

CHAPTER XIV
MANUFACTURE OF PICRIC ACID

PRINCIPLES OF MANUFACTURE

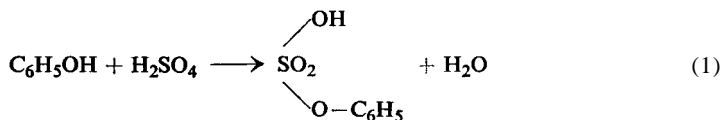
PICRIC acid is produced either by nitrating phenol or by nitrating dinitrophenol prepared by hydrolysis of chlorodinitrobenzene.

NITRATION OF PHENOL

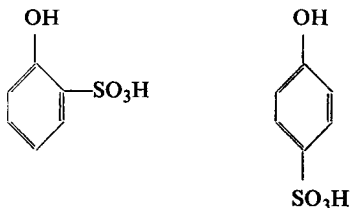
The process is effected in two stages. Phenol is first sulphonated and then the sulphonation product is nitrated with nitric acid (p. 126).

Two features of the process may justify its use. First of all, direct nitration of phenol with a nitrating mixture may lead to the formation of various by-products resulting from oxidation, condensation, resinification etc. (p. 480) which will contaminate the product and lower its yield. In addition, when two separate stages are used - sulphonation and nitration - it is possible to carry out the nitration without any excess of acids, so that the spent acids left after separation of the product may be discharged into the drainage system without further treatment which would increase production costs. This is of great importance, principally because the acids are not suitable for concentration as they contain picric acid. Picric acid is known to be rather volatile and may escape from sulphuric acid solutions if in the concentration process the H_2SO_4 content becomes higher than 72.5%. Picric acid vapours, after being condensed on metal parts of the equipment, may form picrates, for example, with lead or iron, which explode readily.

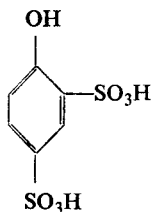
For the first stage of the process, i.e. sulphonation of phenol, sulphuric acid is used in some excess (4-4.5 moles of sulphuric acid per 1 mole of phenol). Initially a sulphuric acid ester is formed:



which is later converted into a mixture of *o*- and *p*- phenolsulphonic acids:



At room temperature the conversion proceeds slowly, whereas it occurs rapidly on heating. The higher the temperature, the more *p*- isomers are formed. At 90-100°C phenoldisulphonic acid is also formed:



Its presence is advisable, as later it will facilitate the nitration process.

Marqueyrol and Loriette [1] investigated the process of phenol sulphonation with varying sulphuric acid concentration, time and temperature of sulphonation. Their results are presented below (Table 117).

TABLE 117
SULPHONATION OF PHENOL UNDER VARIOUS CONDITIONS

H ₂ SO ₄ concentration, %		Per cent of phenol converted into disulphonic acid
92		62
93		66
94		71
96		82
97		91
100		100
Time of sulphonation with 93% H ₂ SO ₄ at 100°C, min		
15		48
30		65
60		66
120		68
240		68.5
Sulphonation with 93% H ₂ SO ₄ , temperature °C	Sulphonation time, min	
75	30	51
75	60	59
150	15	50
150	30	66
150	60	66.5

Phenoltrisulphonic acid is formed only when using an excess of 20% oleum.

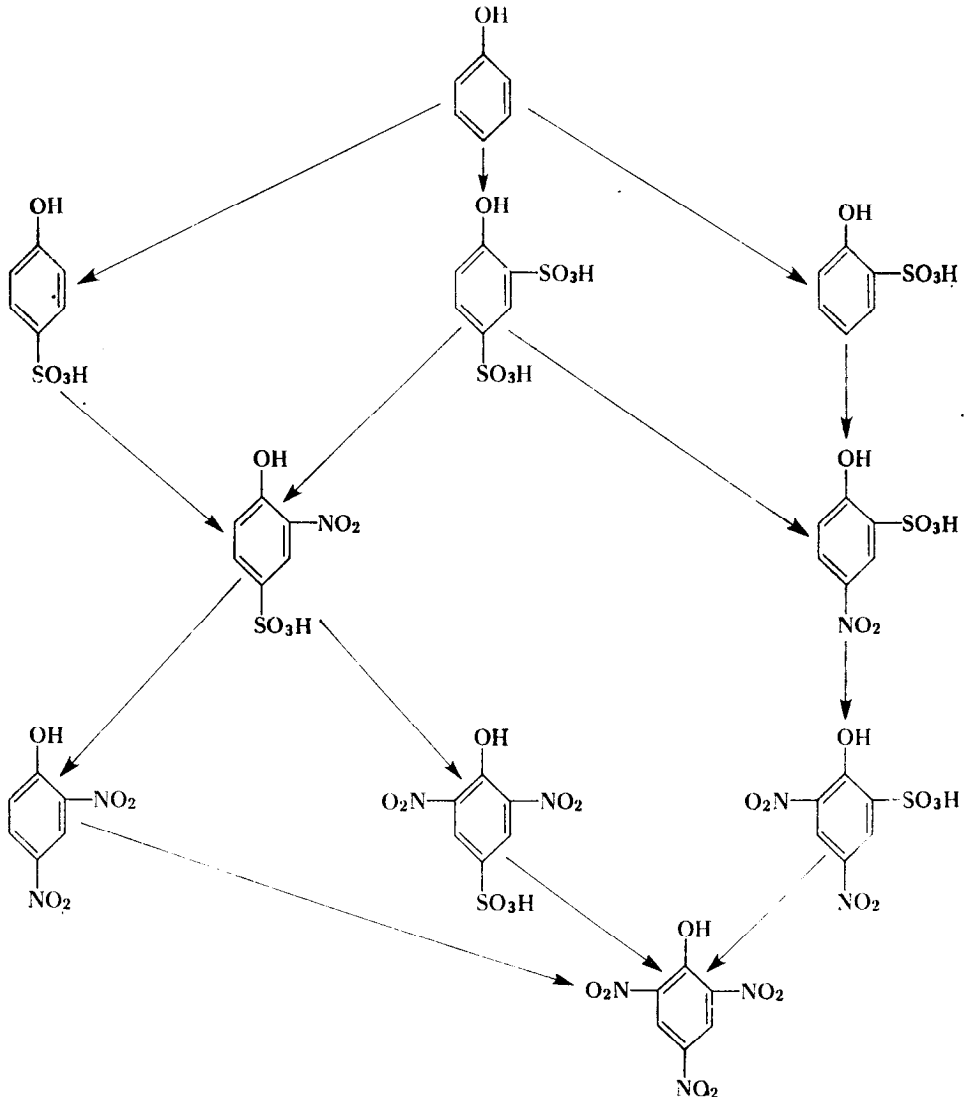
The second stage in the preparation of picric acid is the nitration of the phenol-sulphonic acid obtained in the first stage of the process.

“Sulphophenol”, which is the name of the starting material for the second stage, is a mixture of 1,4-phenolsulphonic and 1,2,4-phenoldisulphonic acids.

For the nitration the following nitrating agents may be used:

- dilute (44-65%) nitric acid;
- mixture of dilute nitric acid and sodium nitrate;
- concentrated nitric acid.

A schematic presentation of the reactions occurring in the process of preparation of picric acid via sulphonic acid is given below (Pascal [2]):



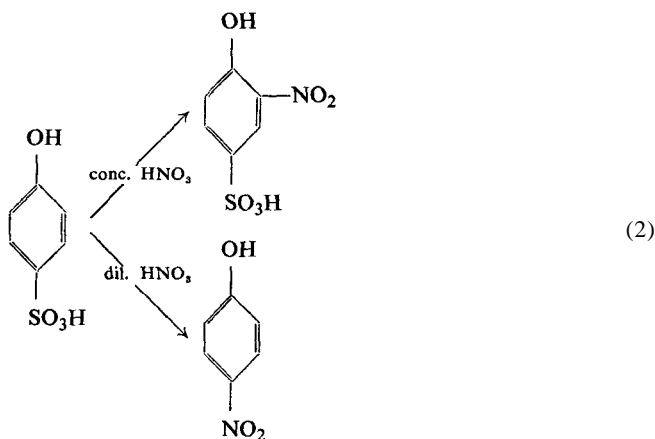
As this scheme indicates, phenolsulphonic acid is first nitrated to 2-nitro-4-sulphonic and 4-nitro-2-sulphonic acids. The former yields 2,4-dinitrophenol and 2,6-dinitro-4-sulphonic acid, and the latter 2,4-dinitro-6-sulphonic acid. All these dinitro compounds are finally converted into picric acid.

The introduction of nitro groups proceeds the more rapidly the more sulpho groups "sulphophenol" contains. The nitration of disulphonic acid is faster than the nitration of monosulphonic acid, but not so fast as the nitration of trisulphonic acid.

Thus, when heating 1-hydroxy-2,4,6-trisulphonic acid with 61% nitric acid at 110°C, picric acid is produced in a yield amounting to 90% of the theoretical (220 parts of picric acid per 100 parts of phenol), whereas from 1,2,4-phenoldisulphonic acid under analogous conditions, the yield of picric acid is 86% of the theoretical (208-210 parts of picric acid per 100 parts of phenol).

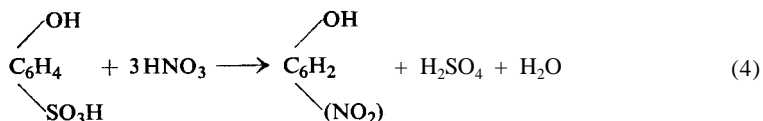
Moreover, it has been proved by Marquyrol and Loriette [1] that the rate of formation of picric acid from 2,6-dinitro-4-sulphonic acid is higher than that from 2,4-dinitro-6-sulphonic acid. Since for the formation of both *p*-phenolsulphonic and 2,4-disulphonic acids high sulphonation temperatures are favourable, it is evident that efforts should be made to attain sulphonation temperature as high as possible. This is especially important if dilute nitric acid is to be used.

King [3] has shown that phenolsulphonic acid can be nitrated by the action of concentrated nitric acid to yield nitrophenolsulphonic acid. On the contrary, reaction with dilute nitric acid leads to the exchange of the sulphonic group by the nitro group:

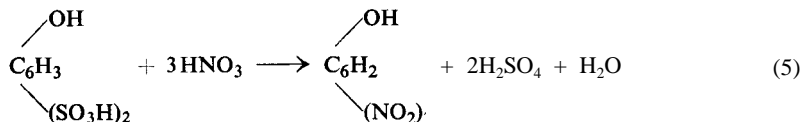


If sulphonation is carried out at a low temperature, nitric acid of higher concentration should be used or a higher temperature should be maintained during the nitration. The latter must, however, be kept within safety limits. Apart from this, higher temperatures naturally favour undesirable side reactions (e.g. oxidation).

The reactions occurring in nitration with sodium nitrate are as follows:



Or



The sulphuric acid formed in reactions (4) and (5) decomposes new portions of sodium nitrate in accordance with reaction (3).

The spent acid from the nitration of phenol by the methods described contains several by-products, among them : 2,4-dinitrophenol-6-sulphonic acid in the proportions of 22 parts per 100 parts of phenol used for the process, which corresponds to a 8% loss of the phenol, and oxalic acid in the proportion of 5-6 parts per 100 parts of phenol. These are the principal by-products that lower the yield of picric acid.

A certain amount of picric acid may be converted into its salts - undesirable products - which may be formed by the contact of picric acid either with metal parts of the plant or with certain salts (e.g. dissolved in the water used for washing the picric acid).

The theoretical yield of picric acid amounts to 243 parts of picric acid from 100 parts of phenol. Because of by-products formation, however, the actual yield hardly exceeds 200-205 parts (82-85%) of the theoretical. During World War I in France a yield of 175 parts of picric acid (72% of the theoretical) was reported.

It should, however, be remembered that commercial picric acid prepared by this method contains lower nitrated phenols. To obtain a chemically pure product, commercial picric acid should be subjected to additional nitration (Arundal, Davies and ICI Ltd. [4]).

NITRATION OF DINITROPHENOL

This is the most modern industrial method for the preparation of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophenol from chlorodinitrobenzene, see p. 484). The nitration of dinitrophenol to picric acid is carried out by conventional methods, using nitrating mixtures containing some 0-5% of water.

The following three grades of purity of picric acid are specified in the U.S.S.R. standard, OST 3515 (Table 118).

TABLE 118

	Grades		
	I	II	III
General appearance	crystalline powder free from foreign matter		
Colour	light yellow		
Setting point, not less than, °C	119.5	119.5	119
Moisture and volatile matters, max.	0.5%	0.5%	0.5%
Insoluble in benzene, max.	0.2%	0.3%	1.0%
this includes :			
picrates	not present	trace	max. 0.03%
SiO ₂ , max.	0.05%	0.05%	0.1%
Sulphuric acid, max.	0.1%	0.2%	0.3%
Halogen	trace	trace	trace

Picric acid should be transported in wooden cases or barrels with thick walls 1.5 cm.

METHODS BASED ON PHENOL NITRATION

Raw materials. A high grade phenol should be used. The U.S.S.R. specifications of 1931, for example, require for nitration top grade phenol with a setting point not below 39°C. A small amount of moisture present, resulting in lowering the setting point to 37°C, does not prove harmful to the nitration process. The purity of the product should be tested by determining the setting point of a dry sample, which should lie within the above mentioned limits.

Nitration grade phenol should be completely soluble in water, giving a clear solution. Not more than 0.1% of non-volatile residue left after the evaporation of phenol, when heated on a steam bath, is permissible.

Acids used for the nitration of phenols should be free from any detectable quantity of lead.

NITRATION METHODS USING DILUTE NITRIC ACID OR MIXTURES OF NITRIC ACID AND SODIUM NITRATE

These are primitive methods (applied during 1914-1918 in Russia, France, Italy and Great Britain), which gained considerable popularity, solely because they enabled large scale production to be achieved rapidly by the hitherto unprepared allied powers.

The main part of the operation consisted in nitrating sulphonated phenol with materials readily available in those days - dilute nitric acid and sodium nitrate. To prevent any corrosion of the nitrators and to prevent any possible formation of metal picrates, the nitrators were built of stone-ware.

Sulphonation of phenol

The first stage of the production process - the preparation of phenolsulphonic acid - may be effected in various ways.

Pascal [2] describes it as follows. Phenol, which is supplied in iron drums, is melted by placing the drums, after removing their lids and bottoms, into steam heated cylinders (I) (Fig. 111). Molten hot (80°C) phenol is collected in the heated tank (2) which also acts as a proportioner. Adjacent to it, is a tank (3) for 92% sulphuric acid.

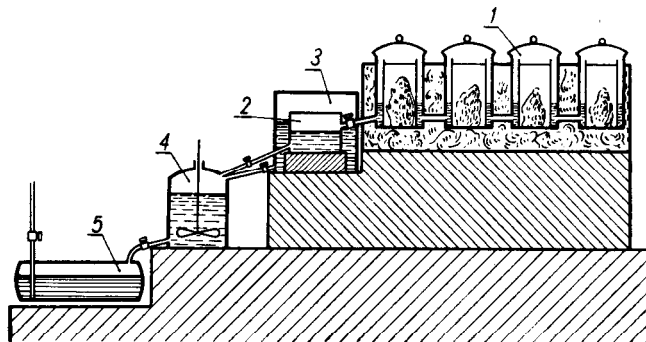


FIG. 111. Diagram of lay-out for sulphonation of phenol (Pascal [2]).

Both liquids flow down to the sulphonator (4), designed for 150-250 kg of phenol. For 100 parts of phenol 500 parts of sulphuric acid is used. The phenol in the sulphonator being hot, the sulphonation reaction starts spontaneously, resulting in a temperature rise to 100°C . After some 10-20 min, sulphonation may be regarded as completed and hot "sulphophenol" is transferred by means of a pressure-egg (5), to the nitrator. The pipeline for conveying the product should be heated, otherwise the phenolsulphonic acids are likely to crystallize.

According to the Lebedev's description [5], phenol is sulphonated with 98% sulphuric acid taken in the proportion of 400-500 parts of acid for 100 parts of phenol. The sulphonation temperature is maintained within $70-80^{\circ}\text{C}$ or $100-110^{\circ}\text{C}$. The reaction time is 4 hr. A temperature of $125-130^{\circ}\text{C}$ may also be maintained, in which case the reaction time may be reduced to 2 hr. Cast iron sulphonators are used, 2 m in diameter and 1.8 m high. The required temperature may be maintained in the sulphonator by heating with a steel heating coil or with a heating jacket.

A schematic design of a sulphonator used in Great Britain is presented in Fig. 112. The reaction temperature is regulated by adjusting the flow of hot phenol. The propeller stirrer (1) is placed in cylinder (2) to get a better circulation of the reaction mixture. Flat blades (3), mounted above the stirrer, break up the stream of liquid raised by the propeller.

The lid of the sulphonator has an exit for the exhaust pipe, two inlets for introducing the reactants, a manhole, an inlet and outlet for steam passed through the coil and a thermometer hole. In addition to this, the lid is equipped with a sight glass and four handles to open the sulphonator. The heating coil is not shown. This vessel is discharged at the bottom.

If concentrated (98%) sulphuric acid has been used for the sulphonation, the sulphophenol should be diluted with water prior to nitration, otherwise the nitration reaction may proceed too violently. Besides some dilution is advantageous to precipitate any salts present, such as lead or ferric sulphates.

Lebedev [5] advises using wash water from the purification of picric acid, as this effects some economy in nitrating and picric acids.

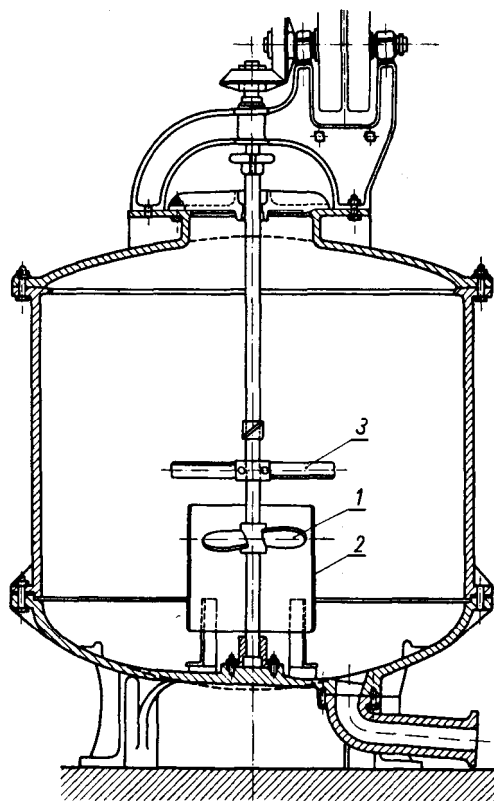


FIG. 112. Sulphonator for phenol (according to Lebedev [5]).

The dilution of sulphophenol is effected in special stoneware vessels. For 95 kg of sulphophenol 72l. of wash water is added. The specific gravity of the sulphophenol after dilution should be 1.35. The diluted sulphophenol is left to settle and then filtered through a sand filter. The temperature of the sulphophenol which is to be nitrated should not be lower than 50°C which is necessary for initiating the nitration reaction.

Nitration of phenolsulphonic acid in movable vessels

The second stage in the manufacture of picric acid is the nitration of the phenolsulphonic acid (sulphophenol) obtained. The simplest reactors used for this process are stoneware jars, "tourills", which may be of various size (e.g. 85 cm diameter

in the widest part, 1.35 m in height). The lids of the jars are equipped with two wide entry holes, 15 cm in diameter (Fig. 113), one for feeding the nitrator with acid and sodium nitrate, the other for connecting the nitrator with the ventilating system. In addition to this, three smaller holes in the lid serve for introducing sulphophenol, inserting a compressed air line that reached down to the bottom of the jar and for inserting a thermometer. Naturally, various modifications of the nitrator construction are possible. These jar-nitrators have the disadvantage of not being equipped with heating or cooling devices: the heat is supplied by the reaction itself and the required temperature is maintained by adjusting the flow of the reactants.

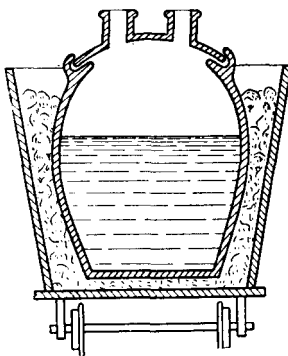


FIG. 113. Jar for the nitration of sulphophenol (Pascal [2]).

To facilitate working and increase output the nitrators are transported in wooden carts from the nitration section to a separate place, where the nitrator contents are allowed to cool prior to their transport to the purification section, where picric acid is separated from the spent acid and washed with water.

Usually the nitrator is tightly enclosed in the cart by a cement layer. This is necessary to isolate and to prevent the nitrator from any damage. Should the jar-nitrator crack because of too high a temperature, the cement layer prevents the reaction mixture from flowing off; sometimes it can even be recovered.

In France nitration was effected in the following way (Pascal [2]).

The jar-nitrator is charged with 275 kg of 44% nitric acid or with the mixture:

nitric acid (44%)	120 kg
sodium nitrate	90 kg

To this 180 kg of warm 50-70°C sulphophenol (corresponding to 30 kg of phenol) is gradually added. At the same time compressed air is passed through the nitrator to mix the reactants well. The rate of addition of sulphophenol should be so adjusted as to prevent the temperature from rising too rapidly at the beginning of the reaction. Hence the sulphophenol should be added carefully at first, although its flow must be rapid enough to attain a temperature of 100°C, at which the main portion of the product nitrates. If the process is operated properly, 95-100°C is attained within 20 min from the beginning of the process (initial temperature 25-30°C).

After one hour a temperature of 115-120°C is attained. All the sulphophenol should be added within one and a quarter hours. By this time the temperature falls to 90-100°C. Then, to remove nitrogen oxides, air is blown through the nitrator for 10-20 min and the nitrator is disconnected from the ventilating pipe and transported to the cooling section.

The nitrator contents are stirred repeatedly with a wooden pole while cooling to prevent picric acid from forming lumps which might retain impurities. After cooling for 34 hr at a temperature of about 60°C, 50-100 l. of water is added, thus preventing the precipitation of sodium bisulphate or, if it has already been precipitated, causing it to go into solution. The diluted acid contains some 45% of H₂SO₄, the concentration at which the solubility of picric acid is lowest. After it has cooled to ambient temperature 12-24 hr, the spent acid is drawn off by a siphon and the picric acid is transported to another section, where it is washed with water. Since the spent acid usually does not contain more than 1% of HNO₃, its recovery is pointless.

As Pascal describes it, a nitrating section is usually designed for 8 nitrators mounted on carts. Every 20 minutes nitration starts (and ends) in a successive nitrator, the whole cycle averaging 2-2.5 hr to complete. Thus during 24 hr, in a battery of 8 nitrators 72 nitrations can be effected. Since each nitrator produces 52 kg per batch, 3744 kg of picric acid will be obtained in 24 hr.

In Russia, as Lebedev reported, the French method gave satisfactory results in summer time only, whereas for the most part of the year (autumn, winter) on account of high heat losses, nitration was never complete and the picric acid yield was low (150-160 parts per 100 parts of phenol). Moreover, the product contained high proportions of mono- and di-nitrophenols.

In this connection various modifications of the process have been developed, consisting first of all in using more nitric acid and less phenol.

The jar-nitrator is charged with 141 kg of 44% nitric acid and 91 kg of NaNO₃. Then 172 kg of sulphophenol (which corresponds to 31 kg of phenol) is run into it over a period of nearly 1 hr 40 min. During the last 10-15 min a temperature of 115°C is maintained. Sulphophenol is added in seven equal portions after the following temperatures have been attained:

	Temperature, °C
I	26-30
II	62-70
III	88-89
IV	96-97
V	106-107
VI	111-113
VII	113-115

Since in winter time the cold compressed air used for mixing might cool the reactants, the sulphophenol should be passed into the nitrator in a weaker stream (or the air should be warmed), otherwise it would be difficult to attain the required

temperature. On the other hand, insufficient mixing may cause the formation of undesired lumps of picric acid. Further operations do not differ from those in the process described above.

Nitrogen oxides, as well as nitric acid vapours, generated in the reaction, flow via the ventilating pipe to a system of jars, coolers and absorption towers, where they are absorbed.

There are also other methods in which the procedure consists in first introducing "sulphophenol" to the nitrator and adding the nitric acid afterwards.

Washing picric acid

The contents of 4-5 nitrators (200-300 kg of picric acid) are transferred by means of wooden ladles to a wooden washing vat (Fig. 114), where picric acid is washed several (mostly five) times with 150-200 l. portions of water. For 100 kg of picric acid 400 l. of water is used. The product is tested for purity by determining the SO_4^{2+} ions in a solution of the picric acid in distilled water. After washing, picric acid is separated from water in a centrifuge usually made of copper, the water content being brought to 5-7%.

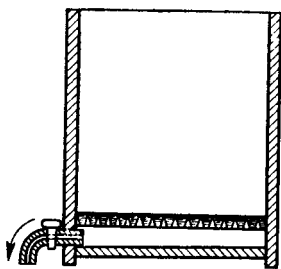


FIG. 114. Wooden vat for washing picric acid (Lebedev [5]).

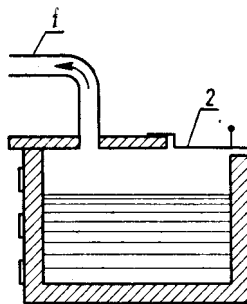


FIG. 115. Nitration tank for the nitration of sulphophenol to picric acid (Pascal [2]).

Washings are collected in special wooden tanks for settling. The spent acid is also added to the washings so as to bring the H_2SO_4 content to 10-30% as in such an "acid water" the solubility of picric acid is at its lowest. The water is decanted from time to time and disposed off into the river, after being neutralized, while the settled picric acid is collected from the bottom of the tank.

The recovered picric acid usually contains large quantities of mineral matter (determined as ash - 0.2%, compared with the permissible limit of 0.03%, as well as H_2SO_4 (0.1% instead of 0.02%). Such a product cannot be used for military purposes without further purification by crystallization from water.

Nitration of phenolsulphonic acid in stationary reactors

The stationary nitrators used in France have the dimensions 2 x 1.8 x 1.0 m (Fig. 115). They are constructed of acid-resistant bricks, joined by an acid-resistant

cement and are reinforced from outside by tarred sheet iron tightened by hoops. The top of the nitrator is partly covered by a Volvic plate equipped with a pipe connected with the ventilating duct (1). An aluminium plate (2) covers the rest of the nitrator top.

In the nitrator described batches of 100-150 kg of phenol may be nitrated: The whole nitration unit is shown in Fig. 116. Nitrators (1) are connected with proportioning tanks for sulphophenol and nitrating acid. Vapours evolving during the nitration flow to jars (3), (4) and (5), passing on their way through the cooling coil (6). Here nitric and nitrous acids are condensed. Non-condensed nitrogen oxides pass to the absorption tower (7), sprayed with water and supplied with air for oxidation. Here the oxides are converted into nitric acid.

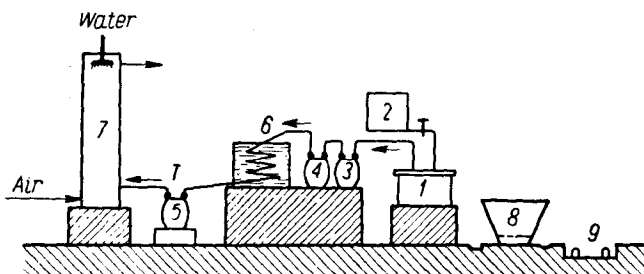


FIG. 116. Flow sheet of the nitration of sulphophenol to picric acid (Pascal [2]).

Next to the nitrator is a wooden double-bottomed tank (8) (the diameter of its upper parts is 1.15 m, height 1.0 m) for separating picric acid from spent acid and for washing the product with water. A narrow gauge railway (9) operates for two lines of nitrators located symmetrically on both its sides.

Similar cylindrical nitrators were in use in Great Britain (Fig. 117).

According to British data, the consumption of raw material for 1 ton of picric acid is:

	British method	French method
Phenol	540 kg	538 kg
NaNO ₃	1990 kg*	1870 kg
H ₂ SO ₄	2930 kg	2620 kg

* The nitric acid recovered in absorbers from nitrogen dioxide generated in the nitration process, has not been taken into account here. Usually 160 kg of HNO₃ (100%) per 1 ton of picric acid can be recovered.

United States method

During World War I a method of manufacture of picric acid was established in the United States.

Olsen and Goldstein [6] described the method as follows.

302.2 kg of phenol are sulphonated with 605 kg 93% sulphuric acid at 95-98°C during 6 hr. The product is composed of 80% phenol-4-sulphonic acid and 20% phenol-2,4-disulphonic acid.



FIG. 117. General view of nitrators for the production of picric acid [8].

The mixture of phenolsulphonic acids is diluted with 737.5 l. of water. Usually wash-waters are used for this purpose. The concentration of phenolsulphonic acid in the resulting solution is 18.4% calculated on phenol.

Nitration is carried out in two stages. In the first stage the nitrator is filled with a nitrating mixture composed of 70% HNO_3 , 10% H_2SO_4 and 20% H_2O . The quantity of the mixture corresponds to that calculated for the introduction of one nitro group. Phenolsulphonic acid is added to the nitrating mixture at 30°C at the beginning and at 52°C at the end. During the first stage mononitro derivatives are formed.

After the first stage the temperature in the nitrator is raised to 60°C and the second stage begins. It consists in adding the same nitrating mixture. During the first hour of mixing the temperature increases to $110\text{--}115^\circ\text{C}$. Altogether 1250 kg of nitrating mixture are added (i.e. 2.75 kg of HNO_3 for 1 kg of phenol).

This method is not accompanied by the evolution of large quantity of nitrogen oxides. The nitration is ended when the content of the nitrator changes colour from red (the colour of phenolsulphonic acids) to yellow (the colour of picric acid).

The yield is 667.6 kg of picric acid, i. e. 220% by weight (theoretical yield 243%).

The spent acid contains 1.0% and 1.5% of picric and oxalic acid respectively. It is diluted with double its weight of water; water from washing picric acid is being

used. The solution is brought to boiling for 5 hr to transform the remaining nitrophenolsulphonic acids into picric acid. After cooling, a second crop of picric acid is obtained in quantity 15% by weight of phenol, i.e. the total yield is 235% by weight. The losses of picric acid in the wash waters correspond to 1% of phenol.

Also Reed [7] described a method of nitrating phenolsulphonic acids in a large pot nitrator of 5500 l. capacity made of acid-proof bricks. Picric acid was settled in a wooden, lead-lined slurry tank and eventually separated in a centrifuge.

CONTINUOUS NITRATION OF PHENOLSULPHONIC ACID

During World War I Brookes [8] introduced in England a continuous method of phenol nitration based on the following principle.

The nitration is performed in a long tank, built of acid resistant bricks joined by a mixture of asbestos and sodium silicate (Fig. 118). The tank is 25 m long,

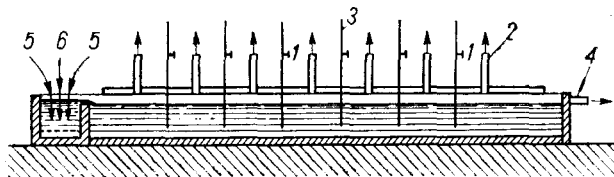


FIG. 118. Diagram of continuous production of picric acid (Pascal [2]).

0.6 m wide, 0.5 m deep inside and with walls 0.2 m thick. At one end of the tank, an area two meters long is separated from the rest of the tank by an inside wall, lower than the walls of the tank. This is a chamber for mixing the reactants. The main part of the tank, 22 m long, is fitted with stoneware covers, equipped with a number of steam pipes (1) for heating up the nitrator content and pipes (2) for conducting away volatile products evolving during the nitration. The reaction mixture flows out continuously through outlet (4) at the other end of the nitrator. A general view of the installation is shown in Fig. 119.

The continuous nitration runs as follows. Phenolsulphonic acid, prepared by reacting 2 moles of H_2SO_4 with 1 mole of phenol, is diluted with water to a sp. gr. of 1.36 and introduced into the mixing chamber by pipe (5). Into it 65% nitric acid and the spent acid from nitration containing about 60% of H_2SO_4 and traces (up to 1%) of HNO_3 are introduced by a set (some 20) of aluminium pipes (6). The total amount of H_2SO_4 introduced is 6 moles per 1 mole of phenol, out of which only 2 moles come from fresh acid. The outlets of all the pipes are arranged below the surface of the liquid. Then the temperature is raised to 102°C by passing steam through the pipes (1). Additional heat may also be supplied by a steam coil, located in this space.

Some picric acid precipitates at the end of the tank and is carried away with the spent acid through the overflow. To facilitate the outflow of picric acid crystals, the reaction mixture coming up to the outlet is agitated now and then by a wooden pole.

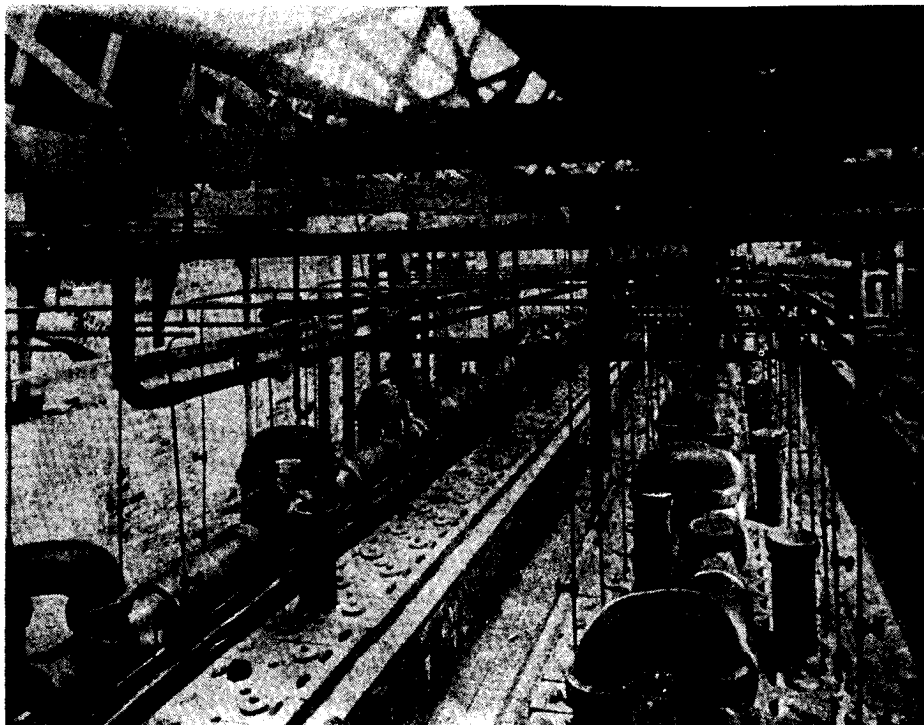


FIG. 119. General view of continuous production of picric acid [8].

The liquid, together with the crystals, is run into a crystallizer equipped with a lead cooling coil and a stirrer rotating at a low speed. Here the rest of the picric acid is precipitated and then separated from the spent acid on a vacuum filter.

Generally the use of lead as a material for construction of a picric acid plant is avoided, except in Great Britain and in the U.S.A. where it is used for the parts of installation which are also in contact with inorganic acids. The latter, being strong acids, are assumed to inhibit the formation of lead picrate.

The spent acid, containing 40-55% of H_2SO_4 , is heated to 120°C in an acid-resistant brick tank equipped with an internal lead heating coil. Here the completion of the nitration (conversion of nitrosulphonic acids to picric acid) takes place along with the concentration of the acid. The acid is subsequently transferred to a cooler: crystallizer, similar to that described above, and from there to a vacuum filter for separating picric acid. The spent acid, now containing 60% of H_2SO_4 , is returned to the nitration.

By the continuous process 190 parts of picric acid are obtained from 100 parts of phenol. The consumption of acids for the output of 1 ton of picric acid is:

HNO_3 (100%)	1270 kg
H_2SO_4 (100%)	2000 kg

NITRATION WITH CONCENTRATED ACID

The low yield of the nitration with the dilute nitric acid is the principal disadvantage of the above methods. Attempts have been made to use more concentrated acids both for sulphonation and nitration, to increase yield. It has been shown, however, that primitive stoneware installations for nitration, without provision for rapid heating or cooling, or for vigorous stirring, are not suitable for concentrated acids. The classical nitration plant, in which the nitrator is equipped with a heating or cooling jacket as well as with a mechanical stirrer, has proved necessary. Nowadays this is the method of nitration generally used.

Nitration with concentrated acid by the Griesheim method is effected in the following way.

To 400 parts of 30% oleum 94 parts (1 mole) of phenol is added with stirring, the temperature being maintained below 90°C. The mixture is heated to 90-100°C during a period of 5 hr. As a result phenoldisulphonic acid is formed.

The oleum solution is then diluted with 200 parts of sulphuric acid (sp. gr. 1.84). The whole is cooled down to 50°C and 80 parts of 80% nitric acid is added. After the temperature has gone up to 60-80°C, a new portion of 80 parts of nitric acid is added. Finally, when the temperature has exceeded 80°C a further 100 parts of nitric acid is added. Altogether, for 94 parts of phenol 260 parts of 80% nitric acid is used, the excess being 16% over the theoretical amount.

The phenoldisulphonic acid thus prepared is then nitrated in conventional iron nitrators with a jacket and a stirrer. 1000-2000 kg of sulphophenol may be nitrated at a time. From 100 parts of phenol 205 parts of picric acid can be obtained.

A flow diagram of picric acid manufacture by a method applied in the U.S.S.R. is presented in Fig. 120 (after Lebedev [5]).

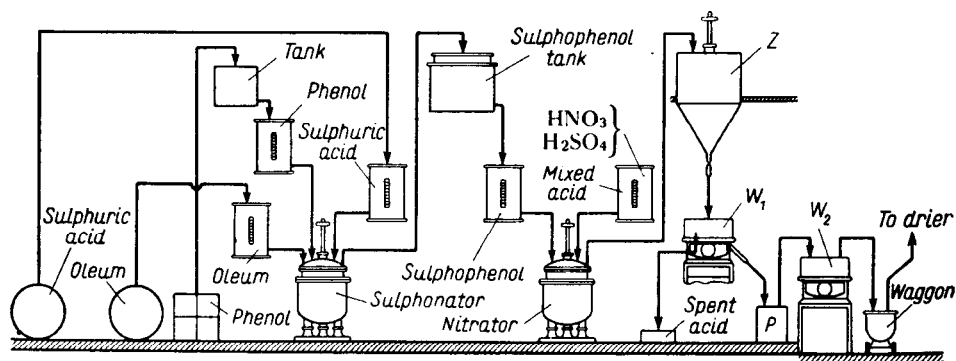


FIG. 120. Flow sheet of the nitration of phenol with concentrated nitrating mixture (Lebedev [5]).

Sulphonation

The first step of the process - sulphonation of phenol - is effected in an iron sulphonator, equipped with a jacket, a heating coil and a stirrer. The construction of the sulphonator is in principle similar to that applied in Great Britain, as described above (Fig. 112, p. 506).

Molten phenol having a temperature of 80°C is transferred to a heated proportioner and from there to the sulphonator, where a quantity of 1750 kg phenol may be sulphonated at a time, this quantity being sufficient for 3-5 nitrations.

After the phenol has been introduced 7800 kg of 20% oleum is fed into the sulphonator. During this operation cold water is passed through the jacket and the coil, the cooling and the flow of oleum being so regulated as to allow the temperature to attain 90°C towards the end of the introduction. Then the cooling is stopped, while the sulphonator content is heated by steam to 100°C and kept at this temperature for 3 hr, before being cooled down again. Then the product is diluted with 3725 kg of sulphuric acid (sp. gr. 1.84). Spent acid may also be used for dilution. This operation should be carried out directly in the nitrator to utilize nitric acid and nitrogen oxides present in the spent acid.

The diluted sulphophenol is cooled down to 35°C before being transferred by compressed air to a sulphophenol tank, heated by a heating coil. The pipe line through which it passes should also be heated up.

The sulphonation takes about 7.5 hr, namely:

Charging with phenol	15 min
Feeding with oleum	21hr
Steam heating	9min
Main reaction	3 h r
Cooling	36 min
Dilution	1 hr
Conveying to the tank	36 min
Total	7hr 36 min

The second stage of picric acid manufacture - sulphophenol nitration - is carried out with a mixture of the following composition:

HNO ₃	70%
H ₂ SO ₄	20%
H ₂ O	10%

For easy control the nitration process is divided into 3 stages: (1) mononitration, (2) dinitration and (3) trinitration. All are effected in one nitrator. The acid required is therefore added in three portions, their weights being in the ratio of 80: 80: 100.

Sulphophenol is subjected to nitration, diluted either with fresh sulphuric acid or with spent acid. The dilution with spent acid usually takes place in the nitrator itself just before the nitration process begins.

For this purpose a portion of 1906 kg of concentrated sulphophenol is run into the nitrator and cooled down to 35°C, then during cooling and stirring, 938 kg of spent acid of the composition:

H ₂ SO ₄	76%
HNO ₃	0.3-1.5%
HNO ₂	2.54%
oxalic acid	2-3%

picric acid	1-2%
total acidity (as H ₂ SO ₄)	83-84%
SP. gr.	1.775

is added. Before starting the nitration the diluted sulphophenol should be cooled down to 40°C.

The separate nitration stages are effected as follows.

Mononitration

To the nitrator containing diluted sulphophenol the first portion of 377.5 kg of the nitrating mixture is run in. During this operation the temperature rises from 40° to 60°C. The addition of the nitrating mixture usually takes 45-60 min (the temperature rises at a mean rate of about 2° per 5 min). At the beginning of the process especially vigorous cooling should be applied to the nitrator contents. Then, as the process goes on, the cooling may be less intense.

Dinitration

In the second nitration stage, another portion of 377.5 kg of the nitrating acid is added. The initial temperature of 60°C rises to 80°C towards the end of the process. The addition of acid takes 45 min. At this stage the nitration proceeds most smoothly and the temperature rises slowly, no cooling being required. If the temperature rises too slowly (less than 2° per 5 min), steam may be passed through the heating coil for a while (not longer than for 1 min) to attain the required temperature by the end of the nitration. If nitration is carried out properly at this stage of the process, it helps the third stage nitration run smoothly. Frothing, which may occur there, may be due to incomplete nitration at the second stage.

Trinitration

At this stage a portion of 470 kg of the nitrating acid is run into the nitrator. The initial temperature is 80°C and towards the end it is 100°C. All the nitrating acid should be added within a period of one hour. The nitrator contents are then kept at 100-110°C for one hour longer. During the addition of the acid the nitrator contents should be cooled. If a rapid rise in temperature occurs the acid flow should be stopped for 1-2 min. After all the acid has been added, the nitrator contents should be heated to prevent the temperature falling below 100°C. On the other hand care should be taken to prevent it rising above 112°C. Higher temperatures should be considered dangerous, although British operating conditions for a similar method permit 115°C as the upper limit. A temperature higher than 100°C and close to 110°C favours the formation of larger crystals on cooling.

Nitration completed, the nitrator contents are cooled down to 35°C to precipitate picric acid. The mixture is then transferred by means of compressed air (4 atm) to a higher mounted tank Z (Fig. 120) and from there to the centrifuge W₁ for separating picric acid from spent acid. For each tank a separate centrifuge is provided.

The sulphophenol nitration takes ca. 64 hr, including:

Charging the nitrator with sulphophenol	30 min
Mononitration	1 h r
Dinitration	45 min
Trinitration	1 h r
Heating	1 hr
Cooling	1 hr 20 min
Discharging	30 min
	<hr/>
Total	6 hr 15 min

Separation and washing picric acid

Picric acid is separated from spent acid by centrifuging. The centrifuge W_1 shown in Fig. 120 is made of V4A stainless steel. It can work at both low and high speeds. As the picric acid suspension in spent acid is drawn off from tank Z_1 the centrifuge is rotated at a low speed (some 200 r. p. m.), then at full speed. Since the crystals of picric acid may be quite minute the centrifuge basket should be lined with stainless steel gauze.

Picric acid is washed with a small quantity of cold water when still in the centrifuge. This wash water is then added to the spent acid. The product is discharged at the bottom and transferred to a wooden or aluminium washing tank P, equipped with a mechanical stirrer or with a bubbler. Here, after mixing with water, the stirrer is stopped and, after settling the water, is drawn off by a siphon. After 5-6 washings, the remaining water is removed in centrifuges, W_2 , made of tinned copper.

The average charge of the washing tank consists of 350 kg picric acid (the quantity produced in one batch) and 1000 l. of water. The washing operation, comprising charging, mixing, decanting, etc., takes 40-46 min. If the product has formed lumps, it should be crushed in a roll crusher before washing.

Counter-current washing processes also are applied. In a system described by Lebedev [5], acid washings containing some 0.007% of H_2SO_4 coming from centrifuge W_2 which is fed with fresh water, are mixed with acid washings from the picric acid washing tank P containing 1.1% of H_2SO_4 . In this way acid water containing 0.85% of H_2SO_4 is obtained. This water is used for washing picric acid in centrifuge W_1 . The water flowing out of it contains 3.2% of H_2SO_4 . A part of this water is introduced into the washing tank P together with fresh water, in such a quantity as to achieve a content of H_2SO_4 in the washings from the tank P equal to 1.1%, as mentioned above.

Centrifuge W_2 is fed initially with the acid water from washer P, finally with fresh water.

Such a system requires 3 m³ of fresh water per 1000 kg of picric acid, whereas conventional methods require 10 m³ of water for the same quantity of picric acid.

After washing, picric acid is centrifuged in centrifuge W_2 so as to reduce its moisture content to 5-6%.

The spent acid flowing out of the centrifuge has a composition as given on p. 515. Its specific gravity 1.775, is similar to that of picric acid (1.813). This is

why the picric acid which has passed through the centrifuge gauze and has precipitated on cooling, does not settle at the bottom but mostly remains suspended in the spent acid. The latter may subsequently be used for dilution of sulphophenol (p. 515).

The spent acid may also be utilized in a different way, namely by diluting with water to a total acidity of 72-75%, further precipitation of picric acid from the solution may be brought about. After a few days standing, the picric acid is separated from the solution on a vacuum filter, as grade II product. The spent acid thus diluted, after being fortified by adding nitric acid and oleum, may be used for the nitration again.

Drying and screening

The construction of picric acid driers presents certain difficulties because of the ready formation of picrates. Having this in mind, wood is mostly used as the construction material for driers, and any metal parts (screws, nails) should be made either of metals that form picrates with difficulty such as copper or aluminium, or of tinned metals or stainless steel. Floors should be made of wood covered with linoleum or concrete coated with asphalt. At the beginning of World War I when concrete floors were commonly in use, picric acid would with time form picrates with cationic constituents of the concrete: calcium, magnesium, sodium and iron. Washing the floor created conditions favourable for the penetration of picric acid into the concrete, and after several months a thick layer of picrates used to form. Any friction, as for example, by moving a bench around or any sort of blow, initiated an explosion of picrates all over the floor, causing fire or explosion in the drier. The inside walls should be plastered with plaster of Paris, since gypsum, being the salt of a strong acid, yields calcium picrate only with difficulty. Lining the walls of the drier section with white glazed wall-paper is recommended. Heaters for heating the drying air should not be placed inside the drying premises. Workman who have to enter the drying section should put on protective wooden-soled shoes with no nails in them. The floor should be swept frequently and washed with water.

To dry picric acid various drying systems are applied. The chamber drier is the simplest. The design of such a drier, used in the U.S.S.R. is shown in Fig. 121 (after Lebedev [5]). On shelves (1) wooden frames covered with linen are placed. Over each of them about 9 kg of picric acid (calculated on dry mass) is spread, so as to obtain a 3-4 cm thick layer. The heater (2) is located in the passage adjacent to the chamber. The natural flow of the heated drying air is shown in the diagram.

The drying of picric acid with a 7% moisture content at 50-60°C usually takes about 2 days. This period can be cut down to 16 hr by passing the drying air through the heater by means of a ventilator.

Tunnel driers may also be applied for drying picric acid.

For this, mechanical sieves made of aluminium or copper gauze, 50 meshes per 1 cm², are used. Figure 122 shows a system which may be used. A wooden funnel (1) serves for leading the product. Lumps of picric acid are retained by gauze (2) and

MANUFACTURE OF PICRIC ACID

may be removed from time to time through door (3). Crystals of the required size pass through the gauze into hopper (4).

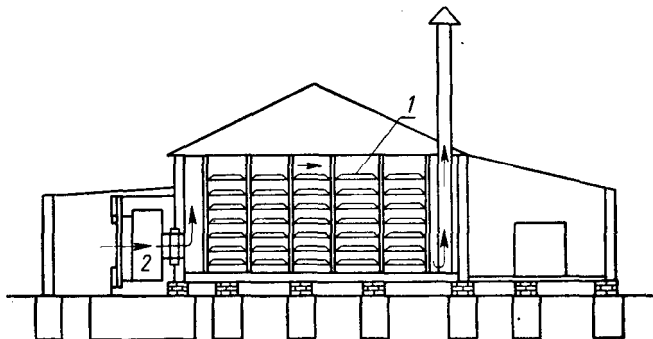


FIG. 121. Chamber drier for picric acid (Lebedev [5]).

The sieve is hung on straps from the ceiling and is kept in oscillating motion by means of an eccentric driven from a compartment adjacent to that in which the screening installation is located. The end product is transported in leakproof chests or in paper-lined barrels.

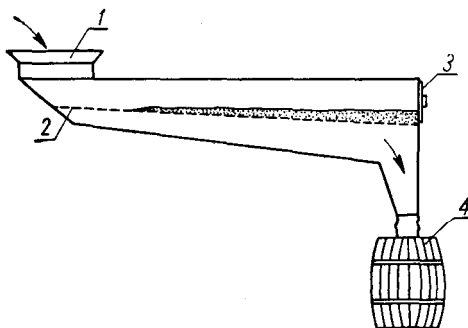


FIG. 122. Sieve for picric acid (Pascal [2]).

DINITROPHENOL NITRATION METHODS

The nitration of dinitrophenol is the most modern commercial method for the production of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophenol from chlorodinitrobenzene, see p. 484).

Both dry and moist dinitrophenol may be nitrated, though the dry product is usually used.

Lebedev [5] describes the production process used in the U.S.S.R. Dinitrophenol from the centrifuge, containing 10-15% of moisture, is dried to obtain a product with only about 0.5% of moisture (drying is effected in picric acid driers).

Since the purity of picric acid depends to a high degree on the purity of the dinitrophenol, the quality standards for the latter should be strictly observed (see p. 486).

The reaction is carried out in a cast iron jacketed nitrator equipped with a stirrer and a stainless steel heating coil 2092 kg of spent acid are run into the nitrator and heated to 50°C. 750 kg of dinitrophenol are then added, the above temperature being maintained during this operation, which will take 30 min. The nitrating mixture prepared from 86% nitric acid (100 parts) and 20% oleum (200 parts) is then run into the nitrator during the course of 23 hr, the excess of the mixture being 25% of HNO₃. During this procedure the temperature should not be allowed to rise over 80°C. After 20 min of stirring, the nitrator contents are heated to 110 - 112°C (1 hr) and subsequently maintained at this temperature for one hour and a half. Altogether the process requires about 8 hr.

The reaction mixture is cooled to 25-30°C as quickly as possible, which takes about 2-3 hr. Picric acid precipitates in fine crystals. The nitrator contents are then drawn off into stainless steel centrifuges or onto iron vacuum filters. The charge of a centrifuge amounts to 250 kg. As a result, 750-780 kg of picric acid can be obtained, which constitutes about 85% of the theoretical yield.

Washing, drying, etc. of picric acid are effected as described above.

A flow sheet of the preparation of picric acid from chlorobenzene is presented in Fig. 123 (after Lebedev [5]).

According to the same author, the material consumption for preparing 1000 kg of picric acid is:

Benzene as feed stock:

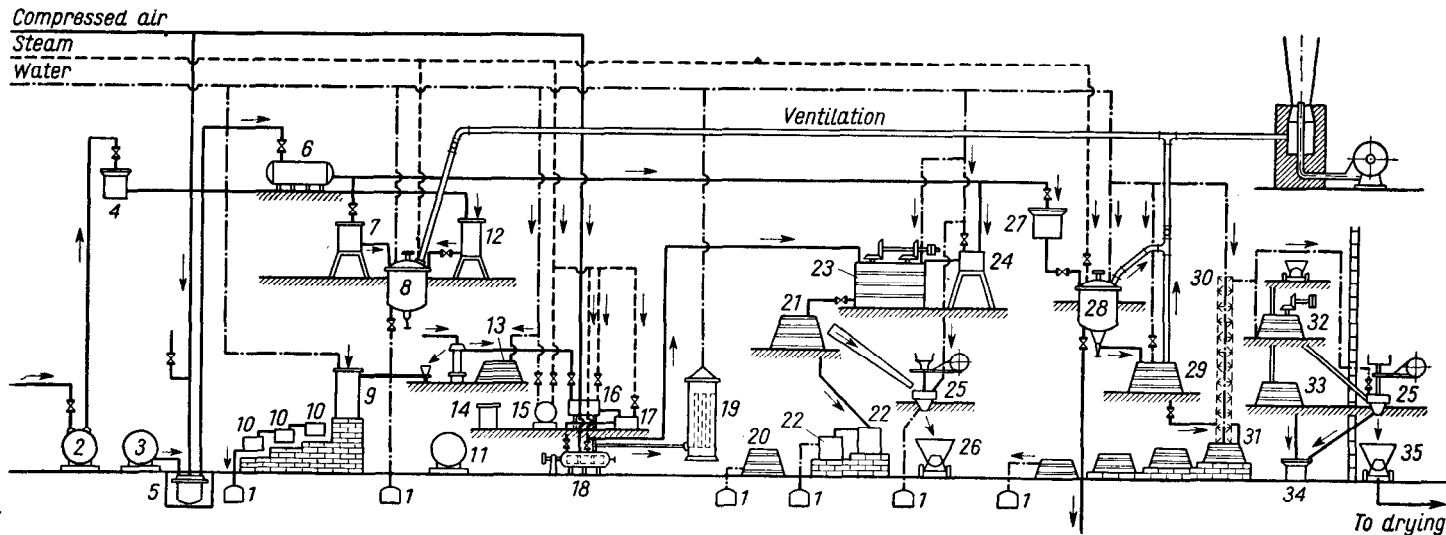
Oleum (20%)	2600 kg
Nitric acid (86%)	1320 „
Benzene	610 „
Sodium carbonate	31 „
Chlorine	540 „
Sodium hydroxide 85%	680 „
Oleum for drying chlorine	95 „

Dinitrophenol as feed stock:

Dinitrophenol	1000 kg
Oleum (20%)	950 „
Nitric acid (86%)	475 „
Spent acid	2370 „

METHODS OF NITRATING BENZENE IN THE PRESENCE OF MERCURIC SALTS

During the 1914-1918 War attempts were made to apply industrially Wolfenstein and Bötters's method [9] of nitration of benzene in the presence of mercuric salts (p. 110). Vignon [10] developed a method in which a mixture of di- and trinitrophenols in the ratio of about 40: 60 was obtained in nearly 85% yield. A mixture prepared in this way might have been applied directly for filling shells. Nevertheless, the method has not been used on an industrial scale due to the large quantities of mercury required for the production, amounting to about 10% of the benzene



Store, of chlorobenzene
and sulphuric acid

Nitration of
chlorobenzene

Hydrolysis to dinitrophenol

Trinitration, Washing

FIG. 123. Flow sheet of the production of picric acid from chlorobenzene (Lebedev [5]).

1 - drain; 2 - storage tank for chlorobenzene; 3 - storage tank for sulphuric acid; 4 - intermediate tank for chlorobenzene; 5 - pressure-egg; 6 - intermediate tank for sulphuric acid; 7 - metering tank for sulphuric acid; 8 - nitrator; 9 - diluting tank; 10 - labyrinth for sedimentation of chlorodinitrobenzene; 11 - tank for caustic soda; 12 - metering tank for chlorobenzene; 13 - vat for washing chlorodinitrobenzene; 14 - metering tank for caustic soda; 15 - tank for hot water; 16 - tank for chlorodinitrobenzene; 17 - metering tank for chlorodinitrobenzene; 18 - reactors for hydrolysis of chlorodinitrobenzene; 19 - condenser; 20 - filter for dinitrophenol from the labyrinth; 21 - filter for dinitrophenol; 22 - labyrinth for the sedimentation of dinitrophenol; 23 - neutralizer; 24 - diluting tank; 25 - centrifuge; 26 - truck with dinitrophenol; 27 - metering tank for sulphuric acid; 28 - nitrator; 29 - filter; 30 - lift; 31 - acid drains; 32 - decantation vat; 33 - titer; 34 - wash-water collector; 35 - truck with picric acid.

used. The recovery of mercury proved to be not worth-while, since its concentration in spent acid and in washing was much too low.

Vignon came to the conclusion that a certain temperature limit should not be exceeded, otherwise oxidation reactions would prevail. In addition, he found that although an excess of benzene resulted in an increased yield, at the same time it favoured the formation of dinitrophenol.

Nitration by Vignon's method on a semi-commercial scale, is carried out as follows: 2.5 parts of mercuric nitrate is dissolved in 100 parts of 52% nitric acid and the solution is mixed with 50 parts of benzene. The mixture is brought to 75-80°C and kept at this temperature for 5-7 hr, then cooled and the layer of benzene, containing nitrobenzene and nitrophenols, is separated by decantation. Benzene is distilled off and nitrobenzene is expelled by steam distillation. The remainder, constituting 125 parts, contains:

dinitrophenol	52%
picric acid	48%

Other authors report the yield obtained does not exceed 140 parts of benzene and the product is contaminated with mercuric picrate.

Broders [11] tried to develop another method of commercial production by passing benzene vapours through nitric acid containing mercuric nitrate. However, he did not succeed in obtaining a yield higher than 20% calculated on the benzene used.

During World War II Wright and his co-workers [12] continued the investigations on this method on large laboratory scale, and developed a process using 1250 ml of benzene for one run.

The reaction was effected at 65°C with 50% nitric acid, containing a dissolved catalyst consisting of

0.28 gramme-atom Al
0.015 gramme-atom Mn
0.0005 gramme-atom Al

calculated on 100 g of benzene. The yield obtained was 150 g of picric acid from 100 g of benzene, i.e. 50% of the theoretical. The consumption of nitric acid amounted to 140-160 g (calculated on HNO₃). Nitrobenzene and dinitrobenzene were formed as by-products.

Wright suggested the recovery of the nitrogen dioxide generated in the reaction and the recycling of spent acid to utilize the catalyst it contains. The results obtained by the author do not differ in principle from those of the earlier investigations. The method, however, like the earlier ones, has not found industrial application.

LITERATURE

1. M. MARQUEYROL and P. LORCETTE, *Bull. soc. chim. France* [4], **25**, 371, (1919); 27, 420 (1920).
2. P. PASCAL. *Poudres, explosifs, gaz de combat*, Hermann, Paris, 1925.
3. R. KING *J. Chem. Soc.* **119**, 2105 (1921).

4. H. ARUNDAL, G. P. DAVIES and I.C.I. Ltd., Brit. Pat. 370436 (1931).
5. I. V. LEBEDEV, *Proizvodstvo pikrinovoi kisloty*, Goskhimtekhiidat, Moskva-Leningrad, 1934.
6. F. OLSEN and J. GOLDSTEIN, *Ind. Eng. Chem.* **16**, 66 (1924).
7. H. S. REED, *Ind. Eng. Chem.* **16**, 72 (1924).
8. Technical Records of Explosives Supply 1914-1918, No. 6. Manufacture of Picric Acid, HMSO, London, 1921.
9. R. WOLFFENSTIZN and O. BÖTERS, Ger. Pat. 194883 (1906); *Ber.* **46**, 586 (1913).
10. L. VIGNON *Bull. soc. chim. France* (4), **27**, 547 (1920).
11. BRODERS, *Rapports de la Poudrerie Nationale de St. Fons*, 1919.
12. G. F. WRIGHT *et al.*, *Ind. Eng. Chem.* **40**, 1281 (1948).