

XIX. *On Colouring Matters derived from Coal Tar.*

BY W. H. PERKIN, ESQ.

THE subject of the present communication is one which is remarkable for the very rapid progress it is making. Previous to the year 1856, the colouring matters derived from "Coal Tar products" were practically unknown; but, owing to recent discoveries, they now rank amongst the most important colouring matters employed. Only a few of them, however, are actually used by the dyer and printer; the rest have merely a scientific interest, and for reasons presently to be mentioned, are not likely to acquire any other.

The coal-tar products which have up to the present yielded colouring matters are numerous. The following is a list of the most important, which are obtained either directly or indirectly from coal-tar:—

* In stating this as my belief, I do not pretend to pronounce what substances are to be regarded as abnormal either to vegetables in general, or to certain species in particular.

The late investigations, carried on by means of the spectrum, have shown, that even lithia is normally present in the ashes of tobacco; and, from the experiment of the Prince of Salm Horstmar, alluded to in p. 214, it might be conjectured that this alkali was present in plants generally.

Copper also was detected in them, as early as 1816, by Dr. Mupner (see Schweigger's Journal), and by Sarzeau, in eleven different kinds, in 1830. (Journal de Pharmacie.) These latter statements, indeed, have been called in question by Danger and Flandin; but they appear to be substantiated by the later researches of Dr. Odling, recorded in the "Guy's Hospital Reports, 1858."

The latter found copper in flour, in grain, in the straw of wheat and barley, in mangel-wurzel, and in Swedish turnips, as well as in a variety of animal substances. But the quantity discovered in these instances was so minute as to lend no countenance to the idea, that so large an amount of sulphate of copper as that taken up by plants in the cases reported by Saussure, could have found its way into their organism, if the vitality of the roots had continued unimpaired.

Aniline and its Homologues,
 Carboic acid,
 Chinoline or Quinoline,
 Naphthaline, and
 Pyrrole bases.

1. *Aniline.*

ANILINE was discovered in 1826 by Unverdorben. The original method employed for its preparation was by digesting indigo with hydrate of potassium, and subjecting the resulting product to distillation. Aniline was also obtained from the basic oils of coal-tar. But the process which is now employed for its preparation is a remarkable instance of the manner in which abstract scientific research becomes in the course of time of the most important practical service.

Benzole was discovered by Faraday, who obtained it from oil gas. After this, it was produced by distilling benzoic acid with baryta, which result determined its formula, and was the cause of its being called benzole. After this, Mansfield found it to exist very abundantly in common coal-tar naphtha, which is the source from which it is now obtained in very large quantities.

Benzole, when studied in the laboratory, was found to yield, under the influence of nitric acid, nitrobenzole. Zinin afterwards discovered the remarkable reaction which sulphide of ammonium exerts upon nitrobenzole, converting it into aniline; and, lastly, Béchamp found that nitrobenzole was converted into aniline when submitted to the action of ferrous acetate. It is Béchamp's process which is now employed for the preparation of aniline by the *ton*. Had it not have been for the investigations briefly cited above, the beautiful aniline colours, now so extensively employed, would still be unknown.

When I discovered aniline purple, nitrobenzole and aniline were only to be met with in the laboratory. In fact, half a pound of aniline was then esteemed quite a treasure; and it was not until a great deal of time and money had been expended, that I succeeded in obtaining these substances in large quantities, and at a price sufficiently low for commercial purposes.

The colouring matters obtainable from aniline are numerous. They are the following:—

Aniline Purple. Violine. Rosine. Fuschine.		Alpha-aniline Purple. Bleu de Paris. Nitrazophenylene. Dinitraniline.
and Nitrophenylene-diamine.		

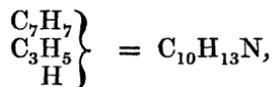
ANILINE PURPLE.

Generally known as Tyrian Purple, Mauve dye, Phenamine, Indisine, &c.

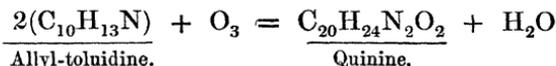
It has been known for many years that the hypochlorites react on aniline and its salts, producing a purple solution. In fact, hypochlorites are the distinguishing test for aniline; but nothing definite was known of the nature of this purple solution, it being simply stated that aniline produced with hypochlorites a purple liquid, but that its colour was very fugitive.

As many very absurd statements have been made respecting the discovery of aniline purple, I will just briefly mention how it was that I first became acquainted with it.

In the early part of 1856, I commenced an investigation on the artificial formation of quinine. To obtain this base, I proposed to act on toluidine with iodide of allyl, so as to form allyl-toluidine, which has the formula:—



thinking it not improbable that by oxidising this, I might obtain the desired result, thus:—



For this purpose, I mixed the neutral sulphate of allyl-toluidine with bichromate of potassium; but, instead of quinine, I obtained a dirty reddish brown precipitate. Nevertheless, being anxious to know more about this curious reaction, I proceeded to examine a more simple base under the same circumstances. For this purpose I selected aniline, and treated its sulphate with bichromate of potassium. This mixture produced nothing but a very un-

promising black precipitate ; but, on investigating this precipitate, I found it to contain that substance which is now, I may say, a commercial necessity, namely, *aniline purple*.

The method adopted for the preparation of aniline purple is as follows :—Solutions of equivalent proportions of sulphate of aniline and bichromate of potassium are mixed and allowed to stand till the reaction is complete. The resulting black precipitate is then thrown on a filter and washed with water, until free from sulphate of potassium. It is then dried. This dried product is afterwards digested several times with coal-tar naphtha until all resinous matter is separated, and the naphtha is no longer coloured brown. After this it is repeatedly boiled with alcohol to extract the colouring matter. This alcoholic solution when distilled leaves the colouring matter at the bottom of the retort, as a beautiful bronze-coloured substance.

Before speaking further of the colouring matter, I will just describe the secondary, or, more properly, the primary products of the action of bichromate of potassium on sulphate of aniline, as nearly nine-tenths of the aniline employed in the preparation of aniline purple are converted into these useless substances.

These products are two in number, namely, the resinous matter which is separated from the black precipitate by means of coal-tar naphtha, and the residue which is left after the colouring matter has been extracted. The resinous matter, when separated from the coal-tar naphtha, consists of a brownish black pitch, which is fusible when heated. It is soluble in alcohol, ether, turpentine, bisulphide of carbon, and many similar solvents. It possesses one remarkable property, viz., that when its solutions in hydrocarbons are acidified with strong acids and well agitated, all the resinous matter is thrown out of solution and precipitated. Alkalies render it soluble again. These facts would make it appear to be a weak organic base.

This substance contains about 10 per cent. of nitrogen. It dissolves in fuming nitric acid, and by ebullition yields a yellowish brown acid. Anhydrous bichloride of tin, when heated with it, does not yield any colouring matter.

The residue which is left after the colouring matter has been separated is a purplish black powder. It contains about 30 p.c. of oxide of chromium. It is insoluble in all solvents, with the exception of strong acids, and is remarkable for the readiness with which it takes fire. It has been used for the manufacture of

black paint and printer's ink. As it contains large quantities of carbon and oxide of chromium, it would form a most valuable product for the preparation of anhydrous chloride of chromium.

The aniline purple prepared according to the process just described, although suitable for practical purposes, is not chemically pure. If required pure, it is best to boil it in a large quantity of water, then filter the resulting coloured solution, and precipitate the colouring matter from it by means of an alkali. The precipitate thus obtained should be collected upon a filter, washed with water until free from alkali, and dried. When dry it is to be dissolved in absolute alcohol, the resulting solution filtered, and then evaporated to dryness over the water bath.

Thus obtained, aniline purple appears as a brittle substance having a beautiful bronze-coloured surface; but if some of its alcoholic solution be evaporated on a glass plate, and viewed by transmitted light, it appears of a beautiful bluish violet colour. If considerable quantities of an alcoholic solution of the colouring matter containing a little water be evaporated to dryness, the surface of the colouring matter next to the evaporating dish, often exhibits a golden green appearance when detached.

Aniline purple is difficultly soluble in cold water, although it imparts a deep purple colour to that liquid: it is more soluble in hot water; but its hot aqueous solution, when left to cool, assumes the form of a purple jelly. It is very soluble in alcohols, though nearly insoluble in ether and hydrocarbons. Aniline dissolves it readily. In properties it seems to be slightly basic, as it is more soluble in acidulated than in pure water. Alkalies and saline substances precipitate it from its aqueous solutions as a dark purplish black powder. Bichloride of mercury precipitates it in a very finely divided state. A little of this precipitate (which appears to be a double compound of chloride of mercury and colouring matter) when suspended in water, and viewed by transmitted light, appears of a blue or violet colour.

A small quantity of hydrate of potassium or sodium added to an alcoholic solution of the colouring matter causes it to assume a violet tint, but without effecting any change in the colouring matter itself. Ebullition with alcoholic potash does not decompose it.

Aniline purple dissolves in concentrated sulphuric acid, forming a dirty green solution which, when slightly diluted, assumes a beautiful blue colour; excess of water restores it to its original purple

colour. It may even be heated for an hour to 100°C. with Nordhausen sulphuric acid without suffering decomposition, being restored to its original colour by means of water, and possessing precisely the same properties it had before being subjected to this powerful agent. Hydrochloric acid acts upon it in the same manner as sulphuric acid. It is decomposed by chlorine, and also by fuming nitric acid. Bichloride of tin is without action upon it.

Powerful reducing agents have a peculiar action upon this colouring matter, somewhat analogous to the action of reducing agents on indigo. An alcoholic solution of sulphide of ammonium mixed with an alcoholic solution of aniline purple, causes it to assume a pale, brownish tint. This solution, when brought in contact with the atmosphere, instantly recovers its original beauty and intensity of colour. An alcoholic solution of the colouring matter mixed with a little protoxide of iron, changes to a pale brown colour. This solution also becomes purple when exposed to the action of the atmosphere; sulphurous acid does not affect the colour of this substance.

Aniline purple forms a remarkable compound with tannin. When an aqueous solution of it is mixed with a solution of tannin, precipitation takes place. The precipitate thus formed after having been well washed, no longer possesses the properties of the pure colouring matter. It is insoluble in water. Like the pure aniline purple, it dissolves in concentrated sulphuric acid, forming a dirty green liquid; but on adding an excess of water to this solution, the new compound is precipitated unchanged; this compound is rather duller in colour than the pure colouring matter itself.

Aniline purple, when agitated with a little moist binoxide of lead, is transformed into *rosine*. It is remarkable for its intensity of colour, a few grains of it colouring a considerable quantity of spirits of wine.

VIOLINE.—This colouring matter, which is a product of the oxidation of aniline, was first obtained by Dr. D. Price, who prepares it by heating an aqueous liquid containing two equivalents of sulphuric acid, and 1 eq. of aniline to the boiling point, and then adding 1 eq. of binoxide of lead, boiling the mixture for some time, and filtering it while hot. The filtrate, which is of a dark purple hue, is boiled with potash, both to separate the

excess of aniline, and also to precipitate the colouring matter; when all the free aniline has volatilized, the residue is thrown on a filter and slightly washed with water, and then dissolved in a dilute solution of tartaric acid. This solution, after filtration, is evaporated to a small bulk, re-filtered, and then precipitated by means of an alkali.

Thus obtained, violine presents itself as a blackish purple powder, which when dissolved in alcohol and evaporated to dryness, appears as a brittle bronze-coloured substance, similar to aniline purple, but possessing a more copper-coloured reflection. It is even less soluble in water than aniline purple. It is very soluble in alcohol, but insoluble in ether and hydrocarbons. Its solutions possess a colour somewhat similar to that of the field violet. Concentrated sulphuric acid dissolves it, forming a green solution, but excess of water restores it to its original colour.

The colour of violine, like that of aniline purple, is destroyed by reducing agents, but restored by the action of the atmosphere. Tannin produces an insoluble compound with it. When agitated with a small quantity of binoxide of lead, it is converted into aniline purple; excess of this re-agent changes it into roseine.

ROSEINE.—This substance almost always accompanies aniline purple, though in very small quantities. It was first noticed publicly by C. Greville Williams, and afterwards by Dr. D. Price. Williams used manganates for its preparation, but Dr. D. Price prepared it by means of binoxide of lead; his process is as follows. To a boiling solution of 1 equivalent of sulphate of aniline, 2 equivalents of binoxide of lead are added, and the mixture is boiled for a short time. The rose-coloured solution is then filtered, and the filtrate evaporated to a small bulk, which causes a certain amount of resinous matter to separate. This evaporated solution is then filtered, and the colouring matter precipitated by means of an alkali; it is then collected on a filter, slightly washed, and then dried. The colouring matter thus prepared readily dissolves in alcohol, forming a fine crimson-coloured liquid which, when evaporated to dryness, leaves the colouring matter as a dark brittle substance, having a slightly metallic reflection. It is much more soluble in water than either aniline purple or violine, but like them, it is insoluble in hydrocarbons, and more soluble in acid than in neutral liquids. Concentrated sulphuric acid dissolves it, forming a green solution;

excess of water restores it to its original colour. It forms a compound with tannin, and is also decolorized, or nearly so, by powerful reducing agents.

The three colouring matters just mentioned, viz., aniline purple, violine, and roseine, are evidently closely allied, for they have nearly the same properties. They are all formed under similar circumstances, namely, by the action of oxidizing agents in the presence of water. They are all slightly soluble in water, though, as the shade of colour becomes redder, so does their solubility increase. Alkalies precipitate them from their aqueous solutions. Concentrated sulphuric acid dissolves them all, forming green solutions, which excess of water restores to the original colour of the colouring matter; powerful reducing agents deprive them of their colour, (or nearly so), but it is restored by the influence of oxygen; and lastly, tannin forms insoluble compounds with them all.

FUCHSINE OR MAGENTA.—This beautiful product, which is often improperly called roseine, is a member of an entirely different series of compounds to the foregoing, being formed under very different circumstances, and possessing very different properties. It was first observed by Natanson, in 1856, when studying the action of chloride of ethylene on aniline, and afterwards (shortly before it was practically introduced into the arts), by Dr. Hofmann, when preparing cyantriphenyl-diamine by the action of bichloride of carbon on aniline. It was M. Verguin who first brought it forward as a dyeing agent, and who, I believe, taught manufacturers how to prepare it on the large scale.

Fuchsine is invariably formed at a temperature ranging from 170° to 190°C. It is produced from aniline, by the action of reducible chlorinized, brominized, iodized, or fluorized substances, as well as by weak oxidizing agents. The substances generally used for its preparation on the large scale, are the perchlorides of tin and of mercury, and the nitrates of mercury.

Preparation of Fuchsine by the action of Bichloride of Tin on Aniline.—Aniline combines with bichloride of tin, evidently producing a double compound; this product is a whitish substance, and may be prepared by adding to aniline bichloride of tin in the anhydrous state, or dissolved in water. Anhydrous bichloride of tin combines with aniline with great energy to form this compound.

To prepare fuchsine from the double compound, it is necessary

that it should be free from water, or nearly so: hence anhydrous bichloride of tin is generally employed for its preparation. The process adopted is as follows.—Anhydrous bichloride of tin is slowly added to an excess of aniline, the mixture being constantly stirred, and the pasty mass thus formed gradually heated. As the temperature increases, it becomes quite liquid, and also brown in colour. As soon as the temperature nearly approaches the boiling point of the mixture, it rapidly changes to a black-looking liquid, which, when viewed in thin layers, presents a rich crimson colour. This is kept at its boiling point some time, and then well boiled with a large quantity of water; by this means, the principal part of the colouring matter is extracted, together with considerable quantities of hydrochlorate of aniline. The residue is a solid, of a brown colour, and contains considerable quantities of tin in the form of a proto-compound.

The aqueous solution of the colouring matter and hydrochlorate of aniline is then boiled, so as to volatilize any free aniline it may contain, and then saturated with chloride of sodium. The chloride of sodium causes the colouring matter to separate as a semi-solid pitchy substance, of a golden-green aspect, while the hydrochlorate of aniline remains in solution. The colouring matter thus obtained may be further purified by digestion with benzole, which dissolves out a certain amount of resinous matter.

Preparation of Fuchsine by the action of Mercurous Nitrate on Aniline.—When mercurous nitrate is left in contact with aniline for some time, it forms a white pasty mass, but when carefully heated to 170°C . or 180°C ., it reacts upon it, forming a brown liquid, which gradually changes to a dark crimson; at the same time the whole of the metal of the mercury-salt collects at the bottom of the vessel. This product, when separated from the metallic mercury, and allowed to cool, becomes semi-solid, being filled with crystals of nitrate of aniline.

To purify this product, it is best to dissolve out the nitrate of aniline it contains in a small quantity of cold water, and then to boil the remaining product several times with fresh quantities of water, until the principal portion of the colouring is extracted, and filtering the resulting aqueous solutions while hot. On cooling, these solutions deposit the colouring matter as a golden green tarry substance, from which benzole separates a small quantity of a brown impurity, leaving the colouring matter as a brittle solid.

I have briefly described the above processes, because they may, to some extent, be regarded as types of most of the methods employed for the production of this colouring matter, the first representing its formation by the action of reducible chlorides upon aniline, and the latter, by the influence of weak oxidizing agents upon aniline.

Fuchsine is undoubtedly an organic base, and a more powerful one than is generally supposed. The product obtained from aniline by means of bichloride of tin, is the hydrochlorate of fuchsine, and that obtained by the oxidizing action of nitrate of mercury is the nitrate of fuchsine.

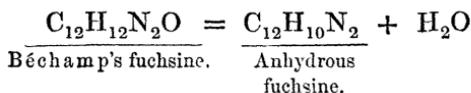
Fuchsine is separated from its salts by precipitation with a small quantity of ammonia.

When freshly precipitated, it is a red, bulky paste, which, on drying, contracts to a purplish red powder. It is but sparingly soluble in water, though moderately soluble in alcohol; it is insoluble in ether and hydrocarbons. A small quantity of hydrochloric acid causes it to dissolve freely in hot water, but an excess of either hydrochloric or sulphuric acid dissolves it, forming a brownish yellow liquid, from which ammonia separates it unchanged; by this reaction it may be distinguished from roseine, which dissolves in strong sulphuric acid, producing the green liquid previously mentioned. Caustic alkalis, or ammonia in excess, partially precipitate fuchsine from its salts, but at the same time, dissolve a considerable quantity of it, forming nearly colourless liquids. Acetic acid added to these alkaline solutions restores the colour of the fuchsine, and if the liquids are concentrated, this base precipitates as a red flocculent substance.

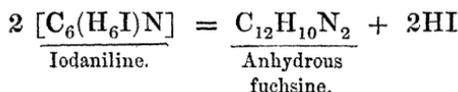
An alcoholic solution of fuchsine, when evaporated to dryness, leaves the colouring matter as a brittle mass, having a remarkably beautiful golden-green metallic reflection.

M. Béchamp has analysed carefully prepared specimens of fuchsine, and found it to have the formula: $C_{12}H_{12}N_2O$, the hydrochlorate being $C_{12}H_{12}N_2O, HCl$, and the hydrochloroplatinate, which is a purple precipitate, having the formula $C_{12}H_{12}N_2O, HPtCl_3$.

The existence of oxygen in this base is remarkable; because, in many instances, it is produced from agents which do not contain a trace of oxygen; as for example, bichloride of tin and aniline. The presence of oxygen in the product analysed, leads to the idea that it was a hydrate; thus—



This is perhaps, to some extent, confirmed by the fact that iodaniline when heated yields fuchsine :



But supposing the fuchsine examined by M. Béchamp, to have been a hydrate, it is remarkable that its hydrochlorate, and more particularly its hydrochloroplatinate, should also be hydrates. But, as our knowledge of this body is as yet but scanty, we must wait for the accumulation of facts before we can form any fixed opinion respecting its constitution.

The compounds investigated by M. Béchamp appear to be uncrystallizable. Sometime back I had upwards of a hundred gallons of a hot aqueous solution of this colouring matter, which had been prepared by means of nitrate of mercury. This solution, on standing until cold, deposited a considerable quantity of the colouring matter in the form of small octahedrons, having a most beautiful green metallic reflection.

Reducing agents decolorize fuchsine ; but the oxygen of the atmosphere restores it to its original tint. If an alcoholic solution of fuchsine be left in contact with sulphide of ammonium until decolorized (or nearly so), and then exposed to the atmosphere, its colour is immediately restored ; but if it be left to stand for several days, and then subjected to the atmosphere, several hours elapse before it assumes its original colour. Like aniline purple, fuchsine is a very intense colouring matter.

Tannin precipitates both fuchsine and its salts, forming difficultly soluble substances ; bichloride of mercury also precipitates this base and its salts, forming double compounds.

When fuchsine is prepared by means of bichloride of tin, and more particularly when nitrate of mercury is used, there are two other colouring matters produced—one possessing an orange and the other a purple colour. It is on account of the presence of the former that some samples of commercial fuchsine possess a scarlet hue. Of this orange colouring matter scarcely anything is known. It is not precipitated from its solutions by alkalis. Of the purple

colouring matter also but little is known. It is formed at the same time as fuchsine, but in very small quantity, and is difficult to separate perfectly. Its properties are similar to those of fuchsine. It dissolves in concentrated sulphuric acid, forming a reddish brown solution, from which part of the colouring matter is separated by dilution with water. Hydrochloric acid dissolves it, forming a dirty yellowish-red liquid.

BLEU DE PARIS.—This is yet another colouring matter, produced under circumstances similar to those which give rise to fuchsine. MM. Persoz, V. de Luynes, and Salvétat give the following account of its preparation and properties:—

Nine grammes of anhydrous bichloride of tin and 16 grammes of aniline, heated for 30 hours to a temperature of about 180° C., in a sealed tube, produce neither a red nor a violet, but a very pure and lively blue. This blue, which resists acids, is darkened in colour by alkalies; but passes to a groselle violet when submitted to this agent in a concentrated state. It preserves its beauty of colour by artificial light, and it dyes animal fibres of a shade whose beauty leaves nothing to be desired.

This colouring matter crystallizes from its alcoholic solutions in fine needles, having an aspect similar to that of ammoniacal sulphate of copper. It is soluble in water, alcohol, wood-spirit, and acetic acid, but insoluble in ether and bisulphide of carbon. With concentrated sulphuric acid it forms an amber-coloured solution, which water converts into a magnificent blue liquid. Strong nitric acid decomposes it. Chromic acid precipitates it from its aqueous solutions without decomposition. Chlorine destroys it. Sulphurous acid does not decolorize it. I find that sulphide of ammonium is also without action upon it. It is precipitated from its aqueous solutions by alkalies and saline compounds.

ANILINE-GREEN OR EMERALDINE—Most chemists who have worked with aniline in the laboratory, must have noticed the peculiar green substance which forms on the outside of the various pieces of chemical apparatus which have been standing in the vicinity of any quantity of this body; this product is aniline-green.

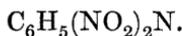
Aniline-green has been known for several years. It may be formed by various processes. One process consists in oxidizing aniline with chloric acid. This is effected by mixing a hydro-

chloric solution of aniline with chlorate of potassium. It may also be obtained by oxidizing a salt of aniline with ferric chloride. Obtained by either of these processes, it presents itself as a dull green precipitate, which, when dried, assumes an olive green colour. It is insoluble in water, alcohol, ether, and benzole. Sulphuric acid dissolves it, forming a dirty purple-coloured solution, from which it is precipitated unchanged by water. With alkaline solutions it assumes a deep colour, somewhat similar to indigo; but acids restore it to its original tint. The colour of aniline-green is much enlivened by the presence of an excess of acid; but, unfortunately, as soon as this acid is removed, it passes back to its normal colour.

Toluidine, xyldine, and cumidine, yield colouring matters under the influence of oxidizing agents, and also when submitted to the action of reducible chlorides at high temperatures, analogous to those obtained from aniline under similar circumstances; but the results are generally not so good, the colour of the products becoming tinged with brown as the bases get higher in the series.

NITROSOPHENYLINE.—This remarkable body is obtained by the action of nascent hydrogen on an alcoholic solution of dinitrobenzole. It is represented by the formula $C_6H_6N_2O$. It is almost insoluble in water, but soluble in acids and in alcohol, producing crimson-coloured solutions; but its colour is not nearly so brilliant as that of fuchsine. It seems gradually to decompose when kept. I have not tried any experiments with it as regards its dyeing properties.

DINITRANILINE.—Dinitraniline is obtained by decomposing dinitrophenyl-citraconimide with carbonate of sodium. When pure it crystallizes in yellow tables. It dissolves very sparingly in water, producing a yellow liquid. It has the formula



It does not combine with acids or alkalies, although it appears to be more soluble in acidulated than in pure water.

Silk can be dyed yellow with dinitraniline.

NITROPHENYLENE-DIAMINE, OR NITRAZOPHENYLAMINE.—Dinitraniline, when submitted to the action of sulphide of ammonium, changes into this beautiful base, which crystallizes in

red needles, somewhat similar in appearance to chromic acid. It dissolves in water, forming a yellow or orange-coloured solution, like that of bichromate of potassium. Alcohol and ether dissolve it freely. It is not at all like fuchsine in its properties, as it forms salts of a yellowish brown or grey colour, whereas, fuchsine forms crimson salts.

This base possesses the power of dyeing silk a very clear golden yellow colour.

PICRIC, OR TRINITROPHENIC ACID.—This beautiful acid was discovered by Hausmann as early as 1788. It may be obtained by the action of heated nitric acid upon a great variety of substances. The following are the names of some of them :—indigo, aniline, carbolic acid, saligenine, salicylous and salicylic acids, salicine, phlorizin, cumarin, silk, aloes, and various gum-resins. It is now prepared for commercial purposes from carbolic acid, and also from certain gum-resins.

I have successfully prepared it from carbolic acid on the large scale in the following manner:—As strong nitric acid acts very violently when brought in contact with carbolic acid, I have found it best to use an acid having a gravity below 1·3, so as partially to convert the carbolic acid, and afterwards to boil it in stronger acid to change it into picric acid. On diluting the acid solution, the impure picric acid precipitates. To purify this further, it should be crystallized from boiling water.

When preparing this product for commercial purposes, it is advantageous to let all the nitrous fumes formed in its preparation, together with a certain amount of atmospheric air, pass over a fresh quantity of carbolic acid: this will absorb them, and, at the same time, be converted into nitro- or dinitro-phenic acid, and consequently diminish the quantity of nitric acid required for its manufacture.

In the preparation of picric acid from carbolic acid there is always a quantity of a yellow resinous matter produced, and at times a considerable quantity of oxalic acid. The latter is always produced when the acid which is used to finally convert the carbolic acid, is too weak: for then it rapidly decomposes the picric acid, yielding carbonic and oxalic acids.

Picric acid was introduced as a yellow dye about five or six years since by Messrs. Guinon, Marnas, and Bonney, eminent silk-dyers, of Lyons. Many of the cheap products sold of picric acid

are of a brown colour, and consist of impure di- and tri-nitrophenic acids, and sometimes of this crude product and ground turmeric.

ROSOLIC ACID.

Runge first noticed this substance in 1834, when studying creosote; but it was almost lost sight of, until again observed by Dr. Hugo Müller, only a short time since. He accidentally observed that when crude phenate of calcium is exposed to a moist heated atmosphere, as that of an ordinary drying stove, it gradually changes in colour, and assumes a dark red tint. This coloration is due to the formation of rosolate of calcium. (I have lately heard that phenate of sodium undergoes a similar change.) Dr. Müller's mode of preparing rosolic acid from this product, and his description of its properties, are given in his paper published in this Journal, vol. xi, p. 1; it is therefore unnecessary to repeat them.*

Mr. Duppa and myself, when investigating some of the derivatives of acetic acid, found that when phenic acid and brom-acetic acid were heated together at 120°C., two products were formed, one possessing all the properties of rosolic acid, while the other had the character of brunolic acid. We also found that a mixture of iodine and carbolic acid, when heated with formic, acetic, butyric, or valerianic acids, produced rosolic acid or a similar substance. A mixture of carbolic acid and iodine did not give a similar result, but a black solid containing iodine.

Rosolic acid has lately been prepared on the large scale, and employed for the purpose of printing muslins. I believe it was the rosolate of magnesium that was employed for this purpose. I do not think it is now used, having been replaced by the more beautiful colouring matter, fuchsine. It was fixed by means of albumin.

COLOURING MATTERS OF QUINOLINE OR CHINOLINE.

Chinoline is found associated with lepidine, cryptidine, and other of the higher nitrile-bases in the basic oils obtained from coal tar, and also in the products obtained by distilling cinchonine with caustic alkalies. It was previously termed *leucoline* or

* See also Tschelnitz (J. pr. Chem. lxxi: 416; and R. Angus Smith, Phil. Mag. (4) xiii, 45; Jahresbericht d. Chem., 1857, p. 447.

quinoline, but the substance described under these two names was found to contain three or more distinct bases. These have been studied by C. Greville Williams, who has applied the name *chinoline* to the product which forms the principal part of the impure substance originally termed quinoline. The substance used for the production of colouring matters need not be pure chinoline, as the product originally termed quinoline is of sufficient purity for this purpose.

Cinchonine appears to be the best source of chinoline, yielding, when distilled with excess of caustic alkali, 65 per cent. of this body sufficiently pure for manufacturing purposes.

Chinoline yields three colouring matters—a violet, a blue, and a green. The following is an account of their preparation by Greville Williams:—

In order to procure the blue colour, one part by weight of chinoline is to be boiled for ten minutes with one and a half parts of iodide of amyl. The mixture from being straw-coloured becomes deep reddish brown, and solidifies on cooling to a mass of crystals. This product of the reaction is to be boiled for ten minutes with about six parts of water, and, when dissolved, filtered through paper. The filtered liquid is to be gently boiled in an enamelled iron pan over a small fire, and excess of ammonia gradually added. The ebullition may be prolonged with advantage for one hour, the evaporation of the liquid being compensated for by the gradual addition of weak solution of ammonia. The latter may be prepared by the admixture of equal volumes of ammonia of density 0.880 and distilled water. The hour having elapsed the whole is allowed to cool, when the colour will almost entirely have precipitated, leaving the supernatant liquid nearly colourless. On pouring the fluid away (preferably through a filter, in order to retain floating particles of colour) the dish will be found to contain resinous looking masses which dissolve readily in alcohol, yielding a rich purplish-blue solution which may be filtered and kept for use.

The colour prepared as above is, as has been said, of a purplish tint, but if a purer blue be required, the following modification is to be resorted to. The filtered aqueous solution of hydriodate of amyl-chinoline is, as before, to be brought to the boiling temperature, but instead of adding ammonia, a solution of caustic potash, containing about one-fifth of its weight of solid potash, is to be substituted. The addition is to be continued at intervals until

three-fourths as much potash has been added as is equivalent to the iodine in the iodide of amyle used. The fluid may, after a quarter of an hour's ebullition, be filtered to separate the resinous colour. The product is a gorgeous blue with scarcely any shade of red. On adding the other fourth of potash to the filtrate while gently boiling, a black mass will be precipitated containing all the red, which otherwise would have been mixed with the blue. This mass dissolves readily in alcohol, yielding a rich purple solution, containing, however, an excess of red. The alcoholic solution on filtration leaves on the filter a dark mass soluble in benzole, and, as sometimes prepared, affording a brilliant emerald-green solution of great beauty. It is not always easy to obtain this green colour.

The properties of chinoline-violet and chinoline-blue are, as far as I have been able to ascertain, identical. They are resinous substances which present a coppery appearance by reflected light, but when in very thin layers, appear of a violet or blue colour by transmitted light. They are bases, and dissolve in acids, forming pale red solutions, which ammonia restores to their original colours. They are slightly soluble in hot water. Tannin precipitates them from their aqueous solutions, apparently forming an insoluble compound. Reducing agents do not affect their shade of colour.

Chinoline green is described by Greville Williams as having a brilliant emerald-green colour of great beauty. I have observed that when chlorine is passed through an alcoholic solution of chinoline blue, it changes into a green; but whether this is the green spoken of by Williams, I am unable to state.

NAPHTHALINE COLOURS.

The beautiful hydrocarbon, naphthaline, which has yielded such a long category of substances to the chemist, has, up to the present time, yielded nothing of practical importance to the dyer. From it the following coloured derivatives have been obtained, namely, *chloroxynaphthalic acid*, *perchloroxynaphthalic acid*, *carminaphtha*, *ninaphthalamine*, *nitrosonaphthalin*, *naphthamein*, and a body of a purple colour.

CHLOROXYNAPHTHALIC AND PERCHLOROXYNAPHTHALIC ACIDS.—These acids were discovered by Laurent. They are produced by digesting their chlorides, namely, the chloride of chloroxynaphthyl and the chloride of perchloroxynaphthyl with an alcoholic solution of hydrate of potassium. They appear to be very difficult substances to obtain in quantity. I have not obtained satisfactory results when endeavouring to prepare them; they have the formulæ $C_{10}(H_5Cl)O_3$ and $C_{10}(HCl_5)O_3$ respectively. They are regarded with great interest, as being very closely allied to alizarine, the colouring matter of madder: in fact, they are viewed as chloralizaric acids; that hypothesis is based upon the idea of alizarine having the formula $C_{10}H_6O_3$; but it happens very unfortunately for this theory that the formula of alizarine itself is still a disputed point.

Chloroxynaphthalic acid is of a yellow colour; its salts are yellow, orange, or crimson, and are described as possessing great beauty. Silk dyed with the ammonium-salt acquires a good golden-yellow colour, little affected by light.

CARMINAPHTHA.—This colouring matter was also discovered by Laurent. It is obtained by heating naphthaline with a solution of bichromate of potassium, and then adding sulphuric or hydrochloric acids. It is described as a fine red substance soluble in alkalis, but precipitated from its alkaline solutions by means of acids. I have never obtained this product when oxidizing naphthalene.

NINAPHTHALAMINE.—Ninaphthalamine is the name given to a remarkable base which was noticed by Laurent and Zinin; but nothing was known of its nature until it was re-subjected to investigation by Mr. Wood, who has both described and analysed it and some of its salts; its formula is, $C_{10}(H_8NO)N$, or naphthalamine in which H is replaced by NO. It is obtained by passing sulphuretted hydrogen through a boiling solution of dinitronaphthaline in weak alcoholic ammonia. The details of the preparation are described in the 12th volume of this Journal, page 154. It has a bright red colour, but I do not think it would be of any value as a dyeing agent, even if it could be obtained cheaply.

NITROSONAPHTHALIN.—This peculiar body is a product of the

action of nitrous acid on naphthalamine. It is prepared by mixing a solution of hydrochlorate of naphthalamine with nitrite of potassium. From this mixture it separates as a reddish-brown precipitate. This, when washed with water on a filter and then dried, is dissolved in alcohol, filtered, and evaporated to dryness on the water-bath. Thus prepared, it is a crystalline dark-coloured substance, having a greenish metallic reflection. It is soluble in alcohol and also in benzole, forming orange-red solutions.

When acids are added to an alcoholic solution of nitrosonaphthalin, it immediately assumes a most beautiful purple or violet colour as fine as any of the aniline purples. Alkalies restore it to its original colour. Silk may be dyed a beautiful purple shade with this substance, provided a certain quantity of hydrochloric or sulphuric acid be present; but what is most unfortunate is, that when the silk thus dyed is rinsed in water, the colour immediately passes back to that of pure nitrosonaphthalin, and, also, that the amount of acid required to keep up the purple shade, if left in the silk, rots it in a few days. Could this purple be fixed, nitrosonaphthalin would become a cheap and most useful dye.

I have endeavoured to produce a sulpho-acid of nitrosonaphthalin, thinking that if such a compound could be obtained, it would possess the purple colour, because it would be an acid itself. But although sulphuric acid does dissolve it, forming a blue solution, no combination takes place. I also endeavoured to produce this desired result by treating sulphonaphthalamine acid with nitrous acid, but obtained only nitrosonaphthalin, the acid of the sulphonaphthalamine acid having apparently separated.

NAPHTHAMEIN.—Piria* observed that naphthalamine and its salts produce blue precipitates, afterwards becoming purple, when brought in contact with perchloride of iron, terchloride of gold, nitrate of silver, and other oxidizing agents. This product of oxidation he terms naphthamein. Silk and cotton may be dyed with it; but the colour of this compound is so inferior as to render it useless as a dyeing agent.

Naphthalamine, when heated with anhydrous bichloride of tin, yields a purple colouring matter, which is insoluble in water, but

* Ann. Ch. Phys. (3) xxxi, 217.

insolubility renders it difficult to use, and its colour is not nearly so good as that of aniline purple.

TAR RED.

This colouring matter was discovered by Mr. Clift, of Manchester, in 1853. It is obtained by exposing a mixture of the more volatile parts of the basic oils of coal tar and hypochlorite of calcium to the air for about three weeks. Of the pure colouring matter I know nothing, except that with tannin it forms an insoluble or difficultly soluble substance, and that with different mordants, it yields different colours.

Professor Calvert has been kind enough to send me a leaf of his Note-book containing the results of different experiments he made upon this colouring matter, which show that the colours obtained from this product are anything but good.

It seems probable that this colouring matter is derived from the pyrrole.

AZULINE.

This substance, which is a beautiful blue dye, has been introduced into England within the last six months. It was discovered by Messrs. Guinon, Marnas, and Bonney, of Lyons, who keep the process for its preparation a secret. It is obtained from coal-tar; but from which of its numerous derivatives is not known.

This colouring matter is a brittle uncrystallizable body, possessing a coppery metallic reflection. It is very difficultly soluble in water, but soluble in alcohol, producing a magnificent blue solution, having but a slight tinge of red. With concentrated sulphuric acid, it forms a blood-red liquid, which when poured into an excess of water, precipitates the colouring matter unchanged. Dilute acids have no effect upon azuline. Its alcoholic solution mixed with an alcoholic solution of hydrate of potassium also changes to a dull-red colour. This, when diluted with water, forms a purple liquid, which is gradually restored to its original blue colour by hydrochloric acid. With excess of ammonia the solutions of azuline change to a reddish-purple colour. This is soluble in alcohol. I have made several experiments with it as a dyeing agent, but have not obtained any satisfactory results. Its

ammoniacal solution treated with sulphide of ammonium, gradually assumes a pale yellowish-brown colour. Iodine destroys the colour of azuline.

In colour it is not quite so fine as chinoline blue, though far superior to Prussian blue.

APPLICATION OF COAL-TAR COLOURS TO THE ARTS OF DYEING SILK AND WOOL.

Silk and wool can be dyed with all the coal-tar colours, with the exception of the rosolates, these fibres possessing in most cases a remarkable affinity (if I may so speak) for these colouring matters. Many of them, as aniline-purple and violine, are taken from their aqueous solutions so perfectly by these substances, that the water in which they were dissolved is left colourless. In fact, silk and wool take them up so rapidly that one of the great difficulties the dyer has to contend with is to get the fibres dyed evenly.

Dyeing Silk with Aniline Purple, Violine, and Roseine.—One process is applicable for dyeing silk with either of these colouring matters, and it is a very simple one. The alcoholic solution of the colouring matter required is to be mixed with about eight times its bulk of hot water, previously acidulated with tartaric acid, and then poured into the dye bath, which consists of cold water slightly acidulated; after being well mixed, the silk is to be worked in it until of the required shade. If a bluer shade than that of the colouring matter is required, a little solution of sulphindigotic acid may be added to the dye-bath, or the silk may previously be dyed blue with Prussian blue or any other blue, and then worked in the dye-bath.

To Dye Silk with Fuchsine, Picric Acid, Chinoline blue, and Chinoline violet.—This process is still more simple than the above, as it is merely necessary to work the silk in cold aqueous solutions of these colouring matters. With fuchsine or picric acid, a little acetic acid may be used; but with chinoline colours, acids must be avoided. With picric acid, a very clear green colour may be obtained by adding a little sulphindigotic acid to the dye-bath.

I may mention that the colour of violine is not so fine as that produced by aniline purple and indigo blue; also that roseine is not so good a colour as fuchsine.

To Dye Silk with Azuline.—The dyeing of silk with this colouring matter is far more difficult than with the preceding, requiring to go through two or three different processes. This difficulty I believe arises from the unsolubility of azuline in water.

The process generally employed is to work the silk in a solution of the colouring matter in water acidulated with sulphuric acid, and when of sufficient depth, to raise the temperature of the dye-bath to the boiling point, and work the silk in it again; after this the silk is well rinsed in water, until free from acid, and worked in a bath of soap lather. It is then again rinsed and finished in a dilute acid bath.

To dye Wool with Aniline purple, Violine, Roseine, Fuchsine, and Chinoline colours.—This operation is generally conducted at a temperature of 50° or 60° centigrade, and the dye-bath is composed of nothing but a dilute aqueous solution of the colouring matter required. Acids should be avoided, or only a very small quantity used, as the resulting colours are not so fine when they are employed.

METHODS OF DYEING COTTON WITH COAL-TAR COLOURS.

When Aniline purple was first introduced, considerable difficulty was experienced in dyeing cotton so as to obtain a colour that would resist the action of soap. Aniline purple is absorbed by vegetable fibres to a certain extent, and very beautiful colours may be obtained by simply working cotton in its aqueous solutions, but when thus dyed, the colours will not stand the action of soap. I have tried the use of tin and other mordants, but without any satisfactory result.

In 1857, Mr. Puller, of Perth, and myself, simultaneously discovered a process by which this colouring matter could be fixed upon vegetable fibres so as to resist the action of soap. This process is based upon the formation of an insoluble compound of the colouring matter with tannin and a metallic base in the fibre.

To effect this, the cotton has to be soaked in a decoction of sumach, galls, or any other substance rich in tannin, for an hour or two, and then passed into a weak solution of stannate of sodium, and worked in it for about an hour; it is then wrung out, turned

in a dilute acid liquor, and then rinsed in water. Cotton thus prepared is of a pale-yellow colour, and has a remarkable power of combining with aniline purple. The above process may be modified, as for example, the stannate of sodium may be applied to the cotton before the tannin, and alum may also be used in the place of stannate of sodium. To dye this prepared cotton with aniline purple, it is only necessary to work it in an acidulated solution of the colouring matter; when thus prepared, the cotton will absorb all the colouring matter of the dye-bath, leaving the water perfectly colourless. It has been found that cotton thus prepared can be dyed with any colouring matter that forms an insoluble compound with tannin. It is therefore used for dyeing with roseine, violine, fuchsine, and chinoline colours.

Cotton may also be dyed a very good and fast colour by mordanting it with a basic lead-salt, and then working it in a hot solution of soap, to which aniline purple has been added.

Oiled cotton, such as is used for dyeing with madder, is also used in dyeing these colours. Cotton simply oiled, and before mordanted with alum and galls, absorbs coal-tar colouring matters with great avidity, producing very fine shades. Oiled cotton mordanted with alum and galls also combines rapidly with these colouring matters: but as the colour of the prepared cotton, is generally rather yellow, it interferes sometimes with the beauty of the result.

Cotton is sometimes washed with albumin, which is coagulated by the action of steam, and the albumin, which covers the cotton, dyed in the usual manner.

I may mention that violine, roseine, fuchsine, and also the chinoline colours, combined with unmordanted vegetable fibres as well as aniline-purple. Picric and rosolic acids are not applicable for dyeing cotton.

PRINTING CALICO WITH COAL-TAR COLOURS.—The process generally employed for printing with these colouring matters is simply to mix them with albumin or lacterine, print this mixture on the fabric, and then to coagulate the albumen or lacterine by the agency of steam.

Mr. Grey, of the Dalmonach Print-works, and myself, discovered the first process of applying these substances to fabrics in a different manner to the above.

It consisted in forming a basic carbonate, or an oxide of lead, on

those parts of the cloth which were to be coloured, and then working the cloth thus prepared in a hot lather containing the colouring matter. Where the cloth was mordanted with the lead-compound, the colouring matter was absorbed; but where immordanted it was left white, because pure cotton is not dyed with these colouring matters in the presence of soap. This process was intended for the application of aniline-purple, for, at the period of this discovery, the other coal-tar colours were unknown. Colours dyed by this process were very pure; but it had many disadvantages which have caused it to be disused.

Lately the process previously described for dyeing colours upon cotton prepared with tannin, has been applied to calico-printing. It consists in printing tannin upon the fabric previously prepared with stannate of sodium, and then dyeing it in a hot dilute acid solution of the colouring matter (in the case of chinoline colours acid must not be used); by this means, the parts of the fabric which are covered with tannin are dyed a deep colour, but the other parts are only slightly coloured. These are cleared by means of well-known processes.

This method of applying these colouring matters is also modified by printing a compound of the colouring matter required and tannin on the prepared cloth, instead of the tannin only, and then steaming the goods.

METHOD OF APPLYING ANILINE GREEN TO FABRICS.—This process, which is interesting, as being the first example of the production of coal-tar colours on the fabric itself, was proposed by Professor Calvert: it is very simple. The design is to be printed on the cloth with a thickened solution of chlorate of potassium, dried, passed through a solution of an aniline salt, again dried, and allowed to hang in a moist atmosphere. In the course of two or three days, the colour will be fully developed. The colour thus produced may be changed into a dark blue by the agency of soap or an alkaline liquid. This process is very inexpensive; the amount of aniline required being very small.

APPLICATION OF NITROSONAPHTHALIN.—If cloth is printed with a thickened solution of a salt of naphthalamine, dried, and then passed through a solution of nitrite of potassium, nitrosonaphthylene will rapidly make its appearance as a reddish-orange

colour; but unfortunately the colour thus obtained will not resist the action of soap.

Many of the coal-tar colours, when viewed by artificial light, are very much modified in tint; and some of them, when compared with similar colours of vegetable origin by daylight, appear of totally different tints by gaslight. The latter case is remarkably illustrated by aniline-purple and archil.

If two silk patterns are dyed, one with aniline purple, and the other with archil, of exactly the same shade of colour when seen by daylight, the colour of the archil pattern when viewed by artificial light, will appear several shades redder than that of the aniline purple.

Dr. Gladstone has examined solutions of these two colouring matters in a hollow wedge by means of the prism, and he finds that a very thin stratum of aniline-purple attacks the spectrum in the yellow (just beyond D), giving rise to a blue-purple colour; and that, as the intensity of the solution increases, the absorption gradually extends very slowly on the less refrangible side, but rapidly on the more refrangible side, till the green entirely disappears, and eventually the true blue.

In the case of archil, the violet and blue rays are absorbed by a strong solution of this colouring matter, though it still permits the extreme *red* ray to pass with great facility: therefore, considering the abundance of red in oil or gas-light, it is not surprising to find that archil colours appear redder by artificial light than those of aniline purple.

The colour of the three coal-tar blues, *bleu de Paris*, *azuline*, and *chinoline-blue*, when viewed by gaslight, are considerably modified. The *bleu de Paris* appears blue; *azuline*, a heavy blueish violet; while the *chinoline-blue* assumes a beautiful violet tint having rather a cast of red.

Dr. Gladstone has also kindly examined these three colouring matters, and gives the following account of his results:—These three blues, in common with aniline purple, attack the spectrum in the yellow (near D), and as the intensity of the colour increases, the absorption extends, especially on the more refrangible side, till the *green* is swallowed up. At the same time the *orange* is absorbed, while the extreme red is transmitted freely.

In the *bleu de Paris* there is an additional band of absorption in

the orange, when very weak solutions are examined; but this is soon merged in the greater band extending from the yellow as the solution increases in intensity.

Strong solutions of azuline absorb the yellow, green, blue, and violet in regular order; but the chinoline blue absorbs the violet when not very deep, and allows the blue to pass for some distance further, after which the *red* alone passes.

Dr. Gladstone states that the chinoline blue is one of the most beautiful dichromatic substances he knows; when viewed in a hollow wedge, with the prism, it passes gradually from a clear blue to a fine red.

Of the numerous colouring matters of which I have briefly spoken, there are only four that are at present employed by the dyer and printer; namely: aniline purple, fuchsine, picric acid, and azuline; but I think it probable that others of them will soon be introduced, such as the bleu de Paris. Nitrophenylene-diamine might also be used for silk-dyeing, as its colour is good, and it resists the action of light well.

Unfortunately the chinoline colours, though very beautiful, are most fugitive. There has been an endeavour to introduce the chinoline blue of late; but, although a considerable quantity of silk was dyed with it at first, it is now scarcely used, because, when exposed to the sun for two or three hours, the dyed silk becomes bleached.

Aniline purple resists the light best. Fuchsine and alpha aniline purple soon fade, especially when on cotton. Azuline and bleu de Paris are not easily acted upon by light when on silk.

When the colouring matters of coal-tar were first introduced, there was great fear that the workmen engaged in their manufacture would suffer in health. All I can say is, that during the few years I have had to do with this branch of manufacture, there has not been a single case of illness among the workmen that has been produced by any of the operations carried on for the production of *aniline purple*.
