# SUMMARY SHOWING A COMPARISON OF PRODUCTS FROM THE ORIGINAL MITSCHERLICH AND HOBEG WASTE SULPHITE LIQUORS WITH NITROBENZENE AT 130° and 160° C.

**Objective:** The reducing action of waste sulphite liquor on nitrobenzene.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Reaction Substance</th>
<th>Waste Liquor</th>
<th>30 min., 130° C</th>
<th>3 hr., 130° C</th>
<th>0 min., 160° C</th>
<th>30 min., 160° C</th>
<th>3 hr., 160° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Azobenzene</td>
<td></td>
<td>9.6</td>
<td>7.0</td>
<td>12.2</td>
<td>5.9*</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>Azoxybenzene</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Sodium azobenzene-p-sulphonate</td>
<td></td>
<td>17.4</td>
<td>19.6</td>
<td>27.6</td>
<td>25.7</td>
<td>34.6</td>
<td>-</td>
</tr>
<tr>
<td>Total reduction products</td>
<td></td>
<td>8.6</td>
<td>7.3</td>
<td>9.0</td>
<td>10.6</td>
<td>9.6</td>
<td>-</td>
</tr>
<tr>
<td>Recovered nitrobenzene</td>
<td></td>
<td>35.6</td>
<td>33.9</td>
<td>48.8</td>
<td>42.2</td>
<td>55.2</td>
<td>-</td>
</tr>
<tr>
<td>Total nitrogen substances accounted for</td>
<td></td>
<td>42.95</td>
<td>44.7</td>
<td>23.6</td>
<td>34.5</td>
<td>16.7</td>
<td>-</td>
</tr>
<tr>
<td>Vanillin</td>
<td>**12.2</td>
<td>19.5</td>
<td>**17.0</td>
<td>**15.2</td>
<td>**15.9</td>
<td>-</td>
<td>16.5</td>
</tr>
</tbody>
</table>

* Low
** Average
The following generalizations are presented from the results of the analyses as summarized on the preceding page:

1. The total quantities of reduction products are greater at the higher temperature (160°C) and are favored during a longer reaction time.
   a. The production of aniline is greater at the higher temperature and a longer reaction time. [The concentrated waste sulphite liquor at the temperature of 160°C gave the largest yields of aniline found in all of the reactions.]
   b. The production of azoxybenzene and azobenzene followed no sharp rules although azobenzene was produced only at the higher temperature and a longer reaction time. Azoxybenzene was produced in all of the reactions but was found in the least amount in the reaction at the higher temperature and long reaction time (the reaction in which the largest amount of azobenzene was produced). The optimum condition, however, for the production of azoxybenzene was found to be 0 minutes at 160°C. This is not unexpected since the greatest amount of reduction occurred at the higher temperature, accompanied by more aniline and more azobenzene for a longer reaction time.
   c. Sodium azobenzene-p-sulphonate was formed in largest amounts at a temperature of 160°C and a reaction time of 30 minutes. This was found to be true for both waste liquors.
   d. The amount of nitrobenzene recovered is greatest in the reactions at the lower temperature (130°C), and a greater quantity of recovered nitrobenzene is accompanied by a low quantity of reduction products. No nitrobenzene was recovered in the reactions at the higher temperature and a long reaction time. [This was found to be true also with the reactions which employed the concentrated liquor.]

2. From an overall standpoint, the results of the original Mitscherlich liquor checked those of the original Hoberg liquor. Certain discrepancies are apparent but are allowable in view of individual reactions and analyses of individual reactions. They show very reasonable agreement in the general trend of the reaction from the standpoint of total reduction, total nitrogen products accounted for, and the amounts of recovered nitrobenzene.

3. The total amounts of nitrogen products accounted for, although rather consistent for given reactions, do not total 100 per
cent. It is to be noted that the higher temperature and the longer reaction time show a marked decrease in the total amounts of products recovered. This inherent factor plus a certain constant error in recovery seem to be the most significant factors to account for this loss. The loss due to incomplete steam distillation was almost negligible since, for three different reactions, an extraction method showed a further isolation of less than five per cent. The loss due to the possible presence of other nitrogen compounds may account for a certain percentage of the total nitrogen compounds. A positive test (qualitative) for nitrogen was found in the reaction-mixture after the isolation of the nitrogen products and an attempt to diazotise three of the reaction mixtures was successful and apparent coupling with alkaline β-naphthol took place.

4. The results for the determination of vanillin are not in agreement and are not considered to be entirely reliable since the method was found to give results which varied considerably. Any question concerning any given vanillin result should be checked by experiment before any final conclusions are drawn. The values, in all probability, are minimum rather than maximum values.

5. Other substances,

a. The presence of a volatile basic substance was questioned throughout the analyses and should be checked if the reactions are performed on a larger scale. A strong odor of a heterocyclic nature was prevalent also.

b. The results of the diazotization reactions suggest the desirability of investigating further the possible presence of sulfanilic acid or some other primary aromatic amine. The total amount of amine present, as calculated from the amount of nitrous acid employed, suggests a maximum of three to four per cent sulfanilic acid. An attempt was made to isolate the sulfanilic acid but was not successful.

The presence of sulfanilic acid in these reactions is very possible since at the higher temperature there is more aniline produced and less azobenzene-β-sulphonic acid. If the aniline results from the reduction of the latter, then sulfanilic acid is formed also in the process.

Samples of the dyed materials, resulting from the diazotization of two different reaction mixtures and the subsequent coupling with β-naphthol.
I. Reaction mixture from XX (Con. Hoberg, 3 hours at 160°C.)

Original, undyed cloth: cotton, silk and wool

Reaction XX Diazoitized and Coupled with \( \beta \)-naphthol

Reaction XX Diazoitized but not Coupled

II. Reaction mixture from XIV (Orig. Hoberg, 30 minutes at 160°C.)

Diazoitized and coupled with \( \beta \)-Naphthol

Files
Brauns
Pearl
Steele
Bossert
OBJECTIVE: The reducing action of waste sulphite liquor on nitrobenzene.

MODE OF ATTACK: This experiment employs the Hoberg waste sulphite liquor which was concentrated and repeats the conditions of Reaction IV (three hours at 160°C). Reaction IV employed the concentrated Mitscherlich waste sulphite liquor. (See book 334 for the details of the reaction; the analysis is given in book 347).

A. Materials used and conditions employed:

Waste sulphite liquor (Hoberg, concentrated) 180 cc. (solids to be same as Reaction IV)

Analysis: Specific gravity (20°C) 1.196
Total solids 491.0 g./liter
Lignin 252.0 g./liter
Per cent solids 51.3

Nitrobenzene
Sodium hydroxide, solid

Conditions: 3 hours at 160°C.

B. Results:

1. Reduction products

Aniline 12.85 g. (23.6 per cent)
Azoxybenzene None detected
Azobenzene 23.6 g. (44.4 per cent)
[Sodium-p-azobenzensulphonate--not determined]

2. Recovered nitrobenzene
None

3. Vanillin
Not determined

4. Other substances; Titration with nitrous acid (See Interpretation)
INTERPRETATION: The analysis was completed through the determinations of the aniline and azobenzene, and recovered nitrobenzene, in order to compare it with the analysis of the reaction with concentrated Mitscherlich waste sulphite liquor. The results are in good agreement as indicated below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Reaction IV (Mitscherlich)</th>
<th>Reaction XX (Hoberg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>25.4</td>
<td>23.6</td>
</tr>
<tr>
<td>Azodyobenzene</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>43.8</td>
<td>44.4</td>
</tr>
<tr>
<td>Recovered nitrobenzene</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Total reduction</td>
<td>69.2</td>
<td>68.0</td>
</tr>
</tbody>
</table>

A portion (150 ml. from a total of 1150 ml.) of the original reaction mixture was cooled and diazotised with the standard NaNO₂ solution in the presence of an excess of acid. This solution was added to a cold, alkaline solution of β-Naphthol. A deep red colored solution was formed, which indicated that coupling had taken place. This was further substantiated by the fact that it produced a dye color on silk and wool cloth. An attempt to produce the same results in a repeated experiment on the same solutions in the absence of the β-Naphthol solution gave negative results. [The quantity of NaNO₂ required for the complete titration of the total volume cannot be used to calculate the quantity of an amine present since there are known to be other substances (phenolic) present which would react with the nitrous acid.] This suggests strongly the presence of another primary aromatic amine.

A similar investigation was made on the reaction mixtures remaining from Reactions X and XIV with similar results. From the results obtained, the total amount of this type of aromatic amine would run between 2 and 3 per cent. This result is obtained by assuming that the amine is sulfanilic acid and calculating on the basis of the amount of nitrous acid used in the titration. [The vanillin and other phenolic substances were removed by ether extraction from acid solution and should not interfere with the titration.]
SUMMARY OF REACTIONS XXI, XVIII, XIV AND XIII

Reactions with the original Hoberg Waste Sulphite Liquor at 130° C. and 160° C.

Objective: The reducing action of waste sulfite liquor on nitro-benzene.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Condition</th>
<th>Vanillin</th>
<th>Aniline Azo-</th>
<th>Sodium Azo-</th>
<th>Red'n</th>
<th>Total Nitro-</th>
<th>Total Product</th>
<th>Accounted for (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXI</td>
<td>Waste liquor 250.0 cc Nitrobenzene 45.0 g. NaOH, solid 28.1 g.</td>
<td>30 min. at 130° C.</td>
<td>13.5</td>
<td>7.0</td>
<td>19.6</td>
<td>7.3</td>
<td>44.7</td>
<td>33.9</td>
<td>73.6</td>
</tr>
<tr>
<td>XVIII</td>
<td>(Same)</td>
<td>3 hours at 130° C.</td>
<td>15.2***</td>
<td>5.9</td>
<td>25.7</td>
<td>10.6</td>
<td>34.5</td>
<td>42.2</td>
<td>76.7</td>
</tr>
<tr>
<td>XIV</td>
<td>(Same)</td>
<td>30 min. at 160° C.</td>
<td>24.5</td>
<td>2.6</td>
<td>5.7**</td>
<td>22.6</td>
<td>13.3</td>
<td>57.3</td>
<td>33.6</td>
</tr>
<tr>
<td>XIII</td>
<td>(Same)</td>
<td>3 hours at 160° C.</td>
<td>13.2</td>
<td>13.4</td>
<td>37.4**</td>
<td>8.3</td>
<td>13.0</td>
<td>00.0</td>
<td>72.1</td>
</tr>
</tbody>
</table>

Notes - * Average
** Azo-benzene
No reaction was performed at 160° C. and 0 minutes.

Analysis of the original Hoberg Waste Sulphite Liquor

Institute File No. 105178 (Sample b)

- Specific Gravity (20° C.) 1.043
- Total solids (g./liter) 117.0
- Lignin (g./liter) 61.0 (56.7 based on methoxyl)
- Percent of total solids 54.0 (Methoxyl was 7.11 %)

76% methoxyl
March 10, 1942

Dear Mr. Mibble:

Res: Lewis-Pearl Patent
Serial No. 430,620

This will acknowledge receipt of the assignment dated February 7, 1942, from Lewis and Pearl to the Institute, of application for patent on Preparation of Asbestos Sulfamate.

Very truly yours,

Harry F. Lewis
Research Associate

Mr. L. D. Mibble
Scans, Pond & Anderson
2157 Field Building
135 South La Salle Street
Chicago, Illinois

nl/51
REPORT ON REACTION XIII

Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment is a continuation of the study of the reducing action of the original Hoberg waste sulfite liquor at 160° C. This reaction parallels Reaction X, in which the original Mitscherlich liquor was employed for 3 hours at 160° C. [See Book 334 for original reaction; Book 347 gives details of the analyses].

A. Materials used and conditions employed:

Waste sulfite liquor (Hoberg, original 250.0 cc.
(Lignin content: 50.7 g./liter; methoxyl)
Nitrobenzene 45.0 g.
Sodium hydroxide, solid 28.1 g.

Conditions: 3 hours at 160° C.

B. Results:

1. Reduction Products

   Aniline 4.57 g. (13.4 %)
   *Azobenzene 12.4 g. (37.4 %)
   *Azodybenzene 3.0 g. (8.3 %)
   **Sodium azobenzene-p-sulfonate 6.74 g. (13.0 %)

2. Recovered Nitrobenzene 0.0 g. (0.0 %)

3. Vanillin (Based on lignin by methoxyl) (13.2 %)

4. Other substances - The usual, volatile basic substance was observed in a very small quantity.

* The separation of the azobenzene from the azodybenzene was not quantitative. The total solid material was distilled under diminished pressure and the purified material was crystallized from ether, which gave two types of crystals.

** The analysis was similar to that in Reaction XXI, Report 13. The alcohol soluble material is called the sodium azobenzene-p-sulfonate.
Interpretation:

The total reduction products amount to 72.1 per cent, which is higher than the amount of total reduction products in Reaction X (61.9 %). The yields of aniline were comparable but the yields of azobenzene, azoxybenzene and the sodium-azobenzene-p-sulfonate were at somewhat of a variance. In both cases, (Reactions X and XIII) no nitrobenzene was recovered. In both cases, the yields of azobenzene were higher than the yields of azoxybenzene. These facts are in agreement with the observations made under similar reaction conditions with the more concentrated waste sulfite liquors.

The vanillin was checked but the result was no higher than that reported. This value is much lower than that of reaction X.

The comparison of results with the other reactions will be found in Report 19. (To be submitted later.)
REPORT ON REACTION XIV

Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment is a continuation of the study of the reducing action of the original waste sulfite liquor at 160° C. This reaction, which employs the original Hoberg waste sulfite liquor, parallels reaction XI (original Mitscherlich waste sulfite liquor, 30 minutes at 160° C.). [See Book 334 for original reaction; the analysis is found in Book 347.]

A. Materials used and conditions employed:

Waste sulfite liquor (Hoberg, original) 250.0 cc.
(Lignin content: 50.7 g./liter; methoxyl)
Nitrobenzene 45.0 g.
Sodium Hydroxide, solid 28.1 g.

Conditions: 30 minutes at 160° C.

B. Results:

1. Reduction Products

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>3.25 g.</td>
<td>(9.2%)</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>1.9 g.</td>
<td>(5.7%)</td>
</tr>
<tr>
<td>Azoxybenzene</td>
<td>10.6 g.</td>
<td>(29.4%)</td>
</tr>
<tr>
<td>Sodium azobenzene-p-sulfonate</td>
<td>11.66 g.</td>
<td>(22.6%)</td>
</tr>
</tbody>
</table>

2. Recovered Nitrobenzene 6.0 g. (13.3%)

3. Vanillin (Based on lignin by methoxyl) (24.5%)

4. Other substances - The amount of the usual, basic substance was small.

** Analysis was similar to that in Reaction XXI, report 13. The alcohol soluble material is called the sodium azobenzene-p-sulfonate.
Interpretation:

The total reduction products amount to 66.9 per cent. This is in good agreement with the results from the original Mitscherlich liquor (Reaction XI, Report 14), which were 65.6 per cent. The amount of nitrobenzene recovered is much greater in this reaction; 13.3 per cent as compared with 2.7 per cent in Reaction XI. The yield of vanillin may be a little high, by analysis. This value is not in agreement with that of Reaction XI; 24.5 per cent as compared with 16.5 per cent in Reaction XI.

The results, from the standpoint of individual reduction products and the sum total of reduction products with both types of waste liquors, are in good agreement. The presence of a small amount of azobenzene in this reaction was expected. The high value of 22.6 per cent for the alcohol soluble material from the original reaction mixture solids agrees reasonably with the value (19.6 per cent) obtained in the study on the Mitscherlich liquor under the same conditions.

rgb/hk
Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack: Report No. 5 presented the results of Reaction X in which the original Mitscherlich waste sulfite liquor was treated according to the method of Freudenberg, which involved treatment at 160°C for 3 hours. This report presents the results from the determination of the sodium azobenzene-p-sulfonate and a check on the vanillin determination.

I. Sodium azobenzene-p-sulfonate (The alcohol-soluble material from the reaction mixture after steam distillation)

Total weight of solid recovered, dry 5.3 g.  
Corrected to original volume 6.3 g.  

A 2.0 g. sample was extracted with ethyl alcohol:  
The 2.0 g. gave 1.5 g. alcohol-soluble, or 75%  
Total yield of alcohol-soluble: 4.73 g.  
% of sodium azobenzene-p-sulfonate: 9.2 (Based on the nitrobenzene)

II. Vanillin-Check determination.  
Method: Ether and NaHSO₃ extraction and precipitation as the 2,4-dinitrophenylhydrazone  
% Vanillin, based on the lignin: 22.8

Interpretation:  
The result on the sodium azobenzene-p-sulfonate checks the previous results in which the Mitscherlich liquor was employed, with the exception of Reaction XI (Report 14).  
The check on the vanillin shows a high result as compared with that reported by Dr. Pearl (7.27%). In the present determination, special care was used in the extraction processes in order to assure complete extraction.

rb/fi
# Summary of Reactions X, XI, XII, XV, and XVII

Reactions with the original Mitscherlich waste sulfite liquor at 130° C. and 160° C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Vanillin %</th>
<th>Aniline %</th>
<th>Azoxybenzene %</th>
<th>Sodium asobenzene p-sulfonate %</th>
<th>Recovered Nitrobenzene %</th>
<th>Total Red'n. %</th>
<th>Accounted For %</th>
</tr>
</thead>
<tbody>
<tr>
<td>XV</td>
<td>30 min. at 130° C.</td>
<td>12.2*</td>
<td>9.6</td>
<td>17.4</td>
<td>8.6</td>
<td>42.95</td>
<td>35.8</td>
<td>78.6</td>
</tr>
<tr>
<td>XVII</td>
<td>3 hrs. at 130° C.</td>
<td>17.0*</td>
<td>12.2</td>
<td>27.6</td>
<td>9.0</td>
<td>23.6</td>
<td>48.8</td>
<td>72.4</td>
</tr>
<tr>
<td>XII</td>
<td>0 min. at 160° C.</td>
<td>15.9*</td>
<td>11.5</td>
<td>34.6</td>
<td>9.1</td>
<td>16.7</td>
<td>55.2</td>
<td>71.9</td>
</tr>
<tr>
<td>XI</td>
<td>30 min. at 160° C.</td>
<td>16.5</td>
<td>12.2</td>
<td>33.8</td>
<td>19.6</td>
<td>2.7</td>
<td>65.6</td>
<td>68.3</td>
</tr>
<tr>
<td>X</td>
<td>3 hrs. at 160° C</td>
<td>7.2**</td>
<td>14.8</td>
<td>13.8</td>
<td>9.2</td>
<td>0.0</td>
<td>61.9</td>
<td>61.9</td>
</tr>
</tbody>
</table>

* Average  
** Probably in error; 22.8 is a check  
# Azobenzene

Reagents used in each of the above reactions:

- Waste liquor - 250 cc.  
  (Lignin Content: 62.1 g./liter; methoxyl; corrected value)
- Nitrobenzene - 45.0 grams
- NaOH, solid - 28.1 grams
Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment repeats Reaction XII in every detail with the exception that this experiment employs a reaction period of 30 minutes, whereas Reaction XII employed 0 minutes at the same temperature (160° C.). This reaction, with the original Mitscherlich liquor, parallels the Hoberg reaction in Reaction XIV [See Book 334 for details of original reaction; analysis, in 347.]

A. Materials used and conditions employed:

Waste sulfite liquor (Mitscherlich, original) 250.0 cc.
(Lignin content: 62.1 g./liter; methoxyl)
Nitrobenzene 45.0 g.
Sodium hydroxide, solid 28.1 g.
Conditions: 30 minutes at 160° C.

B. Results:

1. Reduction products

Aniline 4.16 g. (12.2%)
Azoxybenzene 12.4 g. (33.8%)
Azobenzene 0.0* g. (0.0%)
**Sodium azobenzene-2-sulfonate 10.0 g. (19.6%)

2. Recovered nitrobenzene 1.2 g. (2.7%)

3. Vanillin 16.5 % (based on lignin from methoxyl)

4. Other substances The amount of the usual, volatile basic substance was smaller.

* Presence expected but was not detected.
** Analysis similar to that in Reaction XXI, report 13. The alcohol-soluble material is called the sodium azobenzene-2-sulfonate.
Interpretation:

The total reduction products amount to 65.6 per cent. The total products accounted for amount to 68.3 per cent. The results are similar to those of Reaction XIII (report 7) with the exception of the amount of recovered nitrobenzene.

The above results will be compared with those of the other reactions in which the Mitscherlich liquor was employed. (Report 15, to follow.)
Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment repeats Reaction XV in every detail with the exception that this experiment employs the original Hoberg (quick cook) liquor in place of Mitscherlich liquor as used in Reaction XV. [See Book 334 for the details of the original reaction; the analysis is given in Book 347.]

A. Materials used and conditions employed:

- Waste sulfite liquor (Robert original)
  - Analysis: Sp. gr. (20°C)
  - Solids: 113.0 g./liter
  - Lignin: 50.7 g./liter
  - Lignin (based on methoxyl): 45.0 g.
  - Nitrobenzene: 28.1 g.

- Sodium hydroxide (solid)

- Conditions: 30 minutes at 130°C.

B. Results:

1. Reduction products
   - Aniline: 2.36 g. (7.0%)
   - Azoxybenzene: 7.1 g. (19.5%)
   - Azobenzene: None
   - Sodium azobenzene-p-sulfonate: 3.8 g. (7.3%) (See 4)

2. Recovered nitrobenzene: 20.1 g. (44.7%)

3. Vanillin: 19.5% (based on lignin from methoxyl)

4. Alcohol-soluble portion from the centrifuged reaction mixture (considered to be sodium azobenzene-p-sulfonate)
   - Total solid residue, dry: 5.9 g.
   - Wt. sample employed: 2.4 g.
   - Alcohol-soluble portion: 1.3 g.
   - Alcohol-insoluble portion: 1.0 g.
   - Total alcohol-soluble (corrected to original volume): 3.8 g.

This represents a yield of 7.3%, based on the original nitrobenzene.
5. Other substances; The presence of a small amount of a volatile basic substance was observed, which is similar to previous observations.

**Interpretation:**

The results of the reduction products agree remarkably with those of the experiment in which the original Mitscherlich liquor was employed under the same conditions (Reaction XV). This agreement is somewhat in contrast with the discrepancies found in the two reactions (XVII and XVIII) as reported in report 11 at 130°C for 3 hours. A comparison of the results of the same waste liquor for the reaction time periods of 30 minutes and 3 hours, shows the same general trends for both the Mitscherlich and Hoberg liquors. The vanillin yields are not in line, and it is to be pointed out that the aniline yields for the Hoberg liquor are both low.

The results for both liquors are given below (30 minutes at 130°C) for comparison.

<table>
<thead>
<tr>
<th></th>
<th>(Mitscherlich)</th>
<th>(Hoberg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction XV</td>
<td>Reaction XXI</td>
</tr>
<tr>
<td>1. Reduction products (tot.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Not including the sodium azobenzene-p-sulfonate)</td>
<td>27.0</td>
<td>26.6</td>
</tr>
<tr>
<td>Sodium azobenzene-p-sulfonate</td>
<td>8.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Aniline</td>
<td>9.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Azoxybenzene</td>
<td>17.4</td>
<td>19.6</td>
</tr>
<tr>
<td>2. Recovered nitrobenzene</td>
<td>42.95</td>
<td>44.7</td>
</tr>
<tr>
<td>3. Vanillin</td>
<td>12.1 (Av.)</td>
<td>19.5</td>
</tr>
<tr>
<td>4. Other substances</td>
<td>Presence of small amount of a volatile basic substance observed in both cases. (Not identified)</td>
<td></td>
</tr>
</tbody>
</table>

rb/fl
Report on Isolation of Crystalline Material from Residues of Reactions XII, XV, XVII, and XVIII.

Objective: A study of the alkali-insoluble residues and the estimation of the amount of crystalline material in them. [This material is believed to be the sodium salt of azobenzene-p-sulfonic acid; as per telephone call of Dr. Lewis and Dr. Pearl of December 15, 1941.]

Mode of Attack: The reaction mixture was centrifuged and the solid washed with 5 per cent sodium hydroxide, centrifuged again and heated in an oven at 107°C until completely dry. A weighed quantity was extracted with alcohol until no more dissolved, and this alcohol-soluble substance was considered to be the sodium azobenzene-p-sulfonate.

Results:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total Solid Residue</th>
<th>% Yield Based on Nitrobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry g.</td>
<td>Alcohol Soluble g.</td>
</tr>
<tr>
<td>XII</td>
<td>9.8*</td>
<td>1.2</td>
</tr>
<tr>
<td>XV</td>
<td>8.8*</td>
<td>1.2</td>
</tr>
<tr>
<td>XVII</td>
<td>12.0*</td>
<td>1.0</td>
</tr>
<tr>
<td>XVIII</td>
<td>9.4*</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Corrected weight on basis of material used for the vanillin determinations. **Considered to be the sodium salt of azobenzene-p-sulfonic acid.

Key to Reactions:

- XII -- Original Mitscherlich, 0 min. at 160°C.
- XV -- Original Mitscherlich, 30 min. at 130°C.
- XVII -- Original Mitscherlich, 3 hr. at 130°C.
- XVIII -- Original Hoberg, 3 hr. at 130°C.

Interpretations: The total solid, in each case, was found to be a mixture of crystalline and noncrystalline substances. The alcohol-
soluble substance was distinctly crystalline and definitely of uniform composition. The insoluble material gave qualitative tests for calcium and carbonate. It is probably a mixture of calcium carbonate and calcium hydroxide.

The alcohol-soluble substance was considered to be the sodium salt of azobenzene-p-sulfonic acid. The total yield was calculated for each reaction mixture and the percentage yield, based on the amount of nitrobenzene in the original reaction. The results of the total amounts of reduction products (from report 11) are given below, together with the results given herein:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total Reduction (Report 11)</th>
<th>Sodium Azobenzene-p-sulfonate</th>
<th>Total Reduction</th>
<th>Total Products Etc. Accounted For</th>
</tr>
</thead>
<tbody>
<tr>
<td>XII</td>
<td>46.1</td>
<td>9.1</td>
<td>55.2</td>
<td>71.9</td>
</tr>
<tr>
<td>XIV</td>
<td>27.0</td>
<td>8.6</td>
<td>35.6</td>
<td>78.6</td>
</tr>
<tr>
<td>XVII</td>
<td>39.8</td>
<td>9.0</td>
<td>48.8</td>
<td>72.4</td>
</tr>
<tr>
<td>XVIII</td>
<td>31.6</td>
<td>10.6</td>
<td>42.2</td>
<td>76.7</td>
</tr>
</tbody>
</table>

rb/fl
The result reported in report 10 for aniline was recognized as a low value and a check on the result was to be reported later. This result cannot be reported since an untimely accident resulted in the loss of the aniline in the last stage of the checking process. In the actual process of isolating the aniline, there was reasonable evidence that the yield of aniline would be higher than that reported previously, namely, 5.9 per cent. The analysis of Reaction XIII (Hoberg, original, 3 hours at 160° C.) will offer some help, it is believed, in answering the question concerning the low yield of aniline in this reaction.
### SUMMARY OF REACTIONS XII, XV, XVII, AND XVIII

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Conditions</th>
<th>Aniline</th>
<th>Vanillin</th>
<th>Azoxybenzene</th>
<th>Recovered Nitrobenzene</th>
<th>Total Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>XII</td>
<td>250 cc. w. liquor (Mitscherlich orig.)</td>
<td>0 min. at 160°C</td>
<td>11.5%</td>
<td>15.7%</td>
<td>34.6%</td>
<td>16.7%</td>
<td>46.1%</td>
</tr>
<tr>
<td></td>
<td>45.0 g. nitrobenzene</td>
<td>28.1 g. NaOH, solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XV</td>
<td>DITTO</td>
<td>30 min. at 130°C</td>
<td>9.6%</td>
<td>12.4%</td>
<td>17.4%</td>
<td>42.95%</td>
<td>27.0%</td>
</tr>
<tr>
<td>XVII</td>
<td>DITTO</td>
<td>3 hr. at 130°C</td>
<td>12.2%</td>
<td>16.0%</td>
<td>27.6%</td>
<td>23.6%</td>
<td>39.8%</td>
</tr>
<tr>
<td>XVIII</td>
<td>250 cc. w. liquor (Hoberg orig.)</td>
<td>3 hr. at 130°C</td>
<td>*5.9%</td>
<td>15.8%</td>
<td>25.7%</td>
<td>34.5%</td>
<td>31.6%</td>
</tr>
<tr>
<td></td>
<td>45.0 g. nitrobenzene</td>
<td>28.1 g. NaOH, solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freudenberg (Ber. 73, 167(1949))</td>
<td>3 hr. at 130°C</td>
<td>No report 18.5-20.0</td>
<td>Detected</td>
<td>No report</td>
<td>No report</td>
<td></td>
</tr>
</tbody>
</table>

*To be checked.*

rub/fl Copy Main files, Dr. Lewis, Dr. Pearl, Mr. Steele, Dr. Bossert
Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment repeats Reaction XVII in every detail with the exception that this experiment employs the original Hoberg (Quick Cook) liquor, whereas the Mitscherlich liquor is employed in Reaction XVII. (See book 334 for the details of the reaction; the analysis is given in book 347).

A. Materials used and conditions employed:

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste sulfite liquor (Hoberg original)</td>
<td>250.0 cc.</td>
</tr>
<tr>
<td>Analysis: Sp. gr. (20° C.)</td>
<td>1.048</td>
</tr>
<tr>
<td>Solids</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>113.0 g./liter</td>
</tr>
<tr>
<td>Lignin (based on methoxyl)</td>
<td>61.0 g./liter</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>50.7 g./liter</td>
</tr>
<tr>
<td>Sodium hydroxide (solid)</td>
<td>45.0 g.</td>
</tr>
</tbody>
</table>

Conditions: 3 hours at 130° C.  
(Actually: 3 hours at 127-134° C.)

B. Results:

1. Reduction products

   - Aniline: 2.0 g. (5.9 per cent)
   - Azoxybenzene: 9.3 g. (25.7 per cent)
   - Azobenzene: None

   *(To be checked; this result may be in error.)*
   ***(May be low, if not all steam distilled.)*

2. Recovered nitrobenzene: 15.5 g. (34.5 per cent)

3. Vanillin: 15.8 % (based on lignin 14.6 % from methoxyl)

4. Other substances: None isolated. The usual small amount of volatile base was observed at the beginning of the steam distillation.
Interpretation:

The results show certain agreement with those of Reaction XVII and, at the same time, certain disagreement. The kinds of products formed and the nature of the reactions were the same. The yields of azoxybenzene and vanillin showed reasonable agreement. The discrepancies are found in the total quantities of reduction products, the aniline yields and the amounts of nitrobenzene recovered. The following tabulated results are given for comparison:

<table>
<thead>
<tr>
<th></th>
<th>Reaction XVII</th>
<th>Reaction XVIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Reduction products (total)</td>
<td>39.8</td>
<td>31.6</td>
</tr>
<tr>
<td>Aniline</td>
<td>12.2</td>
<td>15.9</td>
</tr>
<tr>
<td>Azoxybenzene</td>
<td>27.6</td>
<td>25.7</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2. Recovered nitrobenzene</td>
<td>23.6</td>
<td>34.5</td>
</tr>
<tr>
<td>Vanillin</td>
<td>16.9</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>17.9</td>
<td>14.6</td>
</tr>
<tr>
<td>4. Other substances: In both cases, a small amount of an unidentified, volatile basic substance was observed.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>(The yield of aniline is out of line and is to be checked. This will be reported later.)</em></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A comparison of the analyses of the waste sulfite liquors should be considered in view of the above results:

<table>
<thead>
<tr>
<th></th>
<th>Mitscherlich (Orig.) (File No. 104747)</th>
<th>Hoberg (Orig.) (No. 105178)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids, total, g./l.</td>
<td>142</td>
<td>113</td>
</tr>
<tr>
<td>Sp. gr. (20° C.)</td>
<td>1.064</td>
<td>1.045</td>
</tr>
<tr>
<td>Methoxyl</td>
<td>7.95%</td>
<td>7.41%</td>
</tr>
<tr>
<td>Lignin g./l. (Orig. was 83.0); repeat</td>
<td>70.0</td>
<td>61.0</td>
</tr>
<tr>
<td>Lignin, on methoxyl, g./l.</td>
<td>62.1</td>
<td>50.7</td>
</tr>
</tbody>
</table>

The difference in lignin content of the two waste sulfite liquors may be significant in consideration of the amounts of reduction products as well as the amounts of recovered nitrobenzene.

Copy Main files, Dr. Lewis, Dr. Pearl, Mr. Steele, Dr. Bossert
Objective:

The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack:

This experiment repeats the work of Freudenberg in detail with the exception that the total quantities are smaller (but proportional) and the conditions are 30 minutes at 130°C in place of the 3 hours at 160°C. (See book 334 for details of the reaction; the analysis is given in book 347).

A. Materials used and conditions employed:

- Waste sulfite liquor (Mitscherlich, original) 250.0 cc. (Lignin content is 62.1 g./liter)
- Nitrobenzene 45.0 g.
- Sodium hydroxide (solid) 28.1 g.

Conditions: 30 minutes at 130°C. (Actually: 30 min. at 127-137°C.)

B. Results:

1. Reduction products

   - Aniline 3.3 g. (9.6 per cent)
   - Azobenzene None
   - Azoxybenzene *6.3 g. (17.4 per cent)

   *(Probably low, if not all steam distilled)

2. Recovered nitrobenzene 19.3 g. (42.95 per cent)

3. Vanillin 12.4 per cent

   (Vanillin is based on lignin)

4. Other substances: None isolated. It may be desirable to determine vanillic acid. A small amount of a volatile, basic substance was detected at the beginning of the steam distillation; not identified.
Interpretation:

The results of this experiment are best interpreted in comparison with reaction XVII (Mitscherlich liquor at 130°C for 3 hours; Report 8) and reaction XXI (Zoberg liquor under the same conditions; not analyzed as yet).

In this experiment the total yield of reduction products is 27.0 per cent. The percentage of recovered nitrobenzene is 42.95, and the total percentage of substances accounted for is 69.95. The results of this experiment show that the production of aniline, the total amount of reduction products and the production of vanillin are all lower than the amounts of the same substances produced at the same temperature and a longer reaction time (Reaction XVII-3 hours at 130°C). This is substantiated by the fact that the recovery of unreacted nitrobenzene was greater in this reaction.

A summary of the results of this reaction, together with a comparison of the results of the corresponding reactions, will be given later.
OBJECTIVE
A study of the reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK
See Report 5. This experiment attempted to repeat the work of Freudenberg in detail and to give a report on all substances formed in reasonable amounts.

A. Materials and conditions: The Mitscherlich liquor (orig.) (250 cc.) was used with 28.1 g. of NaOH and 45.0 g. of nitrobenzene. The reaction conditions were 3 hours at 160°C.

B. Results
1. Reduction products
   Aniline       5.0 g. (14.5%) Reported previously
   Azobenzene   8.0 g. (24.1%) Reported previously
   Azoxybenzene *5.0 g. (13.8%)
*(Probably low)

2. Recovered nitrobenzene — None

3. Vanillin    **7.27 (As determined by Dr. Pearl)
   **(This value appears to be unusually low)

4. Other substances — Azoxybenzene is reported above. No other substances were identified.

INTERPRETATION
The total yield of reduction products is 52.7 per cent. The fact that no nitrobenzene was recovered suggests again that certain substances are unaccounted for. The results of more recent analyses suggest the possibility that the incomplete recovery of azoxybenzene may be responsible, at least in part, for this repeated discrepancy.

The yellow oil, reported in the previous report, was found to be azoxybenzene.

The report on vanillin is unusually low and suggests the desirability of investigation; either from the standpoint of the analysis or a repeated reaction.
OBJECTIVE
The reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK
This experiment repeats the work of Freudenberg in detail with the exception that the total quantities are smaller (proportional, however) and the conditions are 3 hours at 130° C. (See book 334 for details of reaction.)

A. Materials used and conditions employed:
- Waste sulfite liquor (Mitscherlich, orig.) 250 cc. (Lignin content is 62.1 g./liter)
- Nitrobenzene -- 45.0 g.
- Sodium hydroxide (solid) -- 28.1 g.
- Conditions -- 3 hours at 130° C. (Actually 3 hours at 129-131° C.)

B. Results:
1. Reduction products
   - Aniline 4.17 g. (12.2 per cent)
   - Azobenzene 0.0 (None)
   - Azoxybenzene *10.0 g. (27.6 per cent)
   *(Probably low)
2. Recovered nitrobenzene 10.6 g. (23.6 per cent)
3. Vanillin 16.0 per cent
   17.9 per cent
4. Other substances -- Incomplete at present. It is hoped to determine vanillic acid. A small amount of a volatile, basic substance was observed at the beginning of the steam distillation but its identity was not established.
INTERPRETATION

The results show reasonable agreement with those of Freudenberg. Azoxybenzene is reported, no azobenzene is reported and the vanillin yields are comparable.

The total yield of reduction products is 39.8 per cent. The total per cent of substances accounted for is 63.4. These values are not greatly out of line with the results of Reaction XII (0 minutes at 160° C.) although it will be better to compare the above results with other reactions at 150° C. Since it is believed that some of the azoxybenzene remains behind, upon steam distillation, the results may show closer agreement. The remaining azoxybenzene is to be determined on the alkaline reaction mixture.

The yield of aniline checks the yields of aniline previously reported on reactions in which the 10 per cent NaOH was employed with the given waste liquor (Reactions V, VI, and X, XII).

The results of this reaction will be interpreted better in the light of other reactions at 150° C. (to follow).

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Dr. Lewis
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Dr. Bossert
OBJECTIVE

The reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK

This experiment repeats the work of Freudenberg in detail with the exception that the total quantities are smaller and the time is zero minutes instead of 3 hours.

A. Materials used and conditions employed:

Waste sulfite liquor (Mitscherlich, orig.) 250 cc. (Lignin content is 62.1, based on methoxyl)

Nitrobenzene -- 45.0 g.

Sodium hydroxide (solid) -- 28.1 g.

Conditions: 0 minutes at 1600° C. (See book 334 for details)

B. Results:

1. Reduction products

   Aniline 3.9 g. (11.5 per cent)
   *Azoxybenzene 12.5 g. (34.6 per cent)
   Azobenzene 0.0 g. (None detected)

   *(Probably low)

2. Recovered nitrobenzene 7.5 g. (16.7 per cent)

3. Vanillin 15.7 per cent (based on lignin from methoxyl)

   16.1 per cent (also lignin from methoxyl)

4. Other substances -- Incomplete at present. A small amount of a volatile, basic substance was indicated in steam distillation.
The results show reasonable agreement with those of Freudenberg. The vanillin results probably are somewhat low. The presence of azoxybenzene substantiates the report of Freudenberg also.

The total yield of reduction products is 46.1 per cent. The total per cent of substances accounted for is 62.8. (This includes the recovered nitrobenzene). This leaves the usual per cent of substances unaccounted for; however, this may be explained, in part at least, to the undetermined amount of azoxybenzene which does not distill over with steam. This is to be determined separately on the alkaline reaction mixture.

In this reaction, no azobenzene was detected, which is different from previous reactions. The presence of azobenzene was found to be characteristic of those reactions in which the concentrated waste liquor was used (Report 3). It was found to be present in Reaction X (Mitscherlich under the same conditions as this reaction with the exception that the time in Reaction X was 3 hours). This difference may be due to the difference in time employed for the reaction. In Reaction X, 3 hours at 150° C., a yield of azobenzene was 24.1 per cent, with only a yield of azoxybenzene of 13.8 per cent. Later reports may clarify this difference.

The yield of aniline (11.5 per cent) is comparable to the yields of aniline in previous reactions in which the 10 per cent NaOH was employed (Reactions V, VI, and X).

These results substantiate the previous conclusions (report 3) that higher percentages of reduction products result from the more concentrated liquor and the larger quantities of NaOH. At the same time, however, the yields of vanillin are lower. This suggests the desirability of determining the exact conditions which will give maximum yields of reduction products and vanillin.

No conclusion about the difference in reaction time should be made until the completion of the analyses of the later reactions.

Copy to Main files
Dr. Lewis
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Dr. Bossert
Preliminary Report on Reaction XII

Objective: The reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack

This experiment repeats the work of Freudenberg in detail with the exception that the total quantities are smaller and the time is zero minutes instead of 3 hours.

A. Materials used and conditions employed:

- Waste sulfite liquor (Mitscherlich, orig.) 250 cc.
  (Lignin content is 62.1, based on methoxyl)
- Nitrobenzene 45.0 g.
- Sodium hydroxide 23.1 g. (solid)
- Conditions 0 minutes at 160° C.

B. Results:

1. Reduction products

- Aniline 3.9 g. (11.5 per cent)
- Azoxybenzene Undetermined as yet but indicated to be present.
- Azobenzene Presence doubted

2. Recovered nitrobenzene Undetermined

3. Vanillin 15.7 per cent (based on lignin from methoxyl)

4. Other substances Undetermined

Interpretation

The results thus far show reasonable agreement with those of Freudenberg. Freudenberg reported vanillin yields from 17.7 to 20.0 per cent. The value above is a minimum rather than a maximum. It is being checked at present.
The yield of aniline (11.5 per cent) is comparable to the yields of aniline in previous reactions (V and VI) in which concentrated sulfite waste liquor was used and the percentage of NaOH was the same (10 per cent). Azobenzene, although not indicated in this reaction unless in very small amounts, was found to be one of the reaction products in V and VI. (Report 3).

These results substantiate the previous conclusions (report 3) that higher percentages of reduction products result from the more concentrated liquor and larger quantities of NaOH. At the same time, however, the yield of vanillin is much lower. This suggests the desirability of determining the exact conditions which will give maximum yields of reduction products and vanillin.

The results indicate, again, that the three hour heating period at 1600 C. is unnecessary. This suggests that the completion of the reaction has been accomplished much sooner. The time requirement, as well as the temperature one, will be reported later.
The Use of Sulfite Waste Liquor as a Reducing Agent

The reducing action of sulfite waste liquor has been known for a great many years. Sulfite waste liquor and its chief component, calcium lignosulfonate, have been oxidized by a large number of inorganic oxidizing agents, among which are the following: nitric acid, sodium hydroxide, potassium hydroxide, potassium permanganate, dichromates, hydrogen peroxide, oxides of copper, silver, chlorates, chlorites, chloric, ozone, mercury, cobalt, manganese, and curium, oxygen in the presence of catalysts, etc. Recently the oxidation of sulfite waste liquor with a mild organic oxidizing agent, namely, nitrobenzene, was reported by Freudenberg, Loescher, and Engler [Z. Phys. 71, 187 (1930)] and by Schulte [J. Am. P. 2, 357, 365 (1930)].

In all these experiments emphasis was placed upon the oxidation products of the lignosulfonate or waste liquor and the reduction of the oxidizing agent escaped unnoticed.

The present national emergency and shortage of vital materials has changed this picture. There is a definite shortage of the widely used reducing agent, zinc, and there is a great need for a cheap reducing agent. The possible use of sulfite waste liquor to replace zinc in certain organic reduction processes would be of great value to both the sulfite pulp industry and to the organic reduction industry. The simultaneous oxidation of the sulfite waste liquor to form good yields of valuable organic materials such as vanillin would be a further advantage of processes involving the use of sulfite waste liquor as a reducing agent.

Because the reduction of nitrobenzene with sulfite waste liquor was known, it was decided to use nitrobenzene as the substrate in the first quantitative studies of waste liquor as a reducing agent. Dr. Dessart treated calcium lignosulfonate and sulfite waste liquor with sodium hydroxide and nitrobenzene under conditions similar to those used by Freudenberg, Loescher, and Engler. The effects of varying conditions of concentration ratio, time of reaction, and temperatures of reaction on the yields of vanillin and reduction products of nitrobenzene were determined for the pressure treatment of nitrobenzene with an alkaline sulfite waste liquor solution.

All of Dr. Dessart's reactions were carried out in the same manner, which is illustrated by the following example:
### Materials Used

- Sulfite waste liquor: 64.0 oz. (contains 266 g. lignin/liter)
- Nitrobenzene: 60.0 oz. (72.0 g.)
- Sodium hydroxide: 15.0 g.
- Water: 100.0 oz.

The sodium hydroxide was dissolved in water, mixed with the sulfite waste liquor, and introduced into the stainless steel reaction tube along with the nitrobenzene. The tube was sealed, and with continuous rocking, the temperature of the mixture was increased to 150° within 55 minutes and then heated at 155-160° C. for three hours. The heat was shut off and the tube remained in the shaker for one hour. The tube was cooled to room temperature with tap water, the contents removed, and the mixture subjected to steam distillation. The aqueous steam distillate was acidified with hydrochloric acid to dissolve the basic substances which were then separated mechanically from the acid-insoluble material. The vanillin was recovered by acidifying the alkaline residue from steam distillation and extraction with an organic solvent. The basic substance (aniline) was recovered from the acid steam distillate by adding alkaline, extracting with ether, and distilling. The solid neutral substance (nitrobenzene) was filtered and recrystallized from dilute ethyl alcohol.

A summary of Dr. Ressert's experiments is given in Table I which tabulates the materials used, conditions of the experiments, and the results obtained, together with the work of Freundenberg.

Aniline was determined according to Rubin and Shriver [Chem. Abst. 26, 1270 (1932)] by titrating at a low temperature an aliquot of the acid steam distillate with standard sodium nitrite solution to an end point using potassium iodide-starch paper as an indicator. Yields were reported as percentage theoretically possible from the quantity of nitrobenzene used.

Vanillin was determined by the following method: One-tenth aliquot of the original alkaline residue from steam distillation was

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The sulfite waste liquor used in all of these experiments was a Mitscherlich liquor obtained from Interlake. It had the following analysis:

- Specific gravity (20° O.): 1.064
- Total solids: 182.0 g./liter
- Methoxyl of solids: 7.65 per cent
- lignin (from methoxyl): 6.2 g./liter

The concentrated liquor was made from this original material, and its lignin content was calculated from its total solids content which was 658 g./liter.
acidified with sulfuric acid and repeatedly extracted with ether until
the ether extract appeared colorless (10 to 15 times). The combined
ether extracts were treated with ten separate portions of 5 per cent
sodium bisulfite solution. The combined bisulfite solutions were freed
from sulfur dioxide by warming in the presence of acid and the resulting
acid mixture treated with an excess of an aqueous solution of
2,4-dinitrophenyl hydrazine. The mixture was warmed on the steam plate
for 1/2 hour and allowed to stand overnight. The precipitated vanillin-
2,4-dinitrophenylhydrazone was filtered through a weighed crucible,
dried, and weighed. Yields were calculated as percentage of lignin.
The lignin values of the sulfite waste liquors were determined from
methoxyl values, total solids of liquor, and the known methoxyl content
of spruce wood lignin.

Asbenzene was determined by weighing the recrystallized solid
which separated when the steam distillate was cooled. It was reported
as percentage theoretical of the nitrabenzenes used.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Conditions</th>
<th>Antipyrine</th>
<th>Asphenone</th>
<th>Thiourea</th>
<th>Total</th>
<th>Reduction</th>
<th>Nitrocresol</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsdick, Lentsch, Bayern [Ber. 71, 167 (1938)]</td>
<td>Purified calcium lignosu lignosulfonate sol. a. (3.5% lignin) Nitrobenzene 72 g. Sodium hydroxide 45 g.</td>
<td>3 hr, at 150°</td>
<td>Not report</td>
<td>Not report</td>
<td>12.5-20%</td>
<td>Not report</td>
<td>Not report</td>
<td>18.5%</td>
<td>None</td>
</tr>
</tbody>
</table>

### III

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Conditions</th>
<th>Antipyrine</th>
<th>Asphenone</th>
<th>Thiourea</th>
<th>Total</th>
<th>Reduction</th>
<th>Nitrocresol</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite waste</td>
<td>Liquor (25.6% lignin)</td>
<td>3 hr, at 155-160°</td>
<td>9.6 g.</td>
<td>23.1 g.</td>
<td>1.6</td>
<td>71.0%</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene 72 g.</td>
<td>Sodium hydroxide 45 g.</td>
<td>100 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### IV

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Conditions</th>
<th>Antipyrine</th>
<th>Asphenone</th>
<th>Thiourea</th>
<th>Total</th>
<th>Reduction</th>
<th>Nitrocresol</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite waste</td>
<td>Liquor (25.6% lignin)</td>
<td>3 hr, at 155-161°</td>
<td>13.5 g.</td>
<td>23.1 g.</td>
<td>---</td>
<td>69.2%</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene 72 g.</td>
<td>Sodium hydroxide 45 g.</td>
<td>120 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### V

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Conditions</th>
<th>Antipyrine</th>
<th>Asphenone</th>
<th>Thiourea</th>
<th>Total</th>
<th>Reduction</th>
<th>Nitrocresol</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite waste</td>
<td>Liquor (25.6% lignin)</td>
<td>3 hr, at 155-161°</td>
<td>13.5 g.</td>
<td>23.1 g.</td>
<td>1.6</td>
<td>23.25</td>
<td>27.6 g.</td>
<td>(32.6%)</td>
</tr>
<tr>
<td>Nitrobenzene 72 g.</td>
<td>Sodium hydroxide 23.2 g. (in 10% soln.)</td>
<td>120 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### VI

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Conditions</th>
<th>Antipyrine</th>
<th>Asphenone</th>
<th>Thiourea</th>
<th>Total</th>
<th>Reduction</th>
<th>Nitrocresol</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite waste</td>
<td>Liquor (25.6% lignin)</td>
<td>3 hr, at 155-162°</td>
<td>13.5 g.</td>
<td>23.1 g.</td>
<td>1.6</td>
<td>23.25</td>
<td>27.6 g.</td>
<td>(32.6%)</td>
</tr>
<tr>
<td>Nitrobenzene 72 g.</td>
<td>Sodium hydroxide 23.2 g. (in 10% soln.)</td>
<td>120 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued on page 5)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Conditions</th>
<th>Aniline</th>
<th>Acon benzene</th>
<th>Vanillin</th>
<th>Reduction</th>
<th>Nitrobenzene Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII</td>
<td>Sulfite waste liquor (29.3% lignin) Nitrobenzene Sodium hydroxide Water</td>
<td>1 hr. at 160°</td>
<td>14.1 g.</td>
<td>22.1 g.</td>
<td>7.5%</td>
<td>67.4%</td>
<td>None</td>
</tr>
<tr>
<td>VIII</td>
<td>Sulfite waste liquor (29.3% lignin) Nitrobenzene Sodium hydroxide Water</td>
<td>3 hr. at 156-162°</td>
<td>12.6 g.</td>
<td>25.1 g.</td>
<td>4.1%</td>
<td>70.2%</td>
<td>None</td>
</tr>
<tr>
<td>(Identical with IV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>Sulfite waste liquor (6.3% lignin) Nitrobenzene Sodium hydroxide Water</td>
<td>3 hr. at 158-161°</td>
<td>3.0 g.</td>
<td>5.0 g.</td>
<td>7.3%</td>
<td>35.9%</td>
<td>15.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>IX*</td>
<td>Sulfite waste liquor (29.3% lignin) Acon benzene Sodium hydroxide Water</td>
<td>3 hr. at 156-162°</td>
<td>11.7 g.</td>
<td>M.1%</td>
<td>2.1%</td>
<td>15.3%</td>
<td>Recovered acon benzene 33.49 (60.0%)</td>
</tr>
</tbody>
</table>

*Reaction IX was made to determine whether the large quantities of acon benzene produced in the pressure reduction of nitrobenzene with alkaline sulfite waste liquor could further be reduced to aniline by alkaline waste liquor.

A number of other substances in minute quantities were separated but were not identified.
DISCUSSION

From the data of Table I it is evident that in the pressure reduction of nitrobenzene with alkaline sulfite waste liquor the use of concentrated sulfite liquor with comparatively large amounts of sodium hydroxide results in the production of larger quantities of reduction products. This is shown in a comparison of the results obtained in Reactions IV, VII, and VIII with those obtained in Reactions V and VI. The reasonable agreement of the aniline yields, as well as the total amounts of reduction products, is apparent. Reactions V and VI (in which less sodium hydroxide was used) suggests little difference due to the presence or absence of water under the conditions of the experiments. The yields of anilines in V and VI are higher than the yields of anilines—a fact that is different from the other reactions. Aniline and anisobenzene were the only identified reduction products of nitrobenzene.

Reaction VII, in which the time factor was changed from three to one hour, shows little difference in the total reduction and the amounts of aniline and anisobenzene produced. This fact indicates that in the pressure reduction of nitrobenzene with sulfite waste liquor the longer reaction time is unnecessary.

It is surprising the vanillin yields are so low. However, the data of reactions VII and IX indicate that the vanillin yields are higher when less drastic conditions are used, i.e., less time and lower concentration of alkali.

The cause for the unaccounted 30 per cent of reduction products has not been found. This value was found to be greater in those reactions in which less sodium hydroxide was used (V and VI).

In Reaction IX the amount of reduction of anisobenzene by sulfite waste liquor is surprisingly small. This fact may help to explain the comparatively large amounts of anisobenzene to aniline in previous similar reactions.

FURTHER WORK

A series of experiments to be reported later were performed by Dr. Bussart in which the work of Freundenberg, Lautsch, and Engler was repeated with varying conditions of the time of reaction and the temperature of reaction. The series included the original Interlake (Kitscherlich) liquor and the original quick cook liquor from Haberg. The quantities employed were proportional to those of Freundenberg, Lautsch, and Engler. One reaction was included which employed the concentrated Haberg liquor. The conditions and quantities were similar to those employed in the previous reactions with the concentrated Kitscherlich liquor (Reactions IV to IX).
In addition to the reduction studies at high pressures, it was desired to study the reduction of nitrobenzene with sulfite waste liquor at atmospheric pressure.

The sulfite waste liquor used in this series of experiments was the same Mitscherlich liquor (Interlake) as that used in the earlier pressure reduction studies. The concentrated liquor was also the same. All reductions were performed in the same manner and were identical except for their time of reaction. The same methods of separation were used for the products of reaction in all cases. An example of a reduction experiment is here illustrated:

| Sulfite waste liquor (286 g. lignin/liter) | 126 cc. |
| Nitrobenzene | 60 cc. (72 g.) |
| Sodium hydroxide | 45 g. |
| Water | 123 g. |

The sulfite waste liquor was placed in a three-neck flask of one liter capacity. The flask was fitted with a reflux condenser and a mechanical stirrer under a mercury seal. The stirrer was started and the sodium hydroxide dissolved in the water was added. The flask was stoppered with a rubber stopper carrying a thermometer which reached below the surface of the reaction mixture. The nitrobenzene was then added slowly through the top of the condenser with constant stirring. The temperature due to the reaction rose to 50-70°C. The flask was placed upon a sand bath heated with an electric hot plate. The hot plate was turned on, and the mixture was brought to a gentle boil in a period of approximately one hour. The temperature rose to 103-105°C. Boiling and stirring was continued for the length of time of the experiment, and then the reaction mixture was allowed to cool with stirring. When cool, the mixture was transferred to an apparatus for steam distillation and steam-distilled until no oily material came over with the steam.

The steam distillate was acidified with dilute hydrochloric acid to dissolve the aniline formed. The acid steam distillate was then extracted with ether to remove the unreduced nitrobenzene and the acenaphthene which was volatile with steam. Aniline was determined in the acid aqueous layer by the method of Sabalitschek and Schrader which was described earlier in this report. The unreduced nitrobenzene and the acenaphthene were determined by distilling the ethereal extract under reduced pressure and weighing the pure compounds directly. However, part of the acenaphthene was recovered from the residue from steam distillation.

The vanillin was recovered from the alkaline residue from steam distillation. An aliquot portion (1/10) was acidified with dilute sulfuric acid and repeatedly extracted with ether until the ether extract was colorless (10 to 15 times). The ether solution was repeatedly shaken out with a 5 per cent sodium bicarbonate solution to remove the acidic substances and then with 5 per cent sodium hydroxide
solution. The sodium hydroxide solution containing the vanillin and any other phenolic substances was acidified with hydrochloric acid, filtered, warmed on the steam plate, and treated with an excess of an aqueous solution of 2,4-dinitrophenylhydrazine. The vanillin-2,4-dinitrophenylhydrzone precipitated immediately. The mixture was digested on the steam bath for one-half hour and allowed to stand overnight. The brick red dinitrophenylhydrzone was filtered through a weighed Filtered glass crucible, dried at 105°C, and weighed. The vanillin was calculated from the weight of the vanillin-2,4-dinitrophenylhydrzones (factor = 0.55). The results of the reductions carried out at atmospheric pressure are given in Table II. A number of oxidation products of lignin, such as acetic acid, oxalic acid, vanillic acid, have been separated in small quantities but have not been included in this table. In addition, a number of products have been separated which have not been identified.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagent</th>
<th>Conditions</th>
<th>Acetone</th>
<th>Aroylbenzens</th>
<th>Vanillin</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-I</td>
<td>Sulfite waste liquor (288 g. lignin/liter)</td>
<td>126 cc.</td>
<td>2 hr. at 103-104°</td>
<td>2.68 g.</td>
<td>5.2 g.</td>
<td>4.39 g.</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzene</td>
<td>72 g.</td>
<td></td>
<td>(4.9%)</td>
<td>(9.0%)</td>
<td>(11.8%)</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>65 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>125 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-II</td>
<td>Sulfite waste liquor (288 g. lignin/liter)</td>
<td>126 cc.</td>
<td>1 hr. at 103-104°</td>
<td>4.29 g.</td>
<td>3.6 g.</td>
<td>4.75 g.</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzene</td>
<td>72 g.</td>
<td></td>
<td>(7.8%)</td>
<td>(6.2%)</td>
<td>(13.1%)</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>65 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>125 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-III</td>
<td>Sulfite waste liquor (288 g. lignin/liter)</td>
<td>126 cc.</td>
<td>5 hr. at 103-104°</td>
<td>5.52 g.</td>
<td>5.6 g.</td>
<td>6.81 g.</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzene</td>
<td>72 g.</td>
<td></td>
<td>(10.0%)</td>
<td>(9.3%)</td>
<td>(17.7%)</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>65 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>125 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-IV</td>
<td>Sulfite waste liquor (217 g. lignin/liter)</td>
<td>167 cc.</td>
<td>7.5 hr. at 103-104°</td>
<td>1.61 g.</td>
<td>17.9 g.</td>
<td>7.93 g.</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzene</td>
<td>72 g.</td>
<td></td>
<td>(6.2%)</td>
<td>(31.8)</td>
<td>(20.7%)</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>65 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>84 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-V</td>
<td>Sulfite waste liquor (52 g. lignin/liter)</td>
<td>200 cc.</td>
<td>5 hr. at 103-104°</td>
<td>0.25 g.</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>Picric acid</td>
<td>20 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide</td>
<td>30 g.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued on page 10)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Conditions</th>
<th>Aniline</th>
<th>Acetobenzene</th>
<th>Vanillin</th>
<th>Nitrobenzene</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-VI</td>
<td>Sulfite waste liquor (62 g. lignin/liter) Nitrobenzene Sodium hydroxide</td>
<td>3.5 hr. at 103-104°C</td>
<td>Trace</td>
<td>7.7 g. (13.3%)</td>
<td>1.85 g. (7.4%)</td>
<td>0.7 g. (0.97%)</td>
<td></td>
</tr>
<tr>
<td>A-VII</td>
<td>Sulfite waste liquor (62 g. lignin/liter) Ortho-ntrophenol Sodium hydroxide</td>
<td>6.5 hr. at 103-104°C</td>
<td>(a)</td>
<td>(d)</td>
<td>g-nitrophenol recovered</td>
<td>75 g. (100%)</td>
<td></td>
</tr>
</tbody>
</table>

(a) This value for acetobenzene is the only complete one in the table. It includes both the acetobenzene which distilled with steam and that which remained with the alkaline residues. The acetobenzene values for the alkaline residues of the other experiments will be determined.

(b) Reduction products of picric acid are in the process of recovery.

(c) No reduction products of g-nitrophenol were found. A complete recovery of the starting material was obtained.

(d) Vanillin of this experiment is in process of determination.
DISCUSSION

It is evident from the data in Table II that at the atmospheric pressure reduction of nitrobenzene with concentrated alkaline sulfite waste liquor that the yields of vanillin increase with time of reaction and the yields of aniline increase with time up to a certain point and then drop off.

The yields of anisobenzene, except for experiment A-IV, are meaningless because they are only that portion of the anisobenzene that distilled with the steam during steam distillation. The largest part of the anisobenzene yields remained in the alkaline residue from steam distillation. This fact probably accounts for the unaccounted for nitrobenzene in these and the earlier experiments. It is surprising that at pressures higher than atmospheric pressure the principal reduction product of nitrobenzene when reduced with alkaline sulfite waste liquor is anisobenzene, but at atmospheric pressure, anisobenzene is not produced even in minute quantities—anisobenzene being the principal product.

Experiment A-VII indicates that the presence of a large quantity of water (from the dilute liquor) drives the reduction of nitrobenzene at atmospheric pressure toward the formation of anisobenzene entirely. Only a trace of aniline was found and only a trace of unreacted nitrobenzene was recovered. 11.3 per cent of anisobenzene was recovered from the steam distillate, and if we draw an analogy from experiment A-IV, we can safely say that a much larger quantity is present in the alkaline residue from the steam distillation. This will be recovered, and Table II will be corrected.

Experiments A-V and A-VII were performed to determine if we could produce such useful products as picric acid (useful in dyes and explosives) from the picric acid and ortho-nitrophenol (useful in photography and dyes) from the ortho-nitrophenol. Both of these compounds are made commercially by mild alkaline reduction. The two experiments tried were arbitrary. The picric acid was completely reduced, but the ortho-nitrophenol was recovered unchanged. The vanillin yield of the ortho-nitrophenol run has not been determined.

FURTHER WORK

All of the above experiments were made with the same sodium lignin, nitrobenzene ratio. Some experiments will be made changing this ratio. The effect of time on the atmospheric pressure reduction of nitrobenzene will be carried along further so that we can determine the best conditions for optimum yields of aniline, anisobenzene, vanillin, or asobenzene. The effect of purity, and dilution with water will also be determined.

The reducing action of sulfite waste liquor on a number of organic nitro compounds now commonly reduced by more expensive reducing agents will be investigated.

In addition to these reductions, when the optimum reducing conditions are determined for nitrobenzene, a large experiment will be performed and the reaction mixture worked up to determine the nature and quantity of all the products formed during the reduction.
MEMORANDUM

FROM: Code Office
TO: Dr. Lewis, cc.
SUBJECT: Samples submitted August 25, 1941

<table>
<thead>
<tr>
<th>Institute File No.</th>
<th>Code No.</th>
<th>Specific Gravity (20°C.)</th>
<th>Total Solids g./l.</th>
<th>Lignin Solids g./l.</th>
<th>% of Total Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>105178</td>
<td></td>
<td>1.048</td>
<td>113</td>
<td>61</td>
<td>54.0</td>
</tr>
<tr>
<td>Sample 4: Original Hoberg Waste Sulfite Liquor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105179</td>
<td></td>
<td>1.196</td>
<td>491</td>
<td>252</td>
<td>51.3</td>
</tr>
<tr>
<td>Sample 5: Concentrated Hoberg Waste Sulfite Liquor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105180</td>
<td></td>
<td>1.202</td>
<td>473</td>
<td>250</td>
<td>52.9</td>
</tr>
<tr>
<td>Sample 6: Concentrated Interlake Waste Sulfite Liquor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Method: 111

* 105178 - Methoxyl; 7.41% 

Basis of Report: Oven Dry 
Method: 18
MEMORANDUM

September 16, 1941
File: 509-1

FROM: Code Office
TO: Dr. Lewis, cc. Dr. Pearl
SUBJECT: Additional data on File No. 104747

Code Number: Sample 1 - Sulfite Waste Liquor

Analysis for: Ash on solids:

\[
\text{Ash} = 11.2\% 
\]

Basis of Report: Oven Dry

Method: 4
OBJECTIVE

A study of the reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK

A series of experiments were performed in which the work of Freudenberg was repeated with varying conditions of the time of reaction and the temperature of reaction. The series includes the original Interlake (Mitscherlich) liquor and the original Quick Cook liquor from Hoberg. The quantities employed are proportional to those of Freudenberg. One reaction is included which employs the concentrated Hoberg liquor. The conditions and quantities are similar to those employed in the previous reactions with the concentrated Mitscherlich liquor (IV-IX).

The series of experiments is listed below. The analysis of the series will be reported later.

<table>
<thead>
<tr>
<th>Type of Liquor</th>
<th>Conditions and Number of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Mitscherlich, original</td>
<td>130° C. 130° C. 160° C. 160° C. 160° C.</td>
</tr>
<tr>
<td></td>
<td>30 min. 3 hrs. 0 min. 30 min. 3 hrs.</td>
</tr>
<tr>
<td></td>
<td>XV XVII XII XI X*</td>
</tr>
<tr>
<td></td>
<td>(* Report No. 5)</td>
</tr>
<tr>
<td>B. Hoberg, Original (Quick Cook)</td>
<td>130° C. 130° C.</td>
</tr>
<tr>
<td></td>
<td>30 min. 3 hrs. 50 min. 3 hrs.</td>
</tr>
<tr>
<td></td>
<td>XXI XVIII XIV XIII</td>
</tr>
<tr>
<td>C. Hoberg, concentrated</td>
<td>160° C. 3 hrs. XI</td>
</tr>
</tbody>
</table>

Quantities (In all reactions except XX)

- Waste sulfite liquor, original
- Nitrobenzene
- Sodium hydroxide

- Reaction XX
- Waste sulfite liquor
- Nitrobenzene
- Sodium hydroxide

250.0 cc. 45.0 g. 28.1 g. 180.0 cc. (Total solids are the same as Reactions IV-IX) 72.0 g. 45.0 g.
OBJECTIVE

A study of the reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK

This experiment is the first in a series of reactions which employs the original waste sulfite liquor and follows the method of Freudenberg [Ber. 73, 169(1940)] in detail. The quantities employed are smaller but are proportional. This results from the use of a small reaction vessel. The present waste sulfite liquor is that of Interlake (Mitscherlich) and is the same liquor from which the concentrated liquor, of previous reactions, was prepared. All analyses were similar to those employed in previous experiments.

Reaction X

A. Materials used and conditions employed.

- Waste sulfite liquor: 250 cc. (21.0 g. lignin)
- Sodium hydroxide: 28.1 g.
- Nitrobenzene: 45.0 g.
- Water: None
- Time of reaction: 3.0 hrs.
- Temperature range: 155-162° C. (Chiefly 158-161° C.)

B. Results

1. Reduction products
   - Aniline: 5.0 g. (14.3%)
   - Azobenzene: 8.0 g. (24.1%)
2. Recovered nitrobenzene: Undetermined as yet
3. Vanilla: To be determined by Dr. Pearl
4. Other substances: The presence of another substance is indicated.

INTERPRETATION

The total yield of reduction products, thus far isolated is 35.9%. The amount of nitrobenzene to be recovered will be small, from all indications. At the same time, either the amount of azobenzene will be increased or a new reduction product will result. Toward the end of the steam distillation, a yellow oil distilled over which appeared to turn to an orange solid. The completion of this observation will be reported later.
OBJECTIVE

A study of the reducing action of waste sulfite liquor on azobenzene.

MODE OF ATTACK

An experiment was performed with the use of azobenzene in a proportional quantity which was equivalent to the nitrobenzene employed in reactions III to VIII, inclusive (report 3). The amounts of waste sulfite liquor (concentrated) and sodium hydroxide, also, were proportional to the amounts used in the previous experiments. The origin of the waste sulfite liquor was the same and the conditions of the experiment were identical with the reactions indicated above.

Reaction IX

A. Materials used and conditions employed.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste sulfite liquor</td>
<td>105.0 cc.</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>89.0 g.</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>37.6 g.</td>
</tr>
<tr>
<td>Water</td>
<td>50.0 cc.</td>
</tr>
<tr>
<td>Time of reaction</td>
<td>3.0 hr.</td>
</tr>
<tr>
<td>Temperature range</td>
<td>156-162° C.</td>
</tr>
</tbody>
</table>

B. Results

1. Reduction products
   - Aniline: 13.7 g. (15.2%)
   - Recovered azobenzene: 53.4 g. (60.0%)*
   - Vanillin: To be determined by Dr. Pearl
   - Other substances: Undetermined at present

* A small amount of the reaction mixture was lost but not sufficient to alter the results seriously.

INTERPRETATION

The amount of reduction of azobenzene by the waste sulfite liquor is surprisingly small and not according to expectation. This fact may help to explain the comparatively large amounts of azobenzene to aniline in previous similar reactions. It is possible that the mixing of the reagents is not as efficient in this reaction as in previous ones.

The aniline yield plus the recovered azobenzene shows a total of 75.2 percent recovery. This is higher, but in reasonable agreement with previous reactions.
OBJECTIVE

A continuation of the study of the reducing-action of waste sulfite liquor on nitrobenzene

MODE OF ATTACK

Following the work described in report 2, a series of five experiments was performed in which the amounts of concentrated waste sulfite liquor and nitrobenzene and the temperature remained constant, while the amounts of sodium hydroxide and water were varied and the time factor was changed. Two of the experiments (reactions IV and VIII) were identical in order to check results.

The waste sulfite liquor employed was the concentrated liquor which was used in reaction III (report 2). The analysis of this liquor is as follows: Sp. g. 1.270 (20° C.); Total solids, 65.8%; Lignin, 39.5%. The original liquor came from Interlake, which was the Mitscherlich liquor.

The amount of lignin was increased fifty per cent over that employed in reaction III. The temperature of the reactions was the same as that in the work of Freudenberg (Ber. 73, 167(1941)); otherwise, the amounts of reagents and the experimental conditions were varied. The manner of the addition of reagents, the working conditions of the reaction tube and the general method of the separation of the reaction products were the same as described in reaction III (report 2). The technique employed in cooling the tube was the same in all experiments. The heat was shut off and the tube remained in the shaker for one hour. It was then cooled under the water tap, to room temperature before opening. The newly adopted methods for the estimation of vanillin and aniline are described below.

The method used in the determination of vanillin was a modified Hibbert method [J. Am. Chem. Soc. 58, 345(1938)], which was suggested by Dr. Pearl. In this method, one-tenth of the original, steam-distilled reaction mixture was extracted with diethyl ether (6-8 times, until no color appeared in the ether layer). The ether extract was treated with ten
separate portions of five per cent sodium bisulphite and combined bi-
sulphite solutions freed from SO$_2$ in the presence of acid. The vani-
llin was then precipitated by 2,4 dinitrophenylhydrazine, filtered,
dried and weighed.

The method of determination of aniline was that of Th. Sabalitschka and
H. Shrader [C. A. 15, 1270(1921)] in which an acid solution of standard
sodium nitrite solution to an end point with starch-iodide paper. A
check on the results obtained by this method and those obtained by the
production of aniline hydrochloride indicated reasonable agreement.

A summary of the materials used, the conditions employed and the results
obtained is given on the following page, together with the work of
Freudenberg and the description of reaction III (described in report 2).
A summary of other products is given also.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagents</th>
<th>Conditions</th>
<th>Aniline</th>
<th>Azobenzene</th>
<th>Vanillin</th>
<th>Reduction</th>
<th>Nitrobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freudenberg</td>
<td>400 cc. waste liquor</td>
<td>3 hours at 160°C</td>
<td>No</td>
<td>No report</td>
<td>18.5-20%</td>
<td>No report</td>
<td>None</td>
</tr>
<tr>
<td>[Ber. 73, 167(1940)]</td>
<td>(Sq. g. 1.05; 5.5% lignin) 72.0 g. nitrobenzene 45.0 g. NaOH, solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>84 cc. waste liquor</td>
<td>3 hours at 155-160°C</td>
<td>9.6 g.</td>
<td>28.1 g.</td>
<td>1%</td>
<td>71.0%</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>(Sp. g. 1.27 at 20°C; 39.5% lignin) 72.0 g. nitrobenzene 45.0 g. NaOH, solid 100 cc. water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>126 cc. waste liquor</td>
<td>3 hours at 158-161°C</td>
<td>13.8 g.</td>
<td>23.3 g.</td>
<td>method</td>
<td>69.2%</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>(Same analysis as III) 72.0 g. nitrobenzene 45.0 g. NaOH, solid 60.0 cc. water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>126 cc. waste liquor</td>
<td>3 hours at 158-162°C</td>
<td>7.3 g.</td>
<td>5.8 g.</td>
<td>1.06%</td>
<td>24.3%</td>
<td>27.8 g.</td>
</tr>
<tr>
<td></td>
<td>(Same analysis as III) 72.0 g. nitrobenzene 23.2 g. NaOH (represents 10% NaOH) No water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>126 cc. waste liquor</td>
<td>3 hours at 158-162°C</td>
<td>7.7 g.</td>
<td>6.4 g.</td>
<td>1.90%</td>
<td>26.1%</td>
<td>21.8 g.</td>
</tr>
<tr>
<td></td>
<td>(Same analysis as III) 72.0 g. nitrobenzene 23.2 g. NaOH (Same as V) 60.0 cc. water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>126 cc. waste liquor</td>
<td>1 hour at 160°C</td>
<td>14.1 g.</td>
<td>22.1 g.</td>
<td>5.45%</td>
<td>67.4%</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>(Same analysis as III) 72.0 g. nitrobenzene 45.0 g. NaOH 80 cc. water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIII*</td>
<td>126 cc. waste liquor</td>
<td>3 hours at 158-162°C</td>
<td>12.6 g.</td>
<td>25.1 g.</td>
<td>2.95%</td>
<td>70.4%</td>
<td>None</td>
</tr>
<tr>
<td>(Identical with IV)</td>
<td>(Same analysis as III) 72.0 g. nitrobenzene 45.0 g. NaOH 60 cc. water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* See page 4.
VIII-A is a repetition of VIII. In reaction VIII, the reaction mixture was lost during the process of steam distillation. The estimation of aniline gave 13.24 g. (24.2%), which checks, both reactions, IV and VIII-A.

OTHER SUBSTANCES

In each of the reactions above (especially, IV, V, VI, VII and VIII), a small amount of an acidic oily substance was isolated from the solvent remaining after the vanillin extraction. The amount, in each case, was small and it was not identified. In reaction VI, an attempt to sublime the material resulted in the distillation of a very small amount of a green, semicrystalline substance.

The reaction mixture of IV, after the removal of vanillin, was hydrolyzed with dilute HCL to determine if aniline were liberated from a condensation type of product. The amount of aniline produced (0.1 g.) was negligible. This fails to explain the remaining thirty per cent of unidentified reduction products.

In reaction VII, an ether extraction of the original basic reaction mixture gave about 0.5 g. of an oil which formed an ether insoluble product with dilute HCL. An ether soluble substance was present also. These substances are to be investigated further.

In all reactions involving concentrated sulfite waste liquor, a basic substance with a strong odor of an amine was observed during the first part of the steam distillation. The quantity was small and gave no apparent interference with the estimation of aniline.

INTERPRETATION OF RESULTS

The use of concentrated sulfite liquor with comparatively large amounts of NaOH results in the production of larger quantities of reduction products. This is shown in a comparison of the results obtained in reactions IV, VII, and VIII with V and VI. The reasonable agreement of the aniline yields, as well as the total amounts of reduction products, is apparent. Reactions V and VI (in which less NaOH is used) suggest little difference in the presence or absence of water under the conditions of the experiments. The yields of aniline in V and VI are higher.
than the yields of azobenzene, which is different from the other reactions.

The reaction (VII), in which the time factor was changed from three hours to one hour, shows little difference in the total reduction and the amounts of aniline and azobenzene produced. Apparently, the longer reaction period is unnecessary.

The reason underlying the loss of thirty per cent of the reduction products yet remains to be explained. This value was found to be greater in those reactions (V and VI) in which less NaOH was used. The explanation is not found in the possibility of a condensation reaction between aniline and other reaction products. Further help at this point may result from the experiments on the original liquor (to be reported later).

The formation of other products, although only in small quantities, is worthy of further investigation.

The higher yield of vanillin in reaction VII may result from improved technique in the method of analysis. However, it may be significant that the shorter reaction time produces more vanillin. At best, the yield is low.
OBJECTIVE

A study of the reducing action of waste sulfite liquor on nitrobenzene.

MODE OF ATTACK

The work of Freudenberg [Ber. 73, 167(1941)] was repeated, in which nitrobenzene was heated with waste sulfite liquor and sodium hydroxide at 160° C. for three hours. The quantities and conditions were the same with the exception that the waste sulfite liquor contained 8.38 per cent lignin (analyzed by the 2-naphthylamine method), whereas the lignin content in Freudenberg's work was 5.5 per cent. (Methoxyl method). The vanillin was determined by the method of Tomlinson and Hibbert [J. Am. Chem. Soc. 58, 345(1936)].

Reaction III

A. Materials used and conditions employed.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste sulfite liquor</td>
<td>84.0 cc</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>60.0 cc</td>
</tr>
<tr>
<td>Sodium hydroxide, solid</td>
<td>45.0 g</td>
</tr>
<tr>
<td>Water</td>
<td>100.0 cc</td>
</tr>
</tbody>
</table>

The NaOH was dissolved in water, mixed with the waste sulfite liquor and added to the steel reaction tube with the nitrobenzene. The tube was closed and the temperature increased to 160° within 45 minutes and then heated at 155 - 160° C. for three hours. The tube was cooled to room temperature, the contents removed, and the mixture steam-distilled directly. The aqueous distillate was acidified to remove basic substances, and the remaining solid distillate was separated mechanically. The vanillin was extracted from the remaining reaction mixture with trichloroethylene and one-tenth of volume determined as the m-nitrobenzoyl hydrazone. The basic substance (aniline) was recovered from the acid solution and distilled directly. The solid neutral substance (azobenzene) was recrystallized from ethyl alcohol-water.

B. Results

1. Reduction products and amounts

<table>
<thead>
<tr>
<th>Product</th>
<th>Quantity</th>
<th>(b.p. or m.p.)</th>
<th>% (Based on)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>9.6 g</td>
<td>178-179° C</td>
<td>17.6 per cent (Based on nitrobenzene)</td>
</tr>
<tr>
<td>Azobenzene</td>
<td>28.1 g</td>
<td>68-68.5° C</td>
<td>53.4 per cent (Based on nitrobenzene)</td>
</tr>
</tbody>
</table>
Acidic substance. Less than 0.2 g. of a semisolid substance which had a strong phenolic odor and gave a red color with FeCl₃ solution. It was not identified.

Four further recrystallizations from the mother liquor, from which the azobenzene was recrystallized, gave less than 0.1 g. of a substance which crystallized in colorless plates. It was not identified.

2. Recovered nitrobenzene--None

3. Vanillin

The analysis showed a yield of 1 per cent (approx.) of vanillin.

C. Interpretation

The results show yields of 17.6 per cent aniline, 53.4 per cent azobenzene, and 1 per cent of vanillin. The total amount of reduction products is 71 per cent. The fact that no nitrobenzene was recovered suggests that it was reduced and that certain reduction products were not recovered. This may be due to further reaction between certain reduction products and other reaction products.

The low vanillin yield may be due to the method of analysis or the actual production of less vanillin in the original reaction as a result of the presence of excess lignin. This is substantiated by the fact that the yield of vanillin, as determined by the same method, was approximately ten times higher in the experiment with calcium lignosulfonate in which less lignin was used. The amount of NaOH used in the experiment with calcium lignosulfonate was less also.

In another experiment (Reaction IV - to be reported later), in which the same conditions and quantities were employed with the exception that the amount of waste sulfite liquor was increased 50 per cent, the total yield of aniline was 25.4 per cent and the yield of azobenzene was 43.7 per cent. The total reduction (69.1 per cent) checks, within 2 per cent, the results reported above. No nitrobenzene was recovered in this experiment.
Objective

A study of the reducing action of waste sulfite liquor on nitrobenzene.

Mode of Attack

At the suggestion of Dr. Brauns, the first two experiments were tried with calcium lignosulfonate in place of the sulfite waste liquor. An approximately equivalent quantity of the calcium lignosulfonate, to the lignin content used by Freudenberg [Ber. 73, 167 (1940)], was used. The experimental conditions, otherwise, were the same.

Reaction I

A. Materials used and conditions employed.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium lignosulfonate</td>
<td>20.0 g. (dry basis)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>42.0 g.</td>
</tr>
<tr>
<td>NaOH, solid</td>
<td>4.8 g.</td>
</tr>
<tr>
<td>Water</td>
<td>135.0 cc.</td>
</tr>
<tr>
<td>Total volume</td>
<td>250.0 cc.</td>
</tr>
</tbody>
</table>

A steel bomb, placed in a rocker, was heated with the materials for 3 hours at 155-160°C.

B. Results

1. Reduction products identified and amounts:
   - Aniline         2.0 g.  Approx. 7-8 per cent
   - Azobenzene     0.5 g.  0.8 per cent

2. Recovered nitrobenzene 19.5 g.  46.5 per cent

3. Vanillin   In process of recovery.

C. Interpretation

The above results show that reduction of the nitrobenzene has taken place to produce azobenzene and aniline. No other reduction products were found to be present.
Reaction II

Same as Reaction I, with the exception that a double amount of NaOH was used.

A. Materials and Conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium lignosulfonate</td>
<td>20.0 g. (dry basis)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>42.0 g.</td>
</tr>
<tr>
<td>NaOH</td>
<td>9.6 g.</td>
</tr>
<tr>
<td>Water</td>
<td>135.0 cc.</td>
</tr>
<tr>
<td>Total volume</td>
<td>250.0 cc.</td>
</tr>
<tr>
<td>Time of heating</td>
<td>3 hours at 158-162° C.</td>
</tr>
</tbody>
</table>

B. Results

1. Reduction products

- Aniline 2.5 g. (Identified by boiling point) (8%)
- A higher boiling product (probably azobenzene) 6.0 g.
  (This is in the process of identification.) (Approx. 8%)

2. Recovered nitrobenzene 19.8 g. (47.2%)


C. Interpretation of Results

The results of this experiment are similar to those of Experiment I, although this one shows a higher yield of azobenzene and more reduction. It is probable that the increased quantity of alkali is responsible for the difference.

Reaction III

The experimental conditions of Freudenberg were followed closely and a concentrated solution of waste sulfite liquor was used. The results are not complete as yet, but there is indicated an increased amount of reduction with very little recovery of unreacted nitrobenzene. A large amount of azobenzene was isolated. The amount of aniline has not yet been determined. The complete details of Reaction III will be given in a later report.
MEMORANDUM

FROM: Code Office
TO: Dr. Lewis, cc. Dr. Bossert, Mr. Steele
SUBJECT: Samples submitted July 11, 1941

<table>
<thead>
<tr>
<th>Institute File No.</th>
<th>Code No.</th>
<th>Sample 1— Sulfite Waste Liquor</th>
<th>Sample 2— Sulfite Waste Liquor (Concentrated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>104747</td>
<td>1.064</td>
<td>1.270</td>
</tr>
<tr>
<td>Code No.</td>
<td>104748</td>
<td>142</td>
<td>658</td>
</tr>
<tr>
<td>Specific gravity (20°C.)</td>
<td></td>
<td>83.8</td>
<td>395</td>
</tr>
<tr>
<td>Total Solids, g./l.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin, g./l.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Method: Institute 111
MEMORANDUM

FROM: Code Office
TO: Dr. Lewis, co. Dr. Bossert, Mr. Steels
SUBJECT: Sample submitted July 11, 1941

Institute File No. 104749
Code No. Sample 3-
Calcium Lignosulfonate
Water, % 80.69
Total Sulfur, % 1.33
Inorganic Sulfur, % .60

Basis of Report: As Received
Method: 111