

## Selected Papers.

## On the Aniline or Coal-Tar Colours.

BY W. H. PERKIN, F.R.S.

Continued.

The first apparatus used in the manufacture of nitrobenzol, for the preparation of aniline for the mauve dye, consisted of a large cast-iron cylinder fitted with a stirrer and closed with a door, fastened by a cross-bar and screw. This cylinder was capable of holding between thirty and forty gallons. It was provided with two necks, one for the introduction of the benzol and sulphuric acid, which was supplied through a syphon tube; the other for the exit of nitrous fumes. This last was connected with an earthenware worm, to condense any benzol which might be volatilized by the heat of the reaction. The nitrate of sodium was always introduced into the cylinder before the door was fastened up and luted. Until the preparation of nitrobenzol was understood, there was a great amount of uncertainty in its manufacture, and several explosions occurred, but fortunately without causing any injury to the workmen attending the apparatus. These explosions originated generally from the liberation of too much nitric acid from the nitrate of sodium, by the sulphuric acid, before the formation of the nitrobenzol had begun, so that when it started, the chemical action set in with such energy that an explosion ensued. After a few of these unpleasant occurrences, however, sufficient experience was obtained to get the manufacture under control. Apparatus of a much more extensive character has since been substituted for the cylinders.

This apparatus consists of large cast-iron pots, about 4 feet 6 inches deep, and 4 feet 6 inches wide; they are arranged in rows, and provided with stirrers, worked from a shafting by means of bevel wheels. The covers of these vessels are also made of cast-iron, and are in two pieces, of unequal size, provided with a tall rim, and so arranged that cold water may be kept circulating over their surface; this assists in condensing the benzol, which would otherwise distil away by the heat of the reaction. Through the larger half of the cover the spindle of the stirrer passes, and on account of the difficulty of keeping a stuffing-box in order when using the powerful chemicals necessary in this manufacture, a kind of water-joint has been substituted. It is necessary that it should be deep and rather capacious, instead of filling this joint with water, which would absorb the nitrous fumes, and produce an acid solution which would soon destroy the apparatus, the joint is filled with nitrobenzol; a cast-iron tube passes through the lid to carry away nitrous fumes; this is also cooled so as to condense any benzol vapor which may have escaped the cooling action of the lid; small pipes are introduced through another opening for the purpose of supplying the necessary chemicals. Besides these there is a large opening in the smaller half of the lid, for the purpose of introducing any of the products, which may be added in large quantities at a time. At the bottoms of these large vessels are openings for running out the finished product.

The process of preparing nitrobenzol with

a mixture of sulphuric acid and nitrate of sodium in place of nitric acid, may be carried on very well in this apparatus, provided sufficient sulphuric acid be employed to produce an acid sulphate of sodium, as this will be found quite fluid at the close of the operation, and can be freely run out at the small outlet. A mixture of strong nitric acid and sulphuric acid is now usually employed for the conversion of benzol into nitrobenzol. In working by this latter method the entire charge of benzol is first introduced through the large opening in the lid; this is then closed and the stirrer set moving; the nitric and sulphuric acids are then cautiously run in through the small pipes, care being taken not to add too much nitric acid, until the red fumes begin to appear. After all the charge of acids has been added, and the reaction has perfectly ceased, the product is drawn off. At first a mixture of sulphuric and nitric acids run out, and then the nitrobenzol, this is collected separately and purified, first by agitation with water, and then rendered perfectly neutral by means of a dilute solution of soda. Should it contain any unconverted benzol, this may be distilled off by means of steam. On the continent manufacturers do not appear to have succeeded well in manufacturing nitrobenzol; when it first became a commercial article, their difficulty appeared to have arisen from the fact that they experimented in earthenware vessels, which are both dangerous and unsuitable, and it was not until information was obtained from England, I believe, that they were able to produce this body at a moderate price.

We will now pass on to the processes for converting nitrobenzol into aniline. I have already mentioned that Zinin was the first who discovered that nitrobenzol could be converted into aniline, or, as he termed it, benzidam. His process consisted in treating an alcoholic solution of nitrobenzol with ammonia and sulphuretted hydrogen; but although the discovery of this process was one of great importance from many points of view, still it was very tedious. Bechamp, however, found that by employing a mixture of acetic acid and finely divided iron instead of ammonia and sulphuretted hydrogen, the nitrobenzol was very rapidly converted into aniline, and this process has been found the best yet proposed for manufacturing aniline in large quantities. Many other reagents have been suggested, as arsonite of sodium, powdered zinc, &c., but none of them have been found so advantageous as iron and acetic acid.

In carrying out Bechamp's process, cylinders like those used for nitrobenzol were originally employed. The cylinder was set in brickwork, and heated by means of a small furnace, iron borings were first introduced, and the door fixed in its place airtight. One neck was connected to the upper extremity of the cast-iron worm by means of a pipe called an adapter; the second neck being fitted with a syphon-tube, for the introduction of the nitrobenzol and acetic acid. In working on the large scale it is necessary to add the nitrobenzol and acetic acid in small quantities at a time, otherwise the reaction is so violent as to almost burst the apparatus; by working carefully, however, there is no need to fear any difficulties, especially if the stirrer is well used. By the time all the charge has been introduced a quantity of fluid will have distilled over;

this is returned into the cylinder and the fire lit, and the aniline distilled off.

The principal change which has taken place in this process consists in using high pressure or superheated steam for the distillation instead of fire, and working the apparatus by means of a steam-engine instead of by hand.

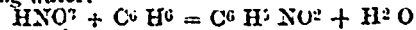
You will observe that the stirrer, which is worked by bevel wheels, has a hollow shaft or spindle, as seen in the section. This is ground to an elbow, connected to the steam main, and held down by a screw, so that when the steam is turned on, it passes through the hollow elbow down the shaft, and then blows out at the bottom among the products; and in this manner the aniline is volatilized, and pass with the steam through the neck, and is condensed by a worm. Aniline thus obtained is generally re-distilled, and sometimes with a little lime or caustic soda, for the purpose of decomposing a body called acetanilide, which is often produced in the manufacture of aniline, especially if the operation is conducted over a fire instead of with steam.

Commercial aniline generally appears of a pale sherry color; when chemically pure it is colorless, but if kept long it becomes quite brown. It possesses a peculiar odor which is slightly vinous when the aniline is pure. It burns with a smoky flame, but is not very inflammable, its boiling point is 182° C. One of its most characteristic reactions is its power of producing a blue or blue-violet coloration with chloride of lime, to which I shall again have occasion to refer. Aniline differs entirely from benzol, and nitrobenzol, being perfectly soluble in dilute acids. This is owing to its being an organic base, and forming compounds with acids. Thus with hydrochloric acid, it forms hydrochlorate of aniline; with sulphuric acid, sulphate of aniline, &c.

We will now, in a very rapid and general way, glance at the chemical changes which take place in connecting benzol with nitrobenzol and aniline.

Benzol, as I have already stated, is a hydrocarbon, i. e., a body composed of hydrogen and carbon only; it is represented by  $C_6H_6$ . This is treated with nitric acid, which contains  $HNO_3$

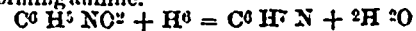
The nitric acts upon the benzol and introduces its nitrogen and parts of its oxygen, at the same time removing hydrogen and forming water.



Nitric acid. Benzol. Nitrobenzol. Water.

Nitrobenzol, when treated with iron and acetic acid, is converted into aniline by the influence of hydrogen gas, in what is termed the nascent state, or the peculiar condition in which it is when liberated from a compound.

This hydrogen unites with the oxygen of nitrobenzol and removes it as water, and at the same time two atoms of hydrogen combined with the deoxygenated nitrobenzol, forming aniline.



Nitrobenzol. Aniline.

Having now seen the various operations which require to be performed for the production of aniline from coal-tar, we are prepared for the consideration of its colored derivatives. We will, therefore, commence at once with the first of the coal-tar colors, "the mauve dye." I have already given you the history