

CCXIV.—*Contributions to our Knowledge of the Sulphide Dyestuffs. Part I.*

By GEORGE HERBERT FRANK.

SINCE the introduction of Vidal black (by R. Vidal, of Paris, in 1893), which, as is well known, is prepared by fusing together *p*-aminophenol (or *p*-aminophenol and other compounds) with sodium polysulphide, a large number of these so-called "sulphide" dyestuffs have been produced in a similar manner from aromatic compounds of varied constitution. The application of these colouring matters, especially to cotton, is of so simple a character, and the colours obtained are of so permanent a nature, that these compounds now constitute one of the most important groups of artificial dyestuffs. Although considerable insight has been gained as to the reactions occurring in their formation (Vidal, *Mon. Sci.*, 1903, [iv], 17, i, 427; Pollak, *Zeitsch. Farb. Ind.*, 1904, 3, 233, 253; Gnehm and Kaufler, *Ber.*, 1904, 37, 2617, 3032), the subject is beset by considerable difficulty, for the dyestuffs are as a rule amorphous, of a comparatively insoluble nature, do not yield well-characterised derivatives, and are accordingly not easily isolated in a pure condition.

During some experiments on the subject it was discovered that the leuco-compounds of many sulphide dyestuffs react with chloroacetic acid, and that the substances thus obtained, when oxidised, yield interesting colouring matters, differing considerably in properties from the parent substance. These new carboxyl derivatives are readily soluble in alkalis, pyridine or phenol, moderately so in boiling alcohol or acetic acid, but insoluble in dilute acids. They are well-defined colouring matters, giving shades similar to those

produced by the original sulphide dyes, and can be readily dyed on wool, but differ from the parent sulphide dyes in that they have very little affinity for cotton.

Among other points of interest attached to these substances it seemed possible that their closer examination would yield an insight as to the true molecular weight of the sulphide dyestuffs from which they were obtained, a point which would be of considerable help in regard to the vexed question of their constitution.

The following investigation deals with the well-known colouring matter, immedial-indone, which is manufactured by heating together *p*-aminophenol and *o*-toluidine with an aqueous solution of sodium sulphide. In order to purify the commercial product, it was repeatedly washed with warm water, treated with dilute hydrochloric acid until the liquor was faintly acid, and well washed. Fifty grams of the finely powdered product were reduced with sodium hydroxide and dextrose at 60—70° in the usual manner, and treated with 20 grams of a solution of sodium chloroacetate. An increase in temperature took place, and after fifteen minutes air was aspirated through the liquid in order to oxidise the leuco-compound. The liquid was now neutralised with dilute hydrochloric acid, the precipitated dye collected, extracted with warm sodium carbonate solution, the extract acidified, and the dye collected and dried; the product was now extracted with warm aniline, filtered from a slight residue, the solution neutralised with acid, and the precipitate again extracted with dilute sodium carbonate solution and acidified. As molecular-weight determinations in pyridine and nitrogen and sulphur estimations indicated that this product was not quite pure, it was submitted to a further treatment with warm aniline and extraction with dilute aqueous sodium carbonate in the manner above described, and finally dried in a vacuum desiccator. The compound obtained in this way contained no ash, and experiments indicated that it was now pure. It was of a deep blue, bronzy colour, readily soluble to a blue solution in aniline, pyridine, phenol, alkalis, or concentrated sulphuric acid, and sparingly so in hot glacial acetic acid or hot alcohol. Experiment indicated the absence of an amino-group, and, unlike the original immedial-indone, it had no affinity for cotton when dyed in a sodium sulphide bath, neither had its sodium salt any affinity for cotton, but the latter could be dyed on wool in the manner of an acid colour, giving a bright blue colour.

After being dried at 98°, it was analysed:

0.1241 gave 0.2494 CO₂ and 0.0459 H₂O. C=54.8; H=4.11.

0.2800 „ 17.3 c.c. N₂ at 13° and 757.7 mm. N=7.40,

0.1121 „ 0.1376 BaSO₄. S=16.88.

0.1312 gave 0.1559 BaSO_4 . $\text{S}=16.72$.

$\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{C}=54.4$; $\text{H}=4.0$; $\text{S}=17.07$;
 $\text{N}=7.48$ per cent.

0.5 Gram of the substance was treated with 10 c.c. of *N*-sodium hydroxide, and the solution was made up to 500 c.c.; by titration with *N*/10-hydrochloric acid and employing phenolphthalein as indicator, the acidity of the compound was first determined, and the neutral liquid thus produced was then treated with sodium tartrate and reduced with standard titanium chloride:

Found, $\text{NaOH}=21.12$ per cent. of the weight of the dye.

$\text{H}_2=0.529$ " " "
 $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{NaOH}=21.39$; $\text{H}_2=0.5347$ per cent.

Hence 189.9 parts of the colouring matter neutralise 40 parts of sodium hydroxide, and for the reduction of 378.2 parts, 2 parts of hydrogen are required.

A determination of the molecular weight was carried out by the cryoscopic method:

0.0854, in 10.3 of phenol, gave $\Delta t = -0.14^\circ$. $\text{M.W.}=377.4$.

$\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$ requires $\text{M.W.}=374$.

When fused with sodium hydroxide, the substance undergoes an interesting change, for not only is sulphur thus removed, but also the carboxyl groups are eliminated. A blue compound insoluble in water or alkalis is thus produced. When reduced, this yields a leuco-derivative, but, unlike the corresponding leuco-derivatives of the sulphide dyestuffs, possesses no affinity for cotton.

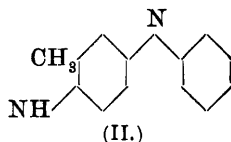
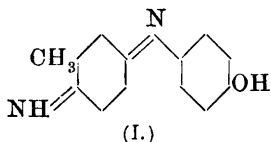
To obtain some further indication as to the nature of the reaction, a quantitative experiment was carried out as follows:

0.5 Gram of the carboxyl derivative was fused at 200° with concentrated aqueous sodium hydrate until a colourless pasty mass, consisting of the leuco-compound of the new substance, was produced. The product when cold was diluted with water, the mixture neutralised with acid, and the colouring matter collected and washed. An estimation of the sulphur present gave the following result:

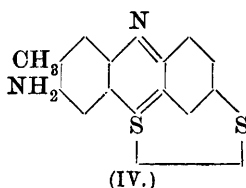
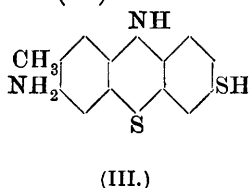
0.154 gave 0.1668 BaSO_4 . $\text{S}=14.89$ per cent.

Hence 215 parts of the substance contain 32 parts of sulphur. If from the found molecular weight of the carboxyl derivative we subtract $2(\text{CH}_2\cdot\text{CO}_2\text{H}) + \text{S}=150$, the new substance should have a molecular weight of 227, which is in fair agreement with the above result. This experiment shows that one atom of sulphur can be removed from the molecule of the original carboxyl derivative, but that on the other hand, the removal does not destroy the chromophoric group of this compound.

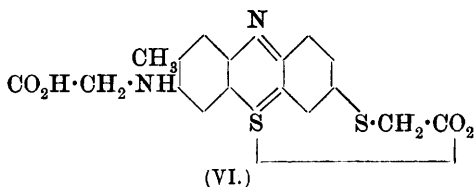
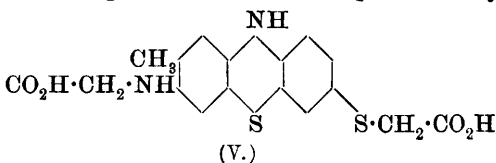
As immedial-indone is formed from the indophenol (I) obtained from *p*-aminophenol and *o*-toluidine, so the resultant dyestuff may be expected to possess the skeleton (II):



If we assume that, as is most probable during the reaction, sulphur enters in the *o*-position with respect to the nitrogen atom, and that the phenolic group is replaced by the thiol group, leuco-immedial-indone would have the constitution (III), and immedial-indone formula (IV):



Such a constitution would offer a ready explanation of the experiments given above. This compound would readily yield with chloroacetic acid a leuco-dicarboxylic derivative having the formula (V), and the colouring matter would be represented by (VI).



This investigation therefore indicates that the most probable constitution of immedial-indone is that given above; further experiments on this difficult subject are in progress.

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