ELECTROLYTIC OXIDATION OF ANILINE OIL.

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In 1856, Perkin discovered the first coal-tar dye, mauve; various oxidizing agents were used by different investigators for producing the red dyes from the crude aniline. It is well known that by the strong oxidizing agents mauve is produced, and by the weak oxidizing agents fuchsine is produced.

The author has intended to ascertain what kind of the red dye is produced by the electrolytic oxidation of the crude aniline.

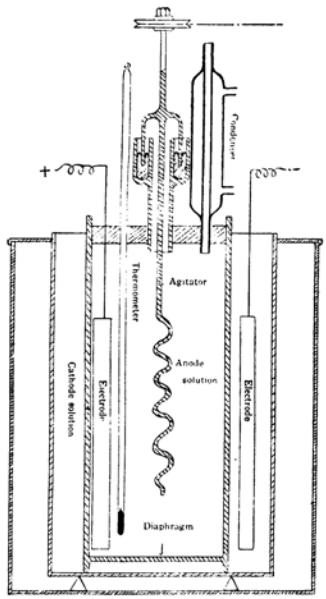


Fig. 1.

The experimental apparatus is shown in Fig. 1. Experimental conditions were as follows: Reagents taken, aniline 15.5 g., *o*-toluidine 17.7 g., and *p*-toluidine 17.7 g. Anode solution, aqueous solution of mineral acid salts of the reagents. Cathode solution, aqueous solution of mineral acid. Electrode, carbon plate. Diaphragm, cylindrical porous cell. Current density, 2 amp./100 sq. cm. Temperature, 80°–90°C. Voltage, 5–6 volts.

I. Quantity of Electricity and Depth of Colour. Under the above conditions, the electrolytic oxidation was applied to aniline oil with a constant agitation of the anode solution. The anode solution became red in short time and by continued treatment it passed into yellow, and finally lost the dying property.

This red dye is difficultly soluble in cold water, fairly soluble in hot water; with alkali it yields a brown precipitate. Its solubility in acid is proportional to the acid concentration, and it becomes colourless by reduction and is gradually recoloured in the air. From these properties it does not belong to triphenylmethane dyes and we may suppose it belongs to the azine group.

At the beginning of the electrolysis, the yield of the dye is proportional to the quantity of electricity; by a further passage of the electrical current the concentration is rather decreased and it is decomposed into foreign substances.

II. Investigation of Absorption Spectrum. It is well known that mauve, safranine, and fuchsine are produced by the oxidation of aniline oil. By comparing the absorption spectra of these dyes with that of the dye which is produced by the electrolytic oxidation, it may be ascertained that the new dye belongs to the series of these dyes, and it is recognized as an intermediate product from the spectra taken at intervals during the oxidation. The absorption curves are shown in Fig. 2. From these curves the dye produced by the electrolytic oxidation is none of mauve, safranine, and fuchsine, but it is situated between mauve and safranine or fuchsine.

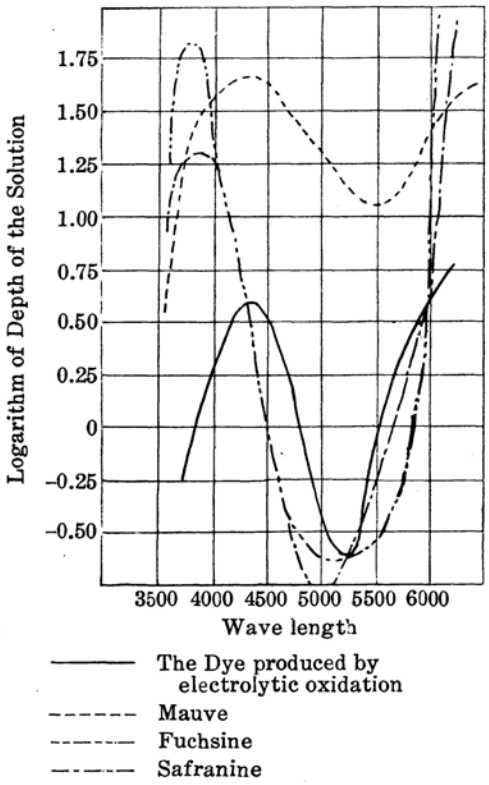


Fig. 2.

At the beginning of the oxidation the absorption takes place at the indigo part and it moves to the purple part, but no definite intermediate product can be recognized by the curves.

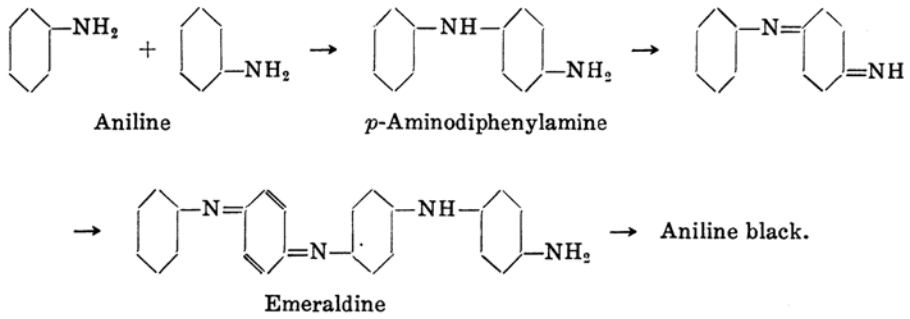
III. The Intermediate Product. From the absorption curves no definite intermediate product can be recognized even though the curves move with progressing oxidation.

By the electrolytic oxidation in the cold, say below 10°C., a blue precipitate is produced, which is scarcely soluble in cold water, fairly soluble in hot water, and easily soluble in alcohol.

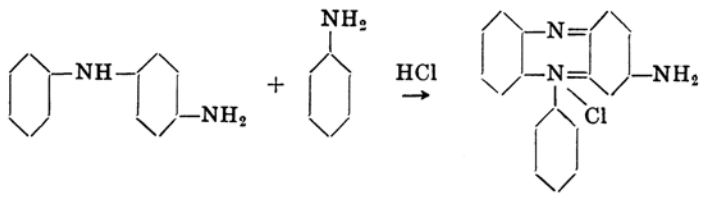
To ascertain the composition of the blue precipitate aniline was first subjected to the electrolytic oxidation at 5–7°C.; the blue precipitate which was soon formed was drawn out from the solution and purified by washing. This blue substance is the same as quinonanil (emeraldine) in all behaviours, which is produced by the ordinary oxidation of aniline.

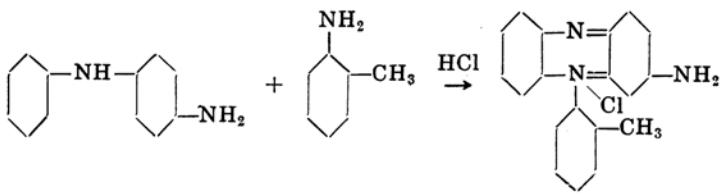
Examination of the properties of the ether soluble substance leaves no doubt that it is *p*-aminodiphenylamine, but the quantity was too small for crystallization.

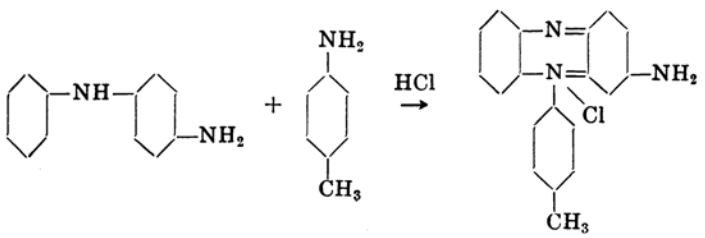
The following equations show the process of the electrolytic oxidation of aniline:



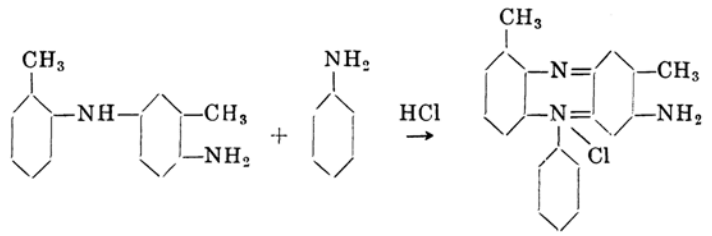
p-Aminodiphenylamine reacts with anilines and produces the red dye, apo-safranine:



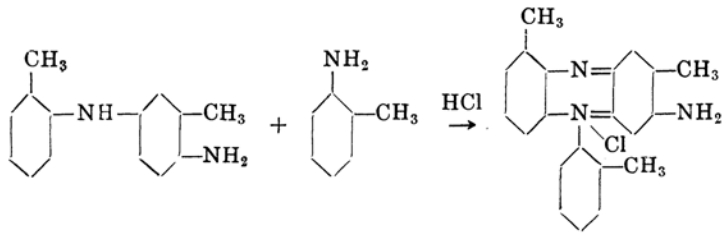




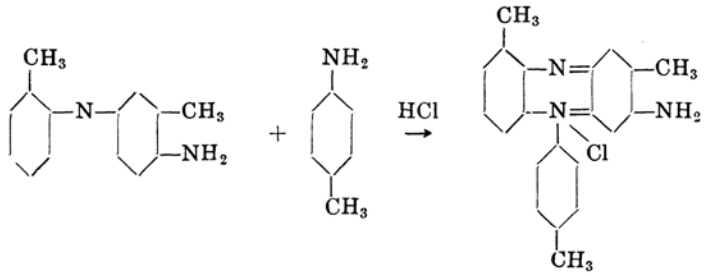
The *p*-aminodiphenylamine produced from *o*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



(IV)



(V)

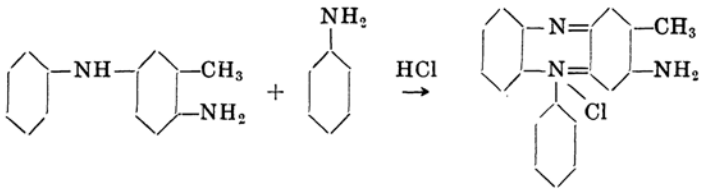


(VI)

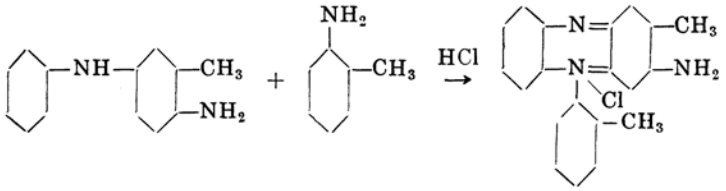
From *p*-toluidine no blue precipitate can be produced. In this case, the basic dyes of reddish-violet are Barsilowsky's and Perkin's bases.

$(C_7H_7N)_3$ (VII) $(C_7H_7N)_3$ (VIII)

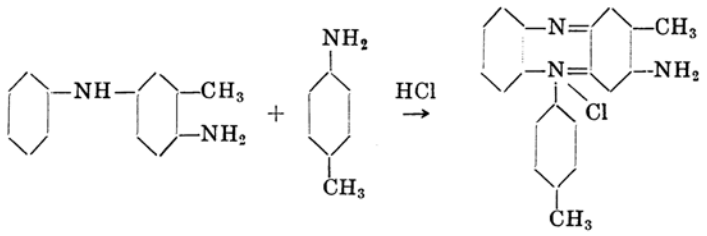
The *p*-aminodiphenylamines from aniline and *o*-toluidine react with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



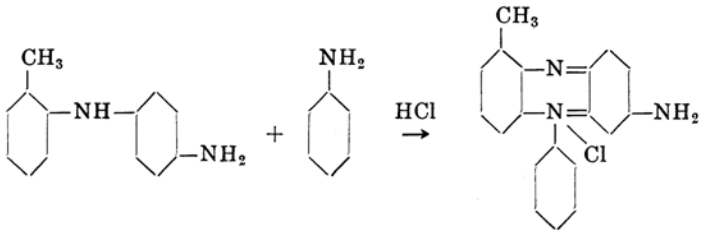
(IX)



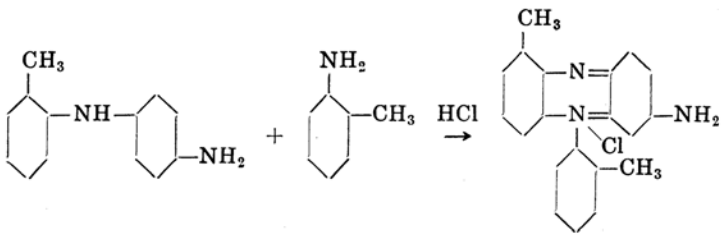
(X)



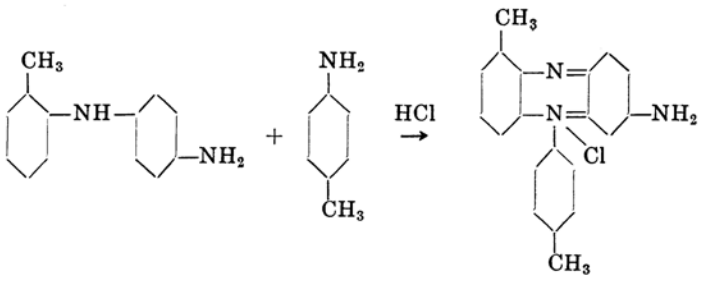
(XI)



(XII)

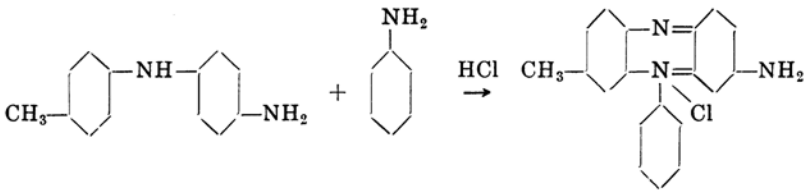


(XIII)

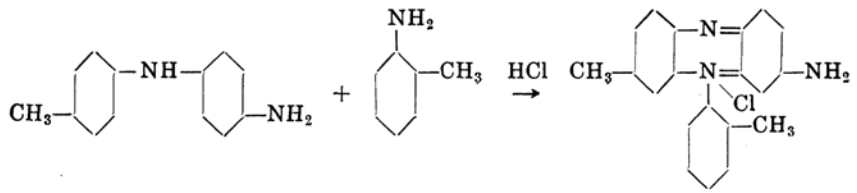


(XIV)

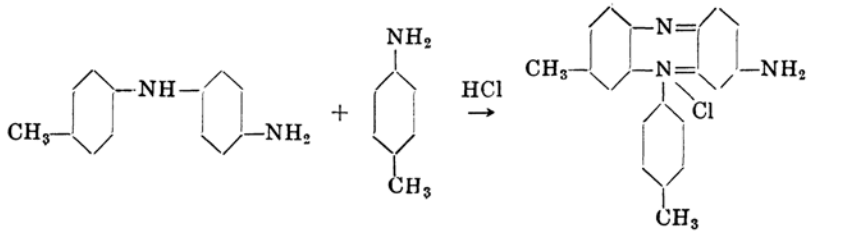
The *p*-aminodiphenylamine from aniline and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



(XV)

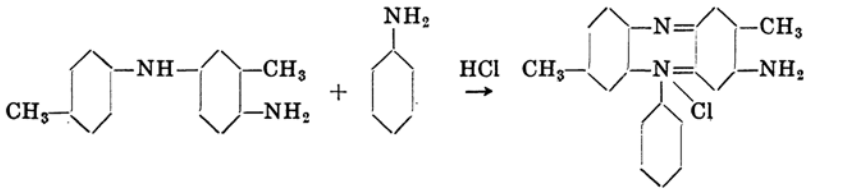


(XVI)

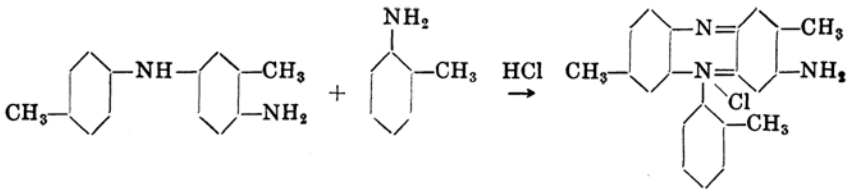


(XVII)

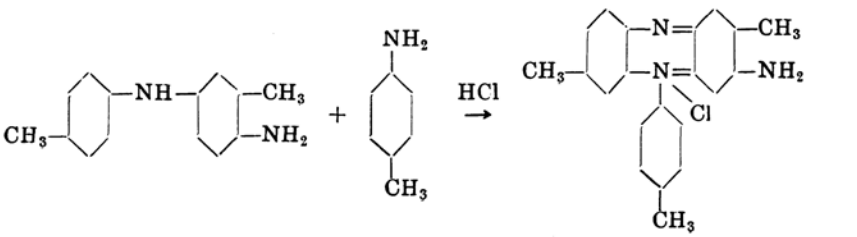
The *p*-aminodiphenylamine from *o*-toluidine and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



(XVIII)



(XIX)



(XX)

As described above, there are produced 20 kinds of the red dyes by the electrolytic oxidation of aniline oil. Among them (II), (III), (IX), (XII), and (XV) form one group of isomers, (IV), (X), (XI), (XIII), (XIV), (XVI), (XVII), and (XVIII) another group and (V), (VI), (VII), (XIX), and (XX) a third group.

Summary.

(1) By the electrolytic oxidation of aniline oil in acid solution neither safranine nor fuchsine is produced.

(2) *p*-Aminodiphenylamine is first produced, it passes into emeraldine and finally into aniline black.

(3) *p*-Aminodiphenylamine reacts with aniline and homologues producing aposafranine.

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