

# THE CHEMICAL NEWS.

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## ON DYER'S CHEMICALS.

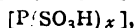
By J. MARZELL.

(Continued from p. 107.)

### PICRIC ACID $[C_6H_2OH(NO_2)_3]$ .

THE manufacture of picric acid from phenol is comparatively old, and intimately connected with the history of tar-distillation. The method stated by Laurent\* in 1874 is still in use, in principle, and the only improvement in this way is the working up of the pure phenol.

Laurent made use of the whole tar. Later on only the fraction passing between  $180^\circ$  to  $200^\circ$  C. was taken, and now the purest market phenol is considered the only rational base for the picric acid manufacture (Crace-Calvert). A disagreeable point in working the pure acid was the very violent action of the nitric acid, and therefore the sulpho-compounds of the carbolic acid were taken as substitutes, either the free sulpho-acids,—



or their soda-salts,  $[P(SO_3Na)_x]$ ,† being brought into reaction with concentrated nitric acid.

Respecting the manufacture from the tar-oils, Quinon Ainé gives a report,‡ but in the present state of that industry it is of mere historical interest.

The picric acid has not been dislodged by the new dyes, and is still used in large quantities. Having a comparatively good market price its manufacture can lucratively be joined with the produce of pure carbolic acid, and therefore it might be of interest to describe in a few words the method of its manufacture.

### Manufacturing Process.

As mentioned above, it consists in the reaction of concentrated nitric acid upon sulpho-compounds of phenol. To produce the sulpho-acids, equal parts of crystallised phenol and concentrated sulphuric acid of 1.843 sp. gr. are heated to about  $100^\circ$  C. till a sample taken out of the mass is completely soluble in water, hereby indicating the transferring of all the phenol into sulpho-compounds. Then the steam is shut off, and the whole allowed to cool down. In some works the sulpho-acids are now diluted in water, and therefore twice the quantity of water is added; a little steam supplied if needed. In other places it is preferred to take the concentrated acids directly into action. For forming the sulpho-acids: this operation either takes place in stone ballons standing in a steam-bath or in wooden tanks lined with lead, a system of steam-pipes lying on the bottom.

The action between the sulpho-compounds and the nitric acid is generally effected in stone ballons, similar to those used for the absorption of hydrochloric acid vapours in the soda works. The round cover is fastened air-tight during the reaction by means of any cement standing the acid. Of the two tubules one serves for carrying away the nitrous, &c., vapours, the other for supplying the sulpho-compounds. The ballons stand in a double line in a steam-bath. At a small distance above them two pipes run along, being joined with each pot by junctions. The one is the main-pipe for the nitrous, &c., vapours, and leads directly into the condensing apparatus; the other has to conduct the sulpho-acids. In the tubulus intended

for this, a funnel is fastened air-tight, leading below the surface of the nitric acid in the pot. From the main pipe there are short pipes with cocks to each of these funnels, allowing the supply to be regulated as wanted. The concentrated nitric acid is put into the pot, and the sulpho-compounds are added slowly. It is of no advantage to hasten the operation, as in this case black resinous products are formed, with a considerable loss of the nitric acid, and causing great difficulty and annoyance in the purifying process.

The principal part of the reaction takes place without requiring any heat, and only at the end of the operation the steam is turned on, by which the action re-commences, and the last traces of unassailed crude products are oxidised. If there is not observed any further development of red nitrous vapours the steam is stopped, and the whole allowed to cool down.

I mentioned above that the sulpho-compounds are also taken without being diluted in water. In this case the reaction has to be moderated by stirring the mass whilst the operation goes on. The apparatus in use for this are analogous to those which have answered all demands in the nitrification of benzol, &c. They are cast-iron pots, with agitator driven by mechanical means, and different arrangements following the supply of the different materials, the carrying away of the arising vapours, and so on. Working in this way, the sulpho-compounds can be formed in the same pot, and then the nitric acid be supplied gradually into the concentrated mixture of  $P(SO_3H)_x$ . The resulting picric acid forms an oily syrup-like mass, forming large and hard crystals in cooling. They are broken, isolated in a centrifugal machine or a filter, washed once or twice with cold water, and finally pressed. They are then diluted in boiling water, slightly acid (40 to 50 grms. of nitric acid per gallon of water generally taken), and allowed to crystallise.

Instead of that purifying by crystallising, it is often much preferred to convert the free acid into an alkali salt, to purify this, and to regain the pure and free acid by decomposing the same.

From the theoretical point of view the potassium salt would indisputably be preferred to the sodium salt. It is much more soluble than the latter, which, besides that, always takes into solution a part of the accompanying oily impurities. The worst difficulty—nearly insurmountable—in working on a large scale is the fact that the potassium salt, so very soluble in boiling water, separates as the liquor cools with an immenserapidly. That disagreeable quality causes much delay in the filtering process, as the precipitating crystals of picrate and potassium stop the pores of the filters and puts them out of work. By heating up the filters by means of indirect steam and different other expedients, trials were made to prevent that mischief, but none of them seemed to answer very well, and as the advantages are after all not so very great, the sodium salt is now adopted in nearly all works.

To convert the acid into soda salt, either the crystals are taken as they come out of the pots, or they are once re-crystallised out of acid water, as by this operation a part of the resinous by-products is already carried away. To get rid of all these impurities entirely, the soda is added in two portions. After having mixed the first part of the alkali to the hot solution of picric acid, it is filtered or digested from the impurities whilst hot. (The oily bodies are not yet diluted in the still acid liquid.) After this the rest of the soda is supplied to the filtrate. The alkali has to be taken in excess, as the picrate of soda is nearly insoluble in the alkaline solution, and therefore separates nearly theoretically.

The picrate of soda is gathered, pressed, washed with cold water, then diluted in boiling water, and oversaturated with sulphuric acid. The picric acid is precipitated, and precipitates nearly entirely, as it is insoluble in the mother-liquor containing the acid modification of sulphate of soda ( $NaHSO_4$ ).

Many experiments have been made on purpose to replace

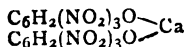
\* *Ann. Chem. et de Phys.*, [3], iii., 221.

† "Rapports de la Jury, International, Paris, 1867," tome vii., Class 443, p. 80.

‡ *Mém. de la Soc. d'Agr. a Lyon*, 1849.

the alkalis by lime; but the results have not proved satisfactory:—

(1.) The basic lime salt formed—



is scarcely soluble. Of course that could be overcome by not saturating entirely, or by adding a certain quantity of free picric acid in filtering.

(2.) The sulphuric acid cannot be taken any more for decomposition, as the sulphate of soda ( $\text{CaSO}_4$ ) formed would precipitate and mix with the settling picric acid, which would again be in contact with the impure mother-liquors. This point is the greatest difficulty. Only nitric and hydrochloric acid, therefore, could be taken in view of their forming salts soluble in water. But both these acids take not by any means unimportant quantities of picric acid into solution, rendering so illusory all advantage which was expected of the difference in price between the crude materials. Concentrated sulphuric acid of 1.843 sp. gr. also keeps a small quantity diluted; but by adding 2 to 3 volumes of water the picric acid is precipitated entirely. Weak  $\text{H}_2\text{SO}_4$  (proportion 1 : 11) does not dilute any picric acid.

For recognising picric acid the following comparing reactions may be of use (L. Kopp):—

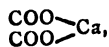
- With  $\text{NaOH}$ , colours yellow.
- With  $\text{SnCl}_2$ , in boiling, slight yellowish precipitate.
- With  $\text{Fe}_2\text{Cl}_6$ , golden-yellow precipitate.
- With  $\text{NaSH}$ , yellowish red; boiling, dark reddish yellow; concentrated, blood-red.
- With  $\text{Am}_2\text{S}$ , like with  $\text{NaSH}$ .
- With  $\text{CaOCl}_2$ , sometimes white, turbid.
- With  $\text{KCN}$ , yellow-red; concentrated, blood-red.

#### Examination.

With the picric acid of commerce very often impurities are mixed, proceeding either from the process or added purposely as adulteration. They can easily be found out by taking advantage of the difference in qualities between them and the picric acid.

(1.) *Resinous Substances*.—They generally come from the picric acid process, but nevertheless they very seldom amount to more than 0.03 to 0.05 per cent; they are only noxious in the dyeing-bath. To separate them, 5 grms. of picric acid are diluted in hot water, a drop of sulphuric acid is added, and filtered. The resinous and oily impurities remain in the filter.

(2.) *Oxalic Acid*.—It is very possible that small quantities of this arise from the process, as that body is easily formed if the reaction of nitric acid is too violent or goes too far; and, as well, it can crystallise out with the picric acid and can escape an even very carefully conducted purifying. But if there are larger quantities found, an intentional adulteration can be concluded. The sample is diluted in hot water, some ammonia and a few drops of a solution of  $\text{CaCl}_2$  are added. The formed oxalate of lime,—



is gathered on a filter, dried at  $100^\circ \text{C}$ ., and weighed. 100 parts of oxalate of lime will answer to 69.7 parts of pure oxalic acid.

(3.) *Saltpetre*.—Can arise from the process, especially if the water used for re-crystallisation was acidified with nitric acid instead of sulphuric acid; but generally it is put in purposely. It can easily be separated, as it is not at all soluble in strong alcohol. 5 grms. of picric acid are digested with about 50 grms. of absolute alcohol. The residue is gathered on a filter, and washed with alcohol till the filtrate is absolutely colourless. The residue on the filter is dried at  $100^\circ \text{C}$ ., and weighed. To examine it properly for  $\text{NO}_3\text{Na}$  an analysis would be wanted, but generally it is enough to know the quantity of impurities, and never mind their theoretical composition. A special test for saltpetre or nitric salts in general is when the

body in question, put upon red-hot coals, detonates, of which fact advantage can easily be taken here.

(4.) *Sulphate of Soda*.—It is detected in the same way as the foregoing. An approximate test upon  $\text{H}_2\text{SO}_4$  can be made in adding a solution of hydrochlorate or nitrate of baryta, which causes a precipitate.

(5.) *Sugar*.—The sample is diluted in boiling water, saturated with carbonate of potassium, evaporated to dryness on the water-bath, and the sugar extracted from the residue by means of alcohol. The usual method of sugar testing is of not much use here, as the picric acid itself is altered by reducing agents. To separate the picric acid from the whole lot of impurities, and to see the percentage of the pure body easily, J. Casthelaz\* constructed an apparatus, which he calls Picrometer. The sample is put into a graduated cylinder and shaken with ether, which only dissolves out the picric acid, so that the remaining impurities can easily be made out. M. Moyret† proposes to take benzol instead of ether, which is generally accepted now. But in this case it is good to hold the cylinder in warm water, as the benzol does not dilute the picric acid so very easily.

#### ON

### SOME SIMPLE LABORATORY MANIPULATIONS.

By Dr. P. TOWNSEND AUSTEN, F.C.S.,  
Assistant Professor of Chemistry in Rutgers' College.

#### THIRD PAPER.

As I see in the CHEMICAL NEWS (vol. xxxvi., p. 57) some allusions made to various forms of wash-bottles, I should like to mention how extremely useful I find a series of different sized jets. It would appear so self-evident that one would think everyone who used a wash-bottle would have a set; yet, indeed, I have known chemists to have a whole series of wash-bottles in order to throw different sized jets. These jets I keep in a division of a drawer. They can be changed in a moment.

Jets are best made by allowing the heated glass to close, until the right size of aperture is obtained. Drawing a tube is not to be recommended, since the stream of water it delivers is rarely round, and hence likely to spray. Moreover, such jets, when made fine, are extremely fragile.

A useful form of jet, and one that I have never seen, although I suppose the idea must have occurred to several, is made in the following manner:—Close the end of a glass tube of about 4 m.m. internal diameter and about 1 m.m. thickness, and blow a bulb about 1 c.m. in diameter. Then heat a platinum wire to a white heat in the flame of a blast-lamp. The flame should be about 5 c.m. long, and the heated spot about 1 c.m. from the end of the wire. By gently pressing the side of the bulb against the wire it is easily pierced. On withdrawing the wire slowly, and at the same time allowing it to cool very slightly (which is effected by holding it higher up in the flame), a small round hole is made in the side of the bulb. The size of the hole depends on the diameter of the wire, its temperature, and the rapidity with which it is withdrawn. The sharp edges are easily removed by carefully filing with a fine file moistened with caustic soda solution.

This form of jet has the advantage that it throws a powerful stream at right angles to the delivery-tube. I find it extremely useful in washing many precipitates, and particularly in dislodging particles adhering to the sides of a filter. It is also useful in washing down precipitates from inverted vessels. Its shape renders it very strong, there being no projecting points to break off.

A bulb-jet with three small holes, in the form of a tri-

\* *Moniteur Scientifique*, 1866, 984.  
† *Ibid* 1866, 1036.