

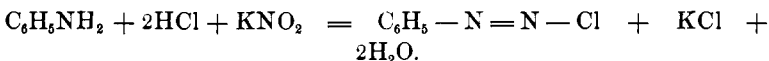
In conclusion, not only is the direct conversion of benzene into phenole by the action of hydrogen peroxide, of much interest, phenole having hitherto been obtained only by some indirect process, but it supplies a satisfactory demonstration of the validity of the third hypothesis above stated.

#### V.—NEW AZO COLORS BELONGING TO THE SO-CALLED TETRAZO GROUP.

BY JAMES H. STEBBINS, JR.

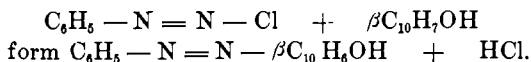
In order to give a clear understanding of this wonderful class of dyes, we will have to go back a few steps and consider the ordinary diazo compounds, their formation, and the azo dyes derived from them.

It is a pretty generally known fact, that when any of the salts of aniline (as the chloride, nitrate, etc.) or its homologues are treated with nitrous acid (either free or in the shape of a nitrite), that diazobenzole chlorides, etc., are formed, viz :



Now from Griess we learn that diazo compounds unite directly with phenoles and amines to form coloring matters which belong to the class of the so-called azo compounds.

As an example of the combination of diazo compounds with phenoles, we may take the action of diazobenzole chloride upon beta naphthole, viz :



If, on the other hand, we allow diazobenzole to react upon an amine (as aniline), we would get an amido-azo compound,



and this is the basis of the new class of colors.

Amido-azobenzole is a yellow basic coloring matter, uniting with one molecule of acids to form salts which, however, are readily decomposed with boiling water.

Now, as we have seen how nitrous acid acted upon amines, it seemed only too probable that if amido-azobenzole chloride were treated with nitrous acid, that a diazo compound would be formed, inasmuch as it contains a free amido radical ( $\text{NH}_2$ ). This hypothesis was fully verified by Kekulé, who describes such a compound in his organic chemistry. This discovery, at that time, presented no value,

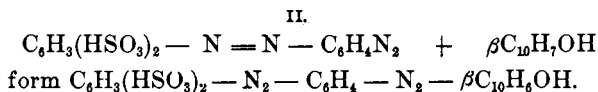
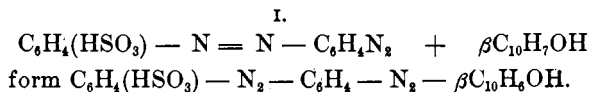
as azo compounds derived therefrom were insoluble in water, and could not be used for technical purposes.

Things remained in this state till a few years since, when it was discovered, that by introducing the sulpho group ( $\text{HSO}_3$ ) into these compounds, they were rendered soluble in water and might be used for dyeing.

Based upon this theory, Graepler took out a patent for converting the hitherto useless amido-azobenzole into its sulpho acid, and since then the manufacture of the tetrazo dyes has made great progress.

One of the first parties to avail themselves of this invention was the firm of Calle & Co., in Biebrich, who shortly after sent into commerce a dye-stuff called "Biebrich scarlet," and this dye is produced by diazotising amido-azobenzolesulpho acids, and combining the so obtained diazobenzolesulpho acids with beta-naphthole, in an alkaline solution.

I say sulpho acids, because, in the preparation of amido-azobenzolesulpho acid, not only the mono, but also the disulpho acid are formed, and we therefore have a mixture of two dye-stuffs as the final result, viz:

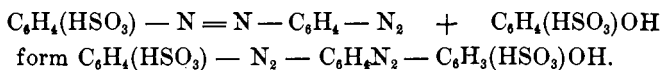


We therefore see, that wherever an aromatic azo compound contains a free amido group, that such a compound is capable of being diazotised, and again combined with phenoles to form new coloring matters.

Basing my experiments on this theory, I have been able to produce a series of new colors, of which the following are examples:

I.

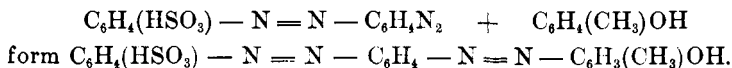
When diazo-azobenzolesulpho acid is allowed to react on an alkaline solution of phenolesulpho acid, a strong yellow dye-stuff is the result.



This color is very soluble in water, and dyes wool of an intense yellow color in an acid bath.

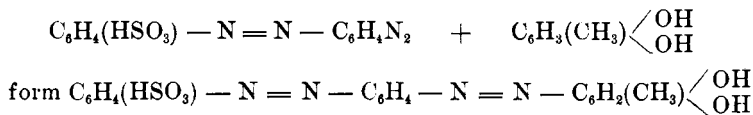
## II.

If diazo-azobenzolesulpho acid is allowed to react on cresole or its sulpho acid, a yellow coloring matter is likewise formed, which does not materially differ from the previous compound.



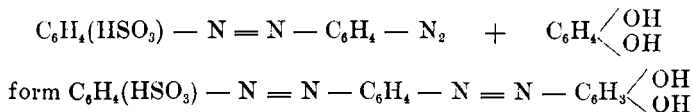
## III.

An alkaline solution of orceine produced an orange color.



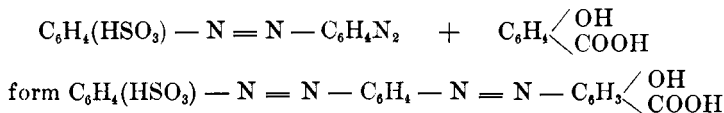
## IV.

Resorcine treated in the same way produced likewise an orange dye-stuff.



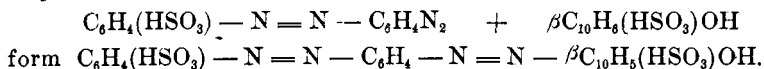
## V.

Salicylic acid brought in contact with diazo-azobenzolesulpho acid produced a yellow dye-stuff.



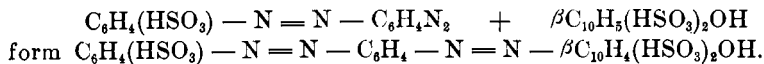
## VI.

In the same way a fine scarlet color is obtained, if beta-naphtholesulpho acid is substituted for salicylic acid.



## VII.

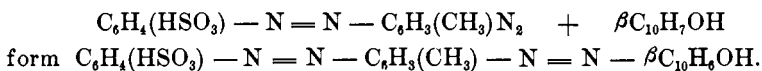
If we substitute beta-naphthoedisulpho acid for the monosulpho acid, a fine red color is the result. (Pat. by Koehler.)



## VIII.

Finally, if we treat azosulphoxybenzole-diazotoluole with an alkaline solution of beta-naphthole, an intense red coloring matter is

obtained. This coloring matter is very similar to Biebrich scarlet, but has a somewhat bluer shade.



These dyes are nearly twice as strong as the ordinary azo dyes, and they may be distinguished from one another by a very sharp reaction. When such a dye-stuff contains the sulpho group ( $\text{HSO}_3$ ) in the benzole nucleus, it is converted into an intense green color by the addition of a few drops of strong  $\text{H}_2\text{SO}_4$ . When the sulpho groups are in both the benzole and naphthole nuclei, an intense blue color is obtained, but, when only in the naphthole nucleus, a purple color is the result.

We can thus tell almost at a glance, the nature of the color under examination.