PRODUCTION OF PICRIC ACID
FROM MONOCHLORBENZOL

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PRODUCTION OF PICRIC ACID
FROM MONOCHLORBENZOL

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Picric Acid from Chlorbenzol.

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Picric Acid from Chlorbenzol.

Preface.

This investigation into the production of picric acid from monochlorbenzol was undertaken because of the lack of literature on the subject although the process is known to be in extensive use. Owing to the very limited amount of time which was available for this work the experimenters were obliged to confine their efforts to the application of a certain series of reactions which appeared to be most practical. As the attainment of maximum yields at all stages was essential to the success of the process considerable attention was paid to this phase of the work.

The authors desire to express their gratitude for the valuable assistance rendered and interest shown throughout the work by Prof. Harry McCormack.
Picric Acid from Chlorbenzol.

Introduction.

Owing to the present international situation the use of picric acid as an explosive has increased enormously. It is also used to a very limited extent in the dye industry but other yellow dyes have been found which are less costly.

Picric acid is the most powerful explosive known and is therefore used extensively as the bursting charge of shells. The pure acid is exploded only by means of a priming charge such as a cap of mercury fulminate, but when traces of its metallic salts are present it is easily exploded by detonation. Because of this fact great care must be taken in its manufacture and use to prevent contamination.

The usual method for the manufacture of picric acid is to nitrate phenol which has been previously sulphonated. With this process it is impossible to obtain a sufficiently
Picric Acid from Chlorbenzol.

pure product without recrystallization, but with the chlorbenzol process the loss due to this operation is eliminated because of the high purity of the picric acid originally obtained.
Picric Acid from Chlorbenzol.

Theoretical Considerations.

When monochlorbenzol is subjected to strong nitration such as with a mixture of concentrated or fuming nitric and sulphuric acids at a moderately high temperature, the resulting product is largely dinitrochlorbenzol. It is impossible to obtain trinitrochlorbenzol by direct nitration, and because of this fact the production of this body as an intermediate could not be considered. The first product of the nitration of chlorbenzol consists of a mixture of ortho, meta, and para mononitrochlorbenzols. The reaction proceeds as follows:

\[ C_6H_5Cl + HNO_3 = C_6H_4Cl(NO_2) + H_2O \]

The three isomers have the following structural formulae:
Picric Acid from Chlorbenzol.

The amount of meta mononitrochlorbenzol formed is less than one percent and can be neglected. The ortho and para derivatives are formed in nearly equal quantities, the exact amounts of each depending upon the temperature. The physical properties of the ortho and para mononitrochlorbenzols are tabulated below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Ortho</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp. gr.</td>
<td>1.36822°</td>
<td>1.52418°</td>
</tr>
<tr>
<td>m.p.</td>
<td>32.5°</td>
<td>83°</td>
</tr>
<tr>
<td>b.p.</td>
<td>245°</td>
<td>242°</td>
</tr>
<tr>
<td>Crys. form.</td>
<td>needles</td>
<td>monoclinic prisms</td>
</tr>
</tbody>
</table>

Both forms are insoluble in water but
Picric Acid from Chlorbenzol.

soluble in alcohol and ether. They are hydrolyzed by caustic soda solution only under pressure at 130°.

After all of the chlorbenzol has been converted to the mononitrochlorbenzols the action continues with the production of dinitrochlorbenzol. The reaction proceeds as follows:

\[
\text{Cl} + \text{HNO}_3 \rightarrow \text{Cl} + \text{H}_2\text{O}
\]

The main constituent of this nitration product consists of 1:2:4 dinitrochlorbenzol, the amount of the other possible isomers being limited on account of the small quantity of meta mononitrochlorbenzol entering into the reaction. The physical properties of the 1:2:4 dinitrochlorbenzol are as follows:

sp.gr., 1.697\(^{22}\)°; m.p., 53.5°; b.p., 315°; crystalline form, trimetric crystals: in-
Picric Acid from Chlorobenzol.

soluble in water, very slightly soluble in cold alcohol, very soluble in hot alcohol and ether.

At ordinary pressure and at moderate temperature dinitrochlorobenzol is quantitatively converted into sodium dinitrophenate by the action of caustic soda solution. The reaction proceeds as follows:

\[
\begin{array}{c}
\text{NO}_2 \quad \text{Cl} \\
\text{NO}_2 \\
\end{array}
+ 2 \text{NaOH} \rightarrow
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\end{array}
+ \text{NaCl} + \text{H}_2\text{O}
\]

The sodium dinitrophenate is converted into the dinitrophenol by acidification:

\[
2 \begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\end{array}
+ \text{H}_2\text{SO}_4 \rightarrow
\begin{array}{c}
\text{OH} \\
\text{NO}_2 \\
\end{array}
+ \text{Na}_2\text{SO}_4
\]

The physical properties of dinitrophenol are as follows: sp.gr., 1.683\(\text{^22\degree C}\): m.p., 114\(\degree\): crystalline form, yellow tablets: solubility in water at 20\(\degree\), 5 grams per 100 cc: soluble
Picric Acid from Chlorbenzol.

in alcohol and ether. Dinitrophenol may be easily converted into trinitrophenol or picric acid by moderately strong nitration. The reaction is as follows:

\[
\begin{align*}
\text{Picric Acid} + \text{Nitric Acid} & = \text{Trinitrophenol} + \text{Water}
\end{align*}
\]

The physical properties of picric acid are as follows: sp. gr., 1.767; m.p., 122.5°; crystalline form, yellow leaf; moderately soluble in alcohol and ether. Its solubility in water greatly increases with an increase in temperature as is shown in the following table:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gm. Picric per 100cc. of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.67</td>
</tr>
<tr>
<td>20</td>
<td>1.10</td>
</tr>
<tr>
<td>60</td>
<td>2.77</td>
</tr>
<tr>
<td>80</td>
<td>4.22</td>
</tr>
<tr>
<td>100</td>
<td>6.75</td>
</tr>
</tbody>
</table>
Picric Acid from Chlorbenzol.

THE PROCESS.

Owing to the facility with which mono-chlorbenzol is converted into 1:2:4 dinitrochlor-benzol and the ease with which the chlorine of the latter body is replaced by hydroxyl by means of caustic soda solution, the following process for the production of picric acid from chlorbenzol was decided upon as being the most practical:

The steps involved are given below:

1. The conversion of chlorbenzol to 1:2:4 dinitrochlorbenzol.
2. The hydrolysis of dinitrochlorbenzol to sodium dinitrophenate.
3. The liberation of dinitrophenol from its sodium salt.
4. The nitration of dinitrophenol to picric acid.

In carrying out the above reactions the experimenters attempted to determine the most
Picric Acid from Chlorbenzol.

economical means of production.
Picric Acid from Chlorbenzol.

EXPERIMENTAL WORK.

The experimental work was carried out in four divisions corresponding to the four steps in the process as outlined on page 11.

1. Nitration.

The apparatus used in the nitration of the chlorbenzol is shown in Photo No.1 on p.14. It consisted of a two liter flask supported by an iron stand and provided with a water cooled vertical condenser. Heat was supplied by means of an oil bath heated by a Bunsen burner, and agitation was effected by blowing a slow steady stream of air in at the base of the flask by means of a tube inserted through the condenser. Thermometers were used both in the outside bath and in the nitration mixture. At first considerable difficulty was encountered in obtaining a cork or rubber stopper which would withstand the attacks of the strong hot vapors during one entire period.
Picric Acid from Chlorbenzol.

Photo No.1.

Apparatus for

Nitration and Hydrolysis.
Picric Acid from Chlorbenzol.

of nitration. Several innovations were tried among them being gold foil, lead foil, and cement protective coatings. Of these a barium sulphate-sodium silicate cement proved to be the best. A cork stopper was first bored and fitted for the condenser, thermometer, and flask, the flask end being made somewhat unsized so as to allow for a heavy layer of the cement. The condenser and thermometer were inserted in the cork and a thick layer of the cement forming paste was applied and allowed to harden. The cork was then sealed to the flask with fresh cement. Such a cork withstood the disintegrating influences of all subsequent nitrations. Temperature regulation was easily controlled by not allowing the temperature of the outer bath to exceed that of the nitration mixture by more than 20° at any time.
Picric Acid from Chlorbenzol.

The nitration of the chlorbenzol was effected by the use of several nitrating mixtures. The possibility of a quantitative production of dinitrochlorbenzol by means of ordinary nitric (sp.gr. 1.42) and sulphuric (sp.gr. 1.84) acids was eliminated since the work of Louis Rabinovitz and A.A.Wells: The Chemical Engineer, Feb.-Mar., 1917, p.24, conclusively proved that only small amounts of dinitrochlorbenzol were formed under such conditions even at elevated temperatures (200°C.).

Accordingly the first nitration was made with a mixture of ordinary nitric (sp.gr.1.42) and fuming sulphuric (sp.gr. 1.93, 20% free 303) acids. An excess of 25% over the theoretical amount of nitric acid was used and sufficient sulphuric acid was added to bring the water content of the final waste acid to about 20%. After assuming several ratios of chlorbenzol to sulphuric acid, it was found
Picric Acid from Chlorbenzol.

that with a proportion of 1 to 3 this water content was approximated. A smaple calculation is given below:

$$\text{C}_6\text{H}_5\text{Cl} + 2 \text{HNO}_3 = \text{C}_6\text{H}_3\text{Cl(NO}_2)_2 + 2 \text{H}_2\text{O}$$

112.5 126 202.5 36

Assuming 100 grams of chlorbenzol, the amount of nitric acid (sp.gr. 1.42, 70%) theoretically required is:

$$\frac{126}{112.5} \times \frac{100}{.7} = 160 \text{ gms. HNO}_3 (70\%)$$

With 25% excess = 200 gms. " "

Water in 200 gms. acid equals:

$$200 \times .3 = 60 \text{ gms. water}$$

Water formed in the reaction equals:

$$\frac{36}{112.5} \times \frac{100}{100} = 32 \text{ gms. water}$$

The amount of water absorbed by the 300 gms., of fuming sulphuric is:

$$\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$$

80 18 98
Picric Acid from Chlorbenzol.

\[ 300 \times 0.20 \times 18/30 = 13.5 \text{ gms. water abs.} \]

The amount of water in the spent acid mixture is:

\[ (60 \div 32) - 13.5 = 78.5 \text{ gms. water} \]

The total weight of spent acid is:

\[ \text{H}_2\text{SO}_4(100\%) (300 \div 13.5) = 313.5 \text{ gms.} \]
\[ \text{Water} = 78.5 \text{ gms.} \]
\[ \times \text{HNO}_3(100\%) (40\times.7) = 28.0 \text{ gms.} \]

\[ \text{Total} = 420.0 \text{ gms.} \]

Percent of water in the acid mixture equals:

\[ 100 \times 78.5/420 = 18.7 \% \text{ water} \]

In this calculation the possible loss due to the escape of uncondensed vapors has been neglected.

The first nitration was therefore made with:

- 200 gms. chlorbenzol
- 400 gms. HNO\(_3\) (sp.gr. 1.42)
- 600 gms. H\(_2\)SO\(_4\) (sp.gr. 1.93)

The two acids were poured into the flask and the mixture cooled. The chlorbenzol was then
Picric Acid from Chlorbenzol.

slowly added to the acid mixture with continual shaking and cooling. The flask was then sealed to the condenser. The mixture was continually agitated by air and heated sufficiently to maintain a moderate reaction. The following is a table of the time and temperature throughout the operation:

<table>
<thead>
<tr>
<th>Time_</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:00 P.M.</td>
<td>Start</td>
</tr>
<tr>
<td>2:30</td>
<td>100°C.</td>
</tr>
<tr>
<td>3:00</td>
<td>110</td>
</tr>
<tr>
<td>3:30</td>
<td>140</td>
</tr>
<tr>
<td>4:00</td>
<td>160</td>
</tr>
<tr>
<td>4:30</td>
<td>160</td>
</tr>
<tr>
<td>5:00</td>
<td>160</td>
</tr>
<tr>
<td>5:30</td>
<td>160</td>
</tr>
<tr>
<td>6:00</td>
<td>165</td>
</tr>
</tbody>
</table>

Throughout the run there was a slight evolution of brown NO₂ fumes but the amount of these was never allowed to become great. When the reaction
Picric Acid from Chlorbenzol.

had ceased, after about four hours, the paraffin bath was removed and the contents of the flask allowed to cool slightly. The oily layer of dinitrochlorobenzol was separated from the waste acids in a separating funnel, and was subsequently washed several times with hot water until free from acid. The acid mixture was diluted with water to precipitate dissolved dinitrochlorobenzol, and the flaky crystals were coagulated as an oil by heating. This portion was added to the main bulk which upon cooling to room temperature solidified. The total yield of washed product was 345 grams. Further work with this product showed that it contained 10% of mononitrochlorobenzols. The theoretical yield of dinitrochlorobenzol from 200 grams of chlorbenzol is:

\[
\frac{202.5}{112.5} \times 200 = 355.5 \text{ gms.}
\]

The actual yield of dinitrochlorobenzol was:

\[
345 \times .9 = 310.5 \text{ gms.}
\]
Picric Acid from Chlorbenzol.

The percent of the theoretical yield was therefore:

\[ 100 \times \frac{310.5}{355.5} = 87.4\% \]

Nitration with Fuming Acids.

In order to obtain a greater yield of the dinitrochlorbenzol a stronger nitration mixture was used, the water content of the spent acid being calculated to be about 15\%. The charge taken which corresponded to these conditions was as follows:

- 200 gms. chlorbenzol
- 400 gms. HNO₃ (sp.gr. 1.465, 81\%)
- 600 gms. H₂SO₄ (sp.gr. 1.93, 20\% SO₃)

The treatment was very similar to the previous nitration. The log of the run was:

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:30</td>
<td>Start</td>
</tr>
<tr>
<td>1:00</td>
<td>110°C</td>
</tr>
<tr>
<td>1:30</td>
<td>125°C</td>
</tr>
</tbody>
</table>
Picric Acid from Chlorbenzol.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:00</td>
<td>140°</td>
</tr>
<tr>
<td>2:30</td>
<td>150°</td>
</tr>
<tr>
<td>3:00</td>
<td>155°</td>
</tr>
<tr>
<td>3:30</td>
<td>160°</td>
</tr>
<tr>
<td>4:00</td>
<td>165°</td>
</tr>
<tr>
<td>4:30</td>
<td>165°</td>
</tr>
</tbody>
</table>

The dinitrochlorbenzol was separated from the waste acid in a manner similar to that used in the previously nitration. The total yield of mixed nitrochlorbenzols was 352 gms., of which 1% was later found to be monochlorbenzols. The percent of the theoretical yield was:

\[
100 \times 0.99 \times \frac{352}{355.5} = 98\% \text{ of dinitrochlorbenzol.}
\]

On a similar run with slight variations in time and temperature of nitration substantially the same results were obtained.
Picric Acid from Chlorbenzol.

Nitration with $\text{NaNO}_3$ and $\text{H}_2\text{SO}_4$.

Another method of keeping the water content of the spent nitration acid mixture down to a minimum is to produce the nitric acid during the reaction by the action of sulphuric acid ($\text{sp.gr. } 1.42$) on crude sodium nitrate. A few calculations with various proportions of chlorbenzol, sodium nitrate, and ordinary sulphuric acid showed that it was not practical to reduce the water content of the waste acid mixture below 20% as too much sulphuric would be required. Accordingly in order to influence the reaction to a greater yield of dinitrochlorbenzol a greater excess of nitric acid was employed, this time 100% excess. The amount of sulphuric acid used was calculated to reduce the water content of the final waste acid to about 20%. To satisfy these conditions the following proportions were used:
Picric Acid from Chlorbenzol.

100 gms. chlorbenzol
300 gms. sodium nitrate
600 gms. $\text{H}_2\text{SO}_4$ (sp.gr. 1.84, 93%)

The operations were very much like those in the two previous nitration except that at the beginning of the reaction more careful temperature control was required because of the tendency of the action to become violent.

The data taken from such a run was as follows:

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:30 A.M.</td>
<td>Start</td>
</tr>
<tr>
<td>12:00</td>
<td>70°C</td>
</tr>
<tr>
<td>12:30</td>
<td>100°</td>
</tr>
<tr>
<td>1:00</td>
<td>120°</td>
</tr>
<tr>
<td>1:30</td>
<td>130°</td>
</tr>
<tr>
<td>2:00</td>
<td>140°</td>
</tr>
<tr>
<td>2:30</td>
<td>150°</td>
</tr>
<tr>
<td>3:00</td>
<td>155°</td>
</tr>
<tr>
<td>3:30</td>
<td>160°</td>
</tr>
<tr>
<td>4:00</td>
<td>165°</td>
</tr>
<tr>
<td>4:30</td>
<td>165°</td>
</tr>
</tbody>
</table>
Picric Acid from Chlorbenzol.

While the contents of the flask were still hot, the oily layer of dinitrochlorbenzol was decanted off into a beaker of cold water. The sodium sulphate and acid residue was cooled by the addition of sufficient cold water to dissolve all of the sodium sulphate, all dinitrochlorbenzol which it contained was coagulated as an oil. This was added to the main bulk of the oil which was then washed and allowed to solidify as in the previous nitrations. The yield of the crude product was 177 gms., and since 1% was later found to be mononitrochlorbenzols, the yield of dinitrochlorbenzols was 175.2 gms. The percent of the theoretical yield of dinitrochlorbenzol was therefore:

$$100 \times \frac{175.2}{355.5}/2 = 98.6\%$$

As the sodium nitrate method was obviously the cheapest of the three methods used and the yield was high, it seems to be most adaptable to
Picric Acid from Chlorbenzol.

the process.

2. HYDROLYSIS.

The apparatus used in the hydrolysis of the 1:2:4 dinitrochlorbenzol obtained by the nitration of chlorbenzol was exactly the same as that used in the nitration. A caustic soda solution readily reacted with the dinitrochlorbenzol to form sodium dinitrophenate, no other hydrolyzing reagents were used but several variations of the concentration of the alkali and of the temperature were studied. The amount of NaOH was calculated as follows:

\[
\text{C}_6\text{H}_3\text{Cl(\text{NO}_2)_2} + 2 \text{NaOH} = \text{C}_6\text{H}_3(\text{ONa})(\text{NO}_2)_2 + \text{NaCl}
\]

\[
\frac{202.5}{80} + \text{H}_2\text{O}
\]

Therefore \(100 \times \frac{80}{202.5} = 39.5\) gms., NaOH are required. In all of the experiments 45 gms., were used. The ratios of NaOH to water which were used were 1-5, 1-8, 1-10, 1-12, and 1-14. Very little difficulty was encountered in obtaining a complete hydrolysis when the contents
Picric Acid from Chlorbenzol.

of the flask was kept at just a boiling temperature, but in all cases there was a formation of tarry bodies sufficient to discolor the product. The formation of tarry matter by the decomposition of the phenate was probably due to the more intense hydrolyzing conditions at the start. Accordingly more cautious and slow heating at the start of the reaction resulted in, in the case of the dilute solutions of caustic soda, a product that was practically free from tarry bodies.

The solution of sodium dinitrophenate at this stage was contaminated by small amounts of unhydrolyzed mononitrochlorbenzols, and it was found that these could easily be driven off by steam distillation. A description of the apparatus used is hardly necessary as Photo No. 2 on page 28 shows all the essential details. A steam bath was used under the flask containing
Picric Acid from Chlorobenzol.

Photo No. 2.
Apparatus for Steam Distillation.
Picric Acid from Chlorbenzol.

the sodium dinitrophenate solution so as to keep the contents near 100°C., but yet not high enough to decompose the phenate into tarry bodies. The mononitrochlorbenzols distilling off were weighed and checked against the nitration operation to which they corresponded. As the mononitrochlorbenzols have the odor of nitrobenzene the end of the distillation was easily detected by the absence of that odor. The warm sodium dinitrophenate solution was then filtered in order to free it from a small amount of insoluble impurities.

3. THE LIBERATION OF DINITROPHENOL FROM ITS SODIUM SALT.

The next main reaction, which was the liberation of dinitrophenol from its sodium salt solution, was accomplished by acidification. The equation for this change has been given elsewhere. Since,
Picric Acid from Chlorbenzol.

$$2C_6H_3Cl(NO_2)_2 \rightarrow 2C_6H_3(OH)(NO_2)_2 + H_2SO_4$$

405 368 98 72.9

The amount of sulphuric acid which is required to liberate the dinitrophenol from the sodium salt solution formed by the hydrolysis of 100 grams (which was the charge used in all of the hydrolyses) of dinitrochlorbenzol is:

$$100 \times \frac{98}{405} = 24.2 \text{ gms. } H_2SO_4$$

$$\frac{24.2}{1.84} \times 0.93 = 14.3 \text{ cc.} H_2SO_4(1.84)$$

Because of the excess of caustic soda used in the hydrolysis, 20 cc., of acid were used. When the concentrated acid was added to the slightly cooled phenate solution or visa versa, a very dark brown dinitrophenol contaminated with considerable tarry matter was obtained. After making various changes, a light yellow dinitrophenol precipitate was finally obtained by slowly adding the cooled phenate solution, with continual stirring, to an iced 10% sulphuric acid solution. Even with this procedure it
Picric Acid from Chlorbenzol.

was found impossible to precipitate a light colored dinitrophenol from a phenate solution which had been contaminated with tarry matter during the hydrolysis of the dinitrochlorbenzol, but with careful working and the observance of the proper conditions at all steps an excellent light yellow dinitrophenol was always obtained. The precipitated dinitrophenol was filtered and largely freed from water by means of suction. The precipitated dinitrophenol was washed with cold water. The partially dried phenol was further dried on a porous plate in a steam closet. The theoretical yield of dinitrophenol from 100 grams of dinitrochlorbenzol is

\[
100 \times \frac{368}{405} = 90.8 \text{ gms.}
\]

The actual yield varied from as low as 66 gms., in the case of the dark dinitrophenol to about 95 grams in the case of the good color dinitrophenol. On account of the difficulty of drying the efficiency of the process at this step
Picric Acid from Chlorbenzol.

could not be accurately determined. As would be expected greater yields of dinitrophenol were obtained from the 99% dinitrochlorbenzol than from the 90%. The process did not require the dinitrophenol to be thoroughly dried, the drying having been made to give some idea of the efficiency of the hydrolysis and acidification operations.

4. FINAL NITRATION.

As was indicated on page 11, the last step in the process has for its object the conversion of the dinitrophenol obtained in the third step to trinitrophenol or picric acid. The apparatus used for this nitration was similiar to that used in the nitration of the chlorbenzol. The condenser, however, was not essential on account of the comparatively low temperatures (up to 110°C.) employed. The nitration was carried out with ordinary nitric acid (sp.gr. 1.42, 70%).
Picric Acid from Chlorbenzol.

Since;

$$C_6H_3(OH)(NO_2)_2 + HNO_3 = C_6H_3(OH)(NO_2)_3 + H_2O$$

$$\begin{array}{cc}
184 & 63 \\
229 & 18 \\
\end{array}$$

the amount of acid required for 1 gm. of di-nitrophenol is:

$$\frac{63}{184} = 0.342 \text{ gm. } HNO_3$$

or $$\frac{.342}{.7} = 0.488 \text{ gm. } HNO_3 (\text{sp.gr.})$$

In the nitration 100% excess of nitric was used and sufficient sulphuric acid (sp.gr. 1.84) was added to make the water content of the waste acid about 20%. The proportions of dinitrophenol, nitric, and sulphuric which gave these conditions were 1:1:2 respectively. The calculations are omitted as similar ones have already been given. The charge was agitated and the temperature gradually raised in order to maintain the reaction. After about three hours the reaction was apparently completed and the temperature had risen to about 115°C. The hot mixture was then poured into 3 or 4 times its volume of cold water.
Picric Acid from Chlorbenzol.

This gave a dense crystalline precipitate of picric acid which was light yellow in color. When cold the picric acid was filtered off, washed with cold water, and dried on a porous plate in a warm closet. With light colored dinitrophenol very good picric acid having a melting point in the neighborhood of 120°C., was obtained without recrystallization, but it was not possible to obtain a good picric acid from a dark dinitrophenol by such a procedure. Recrystallization from water gave the acid in the form of beautiful yellow leaves. The theoretical yield of picric acid from 100 grams of dinitrophenol from the equation at the top of the previous page is:

$$100 \times \frac{229}{184} = 124.4 \text{ gms.}$$

In one run where the charge consisted of:

- 100 gms. crude dinitrophenol from 100 gms., of 90% dinitrochlorbenzol.
- 100 gms. $\text{HNO}_3$ (sp. gr. 1.42)
Picric Acid from Chlorbenzol.

200 gms. $H_2SO_4$ (sp.gr. 1.84)

a yield of 82 grams of picric acid was obtained:

$$100 \times .9 \times \frac{229}{202.5} = 101.7 \text{ gms. picric}$$

The combined efficiency of the hydrolysis, acidification, and final nitration operations was:

$$\frac{82}{101.7} = 80.6\%$$

The average efficiency of each of these three operations was therefore:

$$\sqrt[3]{80 \times 100 \times 100} = 93.0\%$$

In another run 80 grams of picric acid was obtained from 90 grams of a total of 95 grams of crude dinitrophenol obtained from 100 gms., of 99% dinitrochlorbenzol. The Theoretical yield would have been:

$$100 \times .99 \times \frac{229}{202.5} \times 90/95 = 106.0 \text{ gms.}$$

The combined efficiency of the three steps was:

$$\frac{80}{106} = 75.4\%$$
Picric Acid from Chlorbenzol.

The average efficiency of each step was therefore:

\[
\sqrt[3]{75.4 \times 100 \times 100} = 91.0\%
\]

In the two runs above the best possible conditions were attained at all steps. The dinitrophenol used was practically free from tarry matter and the picric acid obtained was of excellent color. In other runs where darker dinitrophenol was employed the yields were considerably less than those given above.
Picric Acid from Chlorbenzol.

SUMMARY.

The results obtained throughout the experiments on the production of picric acid from monochlorbenzol on a small scale were considered very favorable, and there is every reason to think that the results could be easily duplicated or possibly surpassed in large scale operations. Since the yield of dinitrochlorbenzol from chlorbenzol in the first step of the process was 98% of the theoretical and as the combined efficiency of the other three steps, involving the hydrolysis of the dinitrochlorbenzol to sodium dinitrophenate, the acidification of the latter to dinitrophenol, and the nitration of the dinitrophenol to picric acid, was from 75.4% to 80.6%, the overall efficiency or percent of the theoretical yield of picric acid from chlorbenzol was from 74% to 79%. Considering the number of operations involved in the process, this recovery can be regarded
Picric Acid from Chlorbenzol.

as excellent as it makes the average efficiency of each operation from
\[
\sqrt{\frac{74x100x100x100}{79x100x100x100}} = 92.7\% \\
\]
to
\[
\sqrt{\frac{79x100x100x100}{74x100x100x100}} = 94.3\%
\]

In the ordinary phenol process 190 parts of picric acid are obtained from 100 parts of phenol, which makes the recovery about 70% of the theoretical. In the absence of authentic data on the costs of production of picric acid in the phenol process and the difficulty of estimating the costs in the chlorbenzol process, a real rigid comparison of the two methods is impossible. With the latest quotations of phenol at 42¢ per lb., and chlorbenzol at 30¢ per lb., and the costs of other chemicals used in the two processes being approximately the same, the other factors of the cost of production could be slightly in favor of the
Picric Acid from Chlorbenzol.

phenol process and still allow a sufficient margin on the side of the chlorbenzol process to permit competition.
Picric Acid from Chlorbenzol.

APPENDIX.

Selected Bibliography.


