particles. This and the removal of the hood seemed to affect the tube so that it was somewhat more partial to the darker particles.

The head sample for the second series assayed only 3.65 per cent $SiO_2$. Using the size of the particle as the variable, this experiment, like the former, did not reduce the silica content below 1 per cent, but tended to show that units larger than −1 +2 should be experimented with. Unfortunately, the −1 +2 mesh product was the largest size available. Series 2 of Table II presents the results.

As the assays showed, an excellent reduction in the silica content was made and, though the acid-spar grade was not attained, the findings of these experiments on fluorite indicated that a future experiment, combining a higher bias voltage and a larger size particle, would probably result in a fluorite the silica content of which would be below the allowable maximum.

### Conclusions

It is believed that these experiments establish the possibility of using color and luster in the mechanical separation of minerals, metals, and their allied products, through the aid of a photo-electric cell. The probability and practicability of the method are dependent to a large extent upon the development of the mechanical phase of the separator.

In addition to the idea of mechanical improvements possible, the following suggestions are offered for the development of the sensitivity of the process:

(1) The use of a condensing lens in the reflected ray.
(2) The use of a more intense illumination and the interposition of color filters in the reflected ray; the possibility of using solutions as filters should be studied at the same time.
(3) The preparation of a table of absorption indices.
(4) The analysis of the reflected ray by means of a spectrometer.
(5) The use of monochromatic light of different wave lengths.
(6) The investigation of the color selectiveness of photo-electric cells whose plates are coated with various light-sensitive elements or compounds.
(7) The study of the possibility of better amplification of a high-frequency pulsating d. c. current rather than straight d. c.
(8) The placing of amplifying tubes in series instead of in parallel, and the use of more than two tubes to increase the amplification.
(9) The study of x-rays and the reactions of a photo-electric cell to x-radiation.

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# Studies in the Friedel-Crafts Reactions

## Naphthalene Series. I—Preparation of Naphthanthraquinone[1,2]

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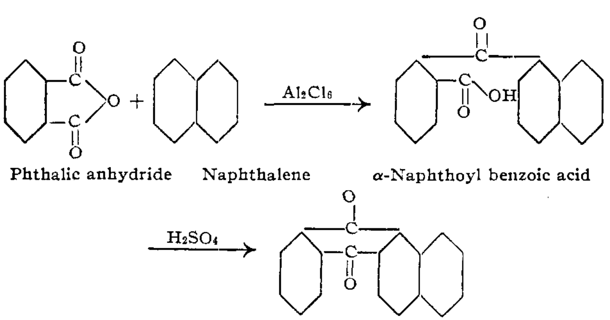
**A practical technic for the preparation of naphthanthraquinone from naphthalene and phthalic anhydride by means of the Friedel-Crafts reaction has been developed. The crude α-naphthoyl benzoic acid approaches the recrystallized product in purity. Naphthanthraquinone prepared from the crude or pure α-naphthoyl benzoic acid is practically identical in purity. Yields of naphthanthraquinone from both the pure and crude α-naphthoyl benzoic acid were in excess of 90 per cent.**

THE preparation of α-naphthoyl benzoic acid according to the Friedel-Crafts reaction has been previously reported by Ador and Crafts (*1*), Gabriel and Coleman (*3*), Graebe (*4*), and Heller and Schulke (*6*). In no case did the crude acid obtained by these investigators possess a high degree of purity. Naphthanthraquinone was first prepared by Elbs (*2*) and later by Gabriel and Coleman (*3*), Graebe (*4*), and Heller and Schulke (*6*). In the preparation of this substance the workers obtained a maximum yield of 80 per cent and a satisfactory purity only by recrystallizations, involving a considerable loss in yield.



Naphthanthraquinone (1,2-benzanthraquinone) (1,2-benzanthrene-7,12-dione)

This investigation was undertaken therefore to develop processes for the manufacture of these two substances which would give products of high purity and at the same time yields that would attract industrial interest.

The foregoing structural formulas represent the reactions involved in the synthesis of naphthanthraquinone.

### Preparation of α-Naphthoyl Benzoic Acid

A study of the following factors was undertaken in order to determine the optimum conditions involved in the preceding synthesis: (1) solvents for the reaction; (2) ratio of naphthalene to phthalic anhydride; (3) ratio of anhydrous aluminum chloride to phthalic anhydride; (4) hydrolysis of the reaction compound; (5) formation of ammonium salt of α-naphthoyl benzoic acid; (6) method of precipitating α-naphthoyl benzoic acid; (7) relation of agitation to yields and purity; (8) relation of reaction temperature to yields and purity.

Condensation was first attempted without the use of solvent and under reduced pressure. Under a pressure of 20 mm. several experiments were made involving the following variations: (*a*) molar ratio of naphthalene to phthalic anhydride from (1:1) to as high as (6:1); (*b*) aluminum chloride and zinc chloride as condensing agents; (*c*) time of reaction from 2 to 6 hours; (*d*) temperature of reaction from 55° to 95° C. In all cases the product, which was dark and resinous, gave a low melting point on account of the presence of phthalides. (Presence of dinaphthylphthalides was indicated by insolubility in hot dilute sodium hydroxide, hot

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[2] Contribution 169 from the Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

ammonium hydroxide, sodium hydrosulfite solution, and a fair degree of solubility in hot alcohol.)

Gabriel and Coleman (*3*) and Graebe (*4*) used carbon disulfide as a solvent while Heller and Schulke (*6*) used benzene. In a previous investigation by the authors in this laboratory, which may be published later, it was found that *o*-dichlorobenzene did not condense with phthalic anhydride in the presence of aluminum chloride at as high a temperature as 50° C. and only to the extent of 5 per cent at 65° C. over a long period of time and under the influence of agitation. It proved to be a very satisfactory solvent and could be recovered from the reaction mixture by steam distillation in almost theoretical quantities. Table I contains the data relating to the experiments in which a comparison has been made of the above-mentioned solvents. The α-naphthoyl benzoic acid was prepared under conditions similar to those employed by the authors in the preparation of 4-chlorobenzoyl benzoic acid (*5*).

**Table I—Comparison of Solvents in Preparation of α-Naphthoyl Benzoic Acid**

| EXPT. | TIME OF REACTION | TEMPERATURE OF REACTION | SOLVENT | SOLVENT RATIO | SOLVENT RECOVERY | YIELD N. B. A. | MELTING POINT[a] |
|---|---|---|---|---|---|---|---|
| | *Hours* | *° C.* | | | *%* | *%* | *° C.* |
| 1 | 2 | 15 | $C_6H_6$ | 12:1 | 97 | 97.6 | 165–168 |
| 2 | 4 | 5 | $C_6H_6$ | 6:1 | 97 | 95.0 | 150–160 |
| 3 | 5 | 0 | $C_6H_6$ | 3:1 | 97 | 92.0 | 140–155 |
| 4 | 2 | 15 | $CS_2$ | 12:1 | 90 | 95.0 | 145–155 |
| 5 | 4 | 5 | $CS_2$ | 6:1 | 90 | 93.0 | 140–150 |
| 6 | 5 | 0 | $CS_2$ | 3:1 | 90 | 92.0 | 135–145 |
| 7 | 2 | 15 | $C_6H_4Cl_2$(1, 2) | 12:1 | 99 | 97.5 | 167–170 |
| 8 | 4 | 5 | $C_6H_4Cl_2$(1, 2) | 6:1 | 99 | 97.0 | 168–171 |
| 9 | 5 | 0 | $C_6H_4Cl_2$(1, 2) | 3:1 | 99 | 97.5 | 170–172 |

Phthalic anhydride, commercial sublimed, 1 mol = 148 grams.
Aluminum chloride, anhydrous, commercial sublimed, 10 per cent excess of 1 mol = 294 grams.
Naphthalene, commercal sublimed, 1 mol plus 5 per cent excess = 134.4 grams.
Agitation continuous.

[a] Melting point of pure material, 176.4° C.

Benzene was not effective as a solvent when a low temperature or a low ratio was used, and the purity dropped off as is shown by the difference in the melting points. In the case of carbon disulfide it was very difficult to free the α-naphthoyl benzoic acid of traces of sulfur. More stream was required to remove the *o*-dichlorobenzene, but it was possible to reduce the quantity of the solvent and yet obtain a product of high purity. Unless otherwise mentioned *o*-dichlorobenzene was used as the solvent in the experiments to be described later.

Naphthalene and phthalic anhydride in molecular proportions yield α-naphthoyl benzoic acid of the highest degree of purity. An excess of naphthalene increased the percentage of phthalides, while an excess of phthalic anhydride gave along with the naphthoyl benzoic acid some *o*-phthalic acid and traces of the benzoyl benzoic acid of the solvent that was used.

As in the preparation of 4-chlorobenzoyl benzoic acid (*5*), it was found that an excess of 10 per cent of aluminum chloride was the most suitable ratio of aluminum chloride to phthalic anhydride for the preparation of α-naphthoyl benzoic acid. An excess of 15 per cent gave a product of a lower degree of purity which contained phthalides, yet when an excess of 5 per cent was used the yield dropped off.

The hydrolysis of the reaction compound was carried out by adding gradually the reaction mixture to iced dilute sulfuric acid, while the acid solution was agitated with a non-swirling motion. In this way the temperature of the hydrolysis was kept low, and at no time was it higher than the temperature attained during the condensation. By this procedure the α-naphthoyl benzoic acid obtained was of a higher degree of purity and much better color than when the cold dilute sulfuric acid was fed gradually to the agitated reaction mixture which was surrounded by an ice bath.

After the removal of the solvent by steam distillation, the reaction mixture was cooled and the crude product separated from the solution of aluminum sulfate by filtration. The residue was then washed free of acid and taken up with ammonium hydroxide to form the ammonium salt of α-naphthoyl benzoic acid. To insure the solution of all the α-naphthoyl benzoic acid, approximately 15 liters of water were added and steam was passed into the mixture until the excess of ammonia had been removed. A small amount of vegetable carbon was then added and steam passed into the mass for an additional 10 minutes. The solution was filtered while still hot and cooled to 15° C. A clear colorless solution was obtained.

The α-naphthoyl benzoic acid was precipitated by gradually feeding the cold ammonium salt into cold dilute sulfuric acid, which was agitated by a continuous non-swirling motion. Coagulation of the precipitate was caused by one of the following: (*a*) too rapid feeding of the ammonium salt; (*b*) utilization of a warm solution of the ammonium salt; or (*c*) the use of a too concentrated solution of sulfuric acid.

It was established in the preparation of 4-chlorobenzoyl benzoic acid (*5*) that with a progressive lowering of the temperature of the reaction it was necessary to have more effective agitation of the reaction mixture in order to obtain a product of higher purity. The data of Table II are presented as evidence of this relationship in the preparation of α-naphthoyl benzoic acid.

**Table II—Relation of Effective Agitation and Temperature upon Purity of α-Naphthoyl Benzoic Acid**

| EXPT. | TIME OF REACTION | TEMPERATURE OF REACTION | SOLVENT RATIO | YIELD N. B. A. | MELTING POINT |
|---|---|---|---|---|---|
| | *Hours* | *° C.* | | *%* | *° C.* |
| 1 | 4.5 | 40 | 3:1 | 96.8 | 145–160 |
| 2 | 4.0 | 25 | 3:1 | 96.3 | 155–165 |
| 3 | 5.0 | 0 | 3:1 | 97.5 | 165–170 |
| 4 | 5.0 | − 5 | 3:1 | 93.7 | 168–170 |

Phthalic anhydride, commercial sublimed, 1 mol = 148 grams.
Aluminum chloride, anhydrous, commercial sublimed, 10 per cent excess of 1 mol = 294 grams.
Naphthalene, commercial sublimed, 1 mol plus 1 per cent excess = 129.3 grams.
Solvent, *o*-dichlorobenzene, b. p. 179° C.
Agitation continuous.

When a solvent ratio of 4:1 was used, it was found that the condensation might be run at a higher reaction temperature and the reaction would still give the α-naphthoyl benzoic acid of the same degree of purity.

The crude α-naphthoyl benzoic acid was purified by successive recrystallizations from glacial acetic acid and then twice from toluene. Combustions on this product gave the following results:

Analysis of substance: 0.0899, 0.0610; $CO_2$, 0.2581, 0.1752; $H_2O$, 0.0352, 0.0240.

Calculated for $C_{18}H_{12}O_3$: C, 78.23; H, 4.38. Found: C, 78.30, 78.29; H, 4.38, 4.40.

McMullen (*7*) reported the melting point of α-naphthoyl benzoic acid to be 176° C.

By a careful fractional precipitation of the hot solution of the ammonium salt of α-naphthoyl benzoic acid, by the addition of dilute hydrochloric acid, fractions of the keto acid with the following melting points were obtained:

| FRACTION | *° C.* | FRACTION | *° C.* |
|---|---|---|---|
| (1) Neutral to litmus | 175.8 | (6) Acid to litmus | 176.4 |
| (2) Acid to litmus | 176.4 | (7) Acid to litmus | 176.4 |
| (3) Acid to litmus | 176.4 | (8) Acid to litmus | 174–174.5 |
| (4) Acid to litmus | 176.4 | (9) Final fraction | 166–169 |
| (5) Acid to litmus | 176.4 | | |

Pure α-naphthoyl benzoic acid melts at 176.4° C. (cor.). Titration with standard 0.2 *N* sulfuric acid indicated a purity of 99.7 per cent. The crude acid with a melting point of 168–170° C. gave a titration value of 99.2 per cent purity. The work of Gabriel and Coleman (*3*) on the structure of the α-naphthoyl benzoic acid was confirmed. Alpha-naphthoic acid and benzoic acid were obtained by caustic fusion.

## Preparation of Naphthanthraquinone

A number of dehydrating agents were tested in determining the best procedure for making naphthanthraquinone from α-naphthoyl benzoic acid. Among the agents examined were the following: concentrated sulfuric acid, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, sulfuryl chloride, anhydrous aluminum chloride, anhydrous ferric chloride, anhydrous zinc chloride, acetic anhydride, and boric acid. Sulfuric acid appeared to be the only reagent capable of producing a sufficient amount of naphthanthraquinone to warrant a detailed study of its use in this synthesis.

The following procedure was adopted after a number of preliminary experiments for the preparation of naphthanthraquinone with sulfuric acid as the ring closure agent. Sulfuric acid was added to α-naphthoyl benzoic acid in a tall beaker, and the mass was agitated with a mechanical stirrer during the entire reaction time. Heat was furnished by an electrical stove, the temperature being regulated by a rheostat within the limits of plus or minus 2° C. At the end of the reaction time the mass was diluted with 20 per cent sulfuric acid until the residual acidity was 50 per cent. The mass was then cooled to 25° C. and filtered; the residue was washed with 50 per cent sulfuric acid, then with hot water until the washings were clear. The mass was then boiled up with 2 per cent caustic and filtered again and washed with hot water until free from alkali. The crude product was then dried and weighed.

A study was made of the effect of temperature on the dehydration of α-naphthoyl benzoic acid to form naphthanthraquinone by means of 95 per cent sulfuric acid.

**Table III—Effect of Temperature on Preparation of Naphthanthraquinone from α-Naphthoyl Benzoic Acid by Ring Closure with 95 Per Cent Sulfuric Acid**

| Expt. | Temperature of Reaction | Time of Reaction | Sulfonation | Color of Product | Yield of Product | Melting Point |
|---|---|---|---|---|---|---|
| | ° C. | Hours | | | % | ° C. |
| 1 | 135 | 4 | Complete | ...... | ... | ..... |
| 2 | 50 | 4 | Some | Yellow | 67.41 | 167–168 |
| 3 | 50 | 5 | Some | Yellow | 72.10 | 168–169 |
| 4 | 45 | 24 | Trace | Light yellow | 81.34 | 167–168 |
| 5 | 40 | 24 | None | Greenish | 76.63 | 167–168 |
| 6 | 35 | 24 | None | Greenish | 64.91 | 167–168 |

Ninety-five per cent sulfuric acid, C. P. (ratio 8:1).
α-Naphthoyl benzoic acid, crude, 50 grams.
Agitation continuous.

It was evident from these results that a high temperature would not be effective in the ring closure with concentrated sulfuric acid on account of sulfonation and poor yields.

A series of experiments was then run to determine the effect of the strength of the sulfuric acid on the ring closure. The data obtained are presented in Table IV.

**Table IV—Effect of Acid Strength on Dehydration of α-Naphthoyl Benzoic Acid to Naphthanthraquinone**

| Expt. | Temperature of Reaction | Time of Reaction | Strength of Sulfuric Acid | Yield of Product | Color of Product | Melting Point |
|---|---|---|---|---|---|---|
| | ° C. | Hours | % | % | | ° C. |
| 1 | 135 | 2 | 73 | 73.40 | Light yellow | 167–168 |
| 2 | 107 | 2 | 80 | 76.80 | Light yellow | 166–168 |
| 3 | 107 | 2 | 83 | 81.25 | Light yellow | 167–168 |
| 4 | 75 | 6 | 90 | 82.50 | Light yellow | 167–168 |
| 5 | 50 | 5 | 95 | 72.10 | Light yellow | 167–168 |
| 6 | 50 | 5 | 99 | 77.00 | Light yellow | 166–168 |
| 7 | 30 | 5 | 3% oleum | Trace | Light yellow | ..... |
| 8 | 30 | 5 | 6% oleum | Trace | Light yellow | ..... |

α-Naphthoyl benzoic acid, crude, 50 grams.
Agitation continuous.
Acid ratio, 8:1.

**Table V—Effect of Acid Ratios upon Ring Closure of α-Naphthoyl Benzoic Acid to Form Naphthanthraquinone**

| Expt. | Yield of Product | Color of Product | Melting Point | Acid Ratio |
|---|---|---|---|---|
| | % | | ° C. | |
| 1 | 20.64 | Green | 165–167 | 2:1 |
| 2 | 47.92 | Green | 167–168 | 4:1 |
| 3 | 60.60 | Light yellow | 167–168 | 6:1 |
| 4 | 79.49 | Yellow | 168 | 8:1 |
| 5 | 80.24 | Yellow | 168 | 10:1 |

Sulfuric acid, 95 per cent, C. P.
α-Naphthoyl benzoic acid, crude, 50 grams.
Agitation continuous.
Temperature of reaction, 40° C.
Time of reaction, 24 hours.

It was then necessary to study the effect of acid ratios upon the ring closure by means of 95 per cent sulfuric acid of the α-naphthoyl benzoic acid to naphthanthraquinone.

From the foregoing tables it was evident that to get a yield of more than 90 per cent of naphthanthraquinone it would be necessary to carry out the ring closure at a high temperature with concentrated sulfuric acid, and with a fairly high ratio of sulfuric acid to naphthoyl benzoic acid. This could not be done without taking steps to inhibit the sulfonation of the α-naphthoyl benzoic acid which takes place along with the ring closure. It was therefore decided to run a group of experiments using different inhibitors. Table VI presents the results of these experiments.

**Table VI—Effect of Several Inhibitors of Sulfonation in the Ring Closure of α-Naphthoyl Benzoic Acid**

| Expt. | Inhibitor | Color of Product | Yield of Product | Melting Point |
|---|---|---|---|---|
| | | | % | ° C. |
| 1 | None | Yellow | Very little | Not taken |
| 2 | 50 g. $C_6H_6$ | Dark green | 75.6 | 160–165 |
| 3 | 50 g. $ZnCl_2$ | Golden yellow | 82.6 | 167–168 |
| 4 | 50 g. $H_3BO_3$ | Golden yellow | 89.6 | 167–168 |

Sulfuric acid, 95 per cent, C. P. (acid ratio 10:1).
α-Naphthoyl benzoic acid, crude, 50 grams.
Time of reaction, 3 hours.
Temperature of reaction, 75° C.

Boric acid was chosen as the best inhibitor of sulfonation, and a large number of ring closures were run to determine the optimum conditions for the preparation of naphthanthraquinone. Table VII presents the ones in which the only variable is temperature.

**Table VII—Effect of Temperature on Ring Closure of α-Naphthoyl Benzoic Acid by 95 Per Cent Sulfuric Acid in Presence of Boric Acid**

| Expt. | Temperature of Reaction | Color of Product | Yield of Product | Melting Point |
|---|---|---|---|---|
| | ° C. | | % | ° C. |
| 1 | 60 | Yellow | 63.40 | 167–168 |
| 2 | 70 | Yellow | 78.50 | 167–168 |
| 3 | 75 | Yellow | 83.60 | 167–168 |
| 4 | 80 | Yellow | 94.20 | 167–168 |
| 5 | 85 | Yellow | 93.90 | 167–168 |
| 6 | 90 | Yellow | 92.50 | 167–168 |
| 7 | 100 | Yellow | 86.40 | 167–168 |

Sulfuric acid, 95 per cent, C. P. (acid ratio 6:1).
α-Naphthoyl benzoic acid, crude, 50 grams.
Boric acid = 50 grams.
Agitation continuous.
Time of reaction, 7 hours.

Other experiments not tabulated indicate that a lower acid ratio tends to incompleteness of the ring closure, that less boric acid allowed sulfonation, and that a higher acid ratio does not increase the amount of naphthanthraquinone formed but increases the amount of sulfonation, that a longer time of reaction does not increase the yield but that a shorter time of reaction indicates a falling off of the yield.

The crude naphthanthraquinone gave a melting point of 168° C. When the same material was recrystallized from 95 per cent sulfuric acid, from glacial acetic acid, and then twice from toluene, or was vatted out of a hydrosulfite bath and then recrystallized from toluene, it gave a melting point of 169° C. (cor.). There was a loss of material in all recrystallizations, and a slight improvement in color of the product.

The structure of naphthanthraquinone as determined by Gabriel and Coleman (*3*) was confirmed. Beta-naphthoic acid and benzoic acid were obtained by caustic fusion. Combustions on the purified product gave the following results:

Analysis of substance: 0.0691, 0.1720; $CO_2$, 0.2123, 0.5276; $H_2O$, 0.0242, 0.0605. Calculated for $C_{18}H_{10}O_2$: C, 83.70; H, 3.92. Found: C, 83.79, 83.66; H, 3.92, 3.94.

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