

Stable Diazo Printing Colours and a New Explanation of the Constitution of Diazo Compounds

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The attempts which have hitherto been made known to replace acetic acid in the diazo printing colours for the beta-naphthol prepare have not been completely successful. As is well known the acetic acid arises from the sodium acetate which is added as a saturating or neutralizing agent for the mineral acid (hydrochloric acid or sulphuric acid) employed.

It is impossible to print the diazo colours containing sulphuric acid, hydrochloric, or phosphoric acid, because of their action on the fibre and also on account of the back greys. Diazo colours which are kept more strongly acid by the acids mentioned do not couple sufficiently.

The acetates of the diazo colours, however, decompose easily, and other organic acids such as formic acid, tartaric acid, citric acid, and oxalic acid act at least no better than acetic acid. The search for a suitable substitute for acetic acid in diazo printing colours has occupied the attention of the colourists of printing establishments and colour works for a long time. I myself took up the problem and found in 1906 that certain mineral acids which do not attack the fibre can very well replace acetic acid, for instance boric acid and tungstic acid.

If boric acid, in the form of commercial boric acid anhydride, is dissolved in hydrochloric acid diazo solutions after they have been neutralized with an excess of calcium carbonate (used in the form of whitening), these solutions and the printing pastes prepared from them can be kept for several days without decomposing or weakening.

If a solution of borax is carefully added directly to hydrochloric acid diazo solutions,

even when cooling, as is done with sodium acetate, the solution froths and decomposition sets in. That is to say, the neutralization of the hydrochloric acid diazo solution beforehand with calcium carbonate cannot be dispensed with.

When tungstic acid is used, it is not necessary to neutralize the solution before adding it in the form of a solution of sodium tungstate. The addition of tungstic acid has proved to be particularly advantageous in the case of p-nitro-o-anisidine red, especially when pink shades are to be printed. Even colours that have been let down as much as 1:24 give clear shades and even these light shades last well.

Pink shades from p-nitro-o-anisidine have a bluish tinge which is much liked, while p-nitraniline red which has been let down becomes yellowish.

Diazo solutions which have been neutralized with calcium carbonate keep better, even in summer, without ice, perhaps even better indeed than the printing colours prepared with the addition of boric acid or tungstic acid.

The use of the acids just mentioned of course is more expensive and it need hardly be specially mentioned that stable diazo printing colours prepared with their aid are more particularly suitable for small prints and as part of multiple colour effects. That is to say, their use is advantageous when not much colour is required, when fresh colour is not often added, and the decomposition of the acetic acid colour soon makes itself noticeable. With heavy prints, on the contrary, where the printing colour must often be freshened up by the addition of more colour, it will be found that the acetic acid colour

will be sufficient. The recipe for the preparation of the stable diazo colours is as follows:

1. 500 grams Base (p-nitraniline, m-nitraniline, or p-nitro-o-anisidine) are made into a paste with
 - 1000 „ boiling water and then
 - 1000 „ hydrochloric acid 19° Bé are added. After having allowed to cool,
 - 3200 „ ice are added and then, all at once,
 - 325 „ nitrite (whereby the temperature sinks to — 5° C). When diazotization is complete, add slowly
 - 500 „ calcium carbonate. After stirring, filtering, and washing
 - 180—240 „ boric acid are added to the filtrate.

The whole is made up to 10 kilos and thickened with 15 kilos gum tragacanth or neutral starch thickening.

2. 500 grams Base are diazotized as directed above.

After diazotizing, neither chalk nor boric acid is added, but a cold solution of 600 grams sodium tungstate in 1200 grams water.

When the diazo compounds are coupled with naphthol on the fibre, the diazo solution should be slightly acid or weakly alkaline; the processes hitherto known all use weakly acid solutions. If treated in the usual way, the diazo solution contains sodium acetate besides free acetic acid.

At a temperature of 25° C acetic acid has the dissociation constant of 1.86×10^{-5} and the acid exponent of 4.73. The presence of sodium acetate reduces the dissociation of the acetic acid and the acid exponent therefore naturally counts higher, that is to say, the acidity becomes less. Boric acid at the same temperature has a dissociation constant of 6.6×10^{-10} , the acid exponent is 9.18. Tungstic acid is an ampholyte with mainly acid properties, and as an ampholyte can only be a weak acid. I was unable to find from the literature the dissociation constant and the acid exponent of tungstic acid, so that I cannot even say whether these constants have already been determined.

It is evident from these figures why boric acid and tungstic acid have proved to be suitable for use in coupling the diazo compounds with naphthol. They are weak acids. In passing it may be remarked that the degree to which

cellulose fibre is injured depends upon the dissociation capacity of the acids, that is to say, the dissociation constants are a measure of the power to injure textile fibre.

Both boric acid and tungstic acid are weaker acids than acetic acid and they can therefore have a more favourable action than the latter. The dissociation constants and the acid exponents of a number of organic acids at 25° C may be tabulated as follows:

oxalic acid	dissoc. const.	3.8×10^{-2}	acid expon.	1.42
tartaric acid	„	9.7×10^{-4}	„	3.01
citric acid	„	8.2×10^{-4}	„	3.09
formic acid	„	2.05×10^{-4}	„	3.69
lactic acid	„	1.55×10^{-4}	„	3.81

Experience has showed that they act more unfavourably on the coupling. (The constants given are taken from J. M. Kolthoff, „Der Gebrauch von Farbenindikatoren“.) When a diazo solution which contains weak acid and also sodium is brought together with the alkaline naphthol prepare it may be supposed that the free alkali of the naphthol prepare acetate is first of all saturated with acetic acid and that the formation of the azo colour proceeds only in the presence of sodium acetate. That would accord with the usual method of working in the manufacture of azo colours when the dyestuffs themselves are actually prepared and not on the fibre, namely coupling with phenols in the presence of a weak alkali. When the diazo solution contains boric acid there are formed under corresponding conditions quite evidently an alkaline borate with an alkaline reaction, and with tungstic acid a weakly alkaline tungstate.

After what has been said there is no need to go further into an explanation of why the stronger acids, such as oxalic acid, tartaric acid, citric acid, formic acid, lactic acid, are less favourable for the formation of the azo colouring matter. It will also be evident why aluminium sulphate, which is used especially in the diazo solution prepared from Fast Red GL Base (Griesheim), can exert the desired favourable action upon the coupling owing to its reaction not being strongly acid. Furthermore it is clear why the formation of an azo colouring matter takes place so smoothly with the use of a neutral diazo solution and a naphthol prepare which contains potassium carbonate and much ricinoleic acid. (I reported upon the process on the Congress last year in Dresden.)

The electrochemical constants cited are only comparatively of value, because the con-

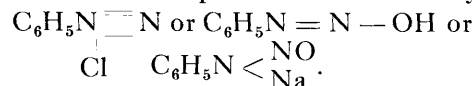
ditions are probably much less simple owing, in particular, to the presence of the diazo compounds or of the components, as has hitherto been supposed, of the diazo compounds. At all events, it can be concluded that acids, the dissociation capacity of which is greater than that of acetic acid, are liable to influence the coupling process less favourably.

These constants evidently influence also the stability of the diazo solutions, for such solutions containing boric acid and tungstic acid are more stable than those with acetic acid, while the neutral solutions are still more stable.

Among the letters which the „Chemiker Zeitung“ published in the Jubilee number of December 29, 1926, on the occasion of its half centenary, is the following communication from R. Wegscheider, of Vienna: “The progress of science is not entirely due to treatises and patents which are or at least should be based upon carefully carried out experiments and deliberations. Suggestions too must not be undervalued which proceed from casual expressions of opinion and chance observations”.

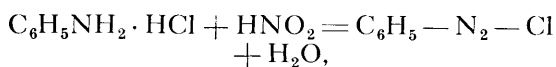
I have these words of Wegscheider's in mind when I communicate to a wider circle of technical colleagues the views which I have formed upon diazo compounds for the most part already more than twenty years ago in consequence of and on the basis of intensive study of the formation of azo colours upon the fibre. These studies would appear to find confirmation in recent investigations, I would mention in particular researches upon molecular compounds, especially organic molecular compounds, and in the changed perceptions gained in this way.

According to the current view, diazo compounds have a composition either of the type



One form can be changed into the other according to the conditions of reaction.

The diazo compounds are supposed to originate in the following way. One molecule of water separates out of one molecule of primary aromatic amino salt and one molecule nitrous acid:



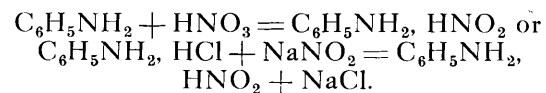
which implies a condensation process. Condensations appear in general at high temperatures, or by the action of agents which have a strong tendency to extract water, or under

the influence of both of these factors. Neither of them is present in the formation of aqueous diazo solutions which takes place at a low temperature, in so far as the production of azo colours on textile fibre comes into consideration, and no condensation agent is present.

The aqueous solutions of diazo compounds behave under the influence of heat like a solution of ammonium nitrite, which decomposes into free nitrogen and water, while diazo compounds form free nitrogen and phenols.

The formulae of diazo compounds given contain three or even four bonds of the nitrogen atoms. V. Meyer, in „Ergebnisse und Ziele der stereochemischen Forschung“, published in 1890, has shown that ethylene compounds are generally formed at high temperatures. I have not been able to find out whether such conditions have been experimentally proved also for organic nitrogen compounds containing multiple linked nitrogen atoms, but there is a presumption that this is the case. The origin of double links according to the usual explanation of the formation of diazo compounds is closely united to a condensation process, since water is split off. This would be explicable if a compound were formed which was insoluble in water, but this is not so. The product formed by the action of nitrous acid upon aromatic amino bodies in the presence of water remains dissolved in water. According to the modern theory, when chemical compounds are dissolved in water, an addition of water first takes place, that is, the formation of a hydrate. It cannot be seen why water should be split off into the water of solution upon the formation of the reaction product of an amino compound and nitrous acid.

The conviction simply forces itself upon the mind that the reaction of amino body and nitrous acid in aqueous solution is, at least first of all, an accumulative reaction. The process in a strongly cooled aqueous solution would probably be that shown by the equation

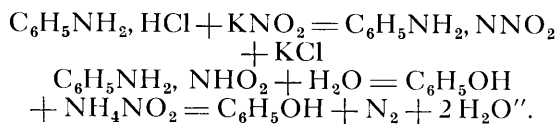


As a matter of fact the action of nitrous acid upon p-nitraniline chlorhydrate without any excess of hydrochloric acid produces at once a diazo compound, as I have shown in my remarks in the article „Anwendung von Kaliumverbindungen in der Druckereipraxis“ (Melliand Textilberichte, 1926, page 615) and

in my paper read before the Congress in Dresden. If an excess of hydrochloric acid is present a labile state of equilibrium arises.

When nitrite is entered into suitable diluted, strongly cooled hydrochloric acid, the nitrous acid set free remains in solution.

That views similar to my own were held long ago is shown by the following passage in Beilstein's „Handbuch der organischen Chemie“, third edition, vol. 1, page 92, with reference to the action of nitrites: “Alkaline nitrites are used in all cases where a definite quantity of nitrous acid is required which must not be exceeded. In order to prepare, for instance, phenols from aniline and its homologues, the hydrochloric acid salts of these bases are treated with (1 molecule) alkali nitrite and then boiled:



There is no hint as to the observations upon which Beilstein based his reaction formula. Here, therefore, in the preparation of phenols from amino bodies and nitrous acid, a diazo compound is not mentioned as intermediate product, but aniline nitrite.

P. Pfeiffer, in „Organische Molekülverbindungen“, page 27, remarks: “One advantage of the coordination theory formulae over the pure valency formulae is, I should say, that in them the components are simply laid close to one another by mutual saturation of affinity, without atoms being separated which were formerly united. *Separations of atoms and transformations should only be assumed when that is absolutely necessary, because otherwise unfruitful speculations arise and undermine the foundations of all determinations of constitution*”. In the reaction amino compound + nitrous acid = nitrite of amino compound, the nitrosamines (Schraube and Schmitt) do not require the constrained explanation of a transplacement if it is assumed that there are accumulation compounds of nitrite at the amino body, the choice being left free to regard nitrite as being constituted according to the scheme NOONa or NaNO_2 .

According to Banchard, nitrous acid at a temperature of 25°C has a dissociation constant of 4×10^4 and an acid exponent of 3.40, so that it is a stronger acid than acetic acid. It will therefore be understood that acetic acid and the still weaker acids do not decompose the nitrite amino compounds and that

azo dyes therefore are produced on the fibre in the presence of weaker acids than nitrous acid, and also why the coupling is either at least incomplete, or does not occur at all, when stronger acids are present. It is well known that no azo dye is formed if an excess of strong acids is present.

The explanation of the origin of azo dye-stuffs from nitrous acid compounds of amino bodies is unconstrained.

There are a number of organic molecular compounds, i. e. accumulation compounds, the origin of which can be compared with the formation of the nitrous acid compounds of amino bodies.

If, however, the classical formula of the diazo compounds is regarded as being correct, then the nitrous acid amino body must be looked upon as an intermediate product. Analogies for the formation of intermediate products, molecular compounds, can be found in considering substitution processes, whereby only those of the aromatic series should be taken for comparison.

In a few cases (for details see P. Pfeiffer, „Organische Molekülverbindungen“, page 264 et seq.) it could be directly proved that an additive process precedes the substitution process in halogen substitutions, by isolation of the primary molecular compound.

In the nitration of aromatic amines (cf. P. Pfeiffer, loc. cit. page 272) a nitrate is first formed which is transformed into a nitranilide under the *influence of an agent which splits off water*, the nitranilide transforming itself to amines nitrated in the nucleus. (I refer in this connection to my remarks upon reactions of condensation.) The sulphonation of aromatic amines (cf. P. Pfeiffer, loc. cit., page 272) proceeds quite according to the scheme of the nitration. If aniline is treated with concentrated sulphuric acid, there is formed first of all acid aniline sulphate which, according to Bamberger, is transformed into phenylsulphaminic acid by splitting off water. This sulphaminic acid is converted by treatment with dilute sulphuric acid into the *o*-sulphonic acid of aniline, and by treatment with concentrated sulphuric acid at a raised temperature isomerized into *p*-aniline-sulphonic acid. (*That is to say, here too a condensation process sets in only after the use of an agent which removes water, at the same time raising the temperature.*) The scope of a lecture which should be kept as short as possible makes it impossible to go into details minutely, but even without this it may be

assumed that the origin of nitrous acid amido bodies by the action of nitrous acid in aqueous solution upon primary amino compounds is, at the lowest, very probable.

About twenty years ago I withdrew myself

from chemistry, but the occurrences of recent times have induced me to resume my chemical studies. Certain extraneous conditions have, however, prevented me from continuing my work upon the subject under discussion.