XXIV.—*On Colouring Matters derived from Diazo-compounds.*

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CHEMISTS who take an interest in one of the youngest branches of applied chemistry, the manufacture of artificial colouring matters, will have remarked that this industry has made during the last three or four years more rapid progress than ever. New colours are being constantly brought out, and a number of them have come into general use, having, if not replaced, at least greatly limited the use of some of the old, costly artificial, and especially of the natural dyes. Although, four or five years ago, the number of artificial colours was very considerable, their range was not perfect. There was a great variety of

magenta, violet, and blue shades; but only one green colour was known until quite recently, and this was of a very fugitive nature. Yellow colours were not known at all, and the only orange, phosphine, was a bye-product of limited production, and consequently very high in price. The dyer was therefore obliged to use for all the mixtures into which yellow or orange colours entered, the natural colours, such as turmeric, anatto, and quercitron, which are both inconvenient in their use, and very fugitive.

The difficulty of selecting from the vast domain of organic compounds those which, being dyes, were likely to fill the existing gaps, induced me to work out a kind of theory of the relation between chemical constitution and the colouring power of aromatic substances, an abstract of which I read three years ago before this Society. In this paper I pointed out that there existed a series of compounds, the colour of which was in close relation to their chemical constitution. The first link of this series is azobenzene.

It is, although of deep yellow colour, not applicable for dyeing, because it is devoid of salt-forming groups. From azobenzene, however, by the successive introduction of amido- or oxy-groups, either basic or acid compounds may be derived, possessing strong affinities to textile fibres, which increase with every new salt-forming group introduced into the molecule.

Of the vast number of possible dyes of this class, all of which are yellow or orange, only two at that time were known, amidoazobenzene,

and triamidoazobenzene,

the first of which was too fugitive, although of a very bright yellow colour, and the second of too dull and reddish a shade, although very fast. It was a natural consequence to assume that the intermediate, then unknown, diamidoazobenzene would combine the freshness and beauty of amidoazobenzene with the strong affinities of the triamido-compound. At the time when I read my paper, I had convinced myself that such was the case, and diamidoazobenzene had become, under the name of *chrysoidine*, an article of commerce.

For its preparation I adopted a method, which divided the two stages of the formation of amidoazo-compounds into two distinct operations. It is generally admitted that, if nitrous acid be allowed to act

on an excess of amido-compounds, one molecule of diazo-compound is formed in the first instance—

This diazo-compound acts on another molecule of the amido-compound, forming the amidoazo-compound—

For the production of chrysoidine I therefore prepared in the first instance a solution of diazobenzene chloride, which on being brought into contact with an aqueous metaphenylenediamine solution, deposited the hydrochlorate of chrysoidine.

Griess has shown that not only amidoazo-compounds may be obtained, but that also the oxy-derivatives of azo-benzene and other azohydrocarbons—which are all dyes—may be prepared by acting with diazo-compounds on the corresponding phenols.

By introducing, therefore, the production of diazo-compounds in a pure state, and on a large scale, into the manufacture of aniline colours, an inexhaustible mine of new and beautiful dyes had been opened. When Hofmann published his paper on chrysoidine, and explained the mode of its preparation, investigations on this class of colouring matters were instituted in the laboratories of almost all aniline colour manufacturers. At the present day the variety of azo-colours in the market, and the number of patents taken out for their production are constantly increasing. Several publications have appeared on the subject, some of which describe more or less accurately even the substances which I first prepared, and which are manufactured by Messrs. Williams, Thomas and Dower. I cannot therefore carry out my original intention of bringing before the Society a full description of the preparation and the properties of all my new azo-colours, and I must content myself with identifying those already described with the names which have been adopted for them in commerce, giving a full description only of some products, which hitherto have not been described by others.

The prototype of these compounds is, of course, chrysoidine, the hydrochloride of metadiamidoazobenzene—

I have given a full description of its properties in a paper published in the *Deut. Chem. Ges. Ber.*, **10**, 654, and in abstract, in this Journal, 1877, **2**, 457, where I described its salts, the free base (m. p. $117\cdot5^\circ$), its acetyl-derivative (m. p. $250\cdot5^\circ$), and its sulpho-compound. I have since also prepared in a state of purity the following analogous substances, which in their properties differ but little from the typical product :—

I have already mentioned that to each basic colour belongs an acid one, which is similar in shade and constitution, and only containing hydroxyl in place of amido groups. Such is also the case with chrysoïdine, the acid counterpart of which has been prepared by Baeyer and Jæger (*Ber.* 8, 51), and carefully studied by Mr. Typke (*Deut. Chem. Ges. Ber.* 10, 1576). This compound is indeed a very beautiful dye, but its metallic salts have so little stability that it could not be employed in the usual way. I therefore introduced a sulpho-group into its molecule, originally by treating dioxiazobenzene with sulphuric acid at 100° ; but very soon I adopted the action of paradiazobenzene-sulphonic acid on resorcin as a simpler method of preparation. This compound has since been described by Griess. Its constitutional formula is that of metadioxiazobenzene sulphonc acid—

and its acid sodium salt is sold under the name of *Tropæoline O*. By acting with diazobenzene sulphonie acid upon other phenols several other colouring matters have been obtained, of which I mention—

Tropæoline Y, the sodium-salt of monoxiazobenzene sulphonie acid, prepared from phenol.

Tropæoline 000 No. 1, oxy- α -naphthyl, and

Tropæoline 000 No. 2, or Orangé 2, the sodium-salt of oxy- β -naphthyl azophenyl sulphonie acid—

Tropæoline 0000, which has been prepared by acting with diazobenzene chloride upon α -naphthol sulphonie acid. It is isomeric with tropæoline 000 No. 1, and 000 No. 2.

Another class of azo-colours may be obtained, if the salt-forming properties of amidoazobenzene and analogous compounds, the beautiful colour of which I mentioned already, be intensified by the introduction of one or several sulpho-groups. It is, however, more advantageous to start, not from amidoazobenzene itself, but from its methylated and phenylated derivatives. Thus we obtain, by acting with paradiazobenzene sulphonic acid on dimethylaniline, a compound which for some time has been manufactured by continental makers. The basic properties of the amidoazo-compounds are, however, still too prominent in it. The smallest quantity of acid introduced into its solution instantaneously reddens it. We may, however, obtain an appropriate equilibrium of basic and acid properties by introducing one phenyl- instead of two methyl-groups into the molecule of amidoazobenzene sulphonic acid, and thus produce perhaps the most beautiful azo-colouring matter known. This compound is manufactured and sold under the name of *Tropæoline OO*. Before describing its properties and derivatives I will make a few remarks on the corresponding non-sulphonated compound, *phenylamidoazobenzene*.

To prepare this compound I dissolve—

17 grams of diphenylamine in
100 c.c. of alcohol.

I also prepare by mixing the appropriate quantities of aniline, hydrochloric acid, and sodic nitrite a solution of

14 grams of diazobenzene chloride in
50 c.c. of alcohol.

I mix the two solutions, whereupon the mixture assumes a deep reddish-brown colour. The flask containing the mixture is surrounded by ice, and from time to time small quantities of an alcoholic trimethylamine solution are added to neutralise the hydrochloric acid liberated in the reaction. Trimethylamine is, on account of the solubility of its hydrochlorate in alcoholic liquids and its indifference to nitrous acid, a very useful reagent in such cases. In the present instance, however, care should be taken only to neutralise, not to basify, the mixture, which would be the case if sufficient trimethylamine were added to produce a yellow coloration. After some time, however, a point is reached when a single drop of trimethylamine solution produces this

yellow colour. The reaction is then finished. A quantity of a thick dark-brown oil has separated out, which may be increased by the addition of water. This oil, which solidifies after some time, is impure phenylamidoazobenzene. To obtain it in a pure state a somewhat lengthy purification is required. The crude product is dissolved in benzene, and the solution is precipitated with gaseous dry hydrochloric acid. The precipitate is collected, washed with benzene, and dried. It is then treated with aqueous ammonia solution, and the yellow mass obtained is carefully washed with cold water. It is then dissolved in alcohol, and for the quantity derived from one operation

50 c.c. of pure amylic nitrite and
25 c.c. of acetic acid are added.

The mixture is heated on the water-bath until it begins to boil. On cooling a beautiful crystallisation of the nitroso-derivative is obtained. The crystals are collected, washed with alcohol, and boiled up with a mixture of equal volumes of alcohol and strong hydrochloric acid, when a reaction takes place. As soon as the formation of ethylic nitrite has ceased, the phenylamidoazobenzene is precipitated by the addition of water. It is collected, washed with ammoniacal water, and crystallised from a small quantity of alcohol, and finally from benzoline (petroleum, b. p. 90—148°), which removes the last traces of a black, tarry substance, tenaciously adhering to the impure product.

Phenylamidoazobenzene forms, when pure, leaflets or needles of a fine golden-yellow colour, m. p. 82°. It is soluble in benzoline, very soluble in alcohol, ether, and benzene. The alcoholic solution assumes a magnificent violet coloration on addition of hydrochloric acid, and after some time steel-grey needles of the hydrochlorate settle out. In concentrated sulphuric acid phenylamidoazobenzene dissolves with a green colour, which, on addition of water, changes into indigo, violet, and red. The analysis gave the following numbers:—

	Theory for $C_{18}H_{15}N_3$.	Found.
C.	79.12	79.66
H.	5.49	5.92
N.	15.39	—
	<hr/> 100.00	

Its constitutional formula may be derived from its mode of formation, and the fact that it gives on reduction aniline and paramidodiphenylamine; it is therefore—

The description of amidodiphenylamine I must reserve for a paper on the reduction of the nitrodiphenylamines. Phenylamidoazobenzene forms, when treated with amyl nitrite and acetic acid as above described, a *nitrosamine* of the formula—

crystallising in beautiful orange needles, difficultly soluble in alcohol and acetic acid, very soluble in benzene, melting at 119.5° . Prolonged boiling with acetic acid causes a decomposition. Mineral acids regenerate phenylamidoazobenzene—

		Found.	
Theory for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}$.		I.	II.
C	71.60	71.54	71.96
H	4.60	5.39	5.37
N	18.50	—	—
O	5.30	—	—
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100.00			

If instead of acting with diazobenzene on diphenylamine, diazobenzene sulphonic acid be used, the product of the reaction is *Tropæoline OO*—

The free acid forms steel-grey needles, very sparingly soluble in water, with pink coloration. It is a powerful acid, and forms well-defined salts with most of the metallic oxides and organic bases, almost all of which are remarkable for their insolubility. The product in commerce is the *potassium salt*, slightly dichroic yellow and orange flat needles of considerable length and extreme fragility. It is very sparingly soluble in cold and easily soluble in boiling water. Very small quantities of mineral salts precipitate it from its solutions. The addition of mineral acids liberates the free acid and changes the colour of the liquid into a reddish-violet. This compound has therefore been proposed as an indicator in alcalimetry—.

	Theory for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{SO}_3\text{K}$.	I.	Found. II.	III.
C	55·25	55·32	55·65	55·70
H	3·38	4·34	2·96	3·80
N	10·73	—	—	—
S	8·18	—	—	—
O	12·41	—	—	—
K	9·98	—	—	—
	<hr/> 100·00			

Sodium Salt.—Similar to the potassium salt, but not so well crystallised.

Ammonium Salt.—Very similar to the potassium salt.

Trimethylamine Salt.—The only salt of Tropæoline OO, which is easily soluble in cold water. It forms very beautiful flat needles.

Barium and calcium salts are insoluble yellow precipitates.

The *aniline salt* shows an extraordinary behaviour when treated with an excess of boiling aniline. It is then suddenly transformed into Induline, $\text{C}_{18}\text{H}_{15}\text{N}_3$, a blue colour, isomeric with phenylamidoazobenzene.

Tropæoline OO, yields on reduction sulphanilic acid and paramido-diphenylamine.

I trust I have succeeded in giving in the present paper a sketch of what I may be permitted to call genuine azo-colours, the true oxy- and amido-derivatives of azobenzene and analogous compounds.

The term *azo-colours* may, however, be extended to compounds derived from amidoazo bodies by the action of amines, and to other colouring substances containing the azo-group—

in their molecule. I hope to have an opportunity of bringing before the Society in another paper an account of my researches in this more intricate chapter of the chemistry of nitrogen.