene-1-azonaphthol during the action of sodium amide on a mixture of nitrobenzene and 2-naphthol in liquid ammonia. Under these conditions, the nitrobenzene is apparently transformed into a diazo compound, coupled to naphthol. During the action of chlorine in hydrochloric acid on 2,5-dinitroaniline it is possible to observe the formation of the diazo compound 2,5-chlorine nitrophenyldiazonium as a consequence of the reaction of nucleophilic substitution of chlorine for the ortho-nitro group with the generation of nitrous acid which diazotizes the amino group [40]:



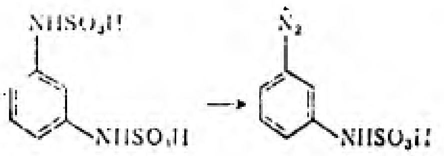
Aromatic Diamines

One benzene ring cannot contain more than two diazo groups [41]. Attempts to introduce a third diazo group lead to the destruction of the benzene ring. In other words, if amino groups are found in various rings of a complex aromatic compound (for example, any kind kind of polyazo dye). In this case it is possible to obtain polydiazo compounds. Only the bis-diazo compounds are of any great practical significance.

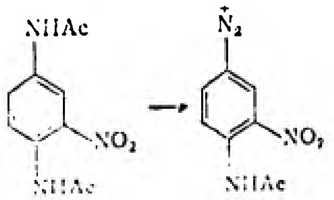
For the case of symmetrical diazo components of the benzidine type, the diazotization of both groups takes place at the same rate, so that rarely is one successful in remaining at the stage of amino-diazo compounds, but rather the bis-diazo compound is formed immediately.

The methods for obtaining mono-diazotized diamines of the benzidine, 1,5 diaminoanthraquinone, diaminostilbenedisulfo acid and other types lead to the conclusion that the bis-diazotized diamine is forced to react with the free diamine [42]. During this, the transfer of a diazo group from a molecule having two such groups to a molecule which does not have even one, takes place via an intermediate stage of diazo amino combination. The nature of the diazo group transfer will be dealt with below. If it is possible to protect one of the amino groups with an acyl radical, then the diazotization of the second amino group and the consequent hydrolysis in an acid medium yields the mono-diazotized diamine [43].

In some cases, mono-diazotization can be achieved by treating the diacylic diamine derivative with nitrous acid. For example, in the diazotization of N,N'-disulfo acid m-phenylenediamine and its analogs, one of the sulfo groups splits off and the resulting amine diazotizes [44]:



In all probability this reaction should be looked upon as a trans-acylation reaction, in which the sulfuric acid radical is replaced by the radical of the nitrous - nitrose group; the resulting nitrosamine is further transformed into the diazonium salt. In a similar fashion, certain aryl nitroamines $ArNHNO_2$ split off the nitro group during diazotation, in being transformed into diazo compounds [45]. An interesting example in which one of the acetyl groups is split off is the diazotization of nitrodiacetyl-n-phenylenediamine. The acetyl group, located in the meta-position with respect to the nitro group, splits off during the reaction [46]:



Here the trans-acylation of a more basic amino group takes place. The second acetyl group, located in the less basic amino group, (in the ortho-position with respect to the nitro group), remains untouched.

The diazotization of m-phenylenediamine leads to the formation of mono- and bis- diazo compounds, as well as products of the interaction of diazo compounds with the original diamine. n-phenylenediamine under usual conditions forms a mono-diazo compound; a bis-diazo compound can also be obtained in a strongly acid medium.

As far as the diamines are concerned, in which the amino group possesses different basic properties, the mono-diazotization of such compounds does not present any particular difficulty. Amino diazo compounds are easily formed from the following diamines: 2,5-diaminobenzoic acid [47], nitro-n-phenylene diamine [48], 1,4-diaminonaphthalene-3-sulfoacid, 4,4'-diaminobenzeneazonaphthalene [49] and others. In all of these cases, the more basic amino group (located in the meta-position with respect to the electron accepting substitute or, in the last example, located in the benzene ring) is more easily diazotized by the second. This again confirms the fact that diazotization is (in the first stage) an acylation reaction, since it obeys analogous rules.

The derivation of bis-diazo compounds from diamines is not complicated. However, in this case there are also pecularities which have to be taken into account. During bis-diazotization, ortho-diamines are transformed into internal diazoamino compounds -- azimines, substances which are very stable and are not decomposed by the action of mineral acids [50]. For this reason, the usual method is incapable of yielding bis-diazo compounds from o-diamines. However, Hodgson proposed carrying out diazotization in iced acetic acid with nitrosylsulfuric acid [51]. A bis-diazo compound was not separated from the o-phenylenediamine. However, this compound diazotizes and both diazonium groups can, according to Sandmeyer, be replaced by iodine. As far as the diamines of the diphenyl, stilbene, naphthalene and anthraquinone series are concerned, their bis-diazotization is carried out with one or the other variant rather easily. In these cases, it is possible to use both the direct [52] and the indirect [53] methods.

The Diazotization Reaction Mechanism

Although in the final analysis treatment with nitrous acid actually leads to the formation of diazo compounds, the first stage of this process is the introduction of an aromatic amine of the nitroso group into the amino group, i.e. a nitrosation reaction. In principle, this reaction is no different than the nitrosation of secondary aliphatic-aromatic amines and belongs to the class of reactions of amine acylation, i.e. the introduction of an acid radical, in this case nitrous. Only the pecularities in the properties of aromatic diazo compounds force the investigator to distinguish the nitrosation reaction of secondary amines from the diazotization of primary ones, drawing a sharp line between them. No one calls the nitrosamine of a secondary aliphatic-aromatic amine a diazo compound, while the nitrosamine derived from the primary amine is numbered among them. Here it is useful to enumerate those compunds which are accepted as diazo compounds. These are first of all, nitrosamine obtained as the first stage in the diazotization reaction; diazohydrate, appearing as we will see later as the tautomer of nitrosamine, their ions which bear the name diazotates; and finally, the diazonium salt:

$ArNHNO$	$ArN{=}NOH$	ArN_2O^-	ArN_2^+
nitrosamine	diazohydrate	diazotate ion	ion of diazonium salt

The following capabilities of all of these particles comprise that set of characteristics which is generally ascribed to aromatic diazo compounds: to quickly change into one another during changes in internal conditions (for example, during a change in the pH of the medium, heating, etc.); to exist simultaneously in solution; some are capable of stereoisomerism, in a word, their unusual variability along with instability. Bamberger was the first to consider that diazotization begins with the formation of nitrosamine, however, direct experimental confirmation of this hypothesis using kinetic methods was accomplished only a relatively short time ago by Ridd [55].

The course of the reaction in an acid medium gives evidence of the fact that an amine salt diazotizes, and it would seem, precludes the possibility of diazotization of the free amine. However, if it is remembered that even in a quite concentrated acid there is always equilibrium between the aryl ammonia ion and the free amine, then the hypothesis that the free amine undergoes nitrosation is not unexpected. Based on various considerations, independently of one another Maki [56], Filippychev [57], Kenner [58], A. E. Poray-Koshits [59], and B. A. Poray-Koshits [60] all came to such a conclusion, though the correctness of the latter was demonstrated by kinetic methods only in 1958 by Hughes, Ingold and

Ridd [61][1].

Insofar as during nitrosation electrophilic substitution of hydrogen takes place, the nitrosating carries a positive charge or a sharply expressed tendency towards it. Taking into account the entire series of equilibria existing in the system, it is possible to lay out all possible nitrosating agents according to their strength in the following order:

nitrose ion > nitrosacidium ion > nitrogen trioxide > nitrous acid

The halogen nitrosyls HalNO [Subscript illegible - translator's note] stand somewhat apart and occupy a position based on their activity in a series with the nitrosacidium, but which are formed only in hydrogen halide acid media. Experimental evidence for the justification of this series was found by Hammett [62], Ingold [63] and others.

The least active nitrosating substance is undissociated nitrous acid, which was previously considered the sole diazotizing particle.

The presence of diverse nitrosating agents in the reaction medium significantly complicates the processes taking place during interaction with the primary amine. Under different conditions the concentrations of active particles change, and one or the other of them becomes the main one, but not the only one taking part in the reaction. The numerous kinetic investigations of Hantzsch [64] which established the second order reaction in comparitively weakly acid solutions, and Schmid [65] who obtained the relationship for the third stage

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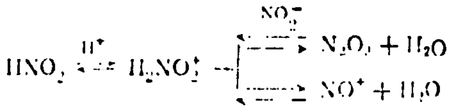
[1] At the present time the possibility of some aryl ammonia salts is admitted (I. H. Ridd et al., J. Chem. Soc. 1966, 533; 1967, 273) [Editor's note].

during an increase in the mineral acid concentration, are in agreement with such a view. Apparently there is some reason behind distinguishing between diazotization in the presence of sulfuric acid which promotes the transformation of nitrous acid into nitrogen trioxide, and in the presence of hydrogen halide acids which lead to the generation of halogen nitrosyls in the medium. The following diagram can represent the transformations of nitrous acid in acid media:

in a sulfuric acid medium



$$HNO_2 \xrightleftharpoons{H^+} H_2NO_2^+ \longrightarrow \begin{cases} \xrightleftharpoons{NO_2^-} N_2O_3 + H_2O \\ \rightleftharpoons NO^+ + H_2O \end{cases}$$

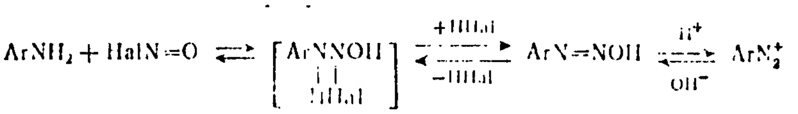
in a medium of hydrogen halide acids

$$HNO_2 \xrightleftharpoons{H^+} H_2NO_2^+ \xrightleftharpoons{HHal} HalNO + H_2O$$

We see in these diagrams that the active nitrosating particle $H_2NO_2^+$ is formed in sulfuric acid which easily generates the nitrose cation, which is indispensable as an electrophilic agent. Halogen nitrosyl with a strongly polarized bond $-\overset{+}{N}\!=\!\bar{O}$, , appears in the hydrogen halide acid medium which also leads to the occurrence of electrophilic particles in the medium.

It seems that in the interaction of nitrose with the base of the aromatic amine, a nitrose ammonium ion should appear. For this, nitrosamine should be at least a little basic. It has been shown by B. A. Poray-Koshits [66] that the basic properties of nitrosamine are extraordinarily low. Thus, if the nitrose ammonium ion is formed (for example, Tsollinger adheres to such a view [67]), then under the reaction conditions it should quickly hydrolyze. Consequently, it should be considered a quasi-stationary intermediate stage of the reaction.

As far as the diazotization in a medium of hydrogen halide acids is concerned, apparently the first reaction product is a complicated addition complex of an amine to the halogen nitrosyl which further is transformed into the diazonium salt:



$$ArNH_2 + HalN{=}O \rightleftarrows \left[\begin{array}{c} ArNNOH \\ |\;\;| \\ H\,Hal \end{array}\right] \underset{-HHal}{\overset{+HHal}{\rightleftarrows}} ArN{=}NOH \underset{OH^-}{\overset{H^+}{\rightleftarrows}} ArN_2^+$$

It has been noted that diazotization proceeds more quickly in hydrochloric acid in many cases [69], than in sulfuric acid, while in the presence of bromine anions it is some ten times faster than in the presence of chlorine anions. Thus on the face of the matter. we have the catalysis of halide ions during the nitrosation reaction. The fact of the matter is probably that a very active nitrosating agent, halogen nitrosyl, is formed in the reaction medium. It has been proposed that this catalysis be utilized in practice by adding hydrobromic salts, most frequently ammonium or postassium bromide [70], to the solution during diazotization. An interesting effect is observed druing diazotization in very dilute solutions (for example, during the titrimetric determination of amines using nitrites), where the addition of hydrobromic salts sometimes determines the possibility of the reaction occurring at all.

The transformation of nitrosamine into the diazonium salt is in general rather clear. Nitrosamine undergoes tautomeric transformation into the diazohydrate which has amphoteric properties [71]. The latter instantly reacts with the mineral acid to form the salt:

$$ArNHNO \rightleftarrows ArN{=}NOH \xrightarrow[-H_2O]{+H^+} ArN_2^+$$

The mechanism of this conversion will be considered in detail later.

The reaction equations given above for diazotization (nitrosation) of primary aromatic amines are apparently not the only ones describing the course of the reaction, since the reaction mixture is a complex system of equilibria in which many diazotizing agents participate, reacting at different rates and forming various intermediate substances. For this reason, the equations given above represent only the important reaction courses, not excluding the secondary ones.

The Structure of Diazo Compounds

As has been stated above, owing to the variability and instability of the aromatic diazo compounds, it is very difficult to determine their structure. For some time it has occasioned sharp arguments and discussions. At the present time, the fundamental questions of the structure of diazo compounds and the principles according to which they change are clear. However, there are some forms of diazo compounds, of whose existence and structure contemporary organic and physical chemists are difficult to convince, since up to now they have not been isolated, and even their existence can be determined only by indirect data, sometimes admitting of two interpretations.

To be distinguished from among the diazo compounds are first of all the salts of the diazo compounds having the general formula ArN_2^+X, in which the diazonium cation is the proton-less Lewis acid. Hundreds of representatives of diazonium salts have been isolated and studied.

The base, coupled to the diazonium cation, which results from its interaction with the first hydroxyl, is the diazohydrate ArN=NOH. Not one representative of the diazohydrates has been isolated up to now. We will determine the reason for this below. Owing to acidic properties, the diazohydrate is capable of reacting with the secondary hydroxyl, with the removal of a proton and the transformation into the so-called syn-diazotate. Syn-diazotates of alkaline metals can be isolated. Equilibrium between the diazonium cation and the syn-diazotate is reached practically instantaneously. For this reason, syn-diazotate is to be considered a conjugate base of the diazoniumcation arising during its complete neutralization. Establishing the thin structure of the diazotate ion, following the solution of problems connected with the structure of the diazonium cation [71, 72, 73], has been given first priority at the present time.

The tautomeric diazohydrate nitrosamine ArNHNO which is formed as noted above in the first stage of the diazotization of aromatic amines, can be successfully isolated (acidification of the anti-diazotate) and studied in detail in a number of cases.

It is impossible not to mention the so-called diazonium hydroxide which Hantzsch [74] unsuccessfully attempted to derive by the action of damp silver oxide on diazonium chloride. At the present time, it is clear that such an interaction will only lead to the formation of two ions in the solution: the diazonium cation and the hydroxyl ion. These ions rapidly react with one another.

Diazonium Salts

The separation of diazonium salts from solutions is of great technical significance. The nature of the anion is a decisive factor in the stability of the salts obtained. Strong acids make it possible to obtain relatively stable preparations in a number of cases, which can be separated and preserved. Particularly reliable are the salts of aryl sulfoacids which are usually obtained by adding the sulfoacids or their salts to concentrated solutions of diazonium chloride.

At low pH values of the medium, the resulting salts are easily separated from the solution. It is possible to filter them out and dry them at elevated temperatures. They do not melt, but only carbonize, are quite soluble in water and their solutions are also stable. On the other hand, isolated incidents involving explosions of the solid salts are known. Saunders feels that their stability in the solid state is explained by the fact that they are not ionized [75]. However, it has been difficult up to now to prove that these salts are completely ionized [76].

There are indications in the literature [77] that the addition of certain sulfo acids to solutions of diazo compounds stabilizes these solutions. It is impossible to hypothesize the presence of non-ionized forms in the solution. Zollinger [78] believes that the aromatic rings of sulfo acids form π-complexes of diazo compounds with the aromatic rings, which are more stable than the usual diazonium salts. The bond between the diazonium and the sulfo group remains purely ionic in this case. Additionally, the introduction of sulfo acids into the solutions can change the pH value, and as is well known, the stability of the diazonium salts depends on the latter [79].

There have been very many proposals for sulfo acids: α- and β-naphthalene sulfo acids [80], disulfo acids of naphthalene [81,82], nitrobenzene sulfo acids, sulfocarbonic acids, acetylsulfanilic acid, sulfo acids and their anthracene derivatives, and many others described in the monograph of Holzach [83].

The salts consisting of a diazonium cation and any other complex anion are of great practical significance. The ability of diazonium salts to form double salts with the halogen metals was known even to Griess [84]. He prepared a double complex salt, diazonium chloride, with stannic chloride of the composition $C_6H_5\overset{+}{N_2} \cdot Sn\overset{-}{Cl_5}$.

The development of methods for deriving diazonium salts with complex anions has occupied many scientists. There have been described complex diazonium salts with arsenous chloride, ferric chloride, antimony chloride, boron trifluoride, iron cyanide and with the salts of cobalt, chrome, tin, lead, cadmium, mercury, copper, silver, gold and platinum. Complex salts with zinc chloride are of particularly great significance. They are obtained by the addition of a zinc chloride solution and aqueous hydrochloric acid solution of diazonium and are easily extracted from the solutions with high yields.

X-ray structural analysis of the crystals of diazonium salts have shown [86] that the anion is located approximately at a distance of 3.2 Å from the diazonium group, thus a bit closer to the end nitrogen atom than to the nitrogen bound directly to the ring. This gives evidence that both nitrogen atoms carry positive charges. The latter is quite important for an understanding of the reactivity of diazonium cations.

The effective radii of the anions and the nitrogen atoms overlap, although to a quite insignificant degree, but nonetheless apparently sufficiently so that the bond between the anion and the cation in remaining ionic somewhat changes its character depending on the properties of the anion. It is probably in this fact that the reason for the difference in the properties of various salts of the same diazonium is to be found: their thermal stability, coloring, etc.

X-ray structural analysis provides confirmation of the fact that the diazonium cation takes the form of a plane system with linearly distributed nitrogen atoms in the plane of the ring. The anion is located along one side of the plane of the organic ion. Figure 1 gives a visual presentation of the spatial structure of the salt of phenyl diazonium.

We note that the structure, outside of which the anion is located in the plane of the aromatic ring and the two nitrogen atoms, makes it possible to understand the formation of spatial isomers when the covalent bond between the end nitrogen atoms and the nucleophilic agent is completed.

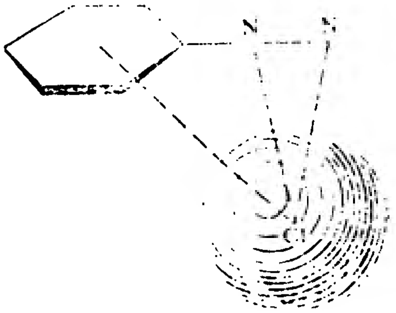
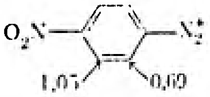


Рис. 1

Figure 1

As a substitute for the aromatic ring, the diazonium group is strongly electron acceptor in nature. Its electron acceptance significantly exceeds such a nitro group.

Reactions have been described in which the nitro group, located in the ortho-position with respect to the diazonium group, is easily replaced by chlorine, the hydroxyl, etc. [87]. The aromatic induction constants σ° for the n-nitro and diazonium groups are equal to 0.89 [88] and 1.86 [89] respectively. It follows from this that the diazonium group is approximately two times stronger than the nitro group as an electron acceptor substitute. Data obtained recently for nuclear magnetic resonance [89] lead to the same conclusions. According to this data the values of electron screening which characterize the reduction in the density of the electron cloud as a result of the electron attraction effect of the nitro and diazonium groups located in the para-position with respect to each other, are 1.05 and 0.69 respectively. This can be illustrated by the following diagram:



In the non-substituted benzene ring these values are equal to 2.72.

It follows from this that in n-nitrophenyldiazonium, the electron cloud is drawn off to the diazonium group, which results in a positive charge and facilitates the nucleophilic substitution of the nitro group by hydroxyl, chlorine, etc. in the para-position of the carbon atom bound to the nitro group.

As far as the bond between both nitrogen atoms is concerned, it has now been established by various methods [71,72,73] that it approaches a triple, where this triple bondedness does not greatly depend on that anion with which the cation is bound. Even in quinonediazides (see below), judging by the infrared spectra, it is not greatly displaced towards the double side. Attention here should be given to the fact that according to the data from x-ray analysis, the positive charge is distributed approximately equally between the two nitrogen atoms. On the other hand, working from the triple bondedness of the latter, the positive charge should be concentrated at the first nitrogen atom. To explain this apparent contradiction, it is possible to introduce the following considerations [89]. Of the three bonds between the nitrogen atoms which are in the sp-hybridization state, only one π-bond whose plane of electron oscillation coincides with the plane of the π-electron clouds of the aromatic ring, is capable of transmitting the coupling. Due to the presence of this bond, a conjugate is realized between the aromatic ring with all of the substitutes existing in it and the end nitrogen atom. This coupling, as can be seen from infrared spectroscopy data, can have a greater or lesser influence on the bond between both nitrogen atoms, either bringing it nearer or conversely, separating it from the purely triple bond.

The second π-bond which is not located in the plane of the π-electron clouds of the aromatic ring, and equally as a third of the σ-bond, can transmit only the induction effect of the positively charged nitrogen atom to the end nitrogen atom carrying as a consequence of this a constant positive charge also.

It is very difficult for the considerations introduced above to reflect in one structural formula the diazonium cation. This formula should reflect the triple bondedness of the nitrogen atoms, the presence of coupling between the aromatic ring and the end nitrogen atom and, finally the positive charge on both nitrogen atoms. It seems that the formula given below reflects the enumerated properties to some extent[1]: 

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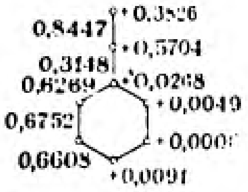
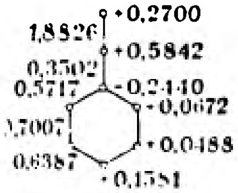
[1] At the present time, quantum-mechanical calculations have been carried out which confirm these qualitative judgments on the structure of the diazonium cation. The calculation data based on the MOKh and SSP-PPP methods [expansion unknown - translator's note] are shown in the following molecular diagrams:



I



II

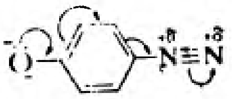
I — MOKh method, D. A. Bochvar, N. P. Gambaryan, V. V. Mishchenko, L. A. Kazitsyna, Proceedings of the Academy of Sciences of the U.S.S.R., 175, 829 (1967); II — SSP-PPP method, V. M. Treyger, I. L. Bagal, B. A. Poray-Koshits, Journal of Organic Chemistry, VI, no. 12, 2535 (1970) (editor's note).

Three bonds are depicted between both nitrogen atoms in this formula. One of them is the actual π-bond capable of effecting coupling between the end nitrogen atom and the aromatic ring, which is pictured with a bent arrow. This coupling, independently of the substitutes in the ring, always leads to a reduction of the positive charge existing at the terminal nitrogen atom. A positive charge on the terminal nitrogen atom arises as a consequence of the constant induction influence of the positively charged nitrogen atom which is directly bound to the aromatic ring. This is reflected in the formula by arrows between the nitrogen atoms. The formula also helps us to understand the influence of the substitutes located in para and ortho–positions on the aromatic ring. If this is an electron acceptor substitute, then the positive charge on the end nitrogen atom is reduced to only the most minimal degree (by only as much as the aromatic induction constant of the diazonium group exceeds that of any electron acceptor substitute) and a similar diazonium salt should be a very active electronophilic reagent (for example, in the nitrogen coupling reaction). On the other hand, an electron donor substitute located in the para or ortho-position with respect to the diazonium group, in reducing the constant positive charge on the end nitrogen atom, lowers the electrophilic reaction ability of the diazonium salt.

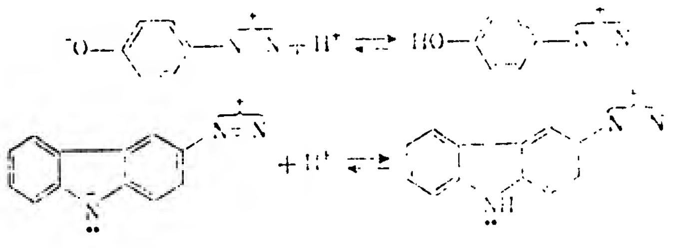
With respect to that noted above, it is impossible not to mention diazonium salts which in the para or ortho–positions with respect to the diazonium group possess electron donor substitutes capable of acidic ionization, – with the hydroxy- or imino group. During the neutralization of diazonium salts, quinonediazides or iminoquinonediazides are obtained from similar compounds, and are internal salts in which the anion serves to ionize the hydroxyl- or imino group. Owing to the clearly expressed electron donor character of these groups, the positive charge of the end nitrogen atom is extinguished to a significant extent. The electrophilic reaction capability of such compounds is reduced because of this, although the capability of nitrogen coupling reactions is still preserved.

As far as the bond between both nitrogen atoms in these compounds is concerned, according to investigations of the infrared spectra it nonetheless approaches a triple bond [71]. The quantum mechanical calculations of the electron density between nitrogen atoms carried out in accordance with the MO LKAO method [expansion unknown - translator's note], in the Khyukkel approximation [90], yield the same conclusion.

Thus, the structure of the quinonediazides and the iminoquinonediazides should reflect the same properties as the usual salts of diazonium: the difference should consist of only the degree of shift of the electron which in the quinonediazides and iminoquinonediazides is greater than in the remaining diazonium salts, for example:



When mineral acid acts on quinonediazides to form oxygen (or correspondingly, nitrogen) a proton is attached and the usual diazonium salt is formed, for example:



Thus, diazonium salts and quinonediazides are bonded together in protolytic relationships.

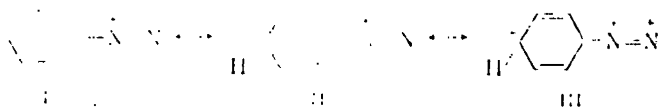
We note that quinonediazides have a considerable practical role as phototropic substances employed in the manufacture of light sensitive papers [91].

The Reactions of Diazonium Salts. Diazo compounds are capable of the most diverse reactions, among them those where nitrogen is liberated from diazo compounds (Zandmeyer's reaction) or reducing processes take place (for example, the transformation into substituted hydrazines) etc. However, the most important are those in which the diazo compounds act as an electrophilic reagent, replacing the hydrogen atom with an aliphatic, aromatic or heterocyclic molecule and in the process of the reaction acquire a covalent azo structure. Various points of view have been advanced concerning the capability of the various forms of a diazo compound to enter into an electrophilic substitution reaction: this ability has been discovered for diazohydrates, sin-diazotates, and for diazonium salts.

Wistar and Bartlett [92] and B. A. Poray-Koshits independently of one another demonstrated by different experimental methods [93] that the only particle capable of a nitrogen coupling reaction is the diazonium cation.

The ability of any diazo compound form to engage in not only a nitrogen coupling reaction but also other reactions in which the diazo compound acts as an electrophilic reagent, is thus connected with the presence of the diazo cation in equilibrium concentrations in the reaction medium. For this reason, in speaking about the activity of diazo compounds, the ability of the corresponding diazonium cations to engage in a nitrogen coupling reaction should be kept in mind. This ability depends first of all on the overall positive charge which the diazocation carries. In other words, it is determined by the strength of the proton-less acid which is the diazonium cation. However, differences in the activity of various diazonium cations also depend from the distribution of electron density within the diazonium cation.

To illustrate this distribution, a set of three valence structures has been used earlier [94]:



the base is the benzoid (I) and two quinoid (II) and (III). Structure (II), which corresponds to the transfer of electron density to the end nitrogen atom, was adduced to explain the properties of diazonium salts with electron donor substitutes in the para position – their reduced reactivity, thermal stability and coloring. Structure (III) corresponds to the transfer of electron density from the diazonium group to the ring. The presence of a positive charge on the end nitrogen atom in this case explains the reason for its reactivity, while the activity of the diazonium cation is determined by the magnitude of the contribution of this structure.

Consequently, structure (III) in which the aromatic ring is an electron accepter, while the diazonium group is a donor, should be excluded from consideration and the differences in reactivity of diazonium salts are to be sought in the differing degrees of extinction of the positive charge of the end nitrogen atom by the electrons of the aromatic ring conjugate with it and with all of the substitutes existing in it.

The stronger the donor properties of the ring with the substitutes are, the more the positive charge is extinguished and the less active the diazonium cation is. On the other hand, the greater the electronegativity of the substitutes in the ring is, the less this charge is extinguished and the more active the diazonium cation is. In summing up what has been said, the following conclusion is to be made: the activity of the diazonium cation depends on the magnitude of the positive charge on the end nitrogen atom, which is determined from the difference between the constant positive charge induced by the neighboring nitrogen atom and the variable negative charge arising because of the coupling between the diazonium group and the ring with various substitutes.

Conant and Peterson [95] in attempting to find a correspondence between the structure and the reactivity of diazonium salts, investigated the nitrogen coupling kinetics in buffer solutions and revealed that the reaction obeys a second order equation.

The first attempt to quantitatively evaluate the activity of substituted phenyldiazoniums was undertaken by Zollinger [96]. He investigated the rate of combination with two azo components of ten diazo compounds and discovered that they correlate with the σ-constants in Hammett's equation [97][1]. These data are in agreement with the views expressed above on the exact structure and activity of diazonium salts.

It is necessary to mention yet another peculiarity, characteristic of the majority of bis-diazo compound reactions (nitrogen coupling, substitution of the diazo group with a hydroxyl group, halogens, reduction to hydrazine derivatives, etc.), which leads to the substitution of the strongly electron accepter diazonium group by either an electron donor or sometimes by a weak electron accepter substitute. Naturally in this case, the influence of this new substitute on the second diazonium group changes sharply, which leads to a significant

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[1] Apart from this, the reactivity of phenyldiazonium in a combination reaction was quantitatively studied in a series of sequential works, for example: L. M. Rozhdestvenskaya, I. L. Bagal, B. A. Poray-Koshits, the reactivity of organic compounds, VI, no 1, 114, no 3, 720 (1969), Tartu. J. Panchartek, V. Sterba, J. Vorlicek, M. Vecera, Coll. Chem. Comm., 33, 894 (1968) (editor's note).

weakening of its activity. This has made it possible to carry out both reactions in stages and was at the base of the method for deriving asymmetrical azo dyes.

Diazohydrates

During the alkalization of diazonium salts it was expected that neutralization of an acid equivalent would lead to addition products of one hydroxyl on the so-called diazohydrates, which should be basic with respect to the original diazonium salt. However, despite all attempts to derive diazohydrates in a manner similar to this, they were unsuccessful.

Bamberger obtained yellow colored compounds which according to the empirical formula were the products from extracting a molecule of water from two diazohydrate molecules [98]. They combine easily with azo components, and with amines yield diazo amine compounds which are explosive. Since they can not only be derived by alkalization, but also by acidification of the diazotate [99], they have been identified as the "diazoanhydride" ArN = NON = NAr.

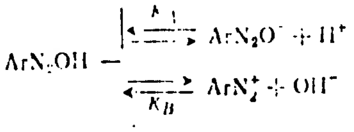
Hantzsch treated diazonium chloride with moist silver oxide [100] and in this way attempted to derive a diazonium base, but obtained solutions of diazo compounds which possessed the same absorption in the ultraviolet portion of the spectrum as the diazonium cation [101]. At the present time it is clear that for these conditions, under which Hantzsch conducted the experiments, the interaction of the hydroxyl with the diazocation did not occur, and the process was limited only by the substitution of the acid anion with the hydroxyl. Morgan and Grist attempted to obtain diazohydrate under special conditions by the acidification of the alkaline salt of a diazo compound [102]. However, as a result of this attempt Bamberger's products were also obtained by the authors — the diazoanhydrides established earlier.

It was demonstrated quite later [103] that the diazoanhydrides are ionic compounds and represent a mixture of the diazonium cation and the diazotate anion which is to be considered as a salt — diazonium diazotate. All the chemical properties and data from potentiometric titration have confirmed this view of their structure.

Relatively recently the reasons have become clear for the lack of success in isolating the diazohydrates. It was initially postulated [104], and thereafter also proven by indirect methods [105] that the diazohydrates are amphoteric compounds. Deciding the acidic or basic properties of diazohydrates is based on the acid-base properties of the diazonium cation and the diazotate anion, i.e. the left and right members in the equation for the neutralization of the diazocation with an alkaline. The diazocation has come to be considered as a strong proton-less Lewis diacid [106]. During the course of its neutralization, an intermediate stage of the formation of the diazohydrate is reached, which is quite easily ionized to a diazotate anion. In this case, it is quite important that the equilibrium constant of the second neutralization stage, K_2, i.e. for the transformation of the diazohydrate into the diazotate anion is much greater than the equilibrium constant of the first stage, K_1, (of the formation of the diazohydrate from the diazonium cation):

$$\mathrm{Ar\overset{+}{N}_2} \underset{\mathrm{OH^-}}{\overset{K_1}{\rightleftharpoons}} \mathrm{ArN_2OH} \underset{\mathrm{OH^-}}{\overset{K_2}{\rightleftharpoons}} \mathrm{ArN_2O^-} \qquad K_2 \gg K_1$$

The diazohydrate is the logically essential stage of neutralization of the diazocation by an alkali. Because of its amphoteric properties, the diazohydrate is capable of both basic K_B and acidic K_A dissociation:



$$ArN_2OH - \begin{cases} \xrightleftharpoons{K_A} ArN_2O^- + H^+ \\ \xrightleftharpoons[K_B]{} ArN_2^+ + OH^- \end{cases}$$

Additionally, it has been shown by Bryuske [105] that if the product $K_A K_B$ is much greater than the ionic water product K_W, then the diazohydrate concentration is insignificantly small, and conversely, for the case of their covariance, the quantity of the latter will likewise be covarient with the quantity of the diazocation and the diazoanion.

The nitrosamines are usually considered along with the diazohydrates in the books and manuals on the chemistry of diazo compounds [107]. Arguments have often taken place about just what a diazohydrate is – is it really that compound which is indicated by this name or is it a nitrosamine ? Hantzsch first advanced the idea that these two compounds are in equilibrium [108]. Since then all investigators have accepted this point of view by incorporating a contemporary concept in it: diazohydrate and nitrosamine are in tautomeric equilibrium. In many handbooks nitrosamine is considered a weakly acid form of a diazo compound and the tautomeric transition of these two compounds has not been and is not now the source of any doubts. Only note has been taken apropos of the extremely rapid proton transitions in this equilibrium [109].

In the work of Ehyges [110], by comparing the absorption spectra in the ultraviolet and infrared ranges (using the MO LKAO method) with spectra of the fixed forms – the alkylated derivatives in which the alkyls are bound either to oxygen or to nitrogen atoms – and by determining the dipole moments of studied nitrosamines it was objectively shown that the acidification products of antidiazotates have the formula of primary nitrosamines ArNHN = 0. It should be emphasized along with this that far from every diazo compound is capable of conversion into a separable one and susceptible to study of the nitrosamine form.

Only the primary nitrosamines are relatively stable and have been separated from n-nitrodiazobenzene, n-benzoyldiazobenzene, n-nitrobenzoyldiazobenzene, polybromo derivatives diazobenzene [111] and several others. Thus, it is clear that relative stability is exhibited only by the primary nitrosamines which contain electron accepter groups in the para or ortho-position. Not one case of the isolation of primary nitrosamines with electron donor groups has been described.

Diazotates

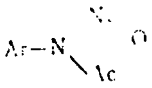
Griess very quickly following his discovery of diazo compounds found that they are capable of transforming into alkaline salts under the action of alkalis [112]. Schraube and Schmidt made the important observation that the alkaline salts of diazo compounds when heated with excesses of concentrated alkalis are capable of changing [113] converting into new compounds which are apparently also diazo compound salts, but which are distinguished by their characteristics from those which Griess synthesized. Griess's salts which Bamberger called normal [114] were in the opinion of the majority of the chemists of that time capable of a nitrogen coupling reaction, are very labile and dissociate easily. Their isolation in solid form presents considerable difficulty, however, Le Fevre and Sousa proposed a few improved methods for deriving them [115] which however did not always lead to the required results.

On the other hand, the first isomeric salts which are called iso-salts are stable and incapable of a nitrogen coupling reaction and are rather easily isolated. Hantzsch in hypothesizing that both salts are stereoisomers, however, did not have direct proof of this and called them sin- and anti-isomers respectively [116]. This name has stuck to them even up to the present time.

In the beginning when the problem of isomerism of these two salt forms was being worked out [117], the discussion centered around the problem of whether the isomeric salts were spatial isomers (Hantzsch) or structural ones. Bamberger defended the latter point of view believing that anti-salts are nitrosamine derivatives, i.e. the metal in them is bound to a nitrogen atom and not the oxygen of the diazohydrate, as Hantzsch supposed.

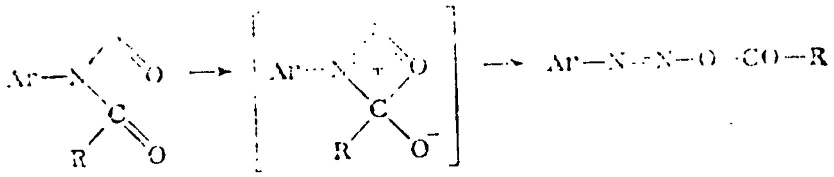
The alkylation of the sodium salt of the diazotate from n-nitroaniline led to the formation of the N-alkyl derivative, and according to the view prevalent at that time was evidence of the nitrosamine structure of the diazotate. However, the alkylation of a silver salt yielded the O-ester. During the alkylation of the anti-diazotate Pechmann and Frobenius obtained nitrosacetanilide [118] which was considered adequate proof of the nitrosamine structure of the diazotate. We now know that the salts of diazo compounds do not have a covalent metal bond with the anion of the acid and consequently, the reactions of these salts can prove nothing in the case of dual reactivity of the anion. As far as the derivation of various derivatives during alkylation is concerned, then the formation of the N- and O- derivatives occurs as a consequence of various mechanisms of these reactions connected with the properties of the resultant metal halide. In the final analysis, Bamberger who was convinced most of all by his own experiments on the oxidation of diazo compound salts [121], accepted Hantzsch's conception.

From the modern point of view it is impossible to accept Hantzsch's theory without criticism and some amendments [120]. B. A. Poray-Koshits and Shaburov [121] spectrally compared the products obtained from the hydrolysis of nitrosacetanilides

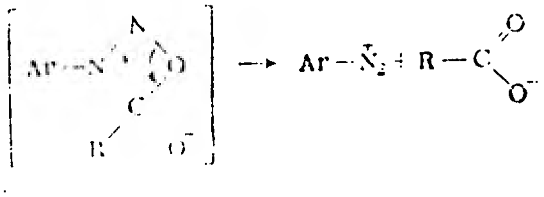


in a weakly alkaline medium and the products of transformation of diazonium salts under the influence of a not very concentrated alkali, which are formed 10–15 seconds following their treatment. It turned out that both substances yield spectrally identical compounds which are neither the stable (anti) diazotate ion nor the diazonium cation, nor finally, acylarylide the formation of which could be hypothesized during the hydrolysis of nitrosacylarylide.

This substance coincides in its properties with the syn-diazotates described earlier. Investigating the kinetics of the hydrolysis process for nitrosacylarylides, the authors came to the conclusion that for various pH values of the medium, the mechanism of the formation of the syn-diazotate varies. According to the works of Huisgen and others [129], at low pH values the transformation process is monomolecular and consists of the rearrangement of nitrosacylarylide into the diazoacetate:



The second stage, the dissociation of the resulting diazoacetate into an aryldiazonium and an acetate ion, runs its course quickly. On the other hand, the transformation of the intermediate complex into a diazo compound cation can be imagined even without the formation of the hypothetical diazoacetate:



For pH values greater than 7.5 (up to 9.5) the reaction is bimolecular and the role of the hydroxyl leads to the detaching of an acyl group from the nitrosacylarylide molecule with the formation of the syn-diazotate even for the n-nitrophenyldiazo compound, a substance for which the transformation rate into the anti-isomer is so great that it is very difficult to replace this stage in the mutual transformations of diazo compounds.

In work with Tomchin and others [123], B. A. Poray-Koshits established the presence of two different anions in the bisdiazotized derivatives of benzidine and its analogs using potentiometric and spectral methods. The second group under the chosen conditions remains in the form of a diazonium cation, while the first diazonium group in reacting with a alkali yields sequentially syn and anti-diazotate groupings.

These facts, along with the work of Littler [124], Luettke [125], Lewis and Suhr [126] are convincing of the fact that there are two isomers of the diazotate ion (and hardly the covalent compounds which Hantzsch imagined). The nature of this isomerism cannot be considered to be finally established. However, there is a significant number of facts which give evidence (if not directly, then indirectly) that both diazotates are spatial isomers and are related to one another as cis- and trans-isomers. It should be noted that even under conditions of complete uniformity of the bonds in the diazotate anion, the shortness of the bond between the two nitrogen atoms will be markedly greater than unity, which makes the existence of two spatial isomers entirely possible. On the other hand, at the present time a rather large number of examples of cis-trans- isomerism has accumulated for diazotate analogues. However, the main concerns here are the azo compounds in the broadest sense of the word, i.e. such substances in which the end nitrogen atom is covalently bound to any other atom (most often with carbon), and because of this the degree of double bondedness of the two nitrogen atoms approaches the double level. For such compounds, the presence of stereoisomerism would be most easily hypothesized. Azobenzene itself, as stated above, is capable of existing in the form of two stereoisomers.

The spatial structure of compounds having an azo group has been proven out by complete x-ray structural analysis [127]. The isomers of diazocyanides, which have been studied in detail ArN=NCN [128], are as has been demonstrated [129, 130], not structural isomers, but in all probability, spatial. The same also applies to diazosulfonates $ArN=NSO_3Na$, which are capable of existing in the form of two isomers. There have been disputes concerning the nature of this isomer [131], which in the final analysis have apparently concluded that the spatial isomerism of these substances is confirmed [132].

The initial works of Hantzsch should be recalled [133], in which he alluded to the steroisomerism of oximes, making an analogy between them and the diazotates. This analogy is all the more justified, since in contrast to the cases given above the oximes are acid compounds and consequently, their stereoisomerism, just as that of the diazotates, leads to stereoisomerism of the organic ions. Thus, one way or another, Hantzsch's initial idea of stereoisomerism has proved to be extremely fruitful and in truth accepted by the majority of contemporary chemists, although with a slightly different interpretation.

The anti-diazotates (they could also be called trans-diazotates) are obtained by treating diazonium salts with concentrated alkalis, sometimes also with vigorous heating. Their formation passes through the diazohydrate and syn- (or cis-) diazotate stages. The formation of the diazohydrate and the syn-diazotate takes place practically instantaneously (see below). Anti-diazotates can be rather easily isolated and extracted from the solution and even dried out. These preparations can be stored for a relatively long time and are one of the stable forms of diazo compounds. As far as the syn-diazotates are concerned, then as was noted above as a consequence of the extraordinary lability, their separation and industrial application is difficult. However, in individual instances they have been separated and described in investigative work.

In summing up all that has been said about alkaline salts of diazo compounds, it is necessary to emphasize that the diazotates (ions) of the alkaline metals are capable of existing in two stereochemical variants, syn- (cis-) and anti- (trans-). The salts of the first are unstable, and their equilibrium with the diazonium cation is achieved practically instantaneously in aqueous solutions (see below). The salts of the second are extremely more stable, and they can be extracted, preserved and employed in industry as a stable form of diazo compounds.

Equilibrium between the anti-diazotate and that of the diazocation is reached slowly, since to carry out the nitrogen coupling reaction, it is necessary to treat the diazotate with a mineral acid solution over some period of time.

EQUILIBRIUM BETWEEN VARIOUS FORMS OF DIAZO COMPOUNDS

Various forms of the class of organic substances known by the general name of diazo compounds were described and briefly characterized above. As we have seen, these include the diazonium salts, diazohydrates, nitrosamines, and diazotates. Quite a bit of material has accumulated to give an account of the interactions of all of the forms enumerated above and to discuss the causes and mechanisms for their mutual transitions from one to the other. Proposals of this type have been made repeatedly, and the most complete is Hantzsch's "system of mutual transformations of diazo compounds" [134]. However, it can not now be considered irreproachable and there is some point in going over all of the relationships which are connected with these forms. First of all, it is hard to establish that all forms of diazo compounds are in mutual equilibrium in aqueous solutions. The state of this equilibrium depends on the acidity of the medium and in certain situations can be shifted to such an extent that one form or the other of a diazo compound becomes susceptible to extraction and detailed study. Some equilibria are easily shifted to one side, and are very difficult to shift to the other.

We shall try initially to consider the individual systems of equilibrium, which make up the overall system of transformations, in which we will arbitrarily separate the purely protolytic equilibria from the tautomeric and stereochemical.

The behavior of a diazocation in aqueous solutions is typical of Lewis acids. When treated with an alkali, the diazocation sequentially reacts with water, and then with the second equivalent of the caustic alkali, converting to a diazotate anion. This acid-base equilibrium is established extraordinarily quickly and exhibits a number of characteristic features.

The first stage in the interaction of a diazonium cation with an alkali is hydroxyl attachment and the formation of the covalent diazohydrate; the second stage consists of the ionization of the diazohydrate under the influence of the second hydroxyl, which removes a proton from it:

$$ArN_2^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} ArN_2OH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} ArN_2O^-$$

B. A. Poray-Koshits and Grachev [135] and later Wittwer and Zollinger [136] used the method of potentiometric titration to investigate diazo compounds and obtain unique neutralization curves. Following the addition of one equivalent of alkali, no jump in potential is revealed in them as is the case for the titration of usual diacids.

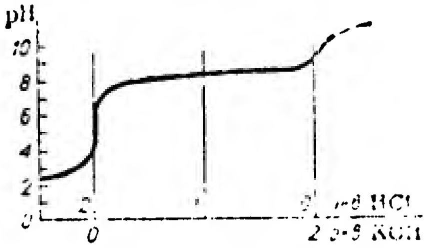


Рис. 2

In all, two jumps are observed in the curve (Fig. 2) of a potentiometric titration of diazonium salt with an alkali: the first corresponds to the neutralization of the excess mineral acid and characterizes the acidic properties of the diazonium cation; the second gives evidence of the appearance of surplus alkali and obviously characterizes the basic properties of the diazotate ion.

Such a shape of the neutralization curve signifies that the equilibrium constant for the first stage of the reaction

$$K_1 = \frac{[ArN_2OH][H^+]}{[ArN_2^+]}$$

is significantly less than the equilibrium constant of its second stage [137]:

$$K_2 = \frac{[ArN_2O^-][H^+]}{[ArN_2OH]}$$

The condition $K_2 >> K_1$ signifies that if exactly one equivalent of alkali is added to the diazonium salt solution, then it is not the diazohydrate which is formed as written in the equations given above, but half quantities of the anion (diazotate) and the cation (diazonium). The amphoteric properties of the diazohydrate are responsible for this interesting phenomenon. At the present time, the equilibrium constants which characterize the attachment of two hydroxyls to the diazonium cation in accordance with the stages below has been successfully accomplished by the potentiometric titration of diazonium salts using a special method of calculation:

$$ArN_2^+ + OH^- \rightleftarrows ArN_2OH$$

$$K_1 = \frac{[ArN_2OH][H^+]}{[ArN_2^+]}$$

$$ArN_2OH \rightleftarrows ArN_2O^- + H^+$$

$$K_2 = \frac{[ArN_2O^-][H^+]}{[ArN_2OH]}$$

The acidity of the diazonium cation can be specified by the constant K_1, which for the compounds which have been studied fluctuates within a range of $10^{-10} - 10^{-13}$. For this reason, the diazonium cation should be considered a weak mono-basic Lewis acid (cf. Zollinger's determination [10]).

The magnitude of K_2 for the same compounds fluctuates in a range of $10^{-9} - 10^{-10}$ and characterizes the diazohydrate as a weak protonic acid.

The ratio of the constants K_1 and K_2 shows that for an acidity of the medium corresponding to the transition region of the diazonium cation into the diazotate, the diazohydrate exists in an aqueous solution in a quantity commensurate with these two diazo forms.

The diazohydrate content from among the other equilibrium forms depends on temperature and is approximately 7% at 0°C, and then reaches 22% at 20°C as this quantity in a number of little m- and n- substituted phenyldiazoniums which have been considered does not depend on the character of the substitute in the benzene ring.

The increase in ionic force increases the acidity and the base dissociation of the diazohydrate. In this respect, the diazohydrate content from among the other diazo forms sharply decreases, other conditions being equal.[1]— editor's note

The transformations described by the equation given above (page 47) are completely reversible and equilibrium between the participants in the reaction is established instantaneously. Related to this is the apparent capability of the syn-diazotate of a nitrogen coupling reaction, which was noted as a typical sign of these salts, and distinguished them from salts of the anti-series by this characteristic.

When one alkali equivalent is added to some diazonium salts, the value of

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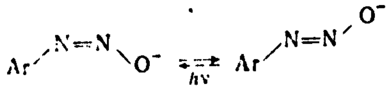
[1] V. A. Ketlinskiy, I. L. Bagal, B. A. Poray-Koshits, the symposium "The Reactivity of organic compounds", VIII, no 2, 463 (1971); VIII, no 3, 475 (1971).

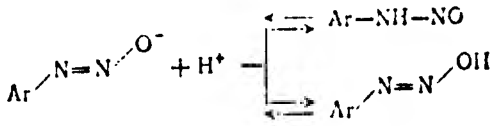
the pH observed right at the start gradually decreases spontaneously [138] to the specified value. This phenomenon was at first taken to be slow neutralization by Poray-Koshits and Passet, and only further investigations convinced the authors that following the instantaneously established equilibrium between the diazocation and the diazotate [135], a new factor enters the process— the rearranging of one spatial ion isomer into another. The syn-diazotate having the greatest basicity, is rearranged into the anti-diazotate with the least basicity, which is of course related to the spontaneous change in the pH value of the solution. The rearrangement of the syn-isomer into the anti-isomer occurs in the majority of cases during heating, but also sometimes when cold. In this case, it should be emphasized that the stronger the Lewis acid is from which the syn-diazotate is obtained, the more rapidly and easily the rearrangement takes place. On the other hand, the more basic the original amine used in the preparation of the diazo compound is (and consequently, the weaker the Lewis acid obtained from it is), the more difficult is the rearrangement. As a matter of fact, for such strong Lewis acids as n-nitrophenyldiazonium, dinitrophenyldiazonium, anthraquinonyldiazonium, etc., the conversion of the syn-isomer into the anti-isomer proceeds so quickly that special measures to fix the syn-isomer during alkalization of the diazonium cation are required [140]. The transformation of the syn-isomer which is obtained from a weak Lewis acid (strongly basic amine, for example aniline) requires quite severe conditions, heating in a concentrated alkali up to 150°C and higher [141].

Tsollinger [142] maintains that the anti-diazotate is in equilibrium with the anti-diazohydrate, based on the not very accurate spectral investigations of Lewis and Suhr [143]. However, as was noted above no one has succeeded in isolating the anti-diazohydrate (see page 52). For this reason, the system of transformations of the syn-diazotate proposed by Tsollinger, seems to have an inadequate basis at the present time.

It would seem that given the equilibrium syn-diazotate ⇌ anti-diazotate. the acidification of the anti-diazotate solution should lead to the formation of a diazonium cation in just the same way as it was converted into the anti-diazotate. However, this does not happen at all. The reverse stereoisomerization of the anti-diazotate into the syn-isomer takes place only in isolated cases and not in the presence of acids, but during radiation with ultraviolet light. Thus, it is of course impossible to include stereochemical transformation in the general protolytic transformation system, since the spontaneous transformation from left to right is accomplished in a reverse direction only in individual cases and when using completely different energy influences on the substance. This is illustrated by the diagram:



For this reason, only the syn-diazotate is to be considered a conjugate base of the diazonium cation (cf. above, page 26). The action of acid on the anti-diazotate leads to the attachment of a proton [144] and the formation of a compound which can be either the anti-diazohydrate or nitrosamine:



The nitrosamine structure of this product is adequately proven only for those cases where it has been possible to extract this substance from solution, i.e. where it has been relatively stable. This in turn, was possible only for diazo compounds which have electron acceptor groups (weakly basic amines, strong Lewis acids, weakly basic diazotates).

Up to now there has been no success in isolating the products, obtained as a result of acidification of the anti-diazotate, from the amines which have more basic properties (analine and all of its derivatives with electron donor substitutes). Perhaps these products have a structure other than the nitrosamine, but there is as yet no data to confirm this hypothesis. The interaction of nitrosamine with an acid leads to the gradual formation of a diazo cation. We will recall that diazotization which is carried out in an acid medium also presupposes the requisite nitrosamine stage, with its further transformation into a diazo cation.

Hantzsch, in condering the process of acidification of the anti-diazotate, took the view [145] that in this case it is not the nitrosamine which is formed, but the anti-diazo hydrate, which is rearranged in an acid medium into the nitrosamine; the latter slowly transforms into a diazonium cation in accordance with an unknown mechanism. In adopting this view of Hantzsch, it would be necessary to maintain that during the diazotization of amines, the anti-diazo hydrate occurs initially and only after this is the nitrosamine formed. The facts given above for the immediate formation of nitrosamine during acidification of the anti-diazotate or during the treatment of an aromatic amine with nitrous acid, refute the views of Hantzsch. The nitrosamine of the primary amine has acidic properties; in spite of this, its transformation into a diazonium cation occurs in an acid medium. Since it is impossible to imagine a direct transformation of nitrosamine into a diazonium cation, it is to be supposed that it passes through a stage of tautomeric transformation of nitrosamine into the diazo hydrate, which instantaneously dissociates into the diazonium cation. It only makes sense that this state is justified independently of the manner in which the nitrosamine is obtained: either from nitrosation of an aromatic amine or acidification of an anti-diazotate.

The tautomeric transformation of nitrosamine into the diazo hydrate presupposes the formation of a common ion for both tautomers, and since it takes place during the catalytic action of protons, then it is necessary to admit that either the primary aromatic nitrosamine possesses minimal basic properties or, more probable, its transformation reaction takes place via a synchronous mechanism. In this case, the attack of the proton is directed to the most nucleophilic oxygen atom [146] in a manner similar to that which takes place during the protonization of nitrosodimethylaniline [147].

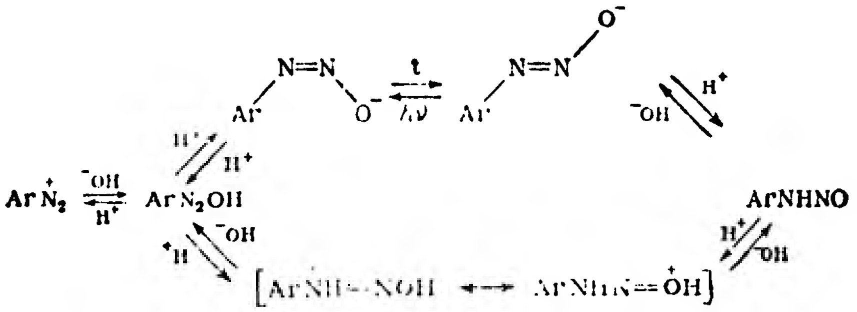
Then the formula for the transformation of nitrosamine into the diazo hydrate can be imagined as follows:

$$\mathrm{ArNHNO} \underset{\mathrm{OH^-}}{\overset{\mathrm{H^+}}{\rightleftarrows}} [\mathrm{ArNHN{=}\overset{+}{O}H} \longleftrightarrow \mathrm{Ar\overset{+}{N}H{=}NOH}] \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{ArN_2OH}$$

The resulting diazo hydrate, regardless of its spatial structure, is instantaneously converted to the diazonium cation:

$$\mathrm{ArN_2OH} \underset{\mathrm{OH^-}}{\overset{\mathrm{H^+}}{\rightleftarrows}} \mathrm{ArN_2^+} + \mathrm{H_2O}$$

In summing up all that has been said above, the representation of proteolytic equilibrium transformations of diazo compounds in aqueous solutions can be presented in the form of the following diagram:



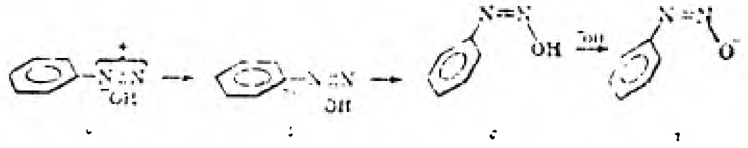
In this system there are both protolytic and tautomeric equilibria, and stereochemical transformations.

The Reactivity of Diazo Compounds

Since it is impossible to consider all of the reactions of which the aromatic diazo compounds are capable, we will take up only those in which the diazonium salt acts as an electrophilic reagent, replacing with the radical which contains two nitrogen atoms any of the hydrogen atoms of a nucleophilic particle. In this case, the diazo group converts to an azo group in which both nitrogen atoms are bound to their partners with covalent bonds. If the nitrogen atoms in the diazonium cation have sp-hybridization, then both nitrogen atoms in the azo compounds are in the sp^2-hybridization state.

In the section on diazo equilibria we have already considered from a thermodynamic aspect the simplest example of such a reaction -- the interaction of a diazonium cation with a hydroxyl ion. The same reaction is now to be considered with a view towards the possible mechanism for it. Both stages of the interaction of a hydroxyl with a diazonium cation do not take place synchronously. This leads to the fact that the first stage of the reaction, the formation of the diazo hydrate, and the second stage, the removal of a proton from a base molecule and the stabilization of the syn-diazotate, take place sequentially, one after the other. The diazo hydrate in this case is to be considered an intermediate product in a fixed state, i.e. one which is never accumulated in the reaction process. In accordance with this, it is possible to hypothesize that the interaction of the diazonium cation with the first hydroxyl is the slowest limiting stage of the process. The detailed mechanism of this interaction can be presented in the following manner. The force of mutual ionic attraction forces the hydroxyl to occupy the same place with respect to the diazonium group that the ion occupied in the crystal salt. In the ion pair which arises in this way, the hydroxyl is oriented by the π-electron system of the aromatic ring and the diazonium group.

The gradual transition of this ion pair (a) into the π-complex (b) takes place in such a manner that the bond of the hydroxyl to the π-electron system of the ring is preserved, which determines the cis-configuration of the complex. The realization of the π-complex is essential for the unfavorable energy aspect of the change from the sp-hybridization of the first nitrogen atom into sp^2-hybridization. In the subsequent stage, the π-complex goes over into the σ-complex (c) with the forced cis-configuration, which is an intermediate product (diazo hydrate). Under the influence of a base,(in the given case, the second hydroxyl), the intermediate product converts to the final reaction product, cis-diazotate (d). This mechanism is explained by the following diagram:



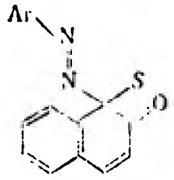
It would seem that the reaction of diazo compounds with alcohols is also quite similar to the reaction with the hydroxyl ion.

However, it is impossible to obtain diazo esters by treating the diazonium salt with aliphatic or aromatic alcohol in an alkaline medium. On analogy with the reaction of the diazonium cation with hydroxyl, which leads to the formation of the diazotate, it is possible to admit that in treating the diazonium salt with liquid or aromatic alcohols in an alkaline medium, diazo esters are formed. Thus, during the interaction of n-bromophenyldiazonium with n-nitrophenolate, instead of an azo compound, a not very stable product having a pale red color is obtained. Dimroth [148] ascribed a diazo ester structure to the compounds obtained, basing this on the fact that an aqueous solution of diazonium salt and potassium n-nitrophenolate had a significantly lower electroconductivity than the mixture of the ions present here should have. Simultaneously Dimroth noted that the diazo esters in interacting with active azo components behave as diazo compounds and form a diazo compound from n-bromodiazobenzene and this azo component. When the diazo ester is heated up to 80°C, it likewise is rearranged into a real azo compound. Similar reactions caused Dimroth to consider diazo esters an intermediate stage in the nitrogen coupling reaction.

Later Poray-Koshits [149] using potentiometric titration where a solution of potassium n-nitrophenolate was used as an alkali agent, showed that in aqueous solutions the diazo ester dissociates into its component ions. It was further shown by Kazitsina [150] using infrared spectroscopy, that in solid form the bond between the diazonium cation and the phenolate ion has an ionic character.

Thus, the product of the interaction of diazonium salt with n-nitrophenolate does not prove to be a covalent diazo ester, but a salt. However, the presence of coloring makes it possible to advance the hypothesis that in the given case the formation of a complex with partial charge transfer takes place.

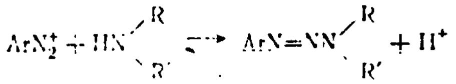
During the interaction of n-nitrophenyldiazonium with 2-naphthol-1-sulfo acid, a diazo ester should be formed in an analogous manner, according to a hypothesis of Buchevev [151]. However, as Zollinger demonstrated [79], the electrophilic substitution of a sulfo group with diazonium takes place in this reaction, while the σ-complex is formed as an intermediate product:



However, the true diazo esters are obtained not from diazonium salt, but from silver salts of anti-diazotates based on Bamberger's method [152] with the treatment of latter halogen alkyls in the absence of light:

$$ArN_2O^-Ag^+ + AlkHal \longrightarrow AgHal + ArN{=}NOAlk$$

Of considerable significance is the electrophilic substitution reaction of hydrogen in the primary or secondary amino group of the aromatic or aliphatic amines, leading to the formation of diazoamine compounds (triazenes):

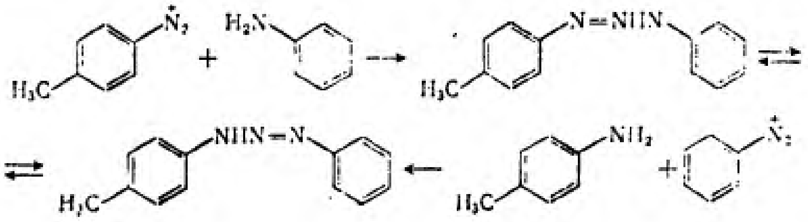


$$ArN_2^+ + HN\begin{matrix} R \\ R' \end{matrix} \rightleftarrows ArN{=}NN\begin{matrix} R \\ R' \end{matrix} + H^+$$

where R is alkyl or aryl, while R' is alkyl or hydrogen.

The derivation of diazoamine compounds was first accomplished by Griess [153]. The general methods for their formation lead to the conclusion that the interaction of a diazo compound with an amine leads to a weakly acid or even an alkaline medium [154]. Aromatic amines which are highly active, yield azo compounds during interaction with a diazonium salt, and the extraction of diazoamine compounds from them presents difficulties. The weakly active amines in an azo compound easily form diazoamine compounds which often appear as side products during diazotization. Apparently, the equilibrium described above for an acid medium is shifted to the left, and in a more acid one, to the right. This also probably explains the ability of diazoamine compounds to break down in acid aqueous solutions with the formation of diazonium salts and an amine. Of course, the state of this equilibrium depends on the acid-base properties of the participants in the reaction. Lukashevich and Lisitsyna determined that some diazoamine compounds which contain halogen atoms, do not dissociate even in 12% sulfuric acid [155]. If an azo component is present in an aqueous medium during the breakdown of triazine, then nitrogen coupling takes place instantaneously with the formation of an azo dye. This property of diazoamine compounds is widely used in industry.

Of the chemical properties of diazoamine compounds it is essential to recall their prototropy, i.e. the ability of the hydrogen atom to transfer from one nitrogen atom to another. Thus, if the diazonium salt from n-toluidine acts on aniline, a product is obtained which is formed during the interaction of diazobenzene with toluidine [156]:



A protracted discussion concerning the structure of diazoamino compounds of a similar type [157] which was based on attempts to prove the structure of a diazoamine compound by purely chemical means (i.e. by the products from its breakdown), concluded with the recognition of tautomerism in this series. Depending on acid-base properties, this tautomerism can lead to various ratios of the tautomers in the mixture. Inadequate attention has been given to one extremely important fact. The fact of the matter is that the prototropy is catalyzed both by hydroxyls [158] and protons [159]. This can only occur in the case where amphoteric properties are admitted for diazoamine compounds. Then in an alkaline medium, the equation for the tautomeric rearrangement will appear as follows:

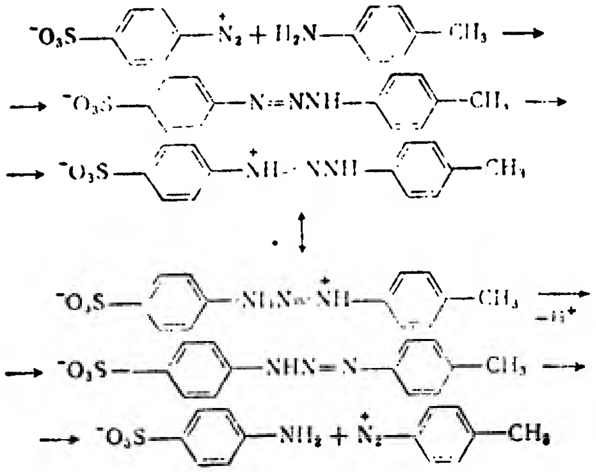
$$\mathrm{ArNHN{=}NAr'} \rightleftarrows \mathrm{H^+} + \mathrm{Ar}\overset{-\delta}{\mathrm{N}}\mathrm{{-}N{=}}\overset{-\delta}{\mathrm{N}}\mathrm{Ar'} \rightleftarrows \mathrm{ArN{=}NNHAr'}$$

while in an acid medium a common ion will be the product of adding a proton to a nitrogen atom:

$$\mathrm{ArNHN{=}NAr'} + \mathrm{H^+} \rightleftarrows \mathrm{Ar}\overset{+\delta}{\mathrm{N}}\mathrm{H{-}N{=}}\overset{+\delta}{\mathrm{N}}\mathrm{HAr'} \rightleftarrows \mathrm{H^+} + \mathrm{ArN{=}NNHAr'}$$

The transformation of one tautomer into another is reminiscent of the transfer mechanism for nitrosamine into diazohydrate during the catalytic action of protons (see above).

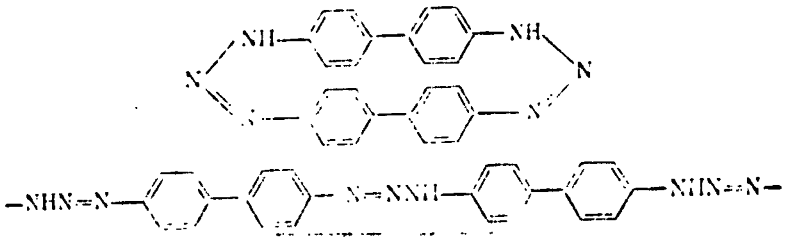
The well known process of diazo group transfer is also connected with the tautomerism phenomenon, and consists of the resulting diazoamine compound decomposing in an acid medium due to the tautomerism with the formation of a diazo compound of another then that one which was taken for the synthesis of the diazoamino compound. For example, during the action of phenyldiazonium-sulfo acid on n-toluidine, n-tolyldiazonium and sulfanilic acid are formed in an acid medium via the intermediate stage of a diazoamino compound [160]:



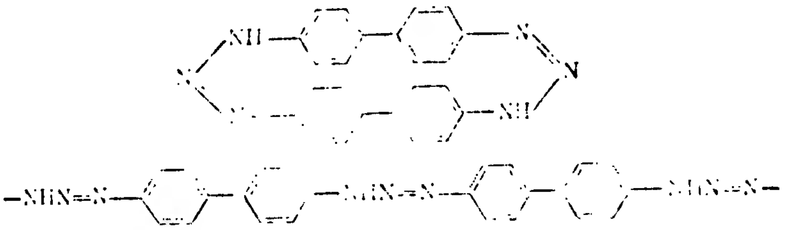
Another explanation which admits of the attaching of a second molecule of the diazo compound to triazene which was given by Tsollinger, is not convincing.

The transfer of a diazo group is utilized for example, to derive monodiazotised benzidine.

The diazoamine compound formed from the completely diazotized benzidine and the benzidine itself, which has a cyclic or a linear structure

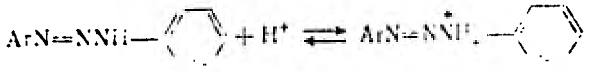


is allowed to stand for an extended period in an acid medium. The tautomeric transformation gradually takes place with the transposition of a proton:



The new symmetrically constructed diazoamine compound is decomposed by the acid and monodiazotized benzidine [162].

Diazoamine compounds are widely employed in the aniline dye industry as stable forms of diazo compounds. The diazoamino compounds (triazenes) when acted upon by mineral acids transform into aminoazo compounds. This reaction belongs to the series of acid catalyzed intermolecular rearrangements and occurs in two stages [163]. At the outset a proton is attached to the diazoamine compound molecule and a diazammonia ion is formed:



which breaks up into a diazonium cation and an amine:

The latter under these conditions enters into a nitrogen coupling reaction with the diazonium ion:

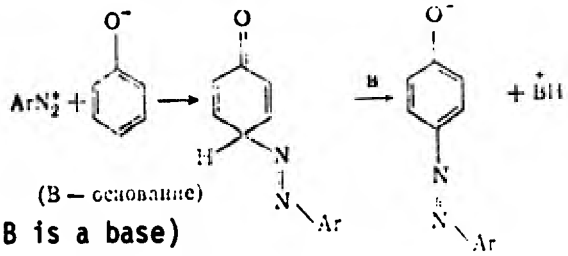
If another aromatic amine which is a more active azo component, is added to the reaction mixture, then the nitrogen coupling takes place with it, and not with the amine which was earlier a component of the diazoamino compound.

The derivation of stable forms of diazo compounds is an important practical problem. By deriving diazoamino compounds, substances which are durable, capable of being stored for a long time without decomposing and of decomposing instantaneously when acted upon by acids or other reagents, the diazo compounds are fixed, which makes it possible to use them at the necessary time as circumstances require. Because of this, the textile plants are freed from the necessity of diazotizing aromatic amines during cold dyeing. This is hardly the only "stable form" of diazo compounds and is not even the most convenient.

However, the significance of diazoamino compounds is nonetheless rather great, particularly for printing and for the derivation of the so-called diazoaminols (rapidogenes), which are mixtures of diazoamino compounds with any azo component. Both the diazoamino compound in its diazonium portion and the azo component should not have any anionic groups which cause them to be soluble in water. On the other hand, an amine-stabilizer for the preparation of a diazoamino compound, should have any group which makes it soluble in water, and because of which it is easily removed by a simple washing following detachment. Secondary amines containing a carboxyl or a sulfo group are the amine-stabilizers of choice in order to avoid the possible transfer of diazo groups. Thus, the following are employed as amine-stabilizers: phenylglycine-o-(or m-) carboxylic acid, methylsulfanthranilic acid [164], N-hydroxyethylanthranilic acid, N-methylanthranilic acid, sarcosine, and methyltaurine (methylaminoethanesulfo acid). Diazoamino compounds from these amino-stabilizers decompose easily, sometimes even in a neutral medium (neutrogenes), and the resulting amine is removed from the sphere of the reaction because of its solubility [165].

Certain diazoamine compounds prepared from the amines enumerated here, in particular the phenylglycene derivatives, have such a rate of breakdown that they can decompose even in a neutral medium, which is very important for ice dyeing processes. The most important of all of the reactions of the aromatic diazo compounds is the nitrogen coupling reaction which leads to the formation of azo compounds.

We will omit here descriptions of various classical theories of nitrogen coupling and refer the reader to the appropriate literature [166]. We shall indicate only that in a nitrogen coupling reaction the formation of various intermediate products has always been suspected, and in certain cases such intermediate products have been ascertained or separated [167]. Kinetic investigations with which it has been made clear that a nitrogen coupling reaction occurs in two stages [168], confirmed the view that it follows a S_E2-mechanism with a quasi-stationary intermediate stage. Both stages which make up the nitrogen coupling process do not transpire synchronously. In the first which is the slowest, the diazonium cation is attached to the nucleophilic center of the azo component,



(B is a base)

forming a σ-complex, which when acted upon by the basic agents present in the reaction medium (hydroxyl, acetate ion, organic base, etc.) quickly splits off a proton and converts to the final reaction product, the azo compound.

Modern investigations using tagged atoms have shown that in the majority of cases the kinetic isotope effect is absent during the nitrogen coupling reaction [169] which supports the correctness of the view given above on the course of the reaction, since it proves its two stage character and the fact that the second stage goes more quickly than the first.

Thus, the action of a diazonium cation as an electrophilic agent on aromatic compounds is similar in all respects to the usual electrophilic substitution, for example, nitration or sulfation. The substantial difference is that the diazo compounds as a rule are stable only at reduced temperatures, and for this reason react with a significantly more active molecule having an energetic nucleophilic center.

Along with reactions where diazo compounds play the part of electrophilic particles and react without generating nitrogen, forming covalent azo structures, many reactions are well known in which the diazo group breaks down, releasing molecular nitrogen and the aromatic radical is substituted by the new group.

Our problem does not include the detailed consideration of reactions of this type; we are limiting ourselves here to just mentioning them, referring those who are interested in these areas of the chemistry of aromatic diazo compounds to specialized monographs [172].

Almost any diazo compound when heated in an aqueous acid solution undergoes decomposition, in which case molecular nitrogen is released from its molecule and the diazo group is substituted by the hydroxyl:

$$ArN_2^+ + HOH \longrightarrow ArOH + N_2 + H^+$$

The reaction proceeds easily [173] and is a means of preparing aromatic phenols from amines. For example, this reaction is used in industry to derive guaiacol from o-anisidine [174]. With similar treatment, polydiazo compounds convert to polyhydroxy compounds [175]. For difficult reactions, catalysts are sometimes used, the most frequently mentioned of which is copper sulfate [176].

If alcohol is used as a medium instead of water, then phenol esters are formed as a result of the reaction [177]. Sometimes the reaction in an alcohol medium is accompanied by a side reaction: the reduction of the diazo compound, with the splitting off of a diazo group and the formation of a hydrocarbon [178]. This reaction is sometimes employed for preparation purposes.

Sandmeyer's reaction is of great importance. It consists of the decomposition of halide salts of diazo compounds in the presence of cuprous salts:

$$ArN_2^+ + Hal \xrightarrow{CuHal} ArHal + N_2$$

For example, in this way it is possible to derive chlorine, bromine and aromatic amine derivatives [177]. If copper cyanide is used in place of the lower halide salt in a solution of sodium cyanide, then the diazonium group is rather easily substituted by the nitrile [178].

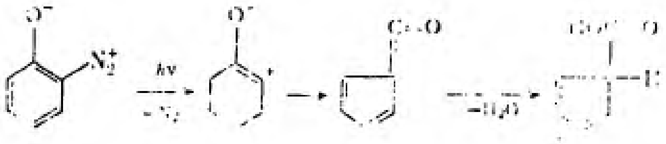
Iodine derivatives can also be derived in the absence of copper salts. For example, to obtain iodine derivatives it is sufficient to add a solution of potassium iodide to the acid diazonium solution and gently heat the reaction mass.

The ability of some diazo compounds to decompose when radiated with ultraviolet light is widely used in industry [179]. The light sensitivity of diazo compounds which have electron donor hydroxy-, dimethylamino-, sulfide and other groups in the para- or ortho-position with respect to the diazonium group, is particularly high. A review of light sensistive compounds, among which the quinonediazides are to be particularly noted, is given monographs [180]. Light sensitive diazo compounds are employed in diazotypy to obtain negative and positive images. The heart of the process consists in the textile material or paper being coated with a layer containing a phototropic diazo compound, where the surface of the material is isolated through an appropriate negative, (for example, a drawing on tracing paper). The diazo compound which is subject to the action of the light decomposes and is thereafter removed, while the undestroyed compound is fixed by means of nitrogen coupling with an azo component.

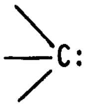
Sometimes the diazonium salt and azo component are applied to the paper simultaneously, but they are forced to react with each other when treated with ammonia pairs only following isolation and decomposition of the diazo compound.

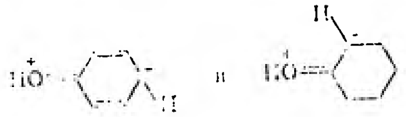
The decomposition of diazo compounds by light can go in various directions, which depend both on the structure of the diazo compound and on the internal conditions, for example, the pH of the medium, temperature, etc. In an aqueous acid medium, the diazonium cation is subject to the same heterolytic decay as during the Sandmeyer reaction, with the formation of an aryl-carbo cation which then reacts either with the hydroxyl forming phenol, or with the anion present in the medium, converting, for example, to a halide derivative.

A ring contracting reaction during the photochemical decomposition of quinonediazides, discovered by Zyus [181], is extremely interesting for phototyping. The essence of this interesting reaction, according to Zyus, is that the quinonediazide in the form of an internal salt releases nitrogen and forms an aryl-carbo cation, which when acted upon by light undergoes a rearrangement of the Wagner - Meierwein type [182] with the formation of a ketene, which is transformed in a reaction with water into cyclopentadienecarboxylic acid or its derivatives:

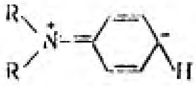


Nitrogen Coupling

At the very beginning of the chapter it was stated that the primary method for deriving azo dyes is a nitrogen coupling reaction -- the interaction of an aromatic diazo compound (as we explained, a diazonium salt) with an azo element or an azo component. Azo component is the name given to a molecule which has a nucleophilic center arising during the ionization or polarization of the molecule. Phenols, amines, and substances with moveable hydrogen atoms in methyl, methylene or methene groups are capable of a nitrogen coupling reaction. All these compounds in one of the saturated electronic structures contain a nucleophilic center in the form of a carbanion  . In phenols, such a nucleophilic center can occur as a consequence of the transfer of electron density from the oxygen atom to the ortho- and para-positions of the benzene rings



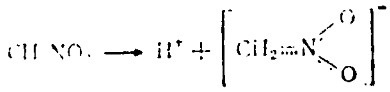
It is natural that the nucleophilic center is located in the para- and ortho-positions with respect to the hydroxy group. The shift of electrons in a phenolate ion takes place significantly more easily than in non-ionized phenol. In this respect, the capability of nitrogen coupling for phenols is expressed a great deal more weakly than for the phenolate ions. The rate of coupling of phenols is 10 - 12 orders of magnitude less that the speed of coupling for phenolates [183]. Owing to the coupling effect, aromatic amines are likewise capable of yielding a nucleophilic center which is necessary for a nitrogen coupling reaction:



Salt formation deprives them of this capacity, since the amines enter into the reaction in the form of a free base [184] and interact with the diazo component only to the extent that there is amine ⇄ aryl ammonia ion equilibrium in the solution.

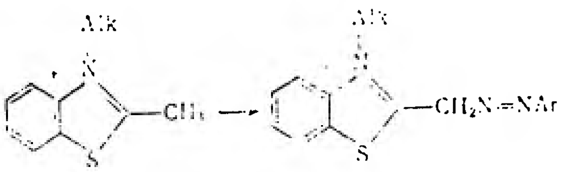
Wistar and Bartlett [186] experimentally confirmed this view of the ability of the free amines to combine. As an azo component, the aromatic amine is somewhat more passive than the phenolate ion, but is more active than phenol insoraf as the coupling effect is expressed more strongly with it. According to Jaffe, the value of the σ_n constant is 0.66 for the amino group, and 0.35 for the hydroxy group [185].

In certain cases, the methyl group exhibits the capability of splitting off a proton, converting directly to a carbanion. Of the substances which possess mobile hydrogen atoms in the methyl group, we will deal first of all with nitromethane. Because of the acidifying action of the nitro group, nitromethane dissociates easily in alkaline media with the formation of a proton and a common ion having balanced bonds:



$$CH_3NO_2 \longrightarrow H^+ + \left[CH_2{=}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}\right]^-$$

This ion, which is a carbanion with a nucleophilic carbon atom, easily enters into a nitrogen coupling reaction. The aromatic and heterocyclic compounds which contain mobile hydrogen atoms in methyl or methylene groups, belong to the same type of azo components. Their mobility is observed in those cases where the methyl or methylene group is coupled with the electron acceptor substitute or electronegative grouping. (The A. E. Poray-Koshits rule [186]). For example, meso-methylacridine in dissociating forms a carbanion with a nucleophilic center in a side chain. A diazonium cation is also attached to this nucleophilic center [187]. The derivatives of 2-methylthiazole [188] and 2-methylimidazole [189], particularly in the form of quaternary salts, have likewise proved to be capable of a nitrogen coupling reaction:

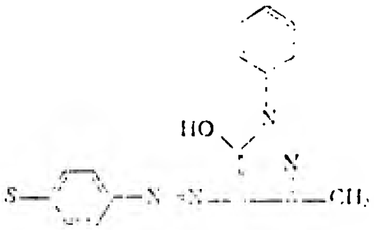


There are communications on the combining of other heterocyclic compounds with an active methyl group of the quinaldine, lepidene types, etc. [190, 191, 192]. Acetoacetic ester, anilides of acetoacetic acid, and phenylmethylpyrazolone

$CH_3COCH_2COOC_2H_5$

$CH_3COCH_2CONHAr$

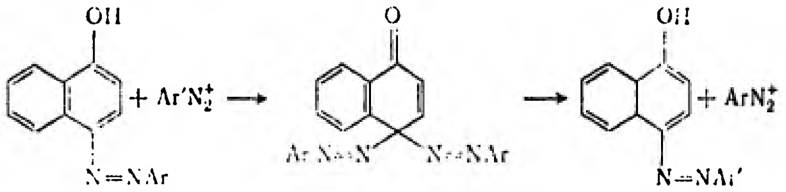
according to the rule of A. E. Poray-Koshits, have mobile hydrogen atoms in the methylene groups, and for this reason are typical keto-enols, and combine easily in an alkaline medium forming azo dyes of practical importance, for example:



Mesitylene [193] and phenylacetylene [194] are examples of hydrocarbons which, because of the specificity of their structure (the possibility of forming carbanions), are capable of participating in a nitrogen coupling reaction with particularly active diazo components.

There are data indicating that toluol and even benzene [195] are capable of a nitrogen coupling reaction with particularly active diazo components, (for example, the diazonium of 2-amino-5,6-dimethyl-1-ethylbenzimideazole).

Up till now, in studying the nitrogen coupling reaction we have worked from the fact that the process of interaction between the diazonium cation and the azo component is irreversible. Actually, the decomposition reaction of azo compounds with the formation of a diazo compound and an azo component has never been observed in pure form. However, Noelting and Granmuzhen [196], and just after them Filippychev and Chekalin [197] described a process of sunplanting one diazo group with another more active group. The process passes through a stage attaching the second diazo component to the azo dye:



Phenols and amines with free para- and ortho-positions can in principle combine both in the para- and in the ortho-positions and form dis- and even trisazo dyes. The proportion between the ortho- and para-isomers is very important in practice, since the ortho-isomers of azo dyes which are more fast due to the presence of an internal molecular hydrogen bond and reduced in indicating properties, are valued for the same reason given above.

The direction of the azo group in the ortho- or para-position depends on many factors, including the nature of the diazo and azo component, the pH of the medium and its character, catalytic additives, temperature, and finally, the presence of groups in the azo component which prevent the introduction of an azo group at one place or another (spatial difficulties). Other conditions being equal, the more active diazo component directs the nitrogen combination to the para-position, and then the less active, to the ortho-position [198]. The substitution of alcohol for an aqueous medium makes it possible to sometimes increase the quantity of the ortho-isomer. The same thing is promoted by an increase in the alkalinity of the medium during coupling with weakly active diazo compounds. Phenol itself combines primarily in the para-position. The ortho-isomer and dys-azo dye yield is in all 1-2% [199]. 1-naphthol combines preferably in the para-position and occasionally in the ortho- [200]; its sulfo acids are capable of yielding ortho-isomers. Thus, Stamm and Zollinger [201] showed that in the combination of o, o-dinitrophenyldiazonium with 1,3-naphthol-sulfo acid, the amount of the para-isomer increases with an increase in the pH of the medium from 4.59 to 5.6. The authors believe that the ratio of the isomers is a function of the usual basic catalysis. Strong bases, for example pyridine, catalyze para-substitution.

The majority of authors maintain that in 1-naphthol the sulfo group in position 3 exhibits spatial difficulty during the introduction of an azo group at position 4 of the naphthalene molecule. This explains the relatively greater quantity of the o-isomer (up to 70%) during combination of this component. Still stronger spatial obstacles are exhibited by the sulfo group located in the pari-position with respect to the possible point of azo group introduction. Thus, 1,5 naphtholsulfo acid combines almost exclusively in the ortho-position. Hydroxy diazo compounds of the naphthalene series, for example 4-sulfoacid-2-hydroxy-1-naphthyldiazonium in an alkaline medium combines with 1-naphthol almost exclusively in the ortho-position [202]:

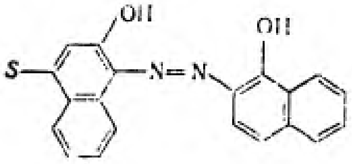
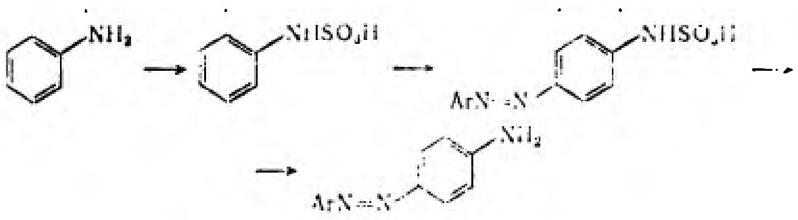


Table 1 is given to show the characteristics of the more important phenols in a practical sense, their activity and direction of combination [203].

The simple phenol esters are also capable of a nitrogen coupling reaction

[204]. However, to successfully carry out the reaction, the presence of two, for example, methoxyl groups in the azo component molecule or the use of a very active diazo component is necessary. It is interesting that in the nitrogen coupling of phenol esters, the hydrolysis of the ester grouping often takes place, so that an azo dye is formed as a result which is a derivative of the phenol itself. We will recall that in general the hydrolysis of simple esters is very difficult. The mechanism of this reaction has not been investigated.

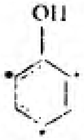
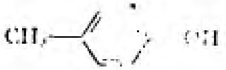
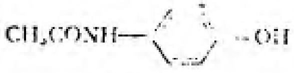
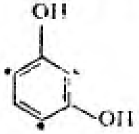
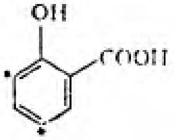
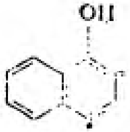
As a rule, the nitrogen coupling reaction of aromatic amines is somewhat more difficult than that of phenolate ions. In this case, the possibility of forming diazoamino compounds should be kept in mind. If there is a danger of this sort, then the primary amino group is transformed by alkylation or acylation into the corresponding derivative and nitrogen coupling is carried out with it. Further, the introduced group is split off and an amino azo compound is obtained. Such protective groups include the sulfo group, the nitro group or the sulfomethylene group, which are easily split off following the nitrogen coupling reaction, for example:

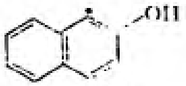
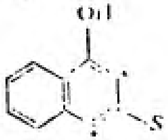
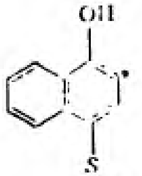
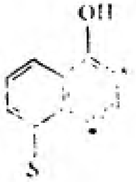
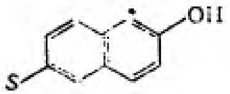
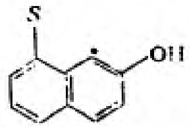


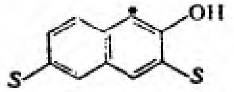
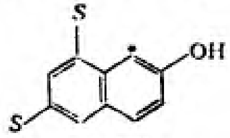
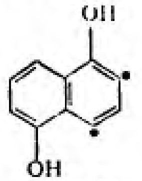
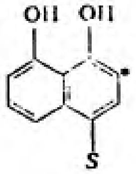
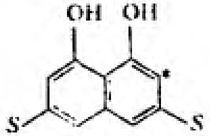
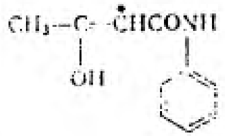
To derive aniline N-methylenesulfo acid and other amines, it is sufficient to heat equivalent quantities of the amine, formaldehyde and a bisulfite solution. A transparent solution is formed as a result of the reaction which can be directly

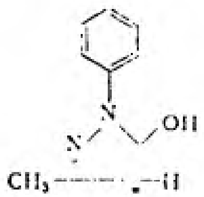
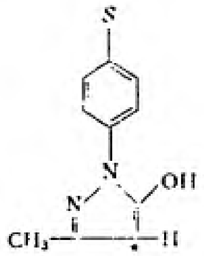
TABLE 1

Combination with Hydroxy Compounds and Derivatives of Acetoacetic Acid and Pyrazolone

Azo component	Formula (point of combination indicated by an asterisk)	Combination medium	Azo component activity in combining	Remarks
Phenol		Alkaline	Average	Combines 3 times: first in position 4, second and third in positions 2 and 6.
n-cresol		"	Low	-
Acetyl-n-aminophenol		"	"	-
Resorcin		Alkaline or weakly acid	High	Combines 3 times: first in position 4, second and third in positions 2 and 6
Salicylic acid		Alkaline	Low	Can combine 2 times: first in the para-position with respect to the hydroxyl group, second in the ortho-position.
1-naphthol		"	High	Combines 2 times: first in position 4, second in position 2; in a strongly alkaline medium and during combination with certain diazo compounds, the first coupling is at position 2

Azo component	Formula (point of combination indicated by an asterisk)	Combination medium	Azo component activity in combining	Remarks
2-naphthol		"	"	Combines with very active diazo compounds in an acid medium
1-naphthol-3-sulfo acid		"	"	Combines primarily in position 2, partially in position 4; in a strongly alkaline medium and with active diazo compounds combines predominately in position 4.
1-naphthol-4-sulfo acid		"	"	-
1-naphthol-5-sulfo acid		"	"	Combines primarily in position 2, partially in position 4; in a strongly alkaline medium and with active diazo compounds combines predominately in position 4
2-naphthol-6-sulfo acid		Alkaline	High	-
2-naphthol-8-sulfo acid (croceic acid)		"	Low	-

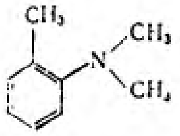
Azo component	Formula (point of combination indicated by an asterisk)	Combination medium	Azo component activity in combining	Remarks
2-naphthol-3,6-disulfo acid (R-acid)		"	High	-
2-naphthol-6,8-disulfo acid (G-acid)		"	Low	-
1,5 dihydroxy-naphthalene		Strongly alkaline (caustic soda)	High	In a weakly alkaline medium combines in position 4; in a strongly alkaline, in position 2.
1,8-dihydroxy-naphthalene-4-sulfo acid		Alkaline	"	-
Chromotropic acid		Alkaline or acetic acid	"	-
Anilide of acetoacetic acid		Acetic acid	"	-

Azo component	Formula (point of combination indicated by an asterisk)	Combination medium	Azo component activity in combining	Remarks
Phenylmethyl-pyrazolone		Alkaline	High	-
n-sulfo acid of phenylmethyl-pyrazolone		"	"	-

used for nitrogen coupling [205]. The methylsulfo group is easily eliminated by hydrolysis.

Electron donor substitutes in the meta-position with respect to the amino group facilitate the nitrogen coupling reaction, probably because of the greater stabilization of the carbanionic center which is in the para-position with respect to the amino group. Thus, m-toluidine combines easily with aniline and without protection of the amino group which is in the para-position with respect to it. n-Xylidine combines even more easily.

It is interesting that in a number of works, the complete inertness of dimethyl-o-toluidine to a nitrogen coupling reaction is noted.



Only with very active diazo compounds does it apparently react to form an azo compound [206]. The explanation for this is found in the fact that dimethyl-o-toluidine because of spatial difficulties arising from the close juxtaposition of two volumetric substitutes – dimethylamino- and methyl groups – is first displaced from the plane of the ring and the joining of the unshared electron pairs of the nitrogen atom to the ring which is essential for the creation of a nucleophilic carbanionic center is made difficult.

In contrast to the phenols, mono-amino compounds of the benzene series are not inclined to form dys-azo dyes. They combine most frequently in the para-position. In the benzene series, in cases where the para-position with respect to the amino group is occupied, coupling rarely occurs in the ortho-position. m-Phenylenediamine, as well as resorcinol, combines very easily – the first azo group assumes the para-position with respect to one of the amino groups; the second azo group enters between both amino groups, i.e. in the ortho-position with respect to both amino groups[1]. Table 2 is given to show the characteristics of the most important amino compounds employed in practice for the synthesis of dyestuff [207].

The nitrogen coupling reaction with bifunctional compounds has features which should be considered here. Resorcinol, one of the most important bifunctional azo components of the phenol series, can combine in various positions. The primary direction is towards the para-position with respect to one hydroxy group and the ortho-position with respect to the other (pp. 66-70).

The fact that there will be three combining resorcinol forms in equilibrium concentrations in an alkaline solution should be taken into account: the non-ionized resorcinol, a singly charged ion and a doubly charged ion. It has been shown that the doubly charged ion reacts approximately 10,000 times faster than the singly charged ion. The non-ionized resorcinol reacts so slowly that its reaction rates can be neglected. In addition to the basic position noted above, the azo group also joins at position 2 of the resorcinol (between hydroxy groups).

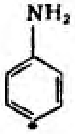
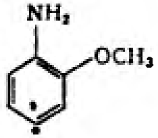
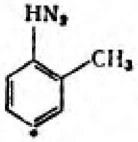
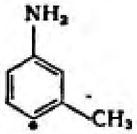
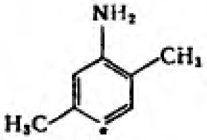
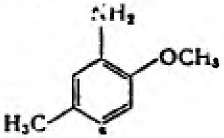
The ratio of the isomers depends on the pH values. Along with the mono-azo dye, a small quantity of the diazo dye is also formed. When a diazo

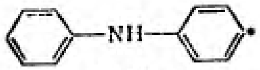
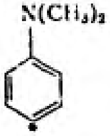
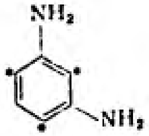
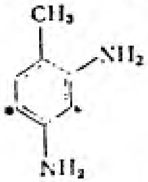
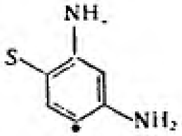
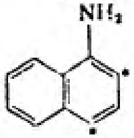
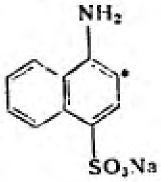
---

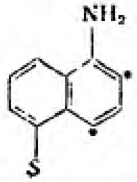
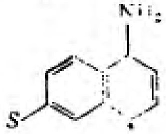
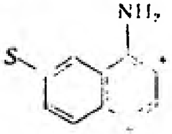
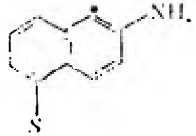
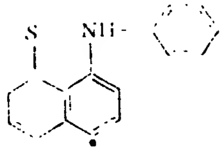
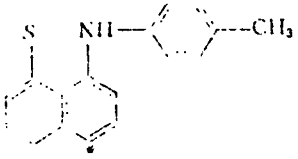
[1] 2-Naphthylamine combines in position 1, 1-naphthylamine combines predominantly in position 4. If there is a substitute (for example, a sulfo group) in position 4 of 1-naphthylamine, the coupling goes to position 2. The same thing happens if there is a volumetric substitute (for example, the same sulfo group) in position 3, spatially hindering the entry of an azo group at position 4.

TABLE 2

Combination With Amino Compounds

Azo component	Formula (point of combination indicated by an asterisk; see remarks)	Combination medium	Azo component activity in combining	Remarks
Aniline		Weakly acidic	Very low	During combination forms a diazoamino compound, which gradually converts to an azo dye when heated.
o-anisidine		"	" "	The same
o-toluidine		"	" "	"
m-toluidine		"	Average	-
n-xylidine		"	"	-
Cresidine		"	Very low	-

Azo component	Formula (point of combination indicated by an asterisk; see remarks)	Combination medium	Azo component activity in combining	Remarks
Diphenylamine		"	Low	-
Dimethylaniline		"	Average	-
m-phenylene-diamine		First combination in an acid medium, second in a alkaline.	High	Can combine three times: first in para-position 4 with respect to the amino group, second in position 2; partially in position 6.
m-toluylene-diamine		The same	"	Combines two times: first in position 5 (para-position with respect to the amino group), second in position 3.
m-phenylene-diaminesulfo acid		Weakly acidic	Average	-
1-naphthyl-amine			High	Combines in position 4, a side product of combination partially forms in position 2.
Naphthionate		Weakly acidic or alkaline	Average	-

Azo component	Formula (point of combination indicated by an asterisk; see remarks)	Combination medium	Azo component activity in combining	Remarks
1-naphthylamine-5-sulfo acid		Weakly acidic	"	Usually combines in position 2; with active diazo compounds, in position 4
1-naphthylamine-6-sulfo acid		Weakly acidic or weakly alkaline	Average	Usually combines in position 4, partially in position 2.
1-naphthylamine-7-sulfo acid		The same	"	The same
2-naphthylamine-5-sulfo acid		Weakly acidic	"	-
Phenyl-peri-acid		Acidic	High	-
Tolyl-peri-acid		"	"	-

compound excess is used, predominantly the 2,4 isomer is formed. Meta-phenylenediamine combines in approximately the same way.

Bifunctional azo components which simultaneously have hydroxy- and amino groups, are extraordinarily important in the industrial production of azo dyes. The bifunctional derivatives of the naphthylene series are particularly diverse and valuable – the aminonaphtholsulfo acids. They are capable of a nitrogen coupling reaction in an alkaline medium just as the phenol, and like the amine, also in an acid medium. The empirical rules based on the different reaction rates have been worked out for some time, and in accordance with which it is possible to initially derive a mono-azo dye, utilizing an amine as an azo component and thereafter also derive a dys-azo dye.

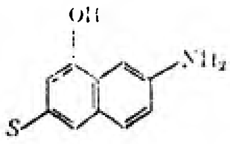
The activity of various substitutes which influence the azo component activity has been discussed above. This is also employed by forcing the bifunctional molecules to combine selectively. If nitrogen coupling is desired at that ring where the hydroxy-group (by the oxy-group) is located, then the reaction is carried out in an alkaline medium where the rate of coupling of the phenolate ion will be greatest, while the amino group in spite of the favorable conditions for coupling (the impossibility of salt formation), possesses significantly less activity than the phenolate group, and does not determine the course of the nitrogen coupling reaction. Conversely, in an acid medium the rate of nitrogen coupling of the non-ionized phenol is significantly less than the combining speed of the amine which is in equilibrium concentration, and for this reason the nitrogen coupling reaction will take place at that ring where the amino group (by the amino group) is located.

By skillfully employing a different medium for the first and second nitrogen coupling, asymmetrical azo dyes with the desired distribution of azo radicals are obtained. Nitrogen coupling in an acid medium is more difficult, particularly for large molecules; in an alkaline medium, the nitrogen coupling rate is rather high, even for large molecules.

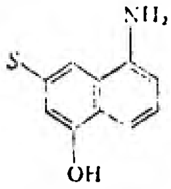
In this case, the most difficult coupling – in an acid medium – is carried out in the first step with the most active diazo component. The more easily effected nitrogen coupling is usually carried out with the already formed azo dye.

Some aminonaphtholsulfo acids are exceptions: having entered into one reaction, they are apparently incapable of repeated combination. Perekalin [208] has determined that the reason for this phenomenon can be the negative influence of the azo group as a electrophilic substitute on the reaction center. Additionally, in the opinion of Perekalin the reactivity of the azo component can be reduced due to the formation of a hydrogen bond between the hydroxyl group and the azo group which has taken the peri-position.

Such a chelate bond greatly passivates the effect of the hydroxy group on the nitrogen coupling reaction. Examples here include γ-acid, M-acid and a few others:



1. γ-кислота



2. М-кислота

1. γ-acid 2. M-acid

Following nitrogen coupling, position 1 or 4 in an acid medium, and 7 and 6 respectively are deactivated by the azo group entering at the right ring.

Table 3 is given to show the characteristics of the most important bifunctional azo components of the naphthalene series [209].

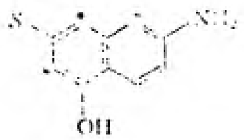
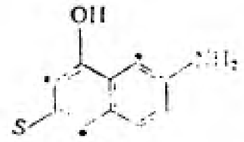
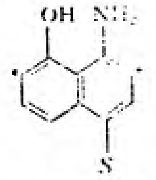
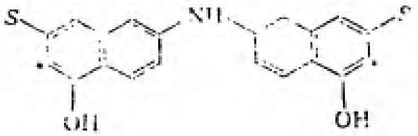
During the synthesis of many poly-azo dyes, particularly those in which aminonaphtholsulfo acid is used as a final reagent and which has a sulfo group in the immediate vicinity of the coupling point, it has been noted that the addition of organic bases catalyze the nitrogen coupling reaction. For example, this applies to dyes which are derived from γ-acid. Quite frequently the large molecule of an already synthesized poly-azo dye having a diazo group, instead of combining, dissociates, if pyridine, quinoline, their homologues, etc. are not added to the reaction.

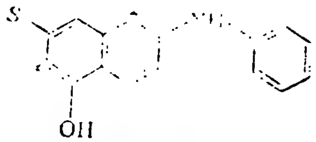
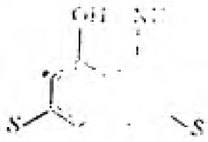
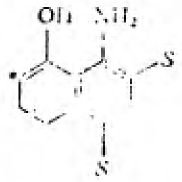
The effect of pyridine and its analogues was clarified by the work of Kozlov and Stepanov [210], Zollinger [211] and others. It was shown that pyridine and its analogues interact with an intermediate product during nitrogen coupling (page 63), taking a proton from it and stabilizing in the form of an azo dye. The strength of the action of the catalysts employed is directly proportional to the constant of their basicity. Consequently, according to Brensted [212] presently catalysis is usually basic. It has been noted that methyl groups in the ortho-positions with respect to the nitrogen atom in pyridine, quinoline and others, reduce the catalytic capability. This is explained by the spatial hindrances during the formation of the transition complex at the proton removal stage [213].

As far as the reactions which are carried out without using these catalysts in an alkaline medium are concerned, it has been found [214] that for pH values of less than 11, a proton is removed by water molecules, while for pH values greater than 11, the hydroxyl ions act as a base.

TABLE 3

Combination with Aminonaphtholsulfo Acids

Azo Component	Formula (point of combination indicated by an asterisk)	Medium and place of combination	Azo component activity in combining	Remarks
J-acid		In an acid medium in position 1, in an alkaline, in position 6	In an acid medium, average; high in an alkaline	Combines two times: first in an acid medium, second in an alkaline; in a strongly alkaline medium, partially combines in position 8.
γ-acid		In an acid medium in position 1, in an alkaline, in position 7	The same	Combines only one time, in a strongly alkaline medium partially combines in position 5.
1-amine-8-naphthol-4-sulfo acid		In an acid medium in position 2, in an alkaline, at position 7.	"	Combines two times, first in an acid medium, second in an alkaline.
Scarlet acid		Alkaline	Average	Forms disazo dyes during combination.
Dinaphthyl-J-acid		"	"	Forms disazo dyes during combination.

Azo component	Formula (point of combination indicated by an asterisk)	Medium and place of combination	Azo component activity in combining	Remarks
Phenyl-J-acid		In an acid medium at position 1; in an alkaline, at position 6.	High	Combines two times: first in an acid medium, second in an alkaline.
H-acid		In an acid medium at position 2; in an alkaline, at position 7	In an acid medium, average; in an alkaline, high	The same
1-amine-8-naphthol-2,4-disulfo acid		Alkaline	High	--

INDIVIDUAL REPRESENTATIVES OF AZO DYES

Because of their multiplicity it is very difficult to classify azo dyes, and there is no generally accepted view on the expedience of employing a particular classification. In principle, any of the classifications can be based on a feature of the chemical structure, technical application or color. There are proposals to consider the large number of azo dyes based on their chemical structure with subdivision into mono-, dis-, tris-, tetra-, and in general poly-azo dyes, depending on the number of azo groups. The further subdivision within each class is based on the order of the nitrogen coupling reactions and on the combinations of the diazo- and azo components employed. For example, if the azo component is capable of combining with two diazo compounds, the dyes are called primary disazo dyes; if a mono-azo dye is capable of diazotizing and combining with a second azo component, the dyes are called secondary asymmetrical dyes; if a bisdiazo compound combines with two like azo components, the dyes are called secondary symmetrical, etc. [215]. All the same, within each group it is necessary to divide the azo dyes according to the nature of their technical application [216]. The further breakdown within each section is made completely arbitrarily – according to the use of one and the same diazo- or azo component, color, certain characteristic chemical properties, the presence of certain substitutes, etc.

In describing the azo dyes which are most interesting from a technical viewpoint, from now on we will adhere to a technical classification for them which divides all azo dyes into three basic groups: water soluble, difficultly soluble in water, and finally, insoluble in water. However, the consideration of dyes based on the principle of their solubility will not always be strictly observed: in some cases a similarity in chemical structure or means of derivation is a more characteristic feature uniting the dyes other than their solubility. For this reason, we will have to deviate from the property of dye solubility and in the same group make reference to soluble, difficultly soluble, and even insoluble dyes. Those dyes which dissolve in organic solvents are also introduced in the group of insoluble dyes. Within the group, depending on the methods employed to dye one or the other substrate, we have divided the dyes into acidic, lac dyes, those easily washed out, mordant, chromic, monochromic, metal containing, direct, fixed, etc. And finally, the sequence for considering the individual representatives will depend on their color; dyes will be studied in order of intensity from yellow to green and black, independently of the molecule size or the number of azo groups, etc.

Water Soluble Azo Dyes

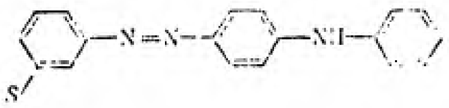
If the dye is a salt consisting of an organic cation (or an anion) and a corresponding inorganic anion (cation), in the majority of cases it will be soluble in water. Not only can inorganic particles act as secondary ions, but in rare cases organic ions can also. This makes the formation of internal salts possible, the water solubility of which is significantly reduced. Dyes in which anions are the colored portion of the salt, are sharply distinguished in their properties from those in which the color carriers are cations. For this reason all water soluble dyes are subdivided into two large groups in accordance with whether an anion or a cation which is a part of their composition, is colored.

Dyes with Colored Anions

Depending on their physical and chemical properties, these dyes are likewise divided into a few subgroups: acidic, direct (substantive), lac, easily washed out dyes, etc. Not all dyes have properties which permit them to be attributed to one and only one group. Some acid dyes have properties making it possible to employ them both as direct or lac dyes and vice versa. For this reason, the division of dyes with colored anions into various groups frequently has a conditional or purely technical character.

Acid Dyes

The simplest representative of acid azo dyes is acid metanil yellow (CI* 13065),



which is obtained from combining diazotized metanil acid with diphenylamine in an alcohol or acetic acid solution. The short coupling chain gives it a high coloration, while the small size of the molecule causes the absence of substantive properties.

Included among the yellow dyes is also acid yellow for rolling (CI 25135),

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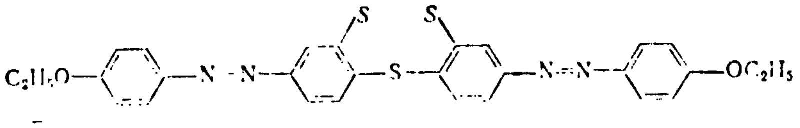
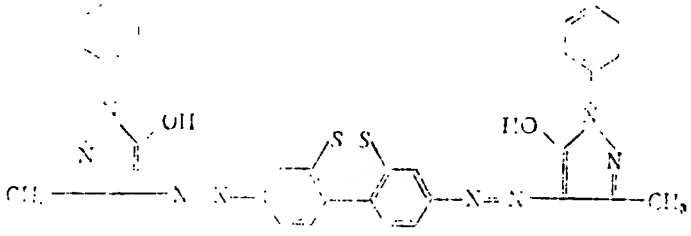
* CI — Color Index (editor's note)

which is obtained by combining the bisdiazotized disulfo acid of diaminodifenylsulfide with two phenol molecules and the subsequent ethylation of the hydroxy groups:



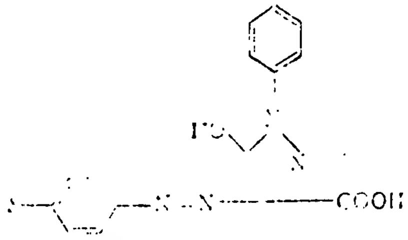
The consideration of this dye is instructive from several points of view. It is well known that resistance to rolling, other conditions being equal, increased with the size of the molecule. It is the ethylation of the hydroxy groups which produce this. On the other hand, an enlarging of a molecule while preserving coupling along the entire chain length should lead to the appearance of substantive properties, which is undesirable for acid dyes. In the dye under consideration, it would seem that both of the central benzene rings are coupled, since the sulfide bridge does not break the link [217]. However, despite the ability of the sulfide bridge to conduct electron influences, this does not occur in the given case due to the rotation of the benzene rings and their displacement from one plane. However, the relatively intense coloration of the dye being considered reveals this: based on its structure which has a large molecule and a long chain of alternating simple and double bonds, it should be colored extremely more deeply than with just a yellow color. However, the color of the dye is approximately the same as it should be for a "halfway one", for example, the nitrogen coupling product of metanil acid with phenol where the combination product is subsequently ethylated. Thus, we see that two important properties, substantivity and color, depend on the same factors and exhibit a sensitive response to the presence or absence of coupling in the atomic chains [218].

Also interesting from the same viewpoint is acid yellow K (CI 22910) which is a product of nitrogen coupling diazotized benzidinedisulfo acid with phenylmethylpyrazole:



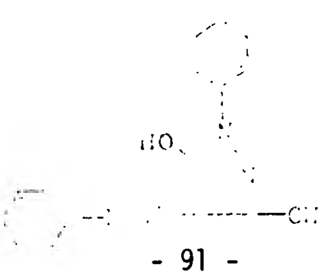
Due to the action of sulfo groups, the benzene rings are removed from one plane. and this interrupts the coupling between both portions of the molecule. The absence of substantive properties and intense color of the dye follows from this. This dye has an increased resistance to light, just as all dyes in which phenylmethylpyrazolone and its diverse derivatives are employed as the azo component. This compound is an important azo component for deriving acid yellow azo dyes which have special light resistance.

The yellow dye Tartrazine (CI 19140) is obtained by combining diazotized sulfanilic acid with phenylmethylpyrazolonecarboxylic acid:

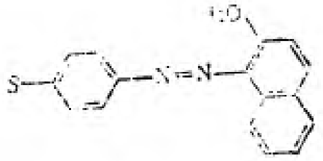


Because of the ease with which a non-toxic, highly pure preparation is obtained, this dye is employed as food coloring.

During combination with phenyldiazonium in an alkaline medium, phenylmethylpyrazolonesulfo acid forms light resistant acid yellow (CI 18820):

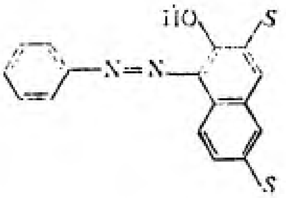


The use of naphthalene derivatives as azo components significantly deepens the color of the derived dyes. Thus, the dye obtained by the nitrogen coupling of diazotized sulfanilic acid with 2-naphthol, acid orange (CI 15510)

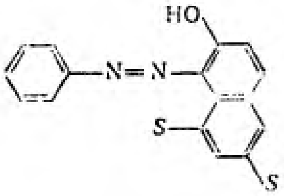


is more deeply colored than the corresponding benzene derivatives. The use of 2-naphthol derivatives, and not 1-naphthol as azo components, is in general quite desirable, since nitrogen coupling takes place at the ortho-position with respect to the hydroxy group and the presence of a hydrogen bond (see page 83), in reducing the acidity of the dye makes it more durable to damp alkaline processing.

Naphtholsulfo acids, particularly R-acid and G-acid, which are obtained by the sulfation of 2-naphthol are very popular as azo components. As a rule, R-acid with various diazo compounds yields dyes which are redder, while G-acid, dyes with yellower hues. The literal names of these dyes are even derived from this (R- from the German rot, and G- from the German gelb, etc. [rot, gelb = red, yellow respectively in German - translator's note]). Acid orange H (CI 16100) is the product of combining diazotized aniline with R-acid:



Light resistant acid orange (CI 16230) — with G-acid:

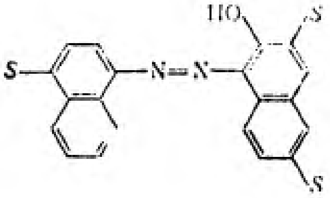


This dye also finds application as one which is easily washed out (see below).

The dye, acid bright orange 4K (CI 23255) is obtained by nitrogen coupling the bis-diazotized m-tolidine first with the anilide of acetylacetic acid and then with G-acid. It is noteworthy that just as in the case of acid yellow (see above), both benzene rings are not situated in the same plane because of the spatial difficulties occasioned by the methyl groups. A break in the linking and the absence of substantive properties and intense dye color follows from this.

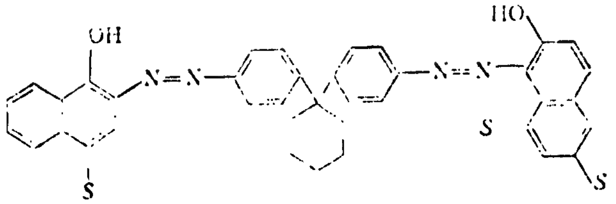
m-Tolidine yields dysazo dyes which are distinguished by a good fastness to friction [219].

Acid scarlet (CI 16150) (m-xylidine ⟶ R-acid) is an example of a dye which has a deeper color due to the use of the same R-acid of a more complex diazo compound. Acid red S (CI 16185) is obtained from naphthionic acid and R-acid



and are employed to color food products, hard candies, soft drinks, creams, etc.

The use of diaminodiphenylcyclohexane as a diazo component to derive acid dyes of a high degree of fastness is interesting. Here it is possible to carry out separate nitrogen coupling with different azo components. Thus, by combination with 1-naphthol-4-sulfo acid (Neville-Winter acid) and thereafter with G-acid, the dye acid scarlet 2Zh (CI 24785) is obtained:

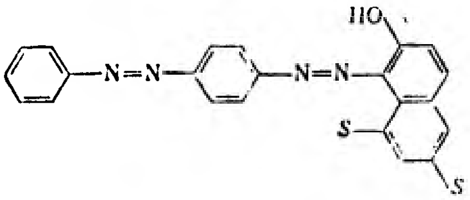


Instead of diaminodiphenylcyclohexane, its methyl and methoxyl substitutes in the benzene rings are employed and dyes having good light resistance and a high degree of fastness to friction are obtained [220]. These dyes do not have substantive properties and are relatively highly colored, in spite of the rather complex molecule. The causes of this are again to be found in the absence of coupling between the benzene rings.

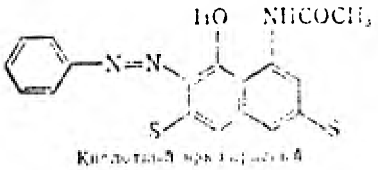
Fast acid scarlet (CI 22245) (G-acid ⟵ benzidine ⟶ phenol, the further esterification of n-toluolsulfochloride) in essence has only one donor group in the G-acid radical. The donor properties of the esterified phenol group are significantly weakened. The same can be said for the dye, fast acid scarlet 2Zh (CI 23265) (1-naphthol-3,6-disulfo acid ⟵ m-tolidine ⟶ phenol, esterification of benzenesulfochloride), and of fast acid red (G-acid ⟵ m-tolidine ⟶ phenol, esterification of n-toluolsulfochloride).

Recently efforts have been made to avoid dyes whose derivation is based on the use of benzidine and its analogues, which have carcinogenic properties. Intensive work on the substitution of benzidine with other diamines is being carried out. However, complete substitution is very difficult and for this reason it is not presently possible to completely exclude benzidine dyes.

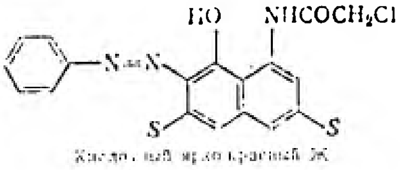
The derivatives of aminoazobenzene and aminoazotoluol, which are obtained as indicated above by the rearranging of the corresponding diazoamino compounds, comprise a special group of dyes. These diazo components yield azo dyes following diazotization and combination with various naphtholsulfo acids, which are used to dye animal fibers. Such a dye is acid red 2Zh (CI 27290), which is obtained by combining aminoazobenzene with G-acid:



The use of H-acid as an azo component for synthesizing acid dyes significantly deepens their color. However, due to the fact that during combination in an alkaline medium a considerable amount of the isomeric dye with the azo group in the o-position with respect to the amino group is formed along with the disazo dye, it is preferable to initially acylate the amino group in the H-acid; this reduces or entirely precludes its participating in the nitrogen coupling. During the combination of diazotized aniline with acetyl-H-acid, acid bright red (CI 18P50) is obtained, and with chloroacetyl-H-acid, acid bright red Zh is obtained:

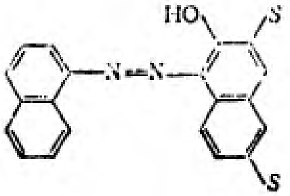


Acid bright red



Acid bright red Zh

A further deepening of the color is achieved by complexing both the diazo components and the azo components. In accordance with the conceptions of dye color intensity, the fusion of the benzene rings and the use of the condensed systems in this respect has a particularly marked effect. Thus, the dye derived from the diazotation of 1-naphthylamine and R-acid, Acid claret color (CI 16180) is colored significantly more deeply than its benzene analogue:

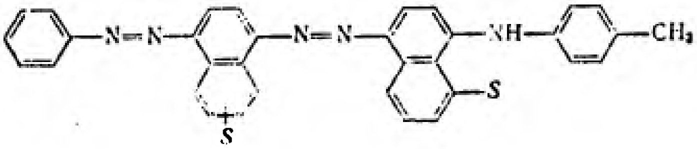


Quite frequently the system employed for the synthesis of polyazo dyes is:

D → I → F

where D is the diazo component, I is the intermediate azo dye containing an amino group capable of diazotization, and F is the final azo component of the 6th and 7-sulfo acid of 1-naphthylamine (Cleve's acid) in the independent form or in the form of a mixture of both isomers.

Thus, acid blue Z (CI 26410) is derived from aniline by combining it with a mixture of 6- and 7- sulfo acids of 1-naphthylamine following diazotization, diazotizing the resulting aminoazo dye, and thereafter combining this diazo compound with tolyl-peri-acid:



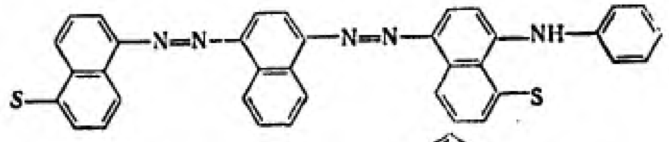
In this example it should again be emphasized that the dye aquires weakly substantive properties and is utilized as an acidic one for dyeing protein fibers. The absence of substantive properties is determined by spatial factors, as well as by the presence of, in all, one comparatively weak electron donor group, the secondary amino group, while the depth of dyeing depends on the large number of condensed rings in the chain lengths of the conjugate bonds.

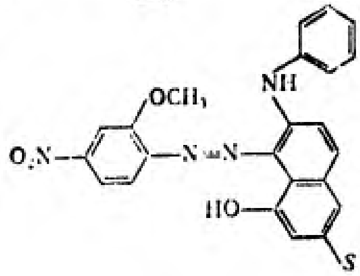
The same can also be said of acid blue K (CI 26400), which is derived in accordance with the formula: metanilic acid → 1-naphthylamine → tolyl-peri-acid. 1-naphthylamine was used here as an intermediate component, while the sulfo group is contained not in an intermediate link, but in the original benzene diazo component. Generally speaking, phenyl-peri- and tolyl-peri-acid when used as the final azo components usually yield deeply colored dyes. The same can also be said of the use of H-acid, regardless of whether it serves as a diazo or an azo component.

Thus, acid azure (CI 13405), in spite of the fact that it is a monoazo dye, is colored a bright blue-light blue and has moderate light resistance and a high degree of fastness to friction [221]. It is derived from the combination of diazotized H-acid with tolyl-peri-acid.

If H-acid is coubly combined (on the hydroxy and amino groups) with benzene diazo components, it is possible to derive acid disazo dyes with deep hues. The not very fast dye, acid blue-black (CI 20470) is an example of this kind of dye and is obtained by combining diazotized n-nitroaniline with H-acid in an acid medium, and thereafter combining the resulting intermediate dye with diazotized aniline in an alkaline medium.

Finally, acidic black dyes can be derived by using more complex diazo and azo components, but in this, not accumulating a large number of electron donor groups in the molecule in order that the dye not acquire strongly pronounced substantive properties for wool (a reduction equalization capability). Of the black acid dyes, acid black S (CI 26370) and acid black 2S (CI 17580) should be mentioned.





The first is derived in accordance with the formula:

1-naphthylamine-5-sulfo acid (Laurent's acid) →

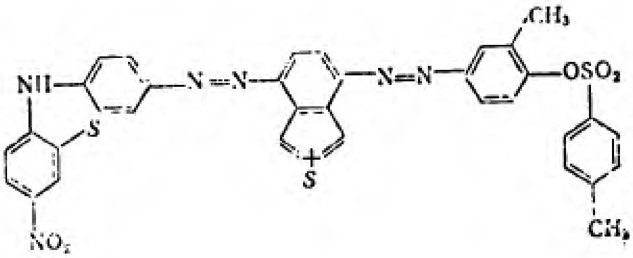
→ 1-naphthylamine → phenyl-peri-acid

while the second in accordance with the formula [222]:

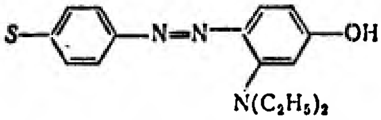
5-nitro-2-aminoanisol $\xrightarrow{(a)}$ phenyl-γ-acid

Due to their ability to easily diffuse in a substrate, some acid dyes are used to color leather and sheepskin furs. Such a dye is acid reddish-brown for leather (CI 26550) which is derived in accordance with the formula 4-nitro-4'-aminodiphenylamine-2-sulfo acid → 1-naphthylamine-6(7)-sulfo acid → o-cresol.

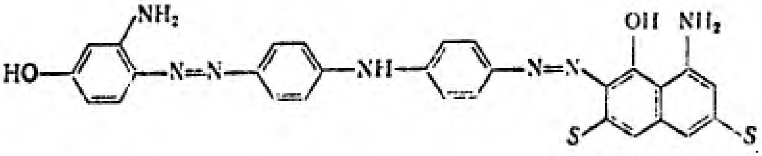
An acyl radical is attached to the hydroxy group by treatment with n-toluolsulfochloride:



It is easy to derive acid brown 2Zh for leather by combining diazotized naphthionic acid with resorcin. Analogous to it is acid brown K for leather which has the structure:



Acid dark blue 2K for leather is derived by combining bis-diazotized diaminodiphenylamine first with H-acid and then with m-aminophenol in an alkaline medium:



An analogous dye from N-phenyl-m-aminophenol is being produced by foreign firms (CI 25060).

Lac Dyes and Lacquers

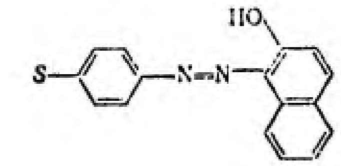
Some typically dyes which yield insoluble salts with alkaline earth metals are employed exclusively in the manufacture of lacquers, i.e. barium or calcium (rarely manganese) salts, which are most often used in polygraphy as well as in the production of wallpapers, pencils, for the preparation of artists' paints, for coloring resin, and sometimes even plastics. As a consequence of their almost complete insolubility in water, they are usually considered along with pigments which are analogous to them from this point of view. However, it is more logical to study them based on the indication of the presence of a colored anion among the acid dyes. These are usually dyes with a small molecule, predominately from yellow to red in color.

The manufacture of just varnishes, the precipitation of the above noted salts from soltuions is carried out in the presence of aluminum hydroxide (transparent varnishes) or barium sulfate (covering paints), on whose particles the insoluble salt precipitates. These substances are called substrates or carriers. The dye adsorbed on the substrate particles is treated with any water soluble barium, calcium or manganese salt. Then an insoluble salt is formed in the thickness of the substrate and the adsorbtion process becomes irreversible. The paint paste is often diluted with fillers to reduce the color intensity; these fillers include titanium white, lithopone, and other substances.

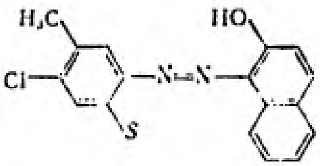
The technology for precipitating insoluble salts of acid dyes, as well as the purity of the original products play a substantial role in obtaining a high quality paint which has the specified hue.

Sometimes paints are obtained in the nitrogen coupling process by intorducing essential ingredients into the reaction mass. However, this method does not have any particular advantages over that described above.

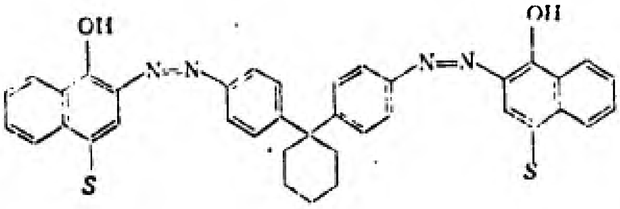
Thus, Paint orange is obtained by the formation of barium salt of the dye from diazotized sulfanilic acid and 2-naphthol:



Paint red Zh (CI 15585) is a barium salt of Paint red Zh derived from the combination of diazotized 2-chloro-5-aminotoluol-4-sulfo acid with 2-naphthol:



Sometimes disazo dyes, which are formed rather seldom with the diazo components used, are sometimes used in this series. Thus, Paint red 2 is a barium salt of acid scarlet 2Zh which is obtained by combining diazotized diaminodiphenylcyclohexane with 1,4-naphtholsulfo acid:



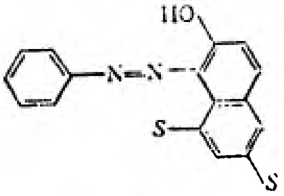
Paint red 2SM is a manganese salt of an azo dye: 2-chloro-5-aminotoluol-4-sulfo acid → 2-hydroxy-3-naphthoic acid.

The use of naphthalene diazo and azo components as always leads to a deepening of the color. Paint red S (CI 15630) takes the form of a barium (or calcium) salt of the dye: 2-naphthylamine-1-sulfo acid → 2-naphthol.

Easily Washed Out Dyes

For purposes of temporarily coloring fibers in a non-fast manner (weak bluing in various tints, marking, etc.), easily washed out acid dyes have been produced. Such dyes have a very weakly expressed substantivity, are quite soluble in water owing to the presence of a large number of sulfo groups and comparatively small molecule, and for this reason can be easily removed from the fiber.

Orange easily washed out dye (CI 16230) is a product of nitrogen coupling diazotized aniline with G-acid:



It is also an acid dye for wool (see above).

Red tinted dyes can be derived by using acetylized H-acid as an azo component. Thus, easily washed out Red (CI 18050) is derived in accordance with the formula aniline $\xrightarrow{\text{al}}$ acetyl-H-acid. Lilac colored easily washed out dye is synthesized from diazotized naphthionic acid and H-acid (alkaline combination), etc.

Complexing Azo Dyes

Complex compounds of chromium, cobalt, nickel and copper have practical significance in the chemistry and engineering of azo dyes. The ions of these elements, which belong to the transition elements of the first long period of the periodic chart, have unfilled inner 3d-, 4s-, and 4p-electron shells. These shells (all or a part of them) can be filled with unshared electron pairs of ligands. Included in the latter can be atoms (for example, nitrogen azo groups), molecules (water, ammonia, amine, and others) or anions (hydroxyl, acid anions, etc.). Only in coordination with a charged ligand is the corresponding charge of the ion neutralized, however, during complexing addition of neutral molecules or groups to a metal ion, the degree of charge on the ion does not change.

It is possible to illustrate this position with examples of various complexes where trivalent chromium plays a part. Chromium, just as the majority of metals of the transition group, has a coordination number of 6 (copper often exhibits only its coordination number of 4). This means that the chromium cation is capable of coupling six more groups or molecules coordinatively without changing their relationships to the anion. The resulting complex can be depicted in the following manner: $[Cr(NH_3)_6]^{3+}3Cl^-$.

If in an analogous example any ion, for example, a hydroxyl, is attached in a coordination linkage to the chromium ion, instead of one uncharged group, then naturally one of the charges on the chromium ion will be neutralized and the complex ion will have in all only two positive charges $[Cr(NH_3)_5OH]^{2+}2Cl^-$, with which it is electrovalently bound to the anions. By carrying out the sequential substitution of uncharged ligands by ions which carry a negative charge, we can introduce three anions into the internal coordiantion sphere, which entirely neutralizes the charges on the chromium. Such a complex will have the structure $[Cr(NH_3)_3(OH)_3]$ and will have no charge. If one, two or three more of the remaining molecules (or groups) are substituted by anions, then the complex ion acquires one, two or three negative charges respectively and is transformed into an anion which is electrovalently bound with one, two or three cations, for example: $[Cr(NH_3)(OH)_5]^{2-}2Na^+$.

It is important to note that in the internal sphere, independently of whether the ions or molecules are ligands, the bonds between them and the chromium atoms are formed, as was stated above, due to the unshared pairs of ligand electrons, i.e. they are covalent. For this reason, the most correct of all approaches is to depict all coordination bonds in the same manner with a solid line.

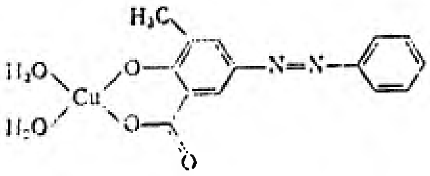
Ortho-hydroxy azo dyes or azo dyes are derivatives of salicylic acid or acids analogous to it and possess a sharply pronounced ability to form complex salts with ions of the metals of the transition group. In this case, phenolate ions and nitrogen atoms of the azo groups act as ligands, while in the case of derivatives of salicylic acid, the phenolate and carboxylate ions which are in ortho-positions with respect to each other, do the same.

We recall that the ortho-positioning of hydroxy groups was a reason for the ease of formation of a hydrogen bond between the hydroxy and azo groups (or between the hydroxy and carboxyl groups), and is responsible for the many specific properties of azo dyes, for example, their reduced acidity, resistance to alkaline treatment, etc. The capacity for forming a hydrogen bond also determines the complexing of these dyes with ions of chromium, cobalt, copper and nickel. The complex salts, in closing a five or six element ring are very durable [223] due to the presence of not less than two ligands in one molecule (a chelate bond), and have interesting hues, in a word they possess those properties which are required of a modern dye [224].

Of itself an azo group is not capable of stably combining with metal ions. Only the presence of a hydroxy group in the ortho-position with respect to it which provides for the completion of a chelate bond, makes it possible to form the stable complex compounds which are used in practice. It is remarkable that although one ortho-hydroxy group is sufficient to complete a chelate bond, the presence of a second ortho group which is capable of acting as a ligand (hydroxy group, amino group, alkoxy group or caroboxylate ion), significantly strengthens the complex.

When o-hydroxy-o'-methoxyazo dye is treated with copper salts, the methoxy group demethylates. Sometimes this is used to advantage by employing a o-methoxyamino derivative as a diazo component, and not an o-hydroxyamino compound, which following diazotization is combined with relative difficulty.

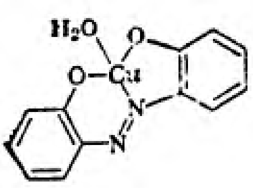
Azo dyes, derivatives of salicylic acid and its analogues, can form complexes with metals without azo groups playing a part. An example of such a complex is given below:



Depending on the relative quantities used for the reaction with metal salts of the dye, as well as on their structure, and circumstances of derivation, the ratio between the metal and the dye radical can fluctuate. One dye radical can be attached to one metal atom. Then we speak of composition complexes of 1:1. o, o'-dioxyazo dyes have a tendency to form complexes of this type. In this case, as can be seen from the examples given below, the ligands which fill the internal sphere of the metal can not only be the groups found in the dye molecule, but also "outside" molecules or ions: water, amines, hydroxyl ions, and what is important to note, electron donor groups (amino or hydroxy groups) of the main chains of protein molecules [225], with whose participation the system fiber-dye is formed.

Complexes 1:1

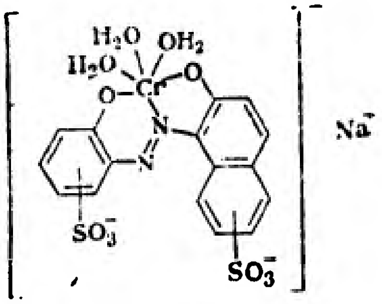
Комплексы 1:1



медьсодержащий комплекс

Complex containing copper

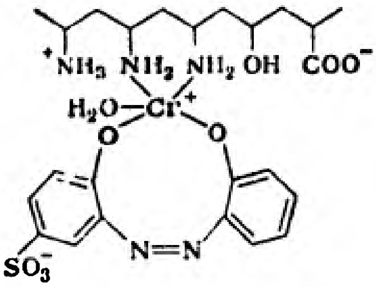
[1]



хромсодержащий комплекс

Complex containing chromium

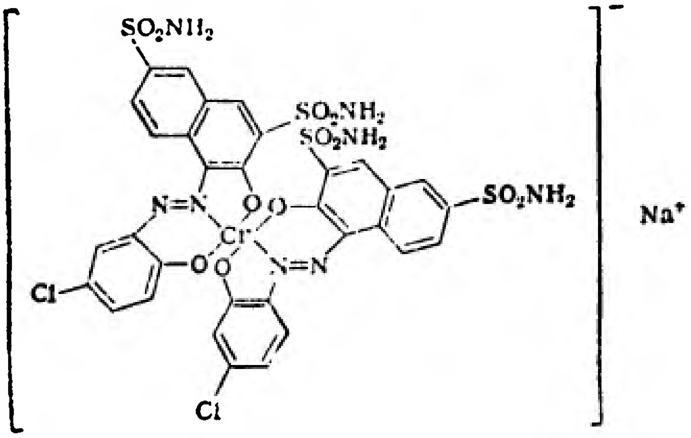
[2]



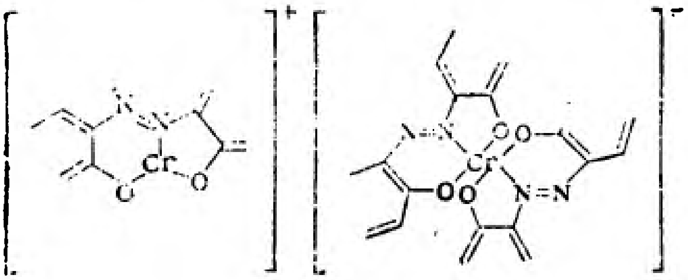
хромсодержащий комплекс
с участием протеинового волокна [3]

1. Complex containing copper 2. Complex containing chromium
3. Complex containing chromium where a protein fiber participates

Complexes of a 1:1 composition contain sulfo groups which give them acid properties. For this reason they are colored in a rather acid medium. Complexes of 1:2, i.e. those in which two dye radicals are attached to one metal atom, are usually formed from o, o'-dioxyazo dyes, which contain sulfamide, sulfo ether and similar groups, which give the complexes only weakly acid properties. An example of such a complex is given below:



Complexes of a 2:3 composition are also known (two metal atoms, three dye molecules). The structure of such a complex can be shown by the diagram:

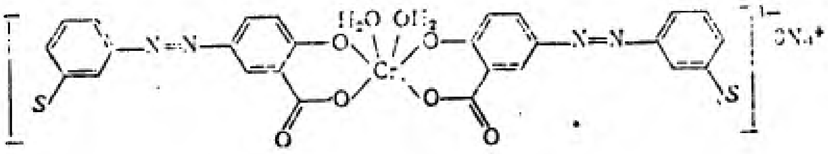


As can be seen from the formula, the 2:3 complex takes the form of an ionic compound in which the role of a cation is played by a 1:1 complex which carries a positive charge, while that of the anion, by a 1:2 complex having a negative charge.

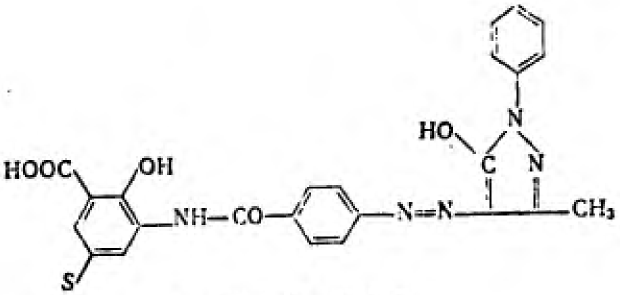
Mordant Dyes

There are various types of mordant dyes among the azo dyes; less than others, the so-called cotton mordant dyes, which are used by preliminarily treating the fiber with metallic mordants, are used almost exclusively for printing. The complex compounds of azo dyes are obtained much more frequently on the protein fibers. The method using preliminary mordant treating is seldom used. More widespread are the chrome dyes which are employed by initially mordanting the protein fiber with chromium salts and then coloring it; also widespread are the monochrome ("metachrome") dyes, where the dyeing is carried out simultaneously with the mordant treatment. For monochrome dyeing, special mixtures are employed (for example, ammonium sulfate and potassium chromate [226]). The structure of the complex which is formed during monochrome dyeing can not be distinguished from the structure of the complexes which result during preliminary or subsequent chromizing.

Dyes which color by the method of subsequent chromizing (chrome dyes). Of the valuable dyes which are treated with chrome salts on the fiber, we will consider Chrome yellow 3. It is obtained by combining diazotized metanil acid with salicylic acid in an alkaline solution. This dye forms complexes with metals because of the salicylic acid radical without an azo group acting as a ligand. The probable structure of the chrome complex of this dye can be shown by the following formula [227]:



The dye, Chrome yellow K, is analogous to the preceding one and is derived from sulfanilic acid instead of metanilic. Chrome yellow 2K which has a complex amine, N-(4-aminobenzoyl)-3-amino-5-sulfosalicylic acid as a diazo component is very interesting; following diazotization it combines with phenylmethylpyrazolone:

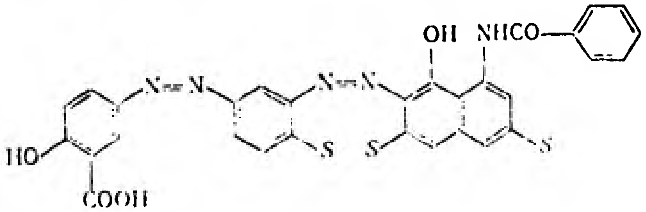


1. Chrome yellow 2K

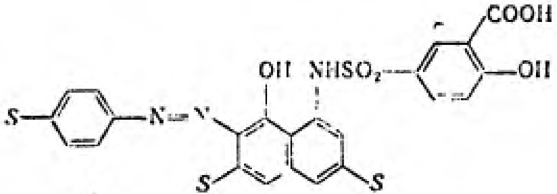
1. Хромовый желтый 2К

The dye forms chrome complexes due to the salicylic acid radical. The addition of phenylmethylpyrazolone to the composition of the molecules assures a yellow color and a high light resistance. Somewhat more complex and more deeply colored is the dye Chrome orange (4-aminoazobenzene-4'-sulfo acid ⟶ salicylic acid).

Chrome bright red is a dysazo dye obtained by combining diazotized 3-nitroaniline-4-sulfo acid with salicylic acid, reducing, and combination with a molecule of benzoyl-H-acid following diazotization:



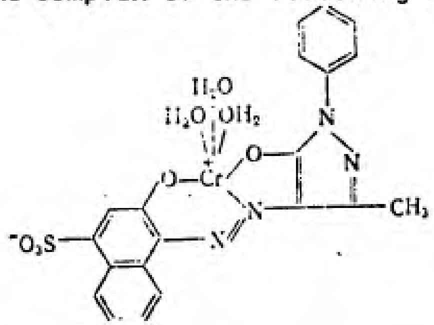
The salicylic acid radical can also be contained in the azo component, not entering into the basic coupling chain of the dye. One such dye is Chrome bright red 2S, obtained by combining diazotized sulfanilic acid with H-acid in which the amino group has been acylated by sulfosalicylic acid:



1. Хромовый прекрасный 2С

1. Chrome bright red 2S

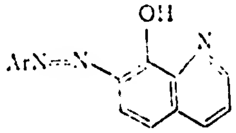
Chrome red (1-amino-2-naphthol-4- sulfo acid ⟶ phenylmethylpyrazolone) (CI 18760) is an example of a o, o'-dioxyazo dye. With chrome chloride it yields a red crystalline complex of the following structure [228]:



In some cases anthranilic acid has been successfully used as a diazo component. In the dye, Chrome claret colored S (anthranilic acid ⟶ 1,4 naphtholsulfo acid) phenolate and carboxylate ions serve as ligands. The fastness of the dye, particularly to light, is good.

Chrome blue K (2-aminophenol-4-sulfo acid ⟶ chromotropic acid) (CI 16675) and Chrome blue 2K (4-chloro-2-aminophenol ⟶ acetyl-H-acid) (CI 18090) are examples of deeply colored o, o'-dioxyazo dyes which yield durable chrome complexes.

Also interesting is the use of 8-hydroxyquinoline as an azo component for deriving analogous dyes and which is coupled with diazo compounds in the ortho-position with respect to the hydroxy group [229]:

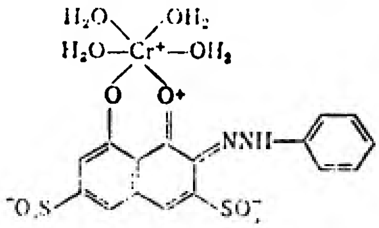


Green colored dyes are derived by using picric acid as a diazo component. Such a dye is Chrome dark green (CI 17235) (picric acid $\xrightarrow{al}$ H-acid). Finally, black dyes can be synthesized by using 6-nitro-1-amino-2-naphthol-4-sulfo acid, combining either with 1-naphthol (CI 14645), or with 2-naphthol (CI 15710).

Chrome black O (CI 20320) is obtained according to the equation:

anthranilic acid $\xrightarrow{(a.)1}$ J-acid $\xleftarrow{(al.)2}$ 4-nitro-2-aminophenol

From the short summary given above for the most important mordant acid dyes, with which animal derived fibers are colored in accordance with the principle of subsequent chromizing, a few conclusions are to be reached. A portion of the dyes considered are derivatives of salicylic acid, and besides this group contain one or a few more sulfo groups. If the dye does not contain a salicylic acid radical, then its mordant properties are at least assured by two hydroxy groups, which are most frequently located in ortho-positions with respect to the azo group. Included in the same group of dyes are those in which one of the hydroxy groups in the ortho-position is substituted by an amino group. Additionally, derivatives of chromotropic acid are also found in it. It was believed earlier that chromotropic acid was oxidized in the chromizing process and yielded derivatives of juglone (hydroxy-1,4-naphthoquinone). It was later revealed [230] that the chrome complexes are formed by the quinonehydrazone form of azo dyes — derivatives of chromotropic acid, for example:

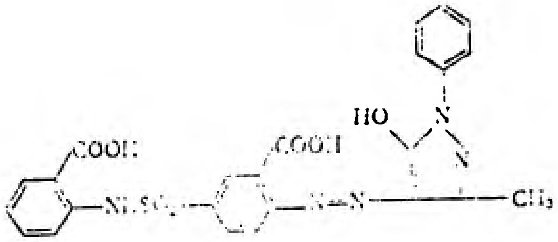


Also found among these dyes are those which can be used in a one dip dyeing method, or by preliminarily separating the complexes with metals and then dyeing with them. However, the most efficient means of employing these mordant dyes, in which it is possible to also obtain good fastness and interesting shadings, is that of subsequent chromizing.

Dyes using the method of simultaneous chromizing. Monochrome (metachrome) dyes are structurally little different from dyes which are used for coloring by subsequent chromizing. We can only mention that the majority of them have a comparatively low molecular weight and contain a carboxyl or sulfonamide group instead of a sulfo group, i.e. those which give the dye extremely weakly acid properties.

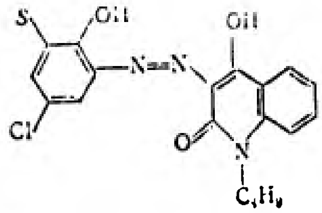
On the other hand, monosulfo acids are also found among the monochrome dyes. The reduced acidic properties of monochrome dyes make it possible to use them for dyeing out of weakly acid or even neutral washes. Either ammonia chromate or a mixture of potassium chromate with any ammonia salts is used as mordanting salts. The ammonia decomposes in proportion to the coloring of the salt and the dyeing bath only gradually becomes weakly acid. This makes it possible not to endanger the formation of a lac dye in the bath, but assures obtaining it in the protein fiber; electron donor groups of protein molecules probably act as ligands during its formation. Monochrome dyes have an advantage over mordant types using subsequent chromizing in that the hues of the dyes do not depend on subsequent chromizing conditions and are more constant, which facilitates the standard utilization of dyes when coloring. Almost any monochrome dye can be employed for subsequent chromizing, but only a few from the group of dyes considered earlier can be employed as monochrome dyes, since in this case it is essential that the lac formation of the mordant dye in a bath does not proceed quickly, but does proceed rather easily in order that the fiber not be subjected to harsh treatment here.

The dye Monochrome yellow 2K (CI 18710) satisfies the requirements given above. It is derived from diazotized 4-aminobenzene-1-sulfanilide-3,2-dicarboxylic acid and phenylmethylpyrazolone:

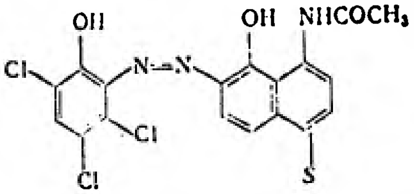


Because of the carboxylic groups and the sulfamide arrangement, it possesses weakly acid properties and additionally contains a hydroxy group in the ortho-position with respect to the azo group which assures mordant properties. It is also possible that imide and carboxyl groups participate in the complexing. Thus, Monochrome orange 4K (CI 14040) (2-chloro-4-nitroaniline ⟶ salicylic acid) does not contain any acid groups other than the carboxylic which simultaneously make possible the mordant properties of the dye.

The use of N-alkylated derivatives of 4-hydroxy-2-quinoline as azo components is also interesting. By combining diazotized 4-chloro-2-aminophenol-6-sulfo acid with N-butyl-4-hydroxy-2-quinolone, the dye Monochrome claret color (CI 19360) is obtained:



A further deepening of the color is achieved by using naphthalene azo components. Monochrome blue Z (3,4,6 trichloro-2-aminophenol ⟶ acetyl-C-acid) (CI 17940)

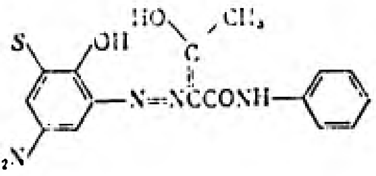


is a very durable monochrome dye having a pleasant blue shade. The dye derived from diazotized picramic acid and S-acid (1-amino-8-naphthol-4-sulfo acid) which is called Monochrome green S (CI 17125) is itself an example of a deepened color where a non-acylated aminohydroxy component is used. Finally, very fast black dyes are well known in this group, which are derived by combining picramic acid with naphtholsulfo acids. Useful as an example here is Monochrome black Z (picramic acid ⟶ 2-naphthol-4-sulfo acid) (CI 15950). In general, the use of picramic acid is advantageous insofar as the hydroxy group is known to be located in the ortho-position with respect to the azo group of the resulting dye. Although the derivatives of o-aminophenol which yield the same result and are widely used, the diazotization and combination of the obtained diazo compound presents well known difficulties for the o-aminophenols (see above).

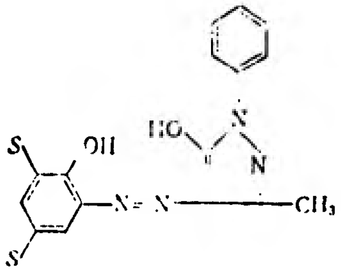
Dyes for anodized aluminum. Included in this group are dyes which are specially chosen to color aluminum, its alloys, as well as products made of them, the surface of which has been coated with an oxide film using the method of anodic oxidation.

All the dyes have mordant groupings, as well as sulfo and carboxyl groups. The molecules of these dyes are comparatively small. Sometimes they take the form of chrome complexes, and it is to be thought that in such a case mixed lacs where two metals participate are formed during the coloring of anodized aluminum. Dyeing with them is accomplished by heating in aqueous solutions. The coloring of aluminum, imitating gold, has found very wide application for consumer products. Other types of dyes have found application in instrument construction, and in the construction industry (for example for coloring architectural decorations, chandeliers, lattices, etc.).

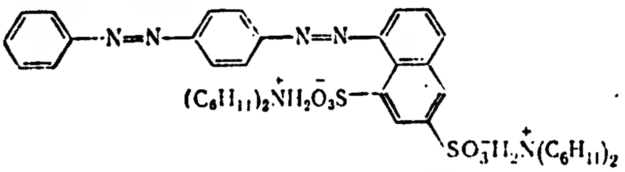
Yellow Z for aluminum (CI 13900) is a chrome complex of an azo dye derived by nitrogen coupling 4-nitro-2-aminophenol-6-sulfo acid with an anilide of acetoacetic acid:



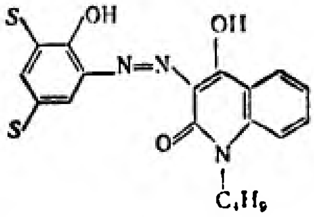
Gold-yellow for aluminum is a copper complex of the product of combining diazotized 2-aminophenol-4,6-disulfo acid with phenylmethylpyrazolone:



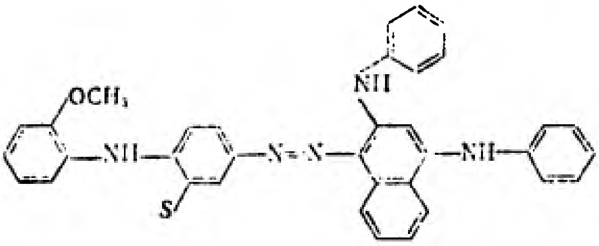
Orange K for aluminum (CI 16105) is obtained by combining diazotized anthranilic acid with R-acid. Scarlet Zh for aluminum which is an azo dye from aminoazobenzene and G-acid is also interesting. A dye with better solubility is manufactured in the form of a dicyclohexylamino salt:



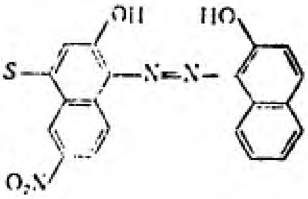
Gold-brown for aluminum is a copper complex of the nitrogen coupling product of diazotized 2-aminophenol-4,6-disulfo acid with 1-butyl-4-hydroxy-2-quinolone:



Blue 2K for aluminum (CI 503020) is synthesized by combining diazotized 4-amino-2'-methoxydipheylamino-2-sulfo acid with 1,3-diphenylaminonaphthalene-8-sulfo acid·



And, finally, Black K for aluminum (CI 15711) is obtained in the form of a chrome complex from an azo dye, the product of nitrogen coupling diazotized 6-nitro-1-amino-2-naphthol-4-sulfo acid with 2-naphthol:



Metal Containing Acid Dyes

A quite important step forward was the invention of metal containing dyes which are prepared from mordant dyes by treating them with metal salts under various conditions.

The preparation of metal containing acid dyes is usually carried out by treating the appropriate dyes with salt of trivalent metals in various proportions and under various conditions [231]. The processing is most frequently carried out in an aqueous solution with heating. The bichromate is not usually employed to derive the metal containing dyes, but rather the salts of organic acids of trivalent chromium are used (for example, salicylic, formic [232]).

In addition to heating the azo dye in an aqueous medium with chrome salts for 4-24 hours [233], it is possible to conduct the process under a small pressure (1.5 – 4 atm). The process of complexing in this case is completed after several hours.

Chrome containing azo dyes for acid dyeing are very fast; as a rule, they withstand heating with acids and alkalis [234]. Dyeing with them is simple and is no different than the usual acid coloring. It is important to note that the color of the original azo dye following complexing, often changes to the darker side.

Metal containing dyes are divided into two groups. Complexes with a 1:1 or 2:3 composition belong to the first of them. They all contain sulfo groups and possess strongly acid properties, and for this reason are as a rule employed for coloring from strongly acid washes [235] (at a pH = 1.9 – 2).

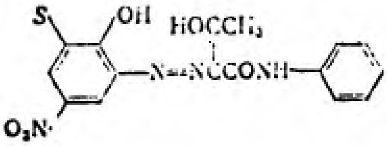
Belonging to the second group are azo dye complexes with a 1:2 composition.

In a chemical respect, they are characterized by the fact that they do not contain substitutes capable of dissociating in a neutral or weakly acid medium (sulfo groups), but have weakly acid properties which increase their hydration ability, and consequently, their water solubility. Alkylsulfone groups have proved to be particularly advantageous in this respect [236]. Sulfamide and acetylamino groups can also be used [237]. Since these dyes are capable of dyeing in a neutral or weakly acid wash, they can be employed for coloring mixed fibers, wool with cotton or polyamide fibers of the nylon, capron [Soviet name for polycaprolactam fiber - translator's note], etc. The complexes have predominantly a 1:2 composition. The most important are chrome and cobalt dyes, but nickel and iron preparations are also known which are of interest both from the viewpoint of durability as well as the hues of the derived complexes.

Metal containing dyes of both the first and the second groups are very convenient in dyeing and yield finished colors which are little different in durability from the mordant chromic or monochrome dyes [238].

Metal containing complexes of 1:2 are usually used for dyeing in a weakly acid bath. However, they can also be used for dyeing in a strongly acid bath; if 4-8% of the fiber weight in sulfuric acid is used for dyeing, then in such a medium the 1:2 complexes are transformed into 1:1 complexes and a dye which does not contain metal. Similar dyes in the foreign literature have names of Neolan or Palatin [239]. Azo components from arylizes of acetoacetic acid, 2,4-dihydroxyquinoline, phenylmethylpyrazolone and others are most frequently used to derive them. The metallic complex is often separated in crystalline form.

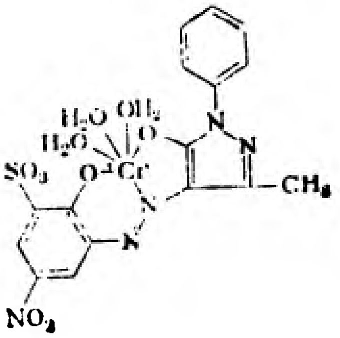
Dyes which are recovered from strongly acid baths. Acid yellow 4KM (CI 13900) belongs to the yellow dyes and is obtained, as are almost all dyes of this group, from the derivatives of o-aminophenol (and naphthol). The anilide of acetoacetic acid is used as an azo component for its synthesis:



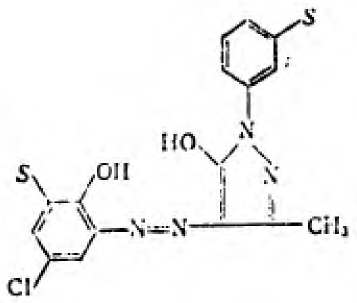
The chrome complex is obtained by heating the dye with an aqueous solution of chromium fluoride or chromium formate for several hours.

Similar to the preceeding dye, acid orange KM (CI 18740) is a chrome complex. The azo dye is derived from the sequence 6-nitro-2-aminophenol-4-sulfo acid → phenylmethylpyrazolone [240]. A complex with a 1:1 composition is obtained when the dye is heated with chromium sulfate and chromium formate at 130° C.

The structure of the lac is expressed by the following formula:



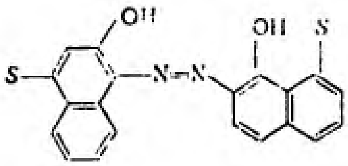
The sulfo group which gives the dye its strongly acid properties can also be contained in the pyrazolone radical. Acid red 4ZhM (CI 18800) is a chromium complex of the dye:



To derive the chrome complex, it is heated with chromium formate in an aqueous solution for several hours at 125° C.

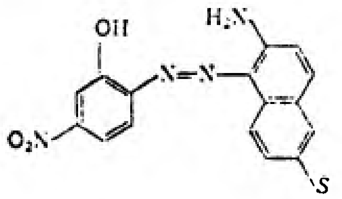
As was stated above, there are rather good reasons for assuming that the molecules of water which act as ligands in complexes of a similar type, are displaced by ligand groups (for example, an amino group) of the protein molecule when dyeing protein fibers.

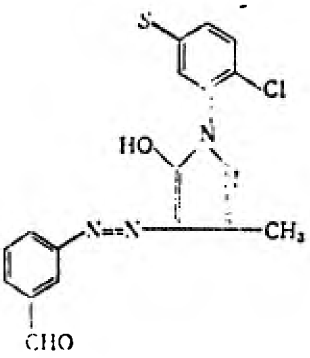
A further deepening of the color is achieved by using an amine of the naphthalene series as a diazo component. Acid pink M (CI 18810) is a chrome complex of the dye which is derived from the combination of 1-diazo-2-naphthol-4-sulfo acid with phenylmethylpyrazolonesulfo acid. There are data in the literature which show that this complex can be successfully separated into optical isomers in cellulose [241]. Acid blue 2ZM is a chrome complex of the dye in which both the diazo component and the azo component are naphthalene derivatives:



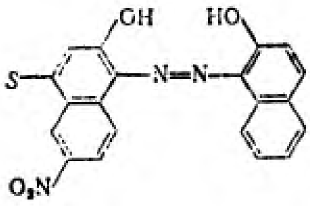
The chrome complex of this dye with a 1:1 composition is obtained by heating it for seven hours in an acid medium with chromium sulfate at 115° C.

An original dye is acid green 4ZhM. It is a mixture of the dye derived from 5-nitro-2-aminophenol and 2-naphthylamine-6-sulfo acid (Brenner's acid) in the form of a chrome complex, and the yellow dye which is formed by combining diazotized m-aminobenzaldehyde with (2'-chloro-5'-sulfo)phenylmethylpyrazolone:





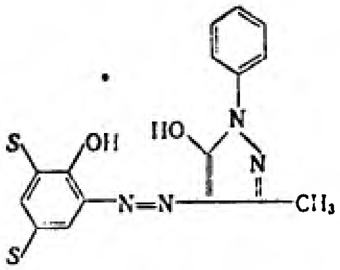
Black colored dyes are obtained by using 6-nitro-1-amino-2-naphthol-4-sulfo acid as a diazo component. During combination with 2-naphthol, the diazo compound derived from this acid forms the dye



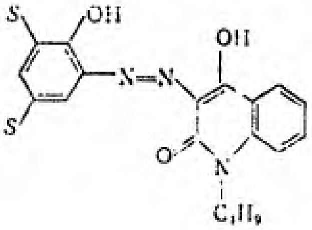
which is produced in the form of a chrome lac of a 2:3 composition [242] under the name of acid black M (CI 15711). The chrome complex is obtained by heating the dye at 115° C for two hours with an aqueous solution of chrome formate Thereafter, the various parts of the chromized and non-chromized dye are mixed and treated with an alkali. Three molecules of the dye are joined to two chromium atoms in the resulting compound.

Naphtholsulfo acid is also used in place of 2-naphthol in the derivation of analogous black dyes.

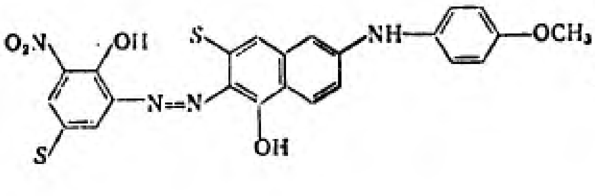
In this group of dyes are also found representatives used to dye leather. We note that the copper complex derived from the product of nitrogen coupling diazotized 2-aminophenol-4,6-disulfo acid with phenylmethylpyrazolone



is known by the name Acid yellow ZM for leather. Analogous to it is Acid orange KM for leather, which is derived by using the same diazo compound which is combined with N-butyl-4-hydroxy-2-quinolone

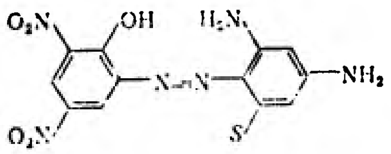


It is used in the form of a copper complex. A chrome complex from the azo dye derived by using 6-nitro-2-aminophenol-4-sulfo acid and n-anisyl-J-acid

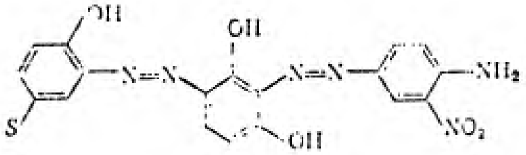


is produced by our industry as Acid blue M for leather.

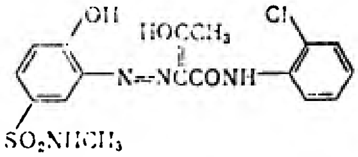
The dye Acid dark brown MSh (CI 13260) in the form of a chrome complex is recommended for coloring sheepskin furs. It is the product of combining diazotized picramic acid with 1,3-phenylenediamine-4-sulfo acid:



Disazo dyes are also well known among these dyes. Acid brown M for leather (CI20250) is very interesting, considering the synthesis. Initially, a copper complex of the dye is obtained form diazotized 2-aminophenol-4-sulfo acid and resorcin, and it is combined with diazotized 1-nitro-2,4-phenylenediamine:



Dyes which are recovered from weakly acid baths. If a derivative of o-aminophenol which contains an alkylsulfone or sulfamide group, which contribute weakly acid properties, is used for a nitrogen coupling reaction with any azo component, then it is possible to obtain the valuable dyes which are known by the names irgalan or cibalan (the firs is produced by the Ciba firm). They yield very interesting and fast colors with various complexing metals. Thus, when diazotized 2-aminophenol-4-methylsulfamide is combined with the o-chloroanilide of acetoacetic acid, the dye



is formed, which yields a cobalt complex of 1:2 (fast Acid yellow NKM)[1],

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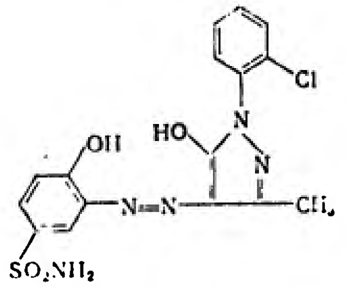
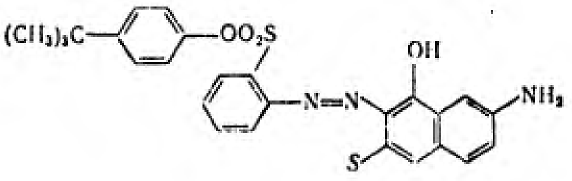
[1] The letter N in the name of the dye indicates that it can be employed in a neutral bath.

which dyes wool an attractive fast yellow color in a weakly acid wash.

An analogous dye which is derived from diazotized 2-aminophenol-4-sulfamide and o-chlorophenylmethylpyrazolone in the form of a chrome complex, and known by the name of Acid orange light resistant N4KM, likewise has outstanding fastness.

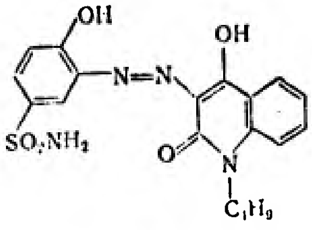


Sulfoesters can also be used in addition to the sulfamide derivatives. A characteristic example of such substances is acid red dye which results from the nitrogen coupling of the diazotized n-tertiary-butylphenyl ester of orthanilic acid with γ-acid:



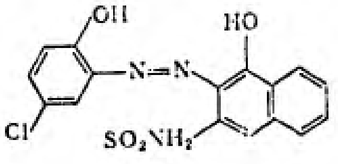
The absence of a weakly acid sulfamide group in this dye is compensated by the sulfo group of the γ-acid which does not have too acid a character, because of the presence in the "quinogenic" position with respect to it of the primary amino group. The chromium or cobalt complex of this dye (Acid red N2S) is used for dyeing in a neutral bath.

A deepening of the color is achieved by using alkylhydroxyquinolones as an azo component. Acid claret color N2SM

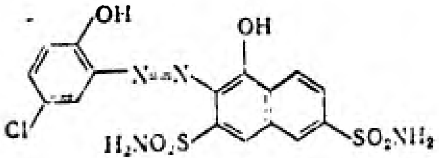


is derived from the combination of diazotized 2-aminophenol-4-sulfamide with N-butyl-4-hydroxy-2-quinolone. It is produced in the form of a chrome complex obtained by heating the dye with chromium salts.

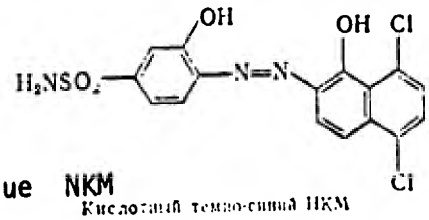
The sulfamide group can also be contained in the azo component. By way of example here we can use Acid violet N2SM, which is a cobalt complex of the dye (4-chloro-2-aminophenol → 1-naphthol-3-sulfamide):



Blue complexes are formed by treating the dyes, for which derivatives of naphthol have been used as an azo component, with chromium salts. Examples include Acid blue N2KM and Acid dark blue NKM:

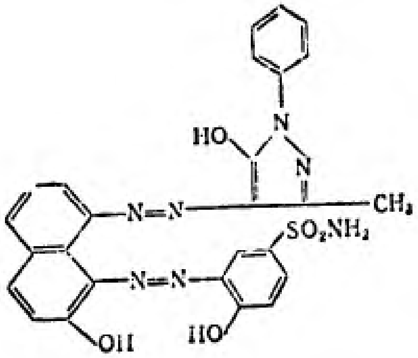


Acid blue H2KM Кислотный синий Н2КМ

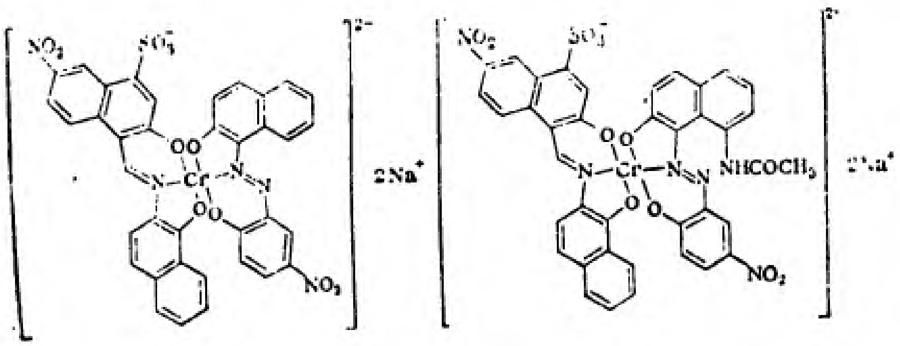


Acid dark blue NKM Кислотный темно-синий НКМ

Of the disazo dyes, we note that Acid brown N2KM is derived by combining diazotized 2-aminophenol-4-sulfamide with 1-acetylamino-7-naphthol, hydrolyzing the acetyl group, secondary diazotization of the resulting monoazo dye and final coupling with phenylmethylpyrazolone:



The dye is sued in the form of a chrome complex. Complex combinations are used to obtain black dyes of this group. An example here is Acid black N23M. Diazotized 6-nitro-1-amino-2-naphthol-4-sulfo acid (we recall that this diazo compound combines specifically in the ortho-position) is combined with 1-naphthol and diazotized 4-nitro-2-aminophenol with 2-naphthol. The mixture of both dyes is treated with chrome salts, obtaining a mixed complex of 1:2. On the other hand, the same 6-nitro-1-amino-2-naphthol-4-sulfo acid is diazotized and combined with 1-naphthol. The latter dye, along with the dye derived from nitrogen coupling diazotized 4-nitro-2-aminophenol with 8-acetylamine-2-naphthol, is likewise treated with chrome salts. Both complexes are mixed together and the dye, Acid black N2ZM is obtained:

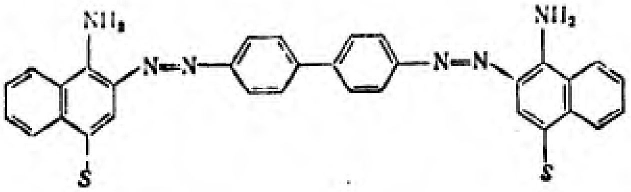


Кислотный черный Н23М

Direct or Substantive Dyes

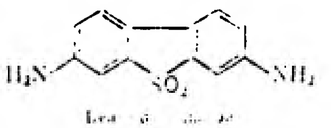
A large group of azo dyes is included in the direct azo dyes for cotton and other plant fibers, as well as for regenerated cellulose fiber. The dyes which are not fixed on the fiber, as a rule have low fastness characteristics. Fixing following dyeing is accomplished by various methods, which are mentioned below.

Historically, the first synthetic substantive dye was Congo red, derived by combining bis-diazotized benzidine with naphthionic acid:

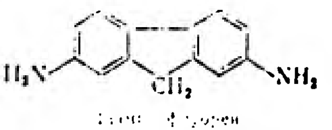


The benzene rings of diphenyl in Congo red are not located precisely in one plane. Nonetheless, the angle between the planes of these rings is not so great that it completely breaks up the overlapping of the π-electron clouds, although both rings also do not entirely interact. Insofar as it is important to preserve even a minimal opportunity for π-function overlapping, it is evident from the fact that the substitutes which are located in meta-positions with respect to the azo groups, even more disrupt the monoplanar structure of the diphenyl radical, and such dyes completely lose substantive properties. Examples here include the dyes which are derivatives of benzidinedisulfo acid, m-tolidine, and others [243].

However, if by using substitutes which are in the ortho-position with respect to the diphenyl bond and which break up the monoplanar disposition of the benzene rings, it is possible to connect a new ring which brings the benzene ring into one plane again, the phenomenon of substantivity is again clearly pronounced. Dyes which are derivatives of benzidine sulfone or diaminofluorene



Benzidine sulfone



Diaminofluorene

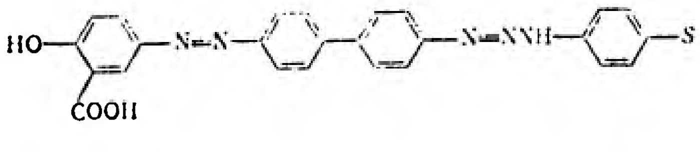
are substantives, in which this property is more sharply pronounced than in dyes which are benzidine derivatives.

Although the use of benzidine and its derivatives (o-tolidine, dianisidine, and others) is very convenient and invariably leads to the formation of substantive dyes, extensive investigations have been undertaken in recent years for the purpose of turning up complete substitues for these diamines, which are carcinogenic substances.

Besides benzidine, other groups are well known which contribute substantive properties to dyes of which they are a part. These include radicals of dehydrothio-n-toluidine, J-acid, acylamino groups, and a few others).

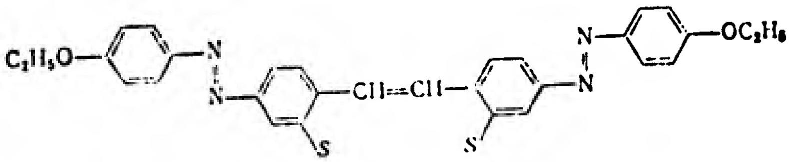
From the viewpoint of their industrial application to dyeing plant fibers, substantive dyes are divided into the usual direct, light resistant direct and fixed by various subsequent treatments.

Direct yellow ZhKh (CI 22010)



is interesting insofar as one part of its molecule is a diazoamino compound; the dye is fixed in the fiber by treatment with chrome salts. It is derived by combining bis-diazotized benzidine with salicylic acid, and subsequently treating the monoazo dye containing the diazo group with sulfanilic acid. Also known is a symmetrical dye, obtained from combining bis-diazotized benzidine with two molecules of salicylic acid (Chrysamine G), but it is of no practical significance in view of its low fastness.

Also interesting is Chrysophenine (CI 24895) which is derived from diaminostilbenedisulfo acid and two phenol molecules; the dye formed in this case is ethylated with ethyl chloride because of its instability in the presence of alkalis:

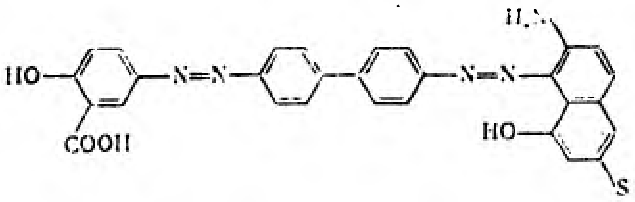


This is one of a few azo dyes to which the quinonehydrazone structure cannot be ascribed.

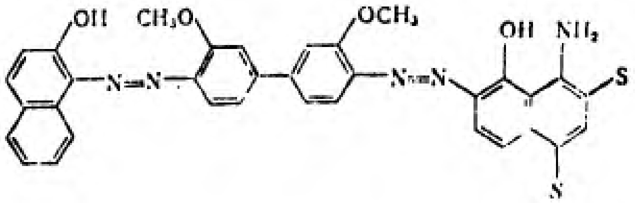
The symmetrical dyes, derivatives of the so-called scarlet acid (phosgene treated J-acid), belong to a group of yellow orange dyes. When two molecules of diazotized aniline are combined with scarlet acid, direct bright orange (CI 29150) is obtained and possesses a satisfactory fastness. The use of naphthalene diazo compounds significantly deepens the color. An example here is Direct red 2S (Ci 29215) which is derived from two moles of 1,5-naphthylaminosulfo acid and one mole of scarlet acid.

The dye, Direct blue for leather (CI 23790) which is derived in accordance with the sequence: o-tolidine ⇉ chromotropic acid (two moles), should also be noted. It dyes leather an attractive blue color and has satisfactory fastness.

An even greater deepening of the color is frequently observed in the derivation of asymmetrical dyes. As was indicated in the chapter on the reactivity of bis-diazotized amines, the nitrogen coupling rate of both diazo groups differ. This is used to derive valuable direct asymmetric dyes by combining the diazotized amine with a less active azo component at first (for example, with an amine or salicylic acid, which exhibit little activity in the nitrogen coupling reaction), and thereafter, effecting a second coupling, this time with an active azo component. An example is Direct red Kh (CI22310), which is obtained by first combining bis-diazotized benzidine with salicylic acid in an alkaline medium, and then with gamma-acid (well known as a rather active azo component) in an acid medium:



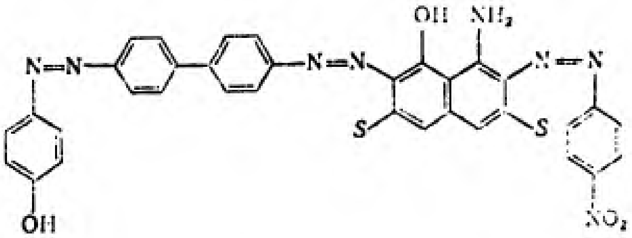
In an analogous manner it is possible to obtain the derivatives of o-tolidine, o-dianisidine, diaminodiphenylamine and other analogues of benzidine. Thus, the not very fast Direct blue (CI 242280) is obtained by first combining bis-diazotized o-dianisidine with 1,8-aminonaphthol-2,4-disulfo acid and then with 2-naphthol:



The symmetrical dye (1,8-aminonaphthol-2,4-disulfo acid ← o-dianisidine → 1,8-aminonaphthol-2,4-disulfo acid) is given the name Direct pure azure.

It also does not have adequate fastness, but is utilized because of the pure light blue hue of the finished colors.

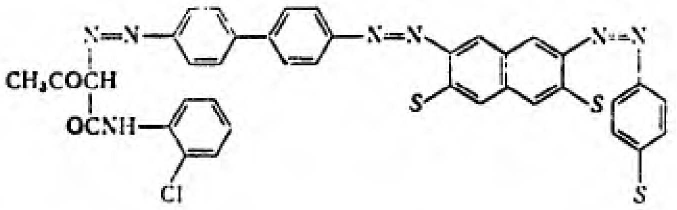
Green and black colors can be derived in this group of dyes by synthesizing more complex trisazo dyes. To derive Direct green (CI 30295), bis-diazotized benzidine is combined in an alkaline medium with the azo dye, which is obatined beforehand from diazotized n-nitroaniline and H-acid in an acid medium. The final coupling is carried out with phenol in an alkaline medium:



A shorter formula for the derivation of this dye appears as follows:

phenol $\xleftarrow{2}$ benzidine $\xrightarrow{1(al)}$ H-acid $\xleftarrow{(a)}$ n-nitroaniline

Direct green for leather is derived by combining bis-diazotized benzidine sequentially with H-acid and the o-chloroanilide of acetoacetic acid. In the final stage, the resulting disazo dye is combined with diazotized sulfanilic acid in an acid medium:



Direct olive colored Kh (CI 31885) is obtained according to the sequence:

$$\text{salicylic acid} \xleftarrow{1(a)} \text{o-tolidine} \xrightarrow{2(a1)}$$

$$\longrightarrow \text{H-acid} \xrightarrow{3} \text{m-phenylenediamine}$$

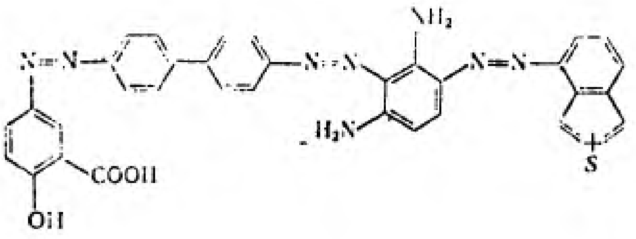
Here it is interesting to note that the azo dye derived from tolidine, salicylic acid and H-acid is subjected to diazotization and final nitrogen coupling. The diazotization of such a complex amine as the above mentioned azo dye sometimes presents considerable technical difficulties.

Direct black Z (CI30235) is derived by combining bis-diazotized benzidine with H-acid in an acid medium. The synthesized monoazo dye is combined in an alkaline medium with diazotized aniline, and finally, following diazotization the resulting complex compound is combined with m-phenylenediamine in an acid medium:

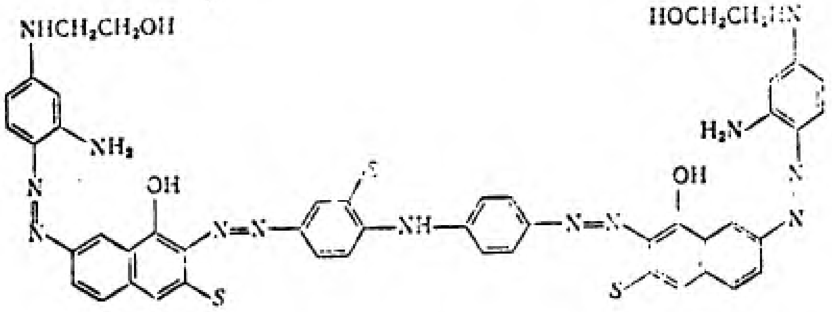
$$\text{m-phenylenediamine} \xleftarrow{3} \text{benzidine} \xrightarrow{1(a)} \text{H-acid} \xleftarrow{2(a1)} \text{aniline}$$

The dye, Direct black K (CI 30245) is obtained by the substitution of m-toluylenediamine for m-phenylenediamine.

If bis-diazotized benzidine is first combined with salicylic and then with the azo dye from diazotized 1-naphthylamine-6(or 7)-sulfo acid and m-phenylenediamine, then Direct brown for chrome leather is obtained:



Found among this group are dyes and the more complex tetracidazo dyes. Direct black 2S (CI 35440) can serve as an example here. In order to derive it, bis-diazotized diaminodiphenylaminosulfo acid is combined in an alkaline medium with two moles of γ-acid. The resulting compound is diazotized and combined with two moles of m-phenylenediamine in an acid medium. Finally, the dye is treated with ethylenechlorohydrin:

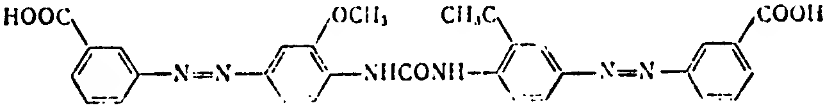


The yellow dyes of this group should also be noted which are not obtained by a nitrogen coupling reaction. When nitrotoluolsulfo acid is heated with caustic alkalis under set conditions, mutual oxidation-reduction of the nitro and methyl groups occurs. The first is reduced to azo and azoxy groups, while the second is oxidized with the formation of stilbene derivatives. In this way, Direct yellow K (CI 40000) is formed, a dye of an undetermined structure, the molecule of which includes azo and azoxy groups. The dye is valued because of the hue purity. Treating it with alkali sulfides (apparently during the reduction of the azoxy group into an azo group) yields fast Direct orange (CI 40003), while treating with benzenesulfochloride yields fast Direct orange K.

There is a particularly large number of similar dyes in the second group of substantive dyes which are direct light resistant azo dyes. Thus, light resistant direct orange 4Zh is a dye of undetermined structure obtained by the interaction of 4,4'-dinitrostilbenedisulfo acid with dehydrothio-n-toluidine; light resistant direct orange 2Zh (CI40215) from interaction with 4-aminoazobenzene-4'-sulfo acid; light resistant direct orange 5K, from the interaction of the same acid with the azo dye obtained by combining diazotized sulfanilic acid with sulfomethyl-o-anisidine with the subsequent hydrolysis of the sulfomethyl group:

In all of these dyes, the nitro groups of dinitrostilbenedisulfo acid react with the amino group of the above listed amino compounds, forming either azo or azoxy groups. The dyes can have either a chain or cyclic structure.

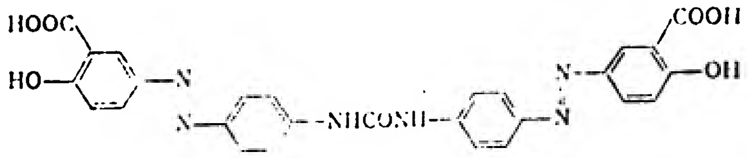
From among the direct light resistant dyes, there are likewise many in which two aminoazo dye radicals are interconnected by a bifunctional group, most often a diacid radical. Such dyes include Direct light resistant yellow (CI 29035), which is derived by combining diazotized m-aminobenzoyl acid with N-sulfomethyl-o-anisidine. Following hydrolysis of the sulfomethyl group, the dye is treated with phosgene, coupling two molecules of the bifunctional carbonyl group:



The introduction of a sulfomethyl group (or one similar to it) into the amino group precludes the formation of diazoamino compounds.

The linking of aminoazo dyes using phosgene, fumaril chloride and cyanur chloride is a frequently used method for deriving substantive dyes.

To derive Direct light resistant yellow ZKh (CI 25300), diazotized n-nitroaniline is combined with salicylic acid; the resulting nitroazo dye is reduced, and finally, the aminoazo compound which is formed is phosgene treated:



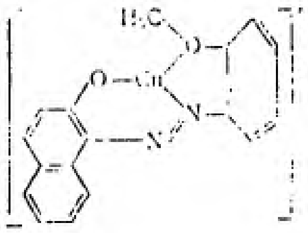
In this case, just as in many others analogous to it, it is necessary to reduce the nitro group found in one of the azo dye rings. The reduction of such a nitro group is completely possible, although it requires gentle handling in order that the reaction is not directed to the azo group during reduction. These conditions usually include the use of alkali sulfates, comparatively low temperatures (40 - 60° C) and the absence of a large surplus of the reducer [244]. The reaction is usually carried out in an aqueous medium. Magnesium sulfate or magnesium chloride is added to the reaction medium during reduction with sodium hydrosulfide.

The joining of two azo dye molecules is also carried out using fumaril chloride. Thus, the dye, Direct light resistant orange 6Zh is obtained in accordance with the following sequence. Initially, 4-aminoazobenzene-3,4'-disulfo acid is diazotized and combined with m-toluidine. The resulting amino azo dye is treated with fumaril chloride and the desired compound is obtained. The amino group in the m-toluidine molecule is not protected, since the methyl group strongly activates the point of entry of the azo group, and diazoamine compounds are almost not formed at all during this nitrogen coupling.

The combining of several azo dyes which contain an amino group, is also carried out using cyanur chloride. Owing to the different reactivities of the three chlorine atoms, the cyanur chloride easily interacts in stages with various amines. For this reason, there is a possibility of obtaining asymmetrical dyes. Additionally, as can be readily seen from the formula given on page , the individual components of the complex dye which are connected together by a triazine ring do not form a unified chain of conjugate double bonds. If two differently colored dyes are joined by a triazine ring, the color of the resulting compound will be a mixture of the colors of both dyes. For example, when blue and yellow dyes are combined using a molecule of cyanur chloride, a green dye is obtained. Such dyes are called dyes with disconnected chromophores, and this method is widely used to derive dyes of a previously specified color.

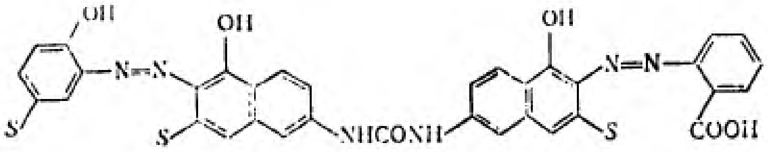
Among the light resistant direct dyes, a rather important position is occupied by complex compounds which are predominately formed with a copper ion.

Dyes having two ligand groups usually form complexes of a 1:1 composition [245]. If a methoxyl group acts as a second ligand, then depending on the method of preparing the complex compound, various results are obtained. When a dye is treated with copper salts (most often copper sulfate) in an aqueous medium at ≈100° C, a singly charged cation of a 1:1 complex is obtained in which a hydroxy group acts as an ionic ligand, while the part of a molecular one is played by the oxygen of a methoxy group and a nitrogen atom of an azo group:

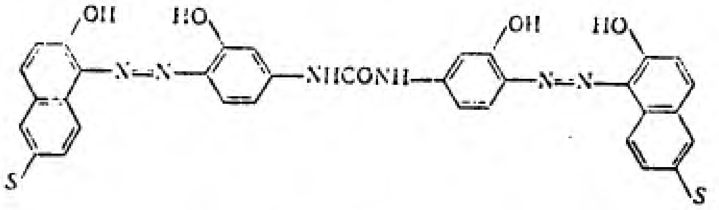


When dyes are treated in the presence of acetic acid, ammonium and an organic base (pyridine, ethanolamine and others) [246], dealkylation occurs -- the splitting off of a methyl group, and exactly the same complex is formed as in the case "coppering" o,o'-dihydroxyazo dye. This method is frequently used to derive dyes of the dihydroxybenzidine series which are difficult to derive by other methods, using dianisidine for their synthesis.

Direct light resistant claret color SM, produced in the form of a copper complex is an example of fast direct dyes. It is a product of nitrogen coupling diazotized 2-aminophenol-4-sulfo acid and anthranilic acid with scarlet acid:

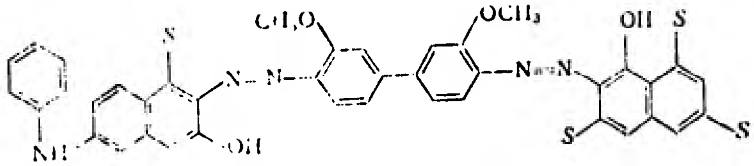


An interesting dye is direct light resistant red-violet 2KM (CI 25410); it is obtained by combining diazotized 5-nitro-2-aminoanisole with Schaffer's acid:

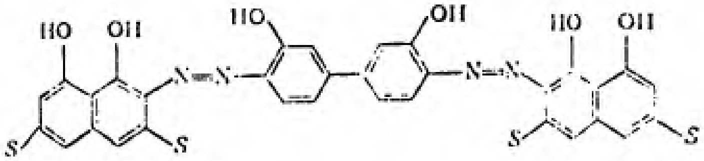


The resulting compound is reduced and treated with phosgene. Finally, the dye is treated with copper sulfate at a high temperature in the presence of bases. In this case, demethylization takes place and a durable dye complex is formed.

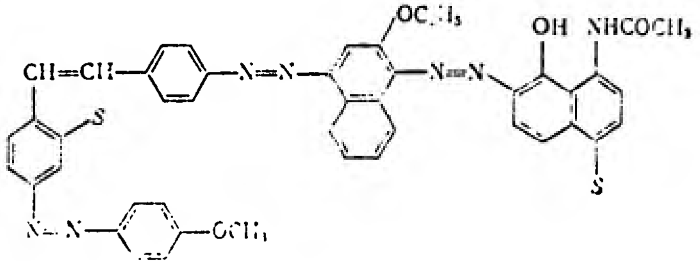
A further deepening of the color is achieved by using dianisidine as a diazo component, while naphthalene derivatives are used as azo components. Direct light resistant blue 2ZM is a copper complex dye formed when bis-diazotized dianisidine is combined with one mole of phenyl-J-acid and one mole of 1-naphthol-3,6,8-trisulfo acid:



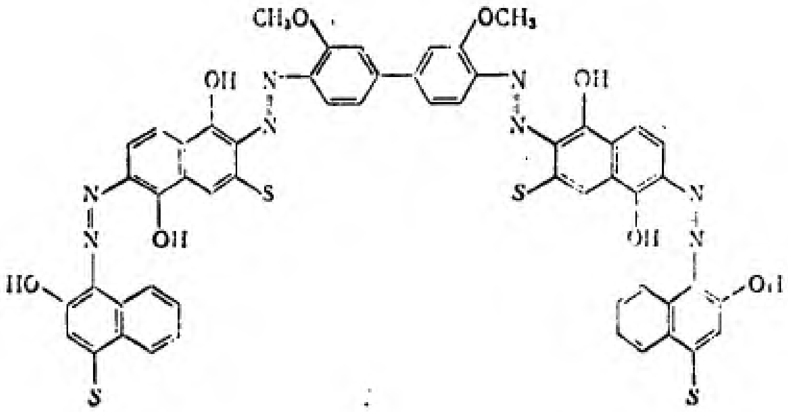
Demethylation sets in during coppering of the dye. Direct light resistant azure ZM (CI 23160), in contrast to the preceding dyes, is a copper complex of a 2:1 composition derived from bis-diazotized dianisidine and chromotropic acid. During coppering, the methyl groups are split off:



It is possible to derive green colored dyes by complexing the molecule and using stilbenedisulfo acid derivatives. Thus, Direct light resistant olive color 2ZM (CI 31985) is derived in accordance with the following formula: 4-nitro-4'-aminostilbenedisulfo acid is diazotized and combined with phenol. Thereafter the phenol hydroxy-group is methylated. The nitro group is reduced, the resulting amine is diazotized, and the diazo compound is combined with 1-amino-2-ethoxynaphthalene-6-sulfo acid; the resulting dye is again diazotized and finally combined with 1-acetylamino-8-naphthol-4-sulfo acid in the presence of pyridine. The ethyl group which is in the ortho-position with respect to the azo group is easily split off during treatment with copper salts. The processes enumerated above lead to the formation of a dye with the following formula:



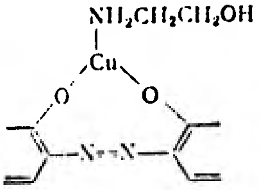
Direct light resistant gray 4SM is a copper complex of the dye



which is derived from dianisidine and two molecules of 1,5-dihydroxynaphthalene-3-sulfo acid. This intermediate dye is combined with two molecules of diazotized 1-amino-2-naphthol-4-sulfo acid. The splitting off of the methyl groups, just as in previous cases, occurs during treatment with copper salts.

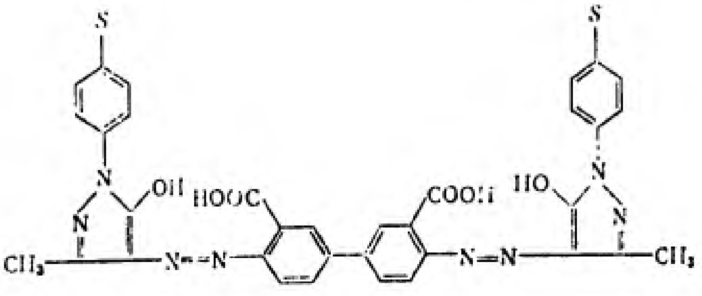
The formation of copper complexes also takes place during copper salt treatment of already dyed fibers at 80° C. For certain dyes where it is necessary to conduct the coppering simultaneously with the dyeing, a complex compound of copper sulfate with sodium tartrate is used as a coppering agent.

It has been proposed that dyeing be conducted in the presence of organic bases of the ethanolamine type for certain difficultly soluble complex compounds of direct dyes and copper salts [247]. During dyeing, a molecule of the organic base is attached to a copper atom, forming a water soluble complex of the type:



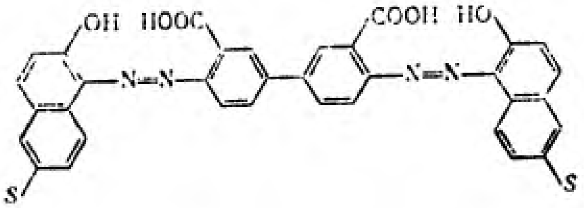
Based on the extent to which the dye is fixed in the fiber, the complex separates out the organic base (in the fiber it is substituted by cellulose groups) and forms fast colors. Such dyes are produced by the Ciba company under the name of cupranones [248].

Of the light resistant direct dyes which are fixed in the fiber by subsequent treatment with copper salts, we will mention Direct light resistand 4KU, which is a product of coupling bis-diazotized benzidinedicarboxylic acid with two moles of phenylmethypyrazolonesulfo acid. The dye is fixed in the fiber with copper sulfate:

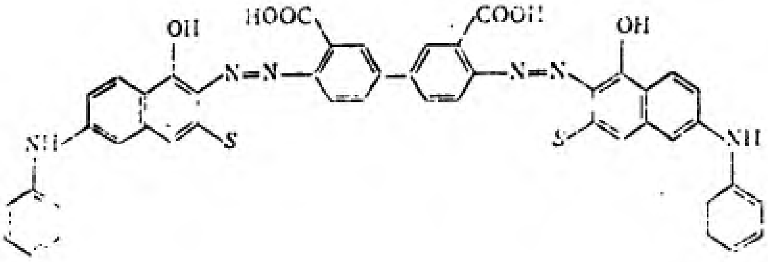


The substitution of phenylmethylpyrazolone by Schaffer's acid leads to

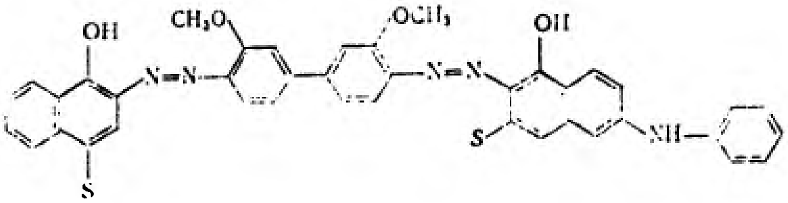
Direct light resistant violet 2KU:



The use of phenyl-J-acid as an azo component makes it possible to derive Direct light resistant violet SU:

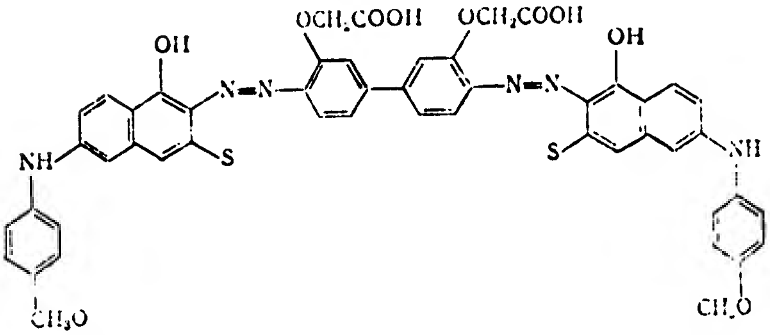


Direct light resistant blue ZU (CI 24185) is derived from dianisidine by diazotizing it and subsequently combining it with phenyl-J-acid and 1-naphthol-4-sulfo acid:

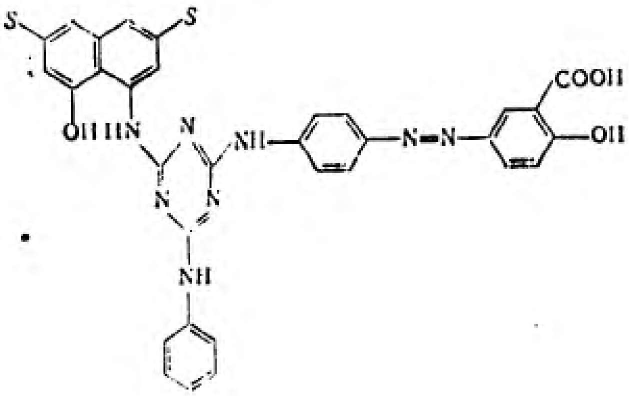


The dye is fixed in the fiber with copper sulfate.

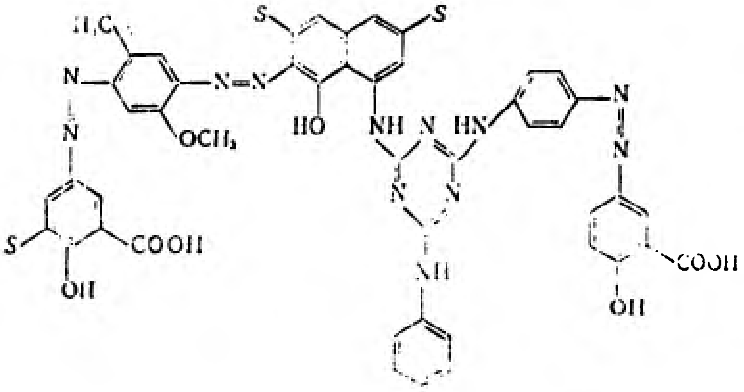
Cometines benzidine-3-3'-dihydroxyacetic acid is used instead of dianisidine. Thus, during its diazotization and combination with n-anisyl-J-acid, the valuable dye, Direct light resistant pure blue 4KU (CI 24555) is obtained:



Following treatment in the fiber with copper salts, the colors thus derived are resistant to the effect of light and wet processing. The dye with disconnected chromophores which is a derivative of cyanuric acid, Direct light resistant green 2ZhU (CI 34040) is very interesting from several points of view. To derive it, the first chlorine atom of cyanur chloride is substituted by the dye derived from the reduction of the nitro group in the product of nitrogen coupling n-nitroaniline with salicylic acid; and the second atom is substituted by H-acid, while the third - by aniline:



Thereafter, the separately prepared azo dye from diazotized 5-aminosulfo-salicylic acid and cresidine is diazotized and combined with the previously derived triply substituted cyanur. As a result, a dye is obtained which is fixed in the fiber with copper sulfate:



The dye, Direct light resistant black KU (CI 30400) is finally derived in accordance with the formula:

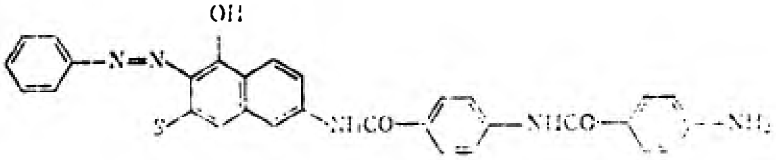
salicylic acid $\xleftarrow{1}$ dianisidine $\xrightarrow{2(a1)}$
5-nitroanthranilic acid $\xrightarrow{(a)}$ J-acid

It is possible that during the fixing with copper salts under relatively gentle conditions the methyl groups of the dianisidine radical are not split off.

The direct dyes which are diazotized in the fiber represent a large group of dyes with substantive properties which are fixed in the fiber. They are characterized by the fact that they contain a primary amino group capable of diazotization. Owing to the substantive properties, these dyes color cellulose fibers, and thereafter are subjected to diazotization in the fiber and nitrogen coupling (often called developing in these cases) with any azo component, most frequently with 2-naphthol, phenylmethylpyrazolone or m-phenylenediamine. The instability of the diazo compound derived in the fiber makes it necessary to carry out the developing as quickly as possible. In this case, the color of the dye changes; on the other hand, this depends on the disposition of the amino group in the primary azo dye. The new dye formed in the fiber is usually enormously more resistant to wet processing, but its light resistance, just as for the majority of direct dyes, is not very good. Usually the prefix diazo- is found in the trademark of dyes which are diazotized in the fiber.

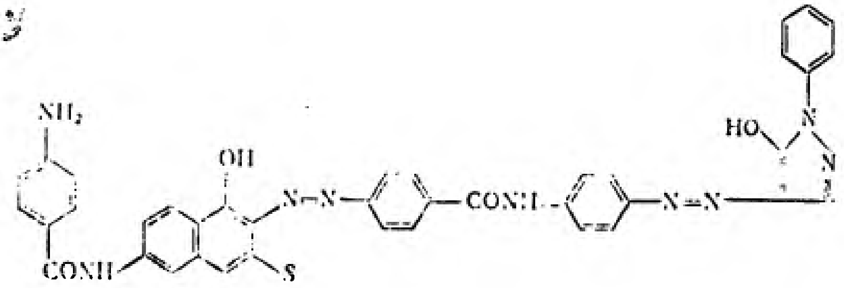
The derivatives of J-acid have acquired considerable significance in this group of dyes. The amino group of J-acid is acylated by n- or m-nitrobenzoylchloride and the nitro group is reduced to amino groups. This process can be repeated, i.e. the amino group acylated once again by n- or m-benzoylchloride and the nitro group again reduced. Such a complexed J-acid is used as an azo component for synthesizing a dye diazotized in the fiber. It is important to note that the accumulation of CO- and NH-groups in the molecule significantly increases the substantivity of the dye and improves its resistance to wet processing. The color of the new, more complex dye does not change very much during diazotization and combination [249]. This is apparently explained by the fact that the junction between the new part of the molecule and the original dye is somewhat encumbered by the carbymide group; for the case of meta-derivatives, it is excluded altogether.

Direct diazo orange is derived in accordance with the formula given above. (4')4"-aminobenzoylamino(benzoyl)-J-acid is synthesized and diazotized aniline is combined with it:



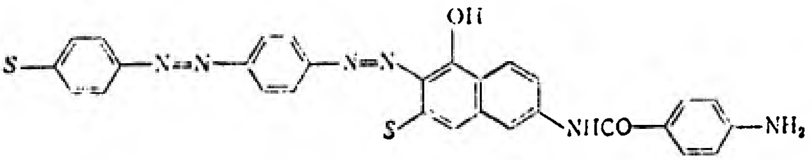
The resulting dye colors plant fibers, and the dye is diazotized in the fibers. The developing is done with 2-naphthol.

To obtain the valuable Direct diazo-scarlet 2Zh (CI 25240), phenylpyrazolonecarboxylic acid is combined diazotized 4-nitro-4'-aminobenzanilide; the nitro group is reduced, and following diazotization is combined with N-n-aminobenzoyl-J-acid:

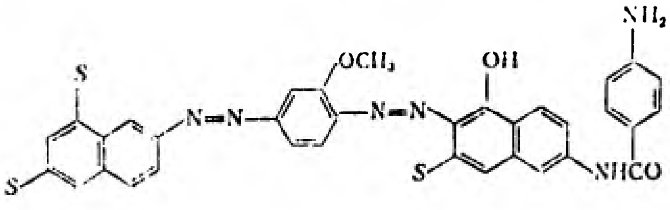


Following diazotization in the fiber and developing with 2-naphthol, scarlet colored dyes which are resistant to wet processing and sufficiently light resistant are obtained.

The complexing of diazo components when deriving the original direct azo dye leads to a deepening of the color. It is possible to obtain the dye, Direct diazo-claret color Zh by combining diazotized 4-aminoazobenzo-4'-sulfo acid with N-(n-aminobenzoyl)-J-acid:

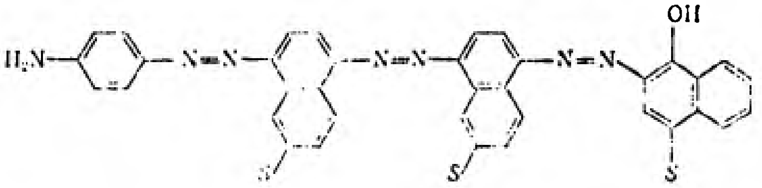


If the amino-G-acid is diazotized,.combined with sulfomethyl-o-anisidine, the sulfomethyl group hydrolyzed, the resulting aminoazo again diazotized, and the diazo compound combined with the same N-(n-aminobenzoyl)-J-acid, then Direct diazo-violet is obtained



which is developed in the fiber following diazotization with 2-naphthol.

Blue colored dyes can be obtained by using 1-naphthylamine derivatives as an intermediate azo component during the synthesis of a complex polyazo dye. For example, N-oxalyl-n-phenylenediamine is diazotized, combined with 1,6-Cleve's acid, diazotized again, combination with the same acid is repeated, which is diazotized and combined with 1-naphthol-4-sulfo acid. In conclusion, the oxalyl group is hydrolyzed by heating it with mineral acids or alkalis. Following all of these operations, the substantive trisazo dye, Direct diazo-blue Z (CI 34085) is obtained:



which, following diazotization in the fiber and developing with 2-naphthol yields attractive and durable blue colors. In this dye, the original amine is an acylated derivative of n-phenylenediamine. It can be derived from n-nitrooxalylaniline by reduction.

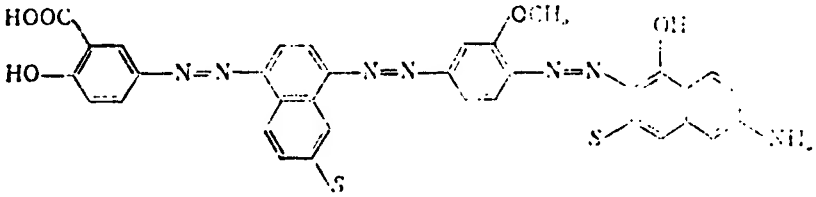
Of the green dyes of this group, we should mention Direct light resistant diazo-greem (CI 34260) which is derived in accordance with the formula:

metanilic acid ⟶ 1,7-Cleve's acid ⟶

1-amino-2-ethoxynaphthalene-6-sulfo acid ⟶

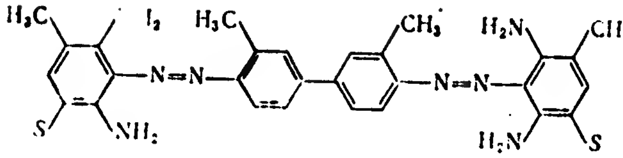
N-(m-aminobenzoyl)-J-acid

Following dyeing, it is diazotized in the fiber and combined with phenylmethylpyrazolone. Black colored dyes are also built up in an analogous manner. For example, Direct light resistant diazo-black Z is derived from aminosalicylic acid, 1,7-Cleve's acid, cresidine and γ-acid; the latter combination is carried out in an alkaline medium:



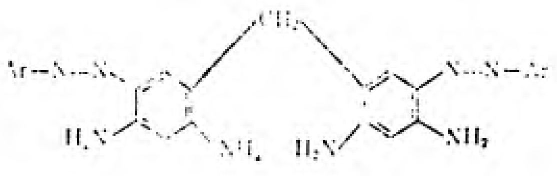
If an azo dye which has substantive properties contains resorcin, m-aminophenol or m-phenylenediamine as an end component, then following application to the fiber, it is able to be combined with diazonium salts as the azo component. The latter should be quite active. n-Nitrophenyldiazonium is employed almost exclusively for this purpose in practice. The colors derived in such a manner are usually deeper than the original ones, and they exhibit an increased resistance to wet processing.

Toluylene orange R (CI 23370) which colors cotton orange, following development with diazotized n-nitroaniline transforms into an attractive, intense reddish brown color very fast to washing:



Along with this, as can be seen from the formula of the dye, there is no place in its molecule for combination with a diazo component. During treatment with an active diazonium salt, the sulfo groups are apparently displaced by an azo radical.

Dyes with a characteristic end group - a radical of m-phenylenediamine, resorcin, or m-aminophenol - are able to be fixed in the fiber if they are treated at 60° C with a weak aqueous solution of formaldehyde in the presence of acetic or formic acid for some time. The chemical mechanism of dye fixing by formaldehyde has not been clarified. There are hypotheses [250] concerning the formation of diphenyl methane derivatives of the type



or the bonding of the dye with methylene bridges to a cellulose molecule [251]. Polyazo dyes which contain resorcin or m-aminophenol as a final component, continue to be patented lately as being fixed in the fiber by formaldehyde.

The formulas for their derivation do not differ from the usual methods of obtaining substantive dyes [252]. By way of example, we show the dyes derived in accordance with the sequence [253]:

m-aminophenol $\xleftarrow{(al)}$ diamine $\xrightarrow{(al)}$ J-acid $\longrightarrow$

1-naphthylamine $\longrightarrow$ resorcin or m-aminophenol

The resistance to wet processing is significantly improved following formaldehyde treatment.

Dyes With Colored Cations

For the dyeing of polyacrylonitrile fibers (prepared both from polyacrylonitrile itself and from its numerous copolymers with other monomers), such as nitron, orlon, curtel and others, dispersed dyes were first used, but now cationic ones are used almost exclusively.

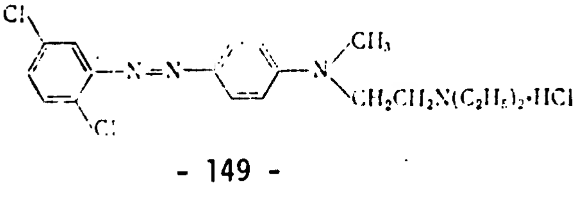
The latter are salts of colored organic bases or quaternary compounds in which the colored part is an organic cation (conjugate proton-less acid).

The salts of organic bases (containing primary, secondary or tertiary amino groups), the so-called basic dyes, are used less often than the quaternary ammonium salts, because of the relatively low light resistance, and sometimes poor water solubility of the former. They are marketed by various firms under the names astrozon, sevron, maxillon, deorlin, etc. The dyeing action of all cationic dyes is based on salt formation between the basic groups of the dye and the anionic groups of the fiber [254]. The latter are formed either by partial hydrolysis of the nitro groups of polyacrylonitrile, or exist in the fiber as end groups of macromolecules in that case where oxidizing agents act as the initiator of polymerization.

In the first dyeing phase, the fiber extracts the cationic dye from the dye wash. In the second, salt formation takes place between the acid groups of the fiber and the basic centers of the cationic dye. In the case where the cationic dye is a quaternary ammonium salt, the dye anion is displaced by an anion of the acid group of the fiber with the isolation of the acid in the dye bath, whose anion previously belonged to the dye transferring to the fiber. Dyeing with cationic dyes usually takes place at high temperatures, which facilitates the dye diffusion in the fiber. It is clear from this that the dye molecule should not be too large. For this reason, cationic dyes of the azo series are most frequently monoazo dyes, and are only disazo dyes in particular cases.

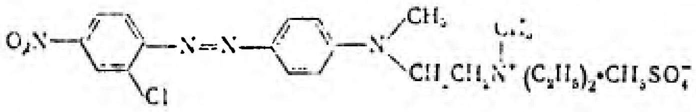
The quaternary ammonium group (or substituted amino group) in the molecules of cationic dyes can be conjugate with the basic chromophore chain of the dye, or separated from it by a small chain of atoms, interrupting the coupling. In the latter case, the character of the basic group has little effect on the dye color. The group which interrupts the coupling is most frequently a polymethylene chain, introduced into the ready dye or the original substances for its derivation. This polymethylene chain is introduced into the amino group directly through an acylamino group or through a carbonyl (or ones similar to it, for example, a sulfone) group. Dyes in which the quaternary ammonium group is bound to the basic chromophore group of the azo dye by a continuous conjugate system, which is most often derivatives of aromatic heterocyclic compounds. In this case, due to the difficulty of diazotizing certain amines of the heterocyclic series, the dyes are sometimes derived not by means of a nitrogen coupling reaction, but form the azo group by other methods which are of great theoretical interest.

Cationic yellow is the product of nitrogen coupling diazotized 2,5-dichloroaniline with N-methyl-n-(2'-diethylaminoethyl)aniline:

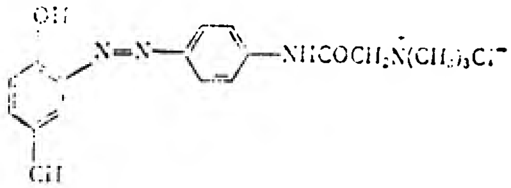


In this dye the basic diethylamine group is removed from the chromophore chain of the azo dye.

Cationic red [255] is derived by combining diazotized 2-chloro-4-nitroaniline with N-methyl-(diethylaminoethyl)-aniline and subsequently treating the dye with dimethylsulfate for conversion to a quaternary salt:

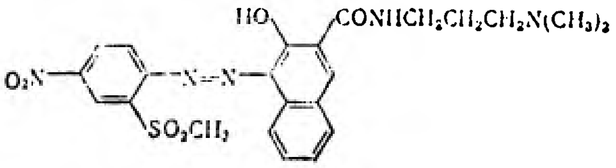


Cationic yellow dye [256] is derived by acylating 4-amino-2'-hydroxy-5'- methylazobenzene with chloracetylchloride, and further treating the resultant compound with trimethylamine:

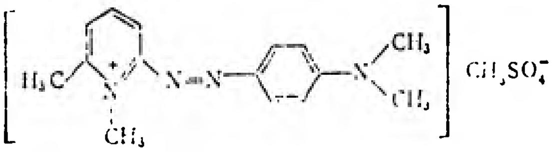


In this dye, the cationic group is bound to the remaining part of the molecule through the acylamine grouping. This dye exhibits a high level of light resistance when used on polyacrylonitrile fiber.

In the patent literature a rather large number of proposals is found for using derivatives of 2,3-hydroxynaphthoic acid for synthesis. Thus, orange cationic dye can be derived [257] by combining diazotized 2-sulfomethyl-4-nitroaniline with the dimethylaminopropylamide of 2,3-hydroxynaphthoic acid:

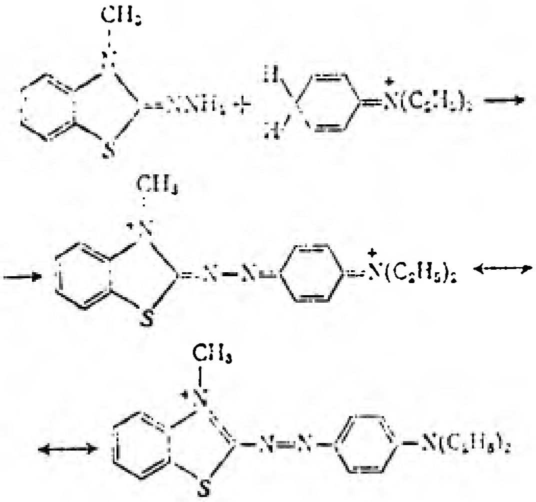


As far as the dyes which are derivatives of heterocyclic compounds are concerned, we should mention a dye derived by condensing 2-amino-6-methylpyridine with n-nitrosodimethylaniline, and further methylating with dimethylsulfate [258]:



The cationic group is coupled with electron donor dimethylamine group in the dye. This leads to deeper shades.

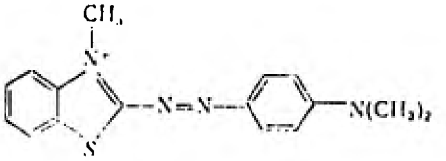
However, in cases where diazotization is difficult, the method worked out by Huhnig and Fritsch [259] can be recommended; the method is one of oxidizing nitrogen coupling, consisting of the simultaneous oxidation of hydrazones of heterocyclic ketones with aromatic amines of phenols. The higher salts of iron, manganese, lead, as well as hydrogen peroxide and other compounds, act as oxidants. The cationic dye formed by the joint oxidation of hydrazone 1-methylbenzo-2-thiozolone with diethylaniline in an acid medium in accordance with the following formula can be used as an example:



A method for deriving cationic dyes has also been patented which is distinguished by the fact that for diazotization of amino derivatives of pyridine, they are first transformed into N-oxides, which are easily diazotized. Following combination with suitable azo components for deriving cationic dyes, oxidizing oxygen is eliminated by treatment with phosphorous, zinc, manganese, iron, etc. trichloride [260].

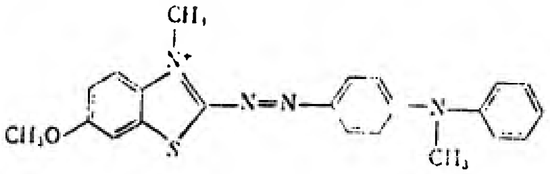
The derivatives of 2-aminobenzothiazole are likewise subjected to diazotization using a specially developed method with nitrosylsulfuric acid in a medium of sulfuric or acetic acid or their mixtures.

Kiprianov for the first time succeeded in synthesizing thiazole dye in 1949 [261]. He diazotized 2-aminobenzothiazole and combined the resulting diazo compound with dimethylaniline. Methylation produces a dye of violet blue color:

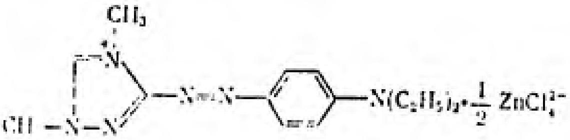


The use of this dye as a cationic dye for coloring nitron was accomplished much later.

Deeper hues are obtained by using N-methyldiphenylamine as an azo component, which easily combines with diazo components in an alcohol or acetic acid medium. For example, a series of valuable cationic dyes can be derived by combining a diazotized amine of the heterocyclic series with N-methyldiphenylamine, and thereafter methylating the azo dye. An example here is the blue cationic dye having the following structure:



Also interesting are dyes of the type Cationic red 2S. It is derived by diazotizing 3-amino-1,2,4-triazole-5-carboxylic acid and combining with diethylaniline. The resulting product is decarboxylated by heating it with acids and is methylated by appropriate methylating substances. The dye is produced in the form of a double salt with zinc chloride:



Besides azo dyes, cationic dyes are widely used which contain azomethine and polymethine groups; also widely used are cationic dyes of the anthraquinone and triarylmethane series.

Difficultly Soluble Azo Dyes

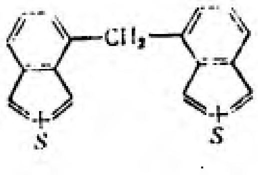
Cellulose fiber has hydroxyl groups which can be used to retain water soluble azo dyes in the fiber. When the number of the hydroxyl groups in the fiber is reduced, or when they are completely lost, the ability to fix dyes from aqueous solutions is lost and the use of special dyes is called for. Thus, for example, cotton dyes do not have any affinity for acetylcellulose [262], which is a source for deriving the important acetylcellulose fiber. But on the other hand, as Meyer demonstrated [263], acetylcellulose dissolves many water repellent dyes in a manner similar to that of ethyl acetate.

Many azo dyes which do not contain salt forming groups are very poorly soluble in water. However, these dyes are capable of dissolving in many organic substances which are the source products in the derivation of artificial and synthetic fibers. In this respect, the latter have an affinity for dyes which a difficultly soluble in water and can combine with them into fast, completely insoluble compounds. Their low level of water solubility is sufficient for dyeing with these dyes, so that throughout the solution stage, the dye penetrates the thickness of the fiber and colors it. Such a dye should be resistant to all water processing.

The majority of synthetic fibers (polyamide, polyester, polyacrylonitrile, polyvinylalcoholic, polyvinylchloride, etc.) require special dyes to color them which often have functional groups to give them solubility in the source substances for deriving the corresponding fibers.

Dispersed dyes have all of the properties essential to dyeing artificial and synthetic fibers [264]. These dyes which are insignificantly soluble in water exist in the form of a thin dispersion (0.5 - 2 microns) in the dye bath, and are adsorbed by the fiber and securely fixed by it. Various authors conceive of the mechanism of adsorption of dispersed dyes by a water repellent substrate in various ways. There are proponents of the formation of a solid solution [265], of a polar interaction arising between the molecules of the dye and the macromolecules of the fiber [266], as well as of the effect of other forces [267].

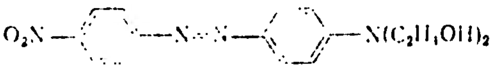
The derivation of difficultly soluble azo dyes in dispersed form sometimes proves to be a complex problem. The method of reprecipitation from suitable solvents is frequently employed, but even more often the synthesized dye is finely broken up, with the simultaneous introduction of dispergators, which make the resulting aqueous dispersion (colloidal suspension) stable during dyeing. The NF dispergator, a complex mixture of which one of the primary components is dinaphthylmethanedisulfo acid, is frequently used:



The transition of difficultly soluble dyes to a dispersed state proceeds more easily if the following are added to the dye molecule: mono- or diethanolamino groups, the ethanolhydroxyethylamino group

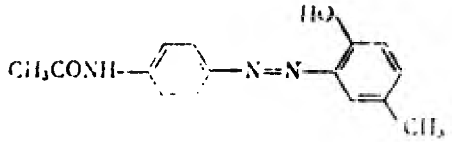
and those similar to it which contain hydroxyl groups. It is possible that the latter effect hydrogen bonds with ester or other groups of acetate, polyester, polyamide and other fibers.

In 1923 Green and Saunders synthesized a dye from diazotized from n-nitroaniline and dihydroxyethylaniline



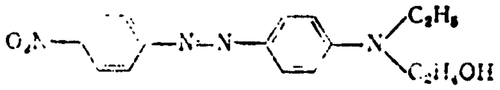
which proved to be capable of effectively dyeing acetylcellulose fiber from an aqueous suspension [268].

The assortment of dyes for acetate fiber is now somewhat expanded. By way of example we will use Dispersed yellow Z (CI 11855) which is the product of coupling diazotized acetyl-n-phenylenediamine with n-cresol in a mixture with NF Dispergator.



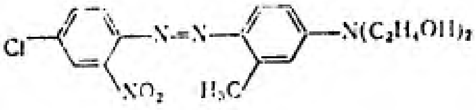
Dispersed yellow 4K (CI 26090) is the product of combining aminoazobenzene with o-cresol. Thus, this dye already contains two azo groups. Its dispersed form in a mixture with NF Dispergator is recommended for dyeing acetylcellulose fibers and lavsan.

Dispersed scarlet Zh (CI 11110) is a mixture of NF Dispergator with the dye which is obtained by combining diazotized n-nitroaniline with N-ethyl-N-hydroxyethylaniline:



Its analogue which has a chlorine atom in the meta-position with respect to the nitro group is known as Dispersed claret color (CI 11115).

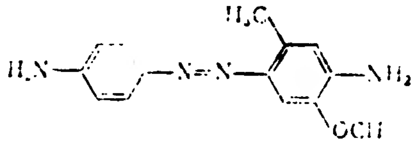
Characteristic is Dispersed orange 2: which is derived from 4-chloro-2-nitroaniline and dihydroxyethyl-m-toluidine:



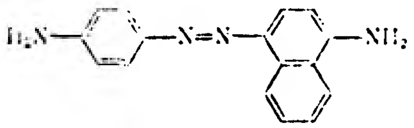
In a mixture with NF Dispergator it effectively colors acetate silk and lavsan an attractive and adequately fast orange color.

If 6-chloro-2,4-dinitroaniline or its bromine analogue as well as certain amines from the heterocyclic series of the 2-amino-6-methoxybenzothiazole type are used as diazo components, then the dyes which are obtained by combining these diazotized amines with derivatives of tetrahydronaphthalene have the valuable property of "dischargeability" [269].

Dispersed azo dyes which contain a free primary amino group, once they are used to color the fiber, can be diazotized in the fiber and combined with appropriate azo components. Such a dye is Dispersed diazo-blue Z (CI 11255) which is derived by reducing the azo dye from diazotized n-nitroaniline and cresidine:



Following dyeing, it is developed in the fiber with 2-naphthol. Dispersed diazo-black S (CI 11365) has just the same properties



and is derived from n-nitroaniline and 1-naphthylamine with subsequent reduction of the nitro group.

Besides 2-naphthol, phenol, resorcin, 2,3-hydroxynaphthoic acid, phenylmethylpyrazolone derivatives and others are used as developers.

Although the ability to dye polyester fiber, as well as acetate, is determined by the presence of complex ester groupings (polyester contain ≈ 46% ester groups by weight of polyethyleneterephthalate, acetate fibers ≈ 41% by weight of the fiber); there is an enormous difference between these types of fibers which is determined by the internal structure, which in polyester fibers is more compact (as a result of the thermal extrusion of the fiber). The fiber has a sharply pronounced water repellent character and high electronegative potential. For this reason, although the mechanism of dyeing a polyester fiber with dispersed dyes is similar to the dyeing of acetylcellulose, there some special demands which are made on dyes when color polyester fibers: for example, the solubility of dispersed dyes and the ability to be effectively dispergated [270].

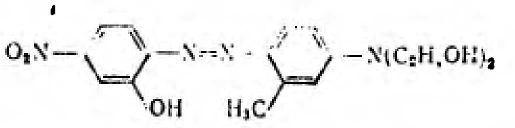
The size of the dye molecule is likewise of very great importance for the successful dyeing of polyester fibers. A factor which determines the dyeing speed is the rate of dye diffusion in the fiber, which is inversely proportional to the size of the dye molecule. Other conditions being equal, the smaller the molecule of the dye, the more easily it diffuses in the fiber.

However, even when the dye requirements for coloring polyester fibers set forth above are met, dyeing with them presents considerable difficulty.

For this reason, special dye methods have been worked out which increase the diffusion rate of the dyes in the fiber: the use of agents which cause the water repellent polyester fiber to swell, and high temperature dyeing. Agents which cause swelling of the fiber are called dye accelerators or carriers. These include phenol, diphenyl, chlorobenzene, a few esters (for example, methylsalicylate, esters of chlorobenzoic acid, etc.), diphenylamine and others. Dyeing at a temperature higher than 100° C has recently found wide application, and is carried out in special autoclaves (of the UKA-1 type), or turbo [271]. A thermosol has successfully been used for dyeing cloth; the essence of the method consists in impregnating the polyester fiber fabric with a thickened dye dispersion, drying, and subjecting it short term heat treatment at 180 - 200° C [272].

In addition to the several dyes used for dyeing acetate silk and which are mentioned above, a large number of dispersed dyes have been proposed for dyeing polyester fibers, of which we will take note of the following.

Dispersed rubin S (CI 11225) is derived by combining diazotized 5-nitro-2-aminophenol with N,N-dihydroxyethyl-m-toluidine:

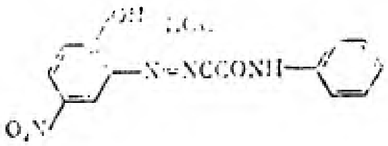


When diazotized 2-chloro-4-nitroaniline is combined with the same azo component, Dispersed claret color 2S (CI 112215) is obtained. When 2,4-dinitroaniline is used for the same purposes, Dispersed violet 4K is obtained.

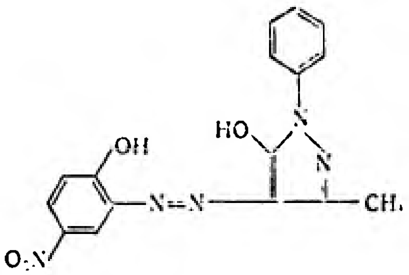
Dispersed red-brown (CI 11100) can be derived from 2,6-dichloro-4-nitroaniline by combining it with N-ethyl-N-hydroxyethylaniline following diazotization.

Polyamide fibers are effectively dyed by dispersed dyes which contain a complexly bound metal. The dyes themselves, for the most part are uncomplicated monoazo compounds which contain mordant groupings. Due to their very low water solubility, they are used in the form of a specially prepared dispersion in dyeing.

Dispersed yellow 2MP is a chrome complex of the dye derived from diazotized anthranilic acid and phenylmethylpyrazolone; Dispersed yellow KMP is a cobalt complex of the azo dye (4-nitro-2-aminophenol → anilide of acetoacetic acid):

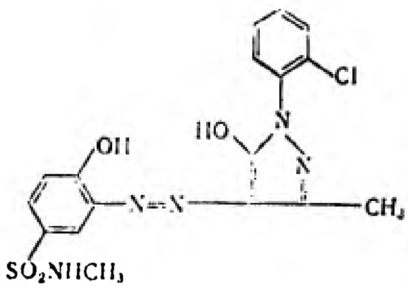


Dispersed red SMP is a chrome complex of the dye



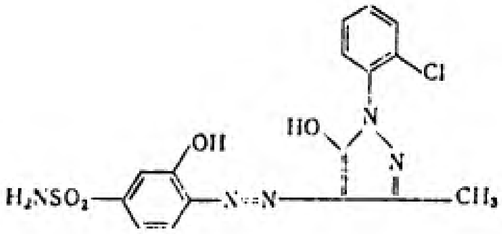
which is derived form diazotized 5-nitro-2-aminophenol and phenylmethylpyrazolone. Dispersed violet is a cobalt complex of the dye from the same diazo component and 2-naphthol. The chrome complex of the same dye bears the name Dispersed gray SMP.

Our industry produces several dyes for dyeing polyamide and polyester fibers in bulk. In essence they are no different than those just considered. Caprosole orange 4K is a chrome complex of the dye



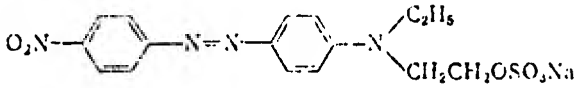
which is derived by diazotizing 2-aminophenol-4-methylsulfamide and combination with o-chlorophenylmethylpyrazolone.

Caprosole scarlet S is a chrome complex of the dye (2-aminophenol-5-sulfamide ⟶ o-chlorophenylmethylpyrazolone):



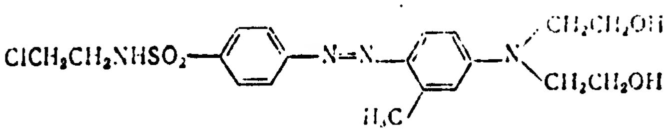
Among the dispersed dyes, there are also those which contain various active groupings, which make it possible for them to bond covalently with various fibers, including the polyamides. These dyes yield colors of sufficiently high fastness and have a good compensating capability. They do not contain sulfo groups and are recovered from suspension by the fiber just as the usual dispersed dyes. Like all active dyes they are capable of hydrolysis. In order to reduce this side reaction to a minimum, in its first stage the dyeing is carried out in a weakly acid medium and only towards the end, following the recovery and equalization of the dye, are alkaline agents added to the dye bath to effect the reaction between the active dye group and the functional nucleophilic group of the fiber, specifically the polyamide (capron, nylon and others). Active dispersed dyes are capable of dyeing not only polyamide fibers, but also woolen ones (the coloring of the latter in this case is somewhat more intense than in the polyamide fiber).

Vinylsulfone dyes are sometimes called solated, if we are dealing with their use for coloring polyamide fibers. The simplest solated dye is the product of combining diazotized n-nitroaniline with the sulfuric acid ester of ethanolethylaniline:



It is water soluble (to a limited extent) and able to dye polyamide fibers from an aqueous suspension. Because of its solubility in acetylcellulose, it also dyes acetate silk.

Active scarlet 1P, which is used for dyeing polyamide fibers and yields colors resistant to wet processing and light, is obtained by nitrogen coupling diazotized 4-β-chloroethylsulfamido-2-chloroaniline with dihydroxyethyl-m-toluidine:



In this case, the active group is the β-chloroethyl group.

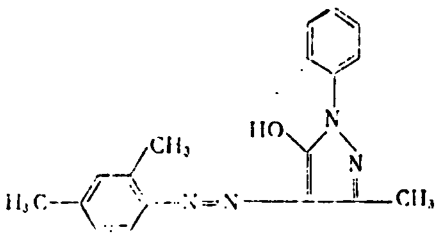
Water Insoluble Azo Dyes

Azo Dyes Which Are Soluble in Organic Solvents

For many industrial purposes it is essential to have an assortment of dyes which are soluble in diverse organic solvents - alcohol, oils, acetone, benzene, etc. Azo dyes which are soluble in organic solvents are monoazo dyes and have a low molecular weight and as a rule do not contain polar groups, which make them water soluble - sulfo, carboxyl groups and others. They also contain alkyl, hydrated aryl and analogous radicals which increase their solubility in organic solvents. Alcohol soluble azo dyes which sometimes contain polar groups, are somewhat of an exception.

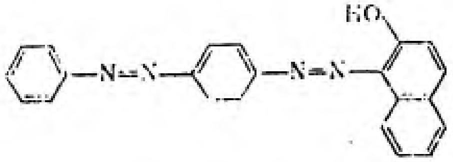
All dyes which are soluble in organic solvents are divided into three basic groups: 1) oil soluble and also soluble in the majority of non-polar solvents; 2) alcohol soluble, suitable for dyeing polar organic solvents; 3) acetone soluble. It stands to reason that this division is of an arbitrary nature since many azo dyes are capable of dissolving simultaneously both in alcohol and acetone, for example, and in oils and alcohol, etc., but for purposes of classification, such a division is rather convenient since it makes it possible to distinguish individual structural features common to the given group of dyes. The association of a dye with one group or the other is reflected in the name of the dye.

The simplest oil soluble dye is n-aminoazobenzene [273] which is derived from the interaction of aniline hydrochloride with diazoaminobenzene at 30 - 40° C. It has now lost its practical significance. Oil soluble yellow Zh (CI 12740) is derived by combining diazotized m-xylidine with phenylmethylpyrazolone. It dyes various oils an attractive yellow color and is widely employed for this purpose:

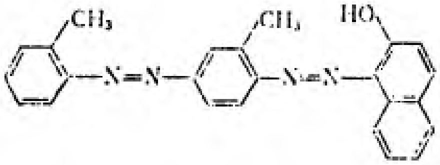


Its analogue derived from aniline and phenylmethylpyrazolone is Oil soluble yellow Z which has somewhat more of a greenish hue.

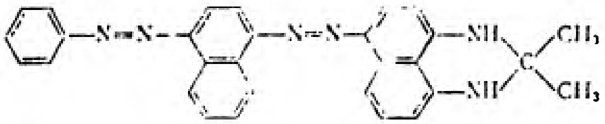
If diazotized aniline is combined with diethylaniline, a dye of a basic character is obtained, Oil soluble yellow 1 which colors oils intensely. A deepening of the color can be achieved by using a naphthalene azo component. Oil soluble orange (CI 12055) is an azo dye derived from diazotized aniline and 2-naphthol. This dye, like many other oil soluble dyes, is produced by several firms under the name of sudan dyes. The quite widely used Oil soluble red Zh (CI 26100) which is also called Sudan III is derived from aminoazobenzene and 2-naphthol:



Oil soluble dark red 1 (26110) (Sudan IV) is synthesized from aminoazotoluol and 2-naphthol:

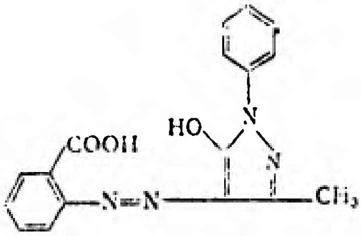


Because of the carcinogenic character of o-aminoazotoluol, its meta-isomer is now used. Besides coloring oils and fuel products it is also used for dyeing plastics [274]. Oil soluble dyes of brown colors are derived by using diazo and azo components of the naphthalene series. Oil soluble brown Zh (CI 11360) is synthesized from diazotized 1-naphthylamine and the same 1-naphthylamine is used as an azo component. Also interesting is the dye, Oil soluble black (CI 26150). It is formed by combining diazotized aniline with 1-naphthylamine. The aminoazo dye is again diazotized and combined with 2,3-dihydro-2,2-dimethylpyridine:



Alcohol soluble azo dyes are derived in a somewhat more complex fashion. Complex compounds of copper, chromium and cobalt are included among them are soluble in alcohol and other organic solvents. In foreign industry many of them have been given the name <u>zanon</u> dyes.

Alcohol soluble yellow (CI 18690) is a chrome complex of a 1:2 composition derived by heating in a formamide medium. obtained from anthranilic acid and phenylmethylpyrazolone,



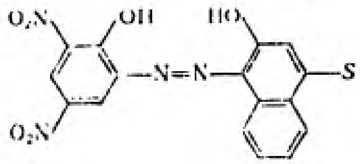
with chromium formate at 113 - 115° C for six hours. If 4-nitro-2-aminophenol-6-sulfo acid is used instead of anthranilic acid, Alcohol soluble orange 2Zh (CI 18745A) is obtained. Its chrome complex is derived by heating the dye with chromium formate at 130° C for three hours.

Alcohol soluble scarlet is very interesting; it is not a metallic complex, but presents itself as a salt with an organic base (of the diphenylguanidine type) of the product from combining diazotized aminoazobenzene with G-acid.

More deeply colored alcohol soluble dyes are obtained by forming chrome complexes of a 1:2 composition from amines which contain nitro groups. For example, Alcohol soluble claret color S (CI 12715) can be derived from 5-

nitro-2-aminophenol and phenylmethylpyrazolone by heating the synthesized dye with chromium formate in a formamide solution at 110° C for 4 - 5 hours.

Alcohol soluble black (CI 15951) contains two nitro groups in the diazo component. It is a chrome complex of the dye synthesized from diazotized picramic acid and 2-naphthol-4-sulfo acid:



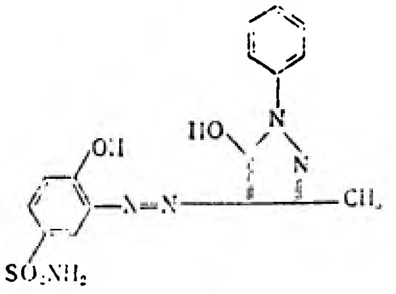
It is a 3-aminoheptane salt which is formed by the sulfo group when the dye is treated with the acetate of 3-aminoheptane.

The ability of some dyes to form salts with organic amines is used to derive dyes which are soluble in various solvents. Thus, the salt of an aliphatic amine and the dye, Alcohol soluble yellow (described above), is quite soluble in acetone and complex esters and is produced as an acetone soluble dye. By using amines of various structures and chain lengths, it is possible to derive dyes with specified solubilities in various organic solvents.

Dyes which are quite soluble in ketones and esters are produced abroad under the trade names of neozanon, orosol, and others. Dyes which are soluble in acetone are in principle little different than dyes which are soluble in alcohol. Perhaps they have somewhat greater acid properties, but the latter are caused by the presence of sulfamide groups or nitro groups. Many of them are cobalt complexes, although chrome complexes are also found.

Acetone soluble yellow 5K is the product of nitrogen coupling 4-nitro-2-aminophenol with the anilide of acetoacetic acid, and is produced in the form of a complex cobalt salt.

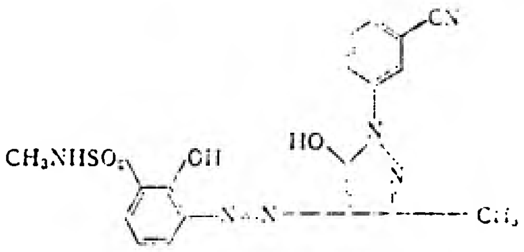
Acetone soluble orange 4Zh is also a cobalt complex of the dye



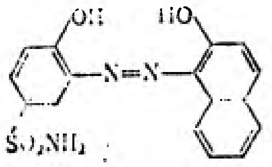
derived from diazotized 2-aminophenol-4-sulfamide and phenylmethylpyrazolone.

Two dyes, Acetone soluble orange Zh and Acetone soluble orange 4K, are respectively a cobalt and chrome complex of 1:2 of the products of nitrogen coupling diazotized 4-nitro-2-aminophenol with phenylpyrazolone. Weakly acid properties are created by the hydroxy group which is located in the para-position with respect to the nitro group. The dyes differ only in their shades: the first is yellowish, the second is reddish.

The dye, Acetone soluble scarlet, is unique and is a chrome complex of 1:2 of the product from nitrogen coupling diazotized 2-aminophenol-6-methylsulfamide with (3'-cyanophenyl)methylpyrazolone:

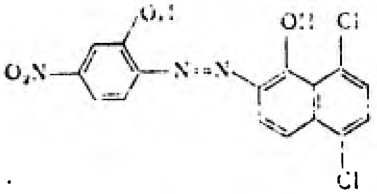


When azo components of the naphthalene series are used, for example, 2-naphthol, more deeply colored dyes are obtained. Acetone soluble red 2S is a cobalt complex of the azo dye derived by nitrogen coupling diazotized 2-aminophenol-4-sulfamide with 2-naphthol,



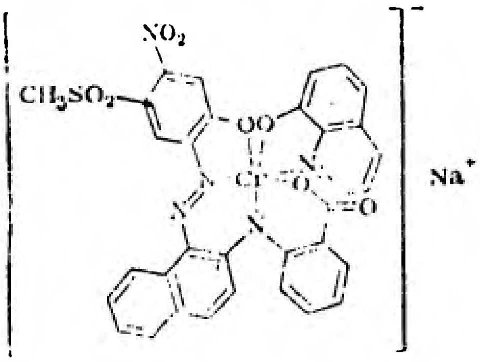
while Acetone soluble blue 2K is a cobalt complex of the dye from 5-nitro-2-aminophenol and 2-naphthol.

By using the same 5-nitro-2-aminophenol and 5,8-dichloro-1-naphthol it is possible to synthesize the dye, Acetone soluble navy blue in the form of a complex cobalt salt



while Acetone soluble greenish-blue (cobalt complex) is derived from the same diazo component and 1-acetylamino-7-naphthol.

The dye, Acetone soluble bright green 1, is theoretically and practically very interesting. It is a complex chrome salt of the azo dye from 4-methylsulfonil-5-nitro-2-aminophenol and 2'-carboxylphenyl-2-naphthylamine. In the formation of the complex, 8-hydroxyquinoline is used as a ligand. The complex carries one negative charge and forms salts with monovalent ions:



Finally, black dyes of this group can be derived by using amines of the naphthalene series as an azo component. The dye, Acetone soluble black, is the product of nitrogen coupling diazotized 5-nitro-2-aminophenol with 2-naphthylamino-1-sulfo acid. It is produced in the form of a cobalt complex.

Pigments

Pigments and lacs comprise a numerous group of dyes which are water insoluble. The latter were considered earlier in the group of soluble cyes, since the base for their derivation is usually water soluble sulfo or carboxylic acid, and only the formation of salts with calcium, barium and other cations leads to the formation of soluble lacs under specified conditions.

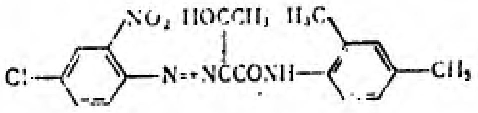
Pigments do not have any groups in the molecule which make them water soluble. They are employed in the manufacture of covering paints for (house) painting, for coloring resin, plastics, in the polygraphy industry, etc. In each of these cases, various demands are made of the pigments concerning their fastness. For example, pigments employed to color resins should be resistant to vulcanization, while those used for coloring plastics should have a high migration stability, i.e. should not come up from the depth of the colored layer to the surface of the dyed products and convert to a non-colored material contiguous with it. The demand for a special resistance to the action of light is made of many pigments, although for some this requirement is not too strict.

It should be especially emphasized that the field of application for pigments in connection with the creation of various types of synthetic fibers and higher polymers is in general, increasing every day. For this reason, both in the domestic and foreign press a large number of works has appeared in recent years which are devoted to the synthesis of new pigments which have one valuable property or another.

On the other hand, detailed investigation of the physical and chemical properties of a large number of pigments shows that they depend not only on the structure of the dyes, but also on the means of their derivation, separation, extent to which they are dispersed, special processes, etc. Even the shadings and color of the derived pigments often depend on the conditions of synthesis and separation. The crystalline structure of the pigments underlies these characteristics and determines the ability to form particles of various sizes, and the change in physical and chemical properties, up to and including a change in hue [275].

Arylamides of acetoacetic, phenylmethylpyrazolone, 2-naphthol as well as diverse azotols, i.e. aromatic compounds with hydroxy or methoxy groups, are frequently used as azo components in deriving azo pigments. Amines from different sources, here given the name <u>azamines</u>, are used as diazo components.

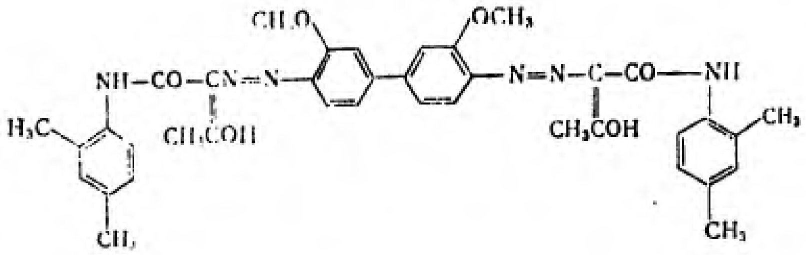
Light resistant pigment yeloow 4K (CI 11730) is derived from diazotized 4-chloro-2-nitroaniline and the m-xylidine of acetoacetic acid:



The presence of a chlorine atom and a nitro group somewhat diminishes the solubility of the pigment in oil, and increases its light resistance.

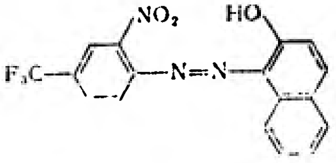
Pigment yellow 5K (CI 21135) is the product of nitrogen coupling the same azo component, but with bis-diazotized o-tolidine. Despite the doubling of the molecule, the color of the dye does not deepen significantly, since probably the angle of rotation of the benzene rings of the central portion of the molecule is so great that the overlapping of the electron clouds in the diphenyl system is already difficult.

The use of dianisidine as a diazo component somewhat deepens the color of the azo pigment. Bis-diazotized dianisidien with the m-xylidine of aceto-acetic acid yields Pigment orange Zh (CI 21165):



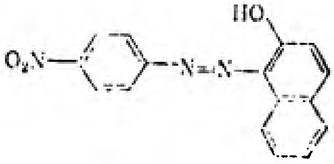
As a rule, disazo dyes have a greater migration stability that the mono-azo dyes.

A particular resistance to the action of light is exhibited which contain a trifluoromethyl group. We note the Lac fast orange ZGL [276]



which is also used for coloring oil products.

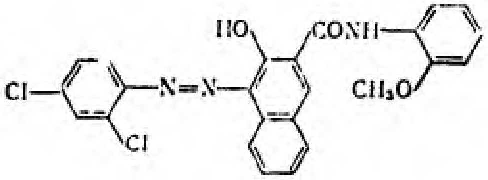
In general, the use of the simplest aniline derivatives in combination with 2-naphthol is a classic example of the derivation of pigments. It is sufficient here to indicate the Pigment red Zh (para-red, para-crimson, CI 12070), widely known as a pigment which can be derived by combining diazotized n-nitroaniline with 2-naphthol:



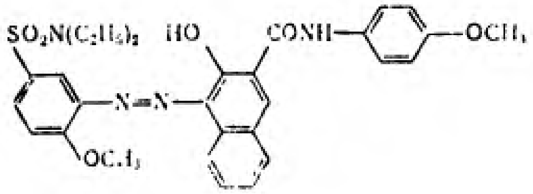
Instead of n-nitroaniline, o-nitro-n-toluidine (concentrated Pigment scarlet, CI 12120), n-nitro-o-chloroaniline (Pigment scarlet Zh, CI 12085) and others are used.

Azotols have found application as azo components in deriving azo pigments; they yield a high degree of resistance to the action of solvents. This property is amplified even more if a sulfamide group or halides are introduced into the molecule of the diazo component. In this way, very valuable pigments are obtained which are resistant to the action of solvents, oil, alkalis and the temperatures used for dyeing resins.

By way of example, we can point out the Pigment bright red 4Zh (CI 12460) which is derived from diazotized 2,5-dichloroaniline and the anisidide of 2-hydroxy-3-naphthoic acid (Azotol OA)



or the Pigment bright red 6Zh which is derived from m-aminobenzoanilide and the n-aniside of 2-hydroxy-3-naphthoic acid (Azotol TA), or the Pigment pink Zh (CI 12490) which is synthesized from diazotized 2-aminoanisol-4-diethyl-sulfamide and Azotol O:



A deeper shade is obtained by using diazo components of the naphthalene series. Thus, Pigment claret color (CI 12170) is formed in conbining diazotized 1-naphthylamine with 2-naphthol. Its copper complex has a brown hue.

The presence of a hetero ring of the imidazole, thiazole or oxazole type in the diazo component significantly increases the heat resistance of pigments synthesized from such amines [277].

Blue and green dyes are rarely found among the azo pigments. For this reason, pigments of these hues which belong to the series of anthraquinone derivatives or the phthalocyanine series have found wide application.

Azide Dyes

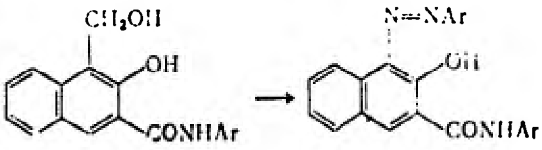
In 1880 Holliday and Sohn made the important discovery that cotton, when impregnated with an alkaline solution of 2-naphthol and dried out, is developed by the diazo compound from n-nitroaniline and dyed a relatively fast and very bright color. Since this method of dyeing did not require heating, and on the contrary was carried out with the addition of ice because of the instability of the diazo compound, and was given the name <u>ice</u> or <u>cold</u> dyeing. These terms are still in use at the present time, although they' have been replaced by the term <u>azide</u> dyeing. The dyes formed in this case in the fiber bear the name <u>azide</u>.

It stands to reason that 2-naphthol and n-nitroaniline were not the sole representatives of azo and diazo components able to dye cotton using the cold dye method. More successful combinations were gradually discovered which led to the rapid flowering of azide dye production.

Impetus in this direction was provided by the synthesis of AS naphthol, the anilide of 2-hydroxy-3-naphthoic acid which was developed in 1911 by the "Griessheim Elektron" company [278]. This anilide proved to be the progenitor of a large number of azo components which are significantly more valuable compounds than 2-naphthol. They have advantages over the latter insofar as they exhibit a significant degree of substantivity. It was initially hypothesized that the substantivity of AS naphthols would free textile plants of the necessity of drying the fabric following impregnation with a solution of AS naphthol. However, better results were obtained in practice when drying was used. In return, the resistance of azide dyes to wet processing and friction, where these preparations were used, was significantly higher than for the use of 2-naphthol.

By varying the diazo and azo components it is possible to obtain practically all shades of dyes from yellow to black. Based on fastness, many of the azide dyes can almost stand up to the most durable of the well known synthetic and natural dyes. It stands to reason that success in synthesizing one or the other azide dye is determined by the correct selection of azotol and azo amine, and the proper method of dyeing with the chosen combination. For this reason, it is not surprising that in patent literature new proposals and substances are appearing all the time, the application of which leads to interesting results. For a long time there was no success in selecting the requisite and achievable combinations for deriving green and black colors. In the end, even this difficulty was overcome.

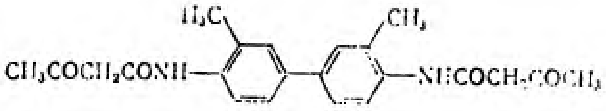
Increasing the substantive properties of azotols is one of the important tasks in the chemistry of this series. It was discovered that during condensation of the arylides of 2-hydroxy-3-naphthoic with formaldehyde, methylol derivatives are formed. The latter have a higher degree of substantivity than azotols themselves. During nitrogen coupling, the diazo group replaces the methylol group and the dye is formed:



The substantivity of the azotols likewise depends on the structure of the amine used in its synthesis. The amines are benzidine derivatives and yield azotols of increased substantive properties. The azotols which are derived from 2,7-diaminofluorene [279] and 2-hydroxy-3-naphthoic acid have a decidedly great affinity for fiber.

For printing purposes, cold dyeing is really even more important. Here it proves to be possible to use diverse mixtures of azotols and stable forms of diazo compounds, which interreact ("develop themselves") only under set conditions.

In increasing the range of azide dyes, investigators came up with the synthesis of diverse azo components, in which different compounds which are also capable of a nitrogen coupling reaction, were used instead of the naphthalene series "of naphthols." They do not have groups which make them water soluble and have the needed substantive properties. Such compounds which yield various shadings when developed with diazo compounds, were discovered in the aliphatic, aromatic and heterocyclic series. So to obtain yellow colors, it is recommended that diacetoacetyl-o-tolidine be employed [280]:

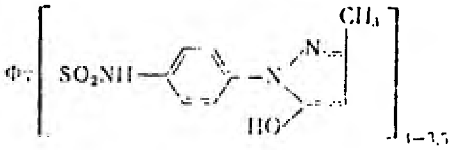


To derive green colors, o-toluidide of 2,3-hydroxyanthracenecarboxylic acid is used; brown, black and olive colors are from the arylides of hydroxycarbazolecarboxylic acid, arylides of hydroxycarboxylic of diphenylene oxide, diphenylenesulfide, fluorene, fluorenone, dibenzonaphthalene and many others [281]. Since all of these azo components are employed the same way as AS naphthols, they are called naphthols in foreign literature, but in ours they are called azotols.

The literal designations of azotols, derivatives of 2,3-hydroxynaphthoic acid, which we have adopted, usually reflect the names of the amines which were used to synthesize the product. For example, the anilide of this acid is designated Azotol A, α-naphthylamide is Azotol ANF, β-naphthylamide is Azotol BNF, m-nitroanilide is Azotol MNA, etc.

The azotols which are most frequently used in azide dyeing are given in Table 4 [282].

Azotol green (Naphthol AS - FGGR) is a molecule of phthalocyanine into which 3 - 3,5 phenylmethylpyrazolone radicals are introduced. Phthalocyaninic Pigment azure is treated with chlorosulfone acid to produce it. The resulting sulfochloride interacts with aminophenylmethylpyrazolone:



Φτ is the radical of phthalocyaninic Pigment azure.

The amines used to derive azide colors are extraordinarily numerous. The single essential requirement for them is the absence of the groups which make them water soluble. The diversity in the amines makes possible combinations with any azo component to derive particularly valuable dyes for their color and shade, their fastness, or for convenience in derivation, or finally for economic considerations.

Painstaking searches for particularly successful combinations of an azoamine and azotol have led to the creation of very durable azide dyes which have the qualities enumerated above, although this work, of course, is continuing, just as the syntheses of new azotols are, which were not previously used in this type of dyeing. Nonetheless, there is now a relatively standard assortment of azoamines which are most popular and widely used in azide dyeing (Table 5) [283].

The designations of azoamines (in foreign literature they are known as bases) include the color of the dyes derived for the azotols which are most used in the textile industry. It is important to note that the fastness of azide colors depends to a significant degree on the structure of the azoamines. It has been discovered, for example, that the presence of a trifluoromethyl group in the meta- and ortho-positions with respect to the amino group of the azoamine greatly increases the light resistance of the colors [284]. Many azoamines which are used to derive red colors contain an ester group in the ortho-position and an electron acceptor in the meta-position with respect to the amino group. Such a structure increases the resistance of the resulting dyes to wet processing.

TABLE 4

Azotols Used For Cold Dyeing

Азотолы, применяемые для холодного крашения

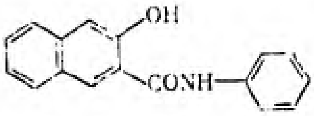
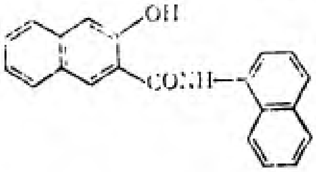
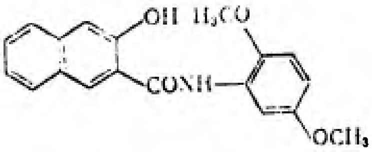
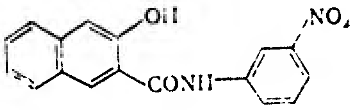
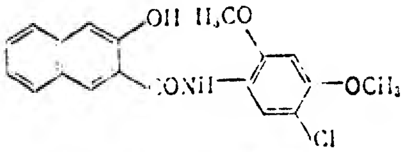
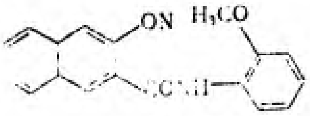
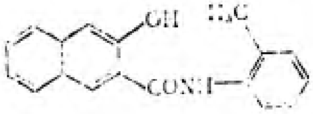
Азотол Azotol	Формула Formula	№ по КИ CI Number
А		37 505
АНФ ANF		37 560
ДМА DMA		37 545
МНА MNA		37 515
О		37 550
ОА		37 530
ОТ		37 520

Table 4 Continued Продолжение

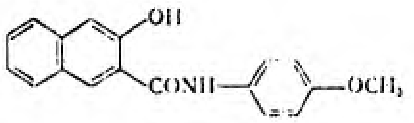
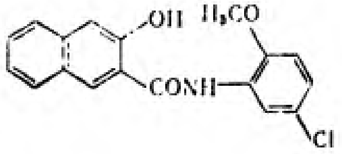
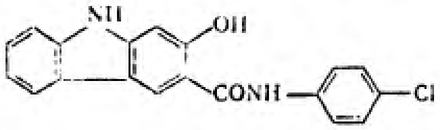
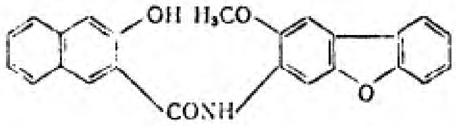
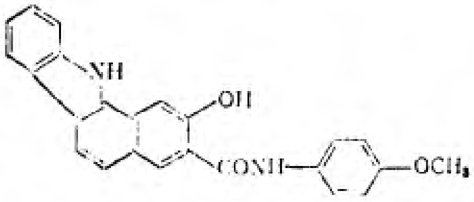
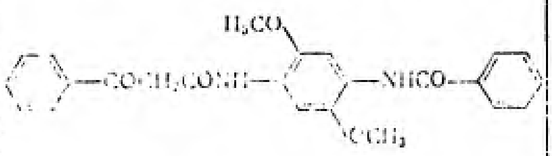
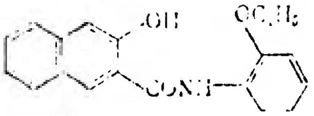
Азотол Azotol	Формула Formula	№ по КИ CI Number
ПА PA		37 532
ХА KhA		37 531
Коричневый Brown		37 600
2		37 580
Черный Black		37 595
ЖН ZhN		37 614
ОФ OF		37 558

TABLE 5

Azoamines Used For Cold Dyeing

Азоамины, применяемые для холодного крашения

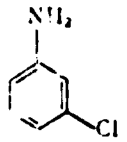
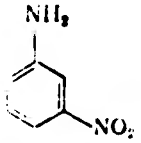
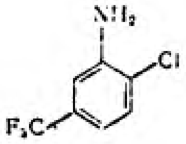
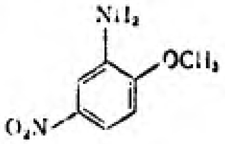
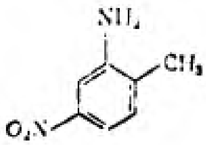
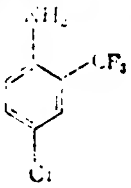
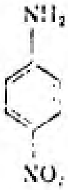
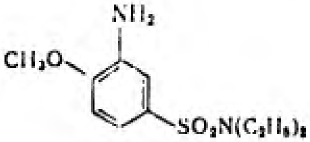
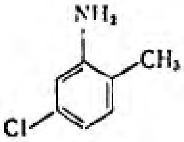
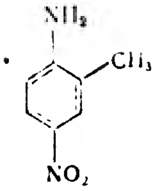
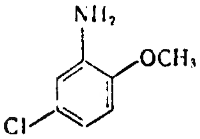
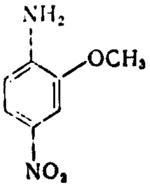
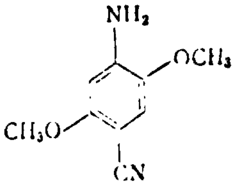
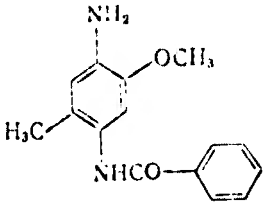
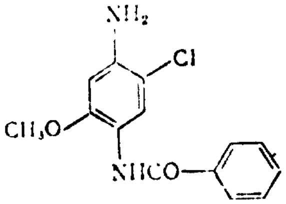
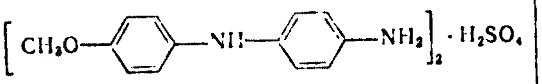
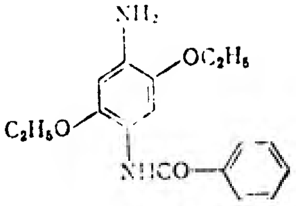
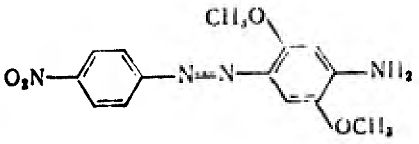
Азоамин Azoamine	Formula Формула	№ по CI CI Number
Оранжевый Ж Orange Zh		37 005
Оранжевый К Orange K		37 030
Ярко-оранжевый К Bright-orange K		37 050
Алый К Scarlet K		37 130
Алый Ж Scarlet Zh		37 105
Ярко-алый Ж Bright-scarlet Zh		37 [illegible]

Table 5 Continued *Продолжение*

Азоамин Azoamine	Formula Формула	№ по КИ CI Number
Красный Ж Red Zh		37 035
Красный О Red O		37 150
Красный С Red S		37 090
Красный 4С Red 4S		37 100
Красный К Red K		37 120
Розовый О Pink O		37 125

Продолжение

Азоамин **Azoamine**	Формула **Formula**	№ по КИ **CI Number**
Бордо К Claret color K		37 170
Фиолетовый Violet		37 165
Темно-фиолетовый 2К Dark violet 2K		37 160
Синий 2К Blue 2K		37 240
Синий О Blue O		37 255
Синий 2С Blue 2S		37 175
Черный К Black K		37 190

The presence of azoamine halide atoms in the molecule likewise improves the light resistance of azide dyes.

As indicated above, there are particularly successful combinations of azotols and azoamines. Lists of such combinations can be found in the specialized literature [285].

As far as printing with azide dyes and coloring smoothly with them are concerned, the use of stable forms of diazo compounds which textile get rid of from chemical operations (diazotization) has proven to be particularly successful. Compounds of this type are prepared at plants using aniline dye chemistry and are supplied to enterprises of the chemical textile industry in a form ready for use in azide dyeing and printing. These are diazonium salts which have increased stability and are called diazoles, which are anti-diazotates, diazoamine compounds and diazo sulfonates. Inasmuch as diazoles contain a diazonium cation capable of a nitrogen coupling reaction without preliminary treatment, they are called active stable forms of diazo compounds, in contrast to the passive (diazoamino compounds, anti-diazotates and diazo sulfonates), which as a rule should be subjected to preliminary treatment with mineral acid for conversion to a diazonium salt which is capable of a nitrogen coupling reaction.

On the other hand, in recent years diazoamino compounds have been proposed which do not require acid treatment for their breakdown and regeneration of an active form of the diazo compound. The rate of decomposition of such diazoamine compounds at increased temperatures is so great that it is sufficient to subject the material, to which the preparations described have been applied, to neutral high pressure steaming in order to form a diazonium cation from them. Such compounds are obtained by using isomers of phenylglycinecarboxylic acid (so-called neutrogenes) and other compounds as an amino stabilizer. For the combination of azide dyes with vat dyes, sometimes a strong, volatile organic base (for example, diethylaminoethanol) is introduced into the print color along with acids instead of a caustic alkali. During steaming it is eliminated, and the paste becomes acidic. The diazoamino coumpound disintegrates with the formation of the active form of the diazo compound.

Above in the chapter on the properties of diazo compounds, we took note of the means of deriving stable salts of diazo compounds, i.e. the synthesis of diazoles. The majority of diazoles used in industry are double complex salts with zinc chloride. They are easily precipitated from sulfuric or hydrochloric acid solutions of diazocompounds by zinc chloride, and following filtration are mixed with any hydrophilic mineral salt (for example, with aluminum hexasulfate). Such an almost dry paste, which contains 20 - 30% diazole, can be stored for a considerable length of time and once dissolved in water, instantly combines with the azo components. Besides double complex salts, diazoles are produced in the form of salts with arylsulfo acids. 1,5-naphthalenedisulfo acid is used quite often for this purpose. A diazo compound solution in mineral acid is treated with the salt of 1,5-naphthalenedisulfo acid, and the deposited precipitate of the diazonium sulfo acid salt, which is usually difficultly soluble in an acid medium, is filtered out and subjected to careful drying using various methods. The chlorides and sulfates of certain diazo compounds can also be employed as diazoles. To derive them, an acid salt of diazonium is mixed with anhydrous sodium sulfate and carefully dried in a vacuum.

Table 6 lists the diazoles which are used for azide dyeing.

The passive forms of stable diazo compounds are prepared using various methods. To derive diazoamino compounds, as noted above, an amine stabilizer is employed which guarantees the absence of diazo group transfer and makes the preparation water soluble. Aqueous solutions of diazonium salts at a set pH are treated with a solution of the amine stabilizer. The resulting diazoamine compound is usually salted out with common salt, filtered out and dried [286]. Phenylglycinecarboxylic acid and its derivatives, sulfoanthranilic acids, N-hydroxyethylanthranilic acid, 5-methylsulfanthranilic acid, sarcosine, methyl taurine, piperidinesulfo acid, etc., are used as amine stabilizers.

To derive the alkaline salts of diazo compounds (anti-diazotates), but often (incorrectly) called (particularly in old literature) nitrosamines, diazo compounds with strong electron acceptor groups are used. They make the formation of anti-diazotates relatively simple, although sometimes they are derived at high temperatures using a concentrated alkali [287]. The diazonium salt solution is gradually added to the alkali at a high temperature and the heating is continued. Following cooling, flakes of the anti-diazotate are crystallized out of solution. They are filtered out and dried.

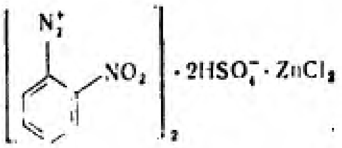
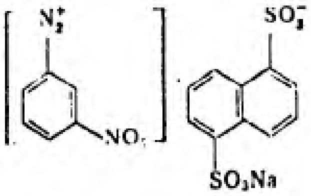
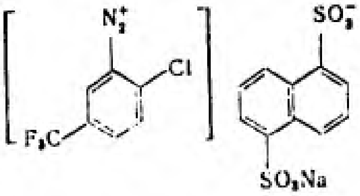
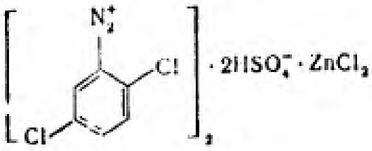
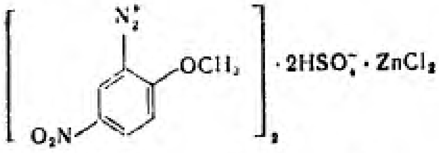
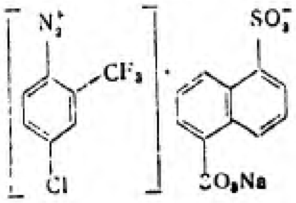
Diazosulfonates, which are somewhat less widespread, can be derived by treating diazonium salts with a solution of alkaline salts of sulfuric acid. Quite important in this case is the maintenance of a set pH value for the solution, since a slightly acid reaction leads to the generation of sulfurous anhydride, while an alkali excess leads to the formation of colored side products. The reaction should be carried out in the most concentrated solution possible [288]. The diazosulfonate salt which is either precipitated or salted out, is filtered out and dried.

TABLE 6

Diazoles Used For Cold Dyeing

Таблица 6

Диазоли, применяемые для холодного крашения

Диазоль Diazole	Formula Формула	№ по КИ CI Number
Оранжевый О Orange O		37 025
Оранжевый К Orange K		37 030
Ярко-оранжевый К Bright orange K		37 050
Алый 2Ж Scarlet 2Zh		37 010
Алый К Scarlet K		37 130
Ярко-алый Ж Bright Scarlet Zh		37 055

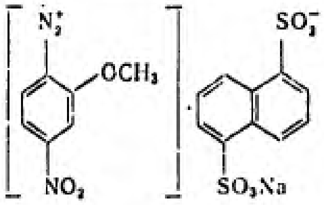
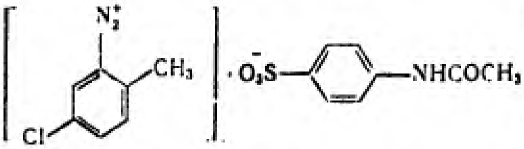
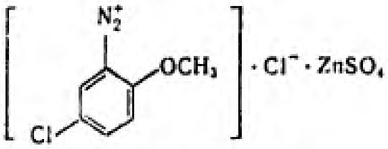
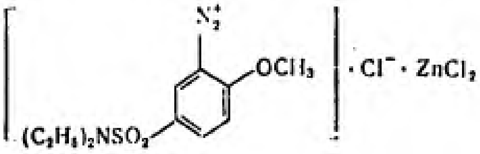
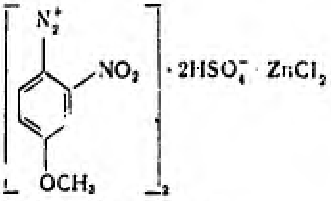
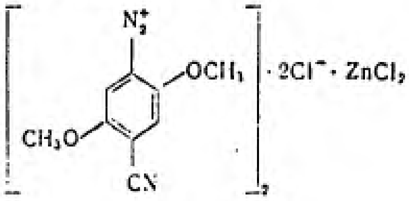
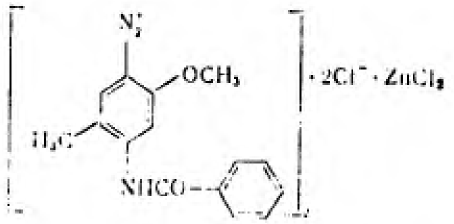
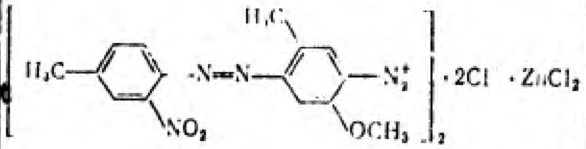
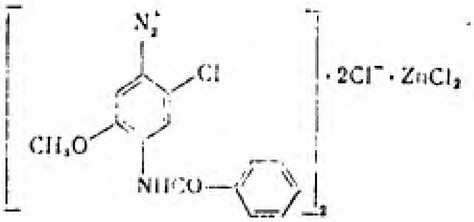
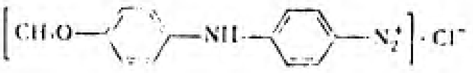
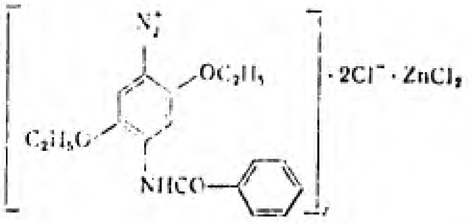
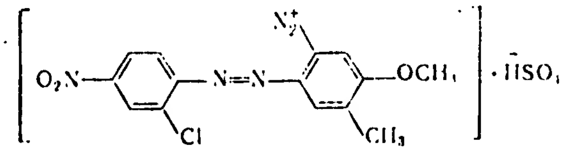
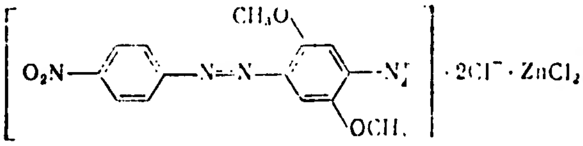
Диазоль Diazole	Formula Формула	№ по CI CI Number
Розовый О Pink O		37 125
Красный С Red S		37 090
Красный К Red K		
Красный О Red O		37 150
Бордо Claret color		37 125
Бордо К Claret color K		37 170

Table 6 **Continued** Продолжение

Диазоль Diazole	Formula Формула	№ по КИ CI Number
Фиолетовый Violet		37 165
Темно-фиолетовый К Dark violet K		37 220
Темно-фиолетовый 2К Dark violet 2K		37 160
Синий 2К Blue 2K		37 240
Синий О Blue O		37 255
Синий 2С Blue 2S		37 175

Continued

Диазоль Diazole	Formula Формула	№ по КИ CI number
Коричневый Brown		37 200
Черный К Black K		37 190
Черный С Black S		37 245

It becomes capable of a nitrogen coupling reaction, just as the other passive forms of stable diazo compounds, only following treatment with mineral acids jointly with oxidants.

Stable diazo compounds are of especially great importance for multicolored decorative printing. For this purpose, mixtures of passive forms of stable diazo compounds are prepared with azotols, which yield particularly valuable azide dyes and they are introduced in an appropriate manner into the printing color and applied to the fabric. Following a drying out (and sometimes even without it), the fabric is usually treated with a solution of mineral acid at a specified temperature or subjected to neutral steaming. The passive form of a diazo compound (anti-diazotate, diazoamino compound, or diazosulfonate) when acted on by an acid converts to a diazonium cation which instantly combines with the azotol present in the printing dye, forming an azide dye in the body of the fiber.

Mixtures of passive forms of stable diazo compounds with azo components can represent different combinations. Mixtures of anti-diazotates with azotols are called diazotols. Abroad they have been given the name rapids [289]. Both the anti-diazotates and the diazotols are combustible, and their mixtures with air are explosive. For this reason, when preparing them it is essential to take the a-propriate precautionary measures.

In addition to diazotols, caustic alkali essential for dissolving the azotol, wetting agents as for example, alizarin oil, and sodium dichromate are also included in printing dyes. The latters promotes an increase in the brilliance of the resulting dyes [290], apparently by preventing the reduction processes of the diazo compound. The dye is developed in the hot vapors of acetic or formic acid and also by neutral steaming with subsequent running of the fabric through a bath containing acetic acid. Under the influence of acetic acid, anti-diazotate converts to a diazonium salt, which instantly combines with the azotol ion, forming an insoluble azide type dye.

The assortment of diazotols is comparitively small, since far from all azoamines are capable of conversion to anti-diazotates. Besides this, they decompose with time. To preclude premature nitrogen coupling in the preparation, the diazotols are protected from the effect of carbon dioxide and are stored in a hermetically sealed container. The list of industrially interesting diazotols which are in use at the present time includes more than 30 representatives [291].

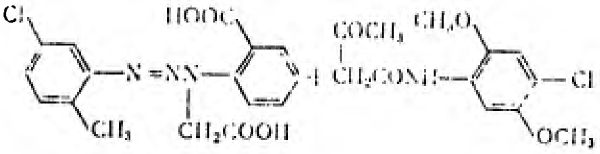
Diazaminols (or rapidogenes) are mixtures of diazoamino compounds with azotols. They are significantly more fast than diazotols, but often require rather severe conditions for their development. The latter is carried out in special acid resistant "maturers" in acetic acid vapors [292]. The severity of the conditions for development is explained by the comparative stability of diazoamino compounds in contrast to the anti-diazotates.

On the other hand, not all of the diazaminols require acid steaming. Diazoamino compounds have been recently developed which decompose with the formation of a diazo compound during so-called neutral development. Such diazaminols have the letter N in our products list in the alphabetical index of names. Sometimes they are called neutrogenes.

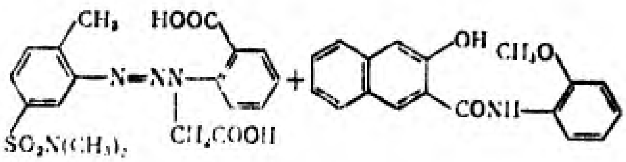
As was stated above, neutral development is possible if an amine stabilizer is used which has an acid group (sulfo or carboxylic). The presence of the latter makes it possible to prepare ammonium salts or salts with volatile organic bases, which decompose when heated, releasing a free acid of the amine stabilizer which breaks down the diazoamino compound [293]. It is also possible to use chlorides of aliphatic amines (for example, dimethylamine) which release acid when heated. The developing is carried out by treating the printed textile with aqueous steam.

By using diazaminols it is possible to derive dyes of all colors, including the dark ones, blue, black, and green.

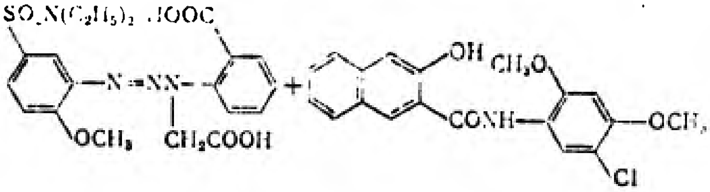
By way of example, we will list a few of the diazaminols. Diazaminol light resistant yellow is a mixture of diazotized Azoamine red S, stabilized by phenylglycine-o-carboxylic acid with Azotol 2Zh:



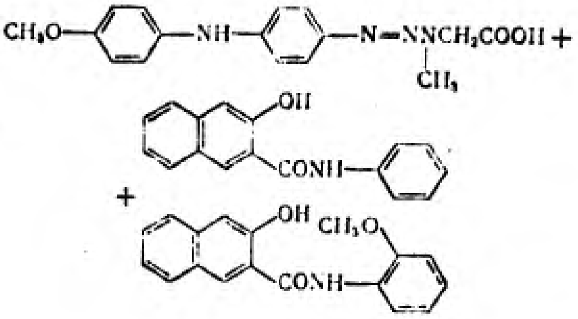
The diazaminol light resistant orange NK is a mixture of Azotol OA with the diazoamino compound derived from diazotized 2-aminotoluol-4-N-dimethylsulfamide and N-hydroxyethylanthranilic acid:



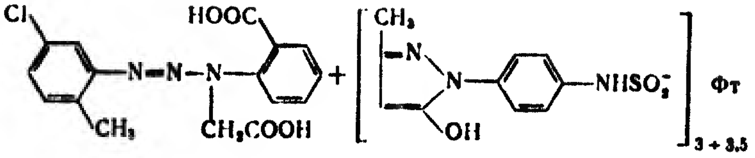
Diazaminol light resistant red N2S is a mixture of the diazoamino compound from Azoamine red O and N-hydroxyethylanthranilic acid and Azotol O:



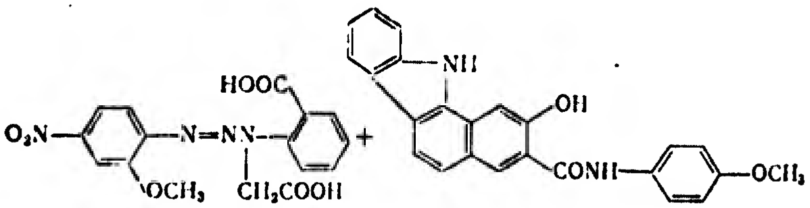
The Diazaminol dark blue NO is also interesting. Azoamine blue O is diazotized and stabilized using sarcosine. A mixture of Azotol A and Azotol OA is used as the azo component:



Finally, Diazaminol light resistant green N is a mixture of the diazoamino compound derived from diazotized Azoamine red S and phenylglycine-o-carboxylic acid and Azotol green is the phthalocyanine derivative of nickel or copper:

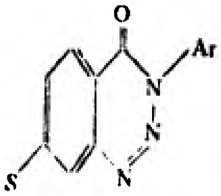


The derivation of black dyes is achieved by using azotols which are derivatives of hydroxycarbazolecarboxylic acids or hydroxybenzocarbazolecarboxylic acids. Thus, Diazaminol light resistant black N is a mixture of Azotol black

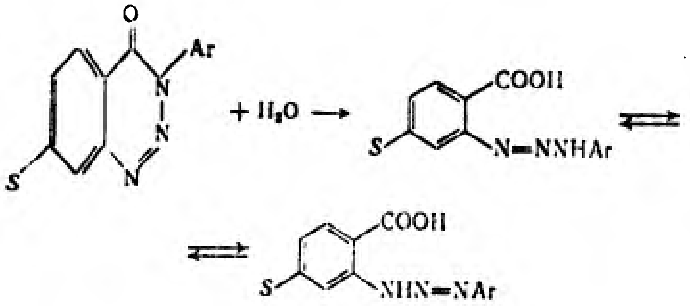


with the diazoamino compound from diazotized Azoamine pink O and phenylglycine-o-carboxylic acid.

Polish chemists have developed original dyes which they have called polagenes. Sulfanthranilic acid is used as an amine stabilizer, and which in interacting with diazo compounds forms triazones under certain conditions, which are internal molecular acyl derivatives of diazoamino compounds:



Triazones are very durable substances which practically do not react with azotols and are capable of being stored in mixtures with the latter for an indefinite period of time. During dyeing or printing with polagenes, they are dissolved in alkalis. In this case, triazones hydrolyze with the formation of a diazoamino compound. Owing to the presence of electron acceptor groups in the amine stabilizer molecule, tautomeric rearrangement takes place with the formation of a diazoamino compound in which the amino component is sulfanthranilic acid:



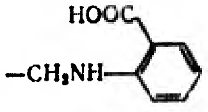
A diazoamino compound decomposes with neutral steaming and the generated diazo compound compound combines with azotols. Finished polagene dyes have an advantage over the usual neutrogenes with their resistance to friction. At the present time about 20 makes of polagenes are produced, from yellow to black in color.

Mixtures of azotols with diazosulfonates are called rapidosoles. The derivation of diazosulfonates is to be carried out in those cases where the formation of anti-diazotates or diazoamino compounds is difficult for some reason. An example here is Diazole blue O (the diazo compound from 4-amino-4'-mehtoxydiphenylamine). It forms neither diazoamino compounds nor the anti-diazotate, but easily enters into a reaction with sodium sulfite forming the diazosulfonate. The latter has a covalent bond of the end nitrogen atom with the sulfur atom. It easily converts to an ionic bond when the sulfurous acid radical is oxidized to a sulfuric radical. This is accomplished during of the rapidozoles with aqueous steam where any oxidant (most often potassium bichromate) is introduced into the printing color.

Azide wool dyes. The principle of azide (cold) dyeing can also be extended to protein fibers. However, the use of azotols which require caustic alkalis for dissolution is not possible in this case. For this reason, the azide dyeing of wool has not been widely used. However, *special azotols* have been worked out for it. The simplest of them is 2-naphthol-1-sulfo acid which requires soda and not a caustic alkali for dissolution. When a mixture of the passive diazo compound form with the kind of azotol as is realized in an acid medium, and this mixture is printed on wool and developed, the sulfo group from the first position of the naphthalene molecule is displaced by an azo group [294]. In accordance with this principle, the usual azotols can also be employed by introducing any group which is easily displaced by an azo group during nitrogen coupling into position one of the naphthalene, and thereby creating the characteristic of solubility in weak alkalis (soda, borax, etc.) or in acids. Methylamino- and dimethylaminomethylene groups, m-carboxyphenylaminomethylene or groups similar to them

$-CH_2NHCH_3$

$-CH_2N(CH_3)_2$



are employed as such groups. These derivatives are obtained using Mannich's reaction [295].

Azoaceto Dyes

The structure of polyester fiber (lavsan, terylene) is such that it is capable of adsorbing phenols and amines which are absorbed by the fiber due to the formation of a hydrogen bond. The so-called azoaceto dyes, mixtures of primary aromatic amines and azo components were proposed for first dyeing acetylcellulose, and then polyester fibers. Following the adsorption of both of these components by the fiber, diazotization and nitrogen coupling in the thickness of the fiber are carried out. It stands to reason that all of these operations do not always proceed easily, since the substance participating in the reaction for forming the azo dye should be insoluble in water and should not be ionized: this would reduce the possibility of their adsorption by the fiber.

Azoaceto dyeing is conducted in just the same way as when using dispersed dyes. Here, accelerators, or high temperature and pressure are also used in the same manner. Following the adsorption, the diazotization and nitrogen coupling operations are carried out. The first proceeds with a mixture of sulfuric acid and sodium nitrite in the cold, or at an elevated temperature for better diffusion of the diazotizing agent into the fiber, while the second proceeds at high temperatures (≈100° C).

We will recall that the azo component on the polyester fiber is in the non-ionized form, and such a form is capable of a nitrogen coupling reaction only with great difficulty.

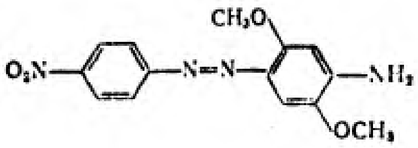
Examples of azoaceto dyes are given below.

Azoaceto orange Zh is a mixture of Azoamine orange K (m-nitroaniline) and Azotol OA (o-anisidide-2-hydroxynaphthoic acid).

Azoaceto scarlet is a mixture of Azoamine scarlet K (m-nitro-o-anisidine) with the same Azotol OA. Quite close to it is Azoaceto red Zh, which is a misture of n-nitro-o-toluidine (Azoamine red 4S) with the same azotol.

Azoaceto claret color is a mixture of the same Azotol OA with Azoamine dark violet 2K. Azoamine blue 2S is widely used as a diazo component. In combination with Azotol A it is known as Azoaceto blue, while in combination with Azotol OA, it is known Azoaceto dark blue.

Azoaceto yellow - brown is a mixture of Azoamine orange K (m-nitroaniline) with Azotol brown (the n-chloroanilide of hydroxycarbazolecarboxylic acid). Finally, Azoaceto black is a mixture of Azoamine black K



with Azotol OT (o-toluidido-2-hydroxynaphthoic acid).

All of the enumerated azoamines are used in the form of bases. The azoaceto dye smooths out well prior to application to the fiber with dispergators. Diethanolamine often serves for the latter.

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