

sulfur. The coke made in the laboratory from the same coal contains 0.75 per cent sulfur, the difference being due to the purging effect of the by-product gases passing through the red-hot coke in the oven. A test, to determine how much the finished coke from the by-product oven could be desulfurized by heating to 1000° and passing hydrogen through for one hour, resulted in a reduction in the coke sulfur from 0.64 to 0.50 per cent, showing that desulfurization of coke by hydrogen was not limited to the actual coking process.

#### CONCLUSIONS

A study has been made of the efficiency of hydrogen and gases containing hydrogen as desulfurizing agents, when passed through finished coke at high temperatures or through coal in the process of coking.

The effect of hydrogen on the removal of sulfur from coke is very noticeable, in most cases the majority of the sulfur being removed during a period of 3 hrs. at 1000° C. With the exception of the decrease in sulfur content, the character of the coke does not seem to be affected by the passage of hydrogen.

Three of the sulfur coking reactions are modified by the passage of hydrogen through the coking mass.

(1) Coal pyrite,  $\text{FeS}_2$ , is caused to decompose at a lower temperature, the decomposition being practically complete at 500°. This change of speed of reaction does not affect the final desulfurization results, however, since complete decomposition of the pyrite is finally attained in the ordinary coking process.

(2) The decomposition of organic sulfur to form hydrogen sulfide is very little affected below 500°, but is enormously increased from 500° to 1000°. All of the desulfurizing effect of the hydrogen is due to this increased decomposition.

(3) A larger amount of sulfide is converted to a "carbon-sulfur" combination. This is due to mass action and results from the modifications in the two reactions given above.

Gaseous mixtures containing hydrogen, such as coke-oven gas, are slower in their desulfurizing action, and even with a longer time of exposure would probably never give the degree of desulfurization attained by the use of pure hydrogen. Their efficiency for the removal of sulfur from coke is high, however, and the repassing of by-product gas through the coking mass may prove of commercial value.

The original state of subdivision of the coal does not affect the desulfurization process. This is because the coal fuses between 350° and 400°, while desulfurization begins above 500°.

The coke produced in coke ovens contains less sulfur than would be accounted for by the primary coking reactions. This is due to the flow of the by-product gas produced through the coking mass.

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#### NAPHTHALENE SULFONIC ACIDS. I—SOME DIFFICULTLY SOLUBLE SALTS OF CERTAIN NAPHTHALENE SULFONIC ACIDS<sup>1</sup>

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In the course of the investigation of the sulfonation products of naphthalene, it became of interest to make and study as many as possible of the more difficultly soluble salts of those acids which might be formed by direct sulfonation, *viz.*, the  $\alpha$ - and  $\beta$ -monosulfonic acids and the 1,5-, 1,6-, 2,6- and 2,7-disulfonic acids of naphthalene. The purpose of investigating these salts was to obtain a characteristic salt of each acid which might serve as the basis of a qualitative test for that acid.

The known difficultly soluble inorganic salts of these acids were found unsuited for the purpose in hand, with the exception of the salts of naphthalene- $\beta$ -sulfonic acid with the heavier metals; such as the nickel, cobalt, copper, cadmium, zinc, and silver salts described by O. N. Witt,<sup>3</sup> and the ferrous salt,<sup>4</sup> known in the industries but not described in any scientific work so far as the author can find.

Erdmann and Süvern<sup>5</sup> are the only ones who have recorded work on the salts of these acids with organic bases. They describe the salts of the  $\alpha$ -,  $\beta$ -, 2,6- and 2,7-sulfonic acids with aniline, benzidine, and *o*-tolidine, but give no analyses of the salts formed.

To investigate this class of salts more thoroughly, salts of various organic bases with the six sulfonic acids were prepared, and those that were difficultly soluble were studied further. The most important of these are described here, and some of their uses in the following paper. Other difficultly soluble salts will probably be described in later contributions from this laboratory.

The method of making the salts was the same in each case. Molecularly equivalent quantities of the acid, or its sodium or potassium salt, and the hydrochloride of the organic base were dissolved separately in hot water, and the two solutions mixed, stirred thoroughly, and allowed to cool. The crystallized salts were filtered, washed with cold water, and dried in a vacuum oven at 100°.

Since they are salts of strong acids with weak bases, they are all easily hydrolyzed by boiling water. In attempting to recrystallize them, a little of the hydrochloride of the base should always be added to counteract this change.

<sup>1</sup> Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

<sup>2</sup> Crystallographic-optical data by Edgar T. Wherry.

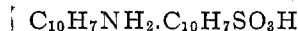
<sup>3</sup> *Ber.*, **48** (1915), 743.

<sup>4</sup> Cain, "Manufacture of Intermediate Products for Dyes," p. 166; Brit. Patent 4459 (1894).

<sup>5</sup> *Ann.*, **275** (1893), 297.

The sulfur in all of these salts was determined as follows: An amount of the salt not exceeding 200 mg. was ignited in a Parr calorimeter bomb with about 5 g. of sodium peroxide. The ignition mass was dissolved in water, the solution acidified, and sulfuric acid<sub>2</sub> was determined as usual by precipitation with barium chloride.

$\alpha$ -NAPHTHYLAMINE NAPHTHALENE- $\alpha$ -SULFONATE,



This salt separates, on cooling the hot solution, in well-defined, glistening, micaceous leaflets, generally arranged in groups. It is soluble in hot water, in hot 95 per cent alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water, but is practically insoluble in cold water and alcohol and in acetone. It melts with decomposition at 232°. Upon analysis, 9.09 and 9.34 per cent of sulfur were found, with the calculated value at 9.13 per cent.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES.<sup>1</sup> *Crystal habit*—When examined under the microscope in ordinary light seen to be made up of overlapping plates.

*Refractive indices* (for D)—[Determined by inserting the polarizer (sub-stage nicol prism) and immersing a small amount of the substance on a microscope slide in liquids of known refractive index one after another until the crystals lying in some definite position disappear, because their index is matched; and repeating for crystals lying in other positions.]

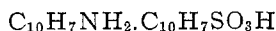
$\alpha = 1.552$ ,  $\beta$  not determined,  $\gamma = 1.795$ ,  $\gamma - \alpha = 0.243$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\gamma$  usually shown.

*Features shown in parallel polarized light, with nicols crossed*—Double refraction extreme, the colors being first to second order, often in beautiful mosaics, on thin plates, but ranging up to fourth or fifth order on thick or upturned ones; extinction parallel to occasional edges; elongation indefinite.

*Features shown in convergent polarized light, with nicols crossed*—None.

*Diagnostic features*—The features likely to be of greatest use in identifying this substance are the crystal habit and the value of the lowest refractive index,  $\alpha$ . If immersed in nitrobenzene ( $n_D = 1.552$ ) or another oily liquid with about the same  $n$ , and examined under the microscope with the polarizer in, the plates disappear practically completely when the direction of index  $\alpha$  lies parallel to the plane of vibration of the polarizer.

$\beta$ -NAPHTHYLAMINE NAPHTHALENE- $\alpha$ -SULFONATE,



This salt crystallizes on cooling from dilute hot solutions in large, glistening, micaceous, diamond-shaped plates. If the hot solution is too concentrated, it forms on cooling a stiff jelly resembling slightly cooked egg albumen. This jelly-like form may partially change, on standing, into a mass of long colorless needles. If this jelly-like form is heated with more water, it dissolves, and the plates are formed on cooling.

The plates are difficultly soluble in cold water, acetone, and 95 per cent alcohol; but soluble in hot water, hot acetone, hot alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water. The salt blackens at 202° and melts at 211°. Analyses gave 9.08 and 8.98 per cent sulfur (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Elongated plates, sometimes showing a 125° termination.

<sup>1</sup> The authors herewith acknowledge the aid of Mr. George L. Keenan of this Bureau in checking some of these data.

*Refractive indices* (D)— $\alpha = 1.620$ ,  $\beta = 1.670$ ,  $\gamma =$  greater than 1.850,  $\gamma - \alpha = 0.23+$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\beta$  are usually shown.

*In parallel polarized light*—Double refraction extreme, the colors being first to second order, sometimes in confused mosaics, on thin plates; extinction parallel to prominent edges; elongation +.

*In convergent polarized light*—A biaxial figure frequently shown, the sign being + and  $2E = 85^\circ \pm 5^\circ$ .

*Diagnostic features*—The features most useful for identifying this substance are the crystal habit, value of the intermediate index,  $\beta$ , and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts  $\alpha$ -monobromonaphthalene with 1 part methylene iodide. When crystals are turned so that their longest dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the index to be 1.670.

$\alpha$ -NAPHTHYLAMINE NAPHTHALENE- $\beta$ -SULFONATE,



This salt forms a voluminous white precipitate in the hot solution, which is made up of microscopic needles. It is soluble in a cold mixture of 4 volumes of alcohol and 1 of water, considerably soluble in hot water and hot 95 per cent alcohol, difficultly soluble in cold water, cold 95 per cent alcohol, and hot and cold acetone. It melts with decomposition at 240° to 242°. The per cent of sulfur found was 9.08 and 9.29 (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

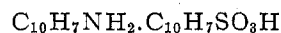
*Refractive indices* (D)— $\alpha = 1.600$ ,  $\beta = 1.650$ ,  $\gamma = 1.725$ ,  $\gamma - \alpha = 0.125$ , all  $\pm 0.005$ ; index  $\gamma$  usually shown lengthwise, and means of  $\alpha$  and  $\beta$  crosswise.

*In parallel polarized light*—Double refraction extreme, bright first order colors being shown even on very minute grains; extinction parallel; elongation +.

*In convergent polarized light*—.....

*Diagnostic features*—The features most useful in identifying this substance are the crystal habit, value of highest index, and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts methylene iodide with 1 part  $\alpha$ -monobromonaphthalene. When the needles are turned so that their long dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the highest index to be 1.725.

$\beta$ -NAPHTHYLAMINE NAPHTHALENE- $\beta$ -SULFONATE,



This salt also forms insoluble microscopic plates in the hot solution. It is slightly soluble in hot water and 95 per cent alcohol, considerably soluble in a cold, and easily soluble in a hot mixture of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and difficultly soluble in cold water and in acetone. It melts with decomposition at 276° to 279°. It contained 9.00 and 9.10 per cent of sulfur (theory 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Minute plates (or rods), with irregular wavy structure.

*Refractive indices* (D)— $\alpha = 1.640$ ,  $\beta = ?$ ,  $\gamma = 1.730$ ,  $\gamma - \alpha = 0.090$ , all  $\pm 0.005$ ; index  $\alpha$  usually shown in one direction.

*In parallel polarized light*—Double refraction extremely strong, first to second order colors being shown even on very minute plates; extinction and elongation indeterminate.

*In convergent polarized light*—Traces of a biaxial figure occa-

sionally shown, but the crystals are too minute for its measurement.

**Diagnostic features**—The feature most useful in identifying this substance is the unusually high value of the lowest index,  $\alpha$ . This index is almost exactly matched by  $\alpha$ -monochloronaphthalene ( $n_D = 1.639$ ), and most of the crystals disappear in one direction or another when immersed in this liquid. For confirmative purposes the other indices may be determined in similar manner, using mixtures of this liquid with methylene iodide of the indices above stated.

FERROUS NAPHTHALENE- $\beta$ -SULFONATE,  $\text{Fe}(\text{C}_{10}\text{H}_7\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}^1$

The author makes no claim to the discovery of this salt which has been extensively made and used in industrial plants. A description of it is given here, since no reference has been found in scientific literature or elsewhere than in the British patent.

The salt separates in large, glistening, colorless, micaceous plates, when ferrous chloride is added to a cold solution of naphthalene- $\beta$ -sulfonic acid or its salts. It is difficultly soluble in cold, but readily soluble in hot water. It is remarkably stable, not being oxidized to any appreciable extent by exposure to air. At  $150^\circ$  to  $160^\circ$  all the water of crystallization is removed and the salt becomes yellowish brown, probably due to slight superficial oxidation of the iron.

Analysis	Calculated Per cent	Found Per cent
Iron.....	9.67	9.52
Water.....	18.69	18.50

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, sometimes showing a  $140^\circ$  termination.

**Refractive indices (D)**— $\alpha = 1.500$ ,  $\beta$  not determined,  $\gamma = 1.660$ ,  $\gamma - \alpha = 0.160$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\gamma$  usually shown.

**In parallel polarized light**—Double refraction extreme, second order colors being shown even on thin plates; extinction parallel to crystal edges occasionally present; elongation indeterminate.

**In convergent polarized light**—Partial biaxial figure occasionally shown, the axial angle being large and the sign apparently +.

**Diagnostic features**—The feature most characteristic of this substance is the unusually low value of the lowest index,  $\alpha$ . The immersion liquid may be benzene ( $n_D = 1.499$ ), or another liquid of about the same  $n$  (for instance, some grades of lubricating oil). Most of the crystals disappear in one direction or another when immersed in this liquid. The other properties may be used for confirmation.

$\alpha$ -NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE,  
 $(\text{C}_{10}\text{H}_7\text{NH}_2)_2 \cdot \text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$

This salt is almost completely insoluble in boiling water. It forms a heavy precipitate of a poorly defined, granular, platy nature. It is very slightly soluble in hot water, 95 per cent alcohol, and a mixture of 4 volumes of alcohol and 1 of water, and practically insoluble in these solvents in the cold, and in acetone. It does not melt below  $280^\circ$ . Analyses gave 10.94 and 10.97 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, irregular in outline.

**Refractive indices (D)**— $\alpha = 1.600$ ,  $\beta$  not determined,  $\gamma = 1.795$ ,  $\gamma - \alpha = 0.195$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\gamma$  often shown.

**In parallel polarized light**—Double refraction extreme, second

order colors being shown even on very thin plates; extinction apparently inclined; elongation indeterminate.

**In convergent polarized light**—Partial biaxial figures rarely shown.

**Diagnostic features**—The value of the lowest refractive index,  $\alpha$ , is characteristic of this substance, when considered in connection with its habit. One other compound in the series studied,  $\alpha$ -naphthylamine naphthalene- $\beta$ -monosulfonate, has the same  $\alpha$  value, but it crystallizes in needles, and is thus readily distinguishable. For immersion, a mixture of equal parts of bromobenzene and  $\alpha$ -monochloronaphthalene ( $n_D = 1.600$ ) may be used. The crystals will disappear in one direction or another in this liquid.

$\beta$ -NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE,  
 $(\text{C}_{10}\text{H}_7\text{NH}_2)_2 \cdot \text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$

This salt precipitates from the boiling solution in a dense voluminous mass of small plates. It is only slightly soluble in hot water and alcohol, and practically insoluble in cold solvents, being slightly more soluble in mixtures of 4 volumes of alcohol and 1 of water. It does not melt below  $280^\circ$ . The results of sulfur determinations were 11.12 and 11.23 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES—Unless care is taken to have an excess of base present, there is a strong tendency for another substance, apparently an acid salt, to crystallize out along with this compound. It has so far been impossible to obtain this other substance in a pure form and no analytical data can be given at present. The acid salt has highly distinctive optical properties, and can be readily recognized when studied under the microscope, but if the two are intimately mixed difficulties may be encountered in confirming the identity of the normal salt. The properties of both are here given.

**Normal salt. Crystal habit**—Plates, irregular in outline.

**Refractive indices (D)**— $\alpha = 1.631$ ,  $\beta = 1.647$ ,  $\gamma = 1.755$ ,  $\gamma - \alpha = 0.124$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\beta$  are usually shown, but  $\gamma$  is exhibited on uptilted plates.

**In parallel polarized light**—Double refraction extreme, bright first order colors being shown on extremely thin plates; extinction and elongation indeterminate.

**In convergent polarized light**—Biaxial figures frequently shown, the sign being +, and  $2E = 75^\circ \pm 5^\circ$  ( $2E$  calculated from  $ns = 77^\circ 06'$ ).

**Diagnostic features**—The features most useful in identifying this substance are the values of the two lower refractive indices,  $\alpha$  and  $\beta$ , and the readiness with which an interference figure can be obtained. In a mixture of 3 parts  $\alpha$ -monobromonaphthalene with one part monobromobenzene ( $n_D = 1.632$ ) practically all of the plates disappear in one direction or the other; and in pure  $\alpha$ -monobromonaphthalene ( $n_D = 1.656$ ) they also disappear. On introducing the substage condenser, using a 4 mm. objective, crossing the nicol prisms, and removing the eyepiece, a fairly distinct biaxial interference figure will usually be seen, the dark brushes lying well within the field. If the microscope is provided with means for measuring axial angles, the numerical value can be obtained; if not, repetition of the procedure, using a thin flake of muscovite mica, will give a figure of practically identical dimensions, showing the axial angle to be not far from  $75^\circ$ .

**Acid salt**—This is distinguished from the normal salt by the extraordinarily strong double refraction, which exceeds 0.30, the value of  $\alpha$  being 1.550, and that of  $\gamma$  being higher than the highest immersion liquid available, the  $n$  of which is 1.850. ( $\beta = 1.700$ .) As a result, the plates of this substance show third or fourth order colors, even when very thin. The axial angle,  $2E$ , is also much larger than is that of the normal salt, so that

<sup>1</sup> Boulton, Haywood, Boulton, and Fergusson, Brit. Patent 4459 (1894).

the dark brushes do not appear in the field of view when the interference figure lies in the diagonal position. These features differentiate this acid salt not only from the corresponding normal salt, but also from all other compounds of the series here studied; and the acid salt, if obtained, can therefore be recognized and excluded from consideration promptly.

$\alpha$ -NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE,  
 $(C_{10}H_7NH_2)_2 \cdot C_{10}H_6(SO_3H)_2$

This salt separates in long, slender needles on cooling a hot solution. It is soluble in hot water, 95 per cent alcohol, soluble in cold mixtures of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It decomposes at  $265^\circ$  to  $267^\circ$ . The value found for sulfur was 11.25 and 11.22 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Well-defined rods, probably belonging to the monoclinic system.

*Refractive indices (D)*— $\alpha = 1.583$ ,  $\beta = 1.730$ ,  $\gamma = 1.770$ ,  $\gamma - \alpha = 0.187$ , all  $\pm 0.005$ ; index  $\alpha$  is usually shown lengthwise, and  $\gamma$  crosswise, of the rods;  $\beta$  is sometimes shown crosswise, especially on rods so turned as to show parallel extinction.

*In parallel polarized light*—Double refraction extreme, the colors being second to third order, even on fairly slender rods; extinction inclined, at an angle of  $17^\circ \pm 1^\circ$ ; elongation negative.

*In convergent polarized light*—Partial biaxial figure occasionally shown, the sign being —, and 2 E large.

*Diagnostic features*—The features most useful in identifying this substance are the value of the lowest refractive index,  $\alpha$ , and the inclined extinction seen in parallel polarized light, with the nicol prisms crossed. The immersion liquid may consist of aniline, which has  $n_D = 1.585$ , which lies so near to the value of  $\alpha$  for this substance that the rods disappear practically completely when immersed in it and turned to the appropriate position. To determine how they should lie in order that this effect shall be shown, each rod should first be examined under crossed nicols, and the stage turned until extinction occurs. If the stage is graduated, this will be found to be the case when the crystal lies at about  $17^\circ$  from parallelism with one or the other cross hair. On throwing out the analyzer, the rods lying near the cross hair indicating the plane of vibration of the polarizer will disappear.

$\beta$ -NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE,  
 $(C_{10}H_7NH_2)_2 \cdot C_{10}H_6(SO_3H)_2$

This salt forms long, flat, silky needles when crystallized from hot water. It is soluble in hot water, 95 per cent alcohol, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It is soluble in a cold mixture of 4 volumes of alcohol and 1 volume of water. It does not melt below  $280^\circ$ . On analysis it gave 10.97 and 11.03 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

*Refractive indices (D)*— $\alpha = 1.550$ ,  $\beta = 1.700$ ,  $\gamma = 1.755$ ,  $\gamma - \alpha = 0.205$ , all  $\pm 0.005$ ; index  $\alpha$  usually shown lengthwise, and means between the others crosswise of the needles.

*In parallel polarized light*—Double refraction extreme, the colors being third or fourth order even on slender needles; extinction parallel; elongation negative.

*In convergent polarized light*—Partial biaxial figures sometimes shown, the sign being apparently —, and 2 E large.

*Diagnostic features*—The features most useful in identifying this substance are the habit, the value of the lowest refractive index,  $\alpha$ , and the extinction. None of the other members of the  $\beta$ -naphthylamine series studied crystallize in needles, although

one (the 2,7-compound) is, to be sure, in rods; but this other substance differs sharply in the other two respects mentioned. The immersion liquid may best consist of nitrobenzene, or other oily liquid with  $n_D$  around 1.55. The needles disappear completely when immersed in this liquid and turned so that their long direction lies parallel to the plane of vibration of the polarizer. They also extinguish in the same position when the analyzer is inserted. The rods of the 2,7-compound, on the other hand, do not disappear in this liquid, and extinguish when lying at an angle of about  $10^\circ$  with a cross hair.

$\alpha$ -NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE,  
 $(C_{10}H_7NH_2)_2 \cdot C_{10}H_6(SO_3H)_2$

This salt separates in minute needles and lumps when a hot solution is cooled. It is moderately soluble in hot water, slightly soluble in hot 95 per cent alcohol, and practically insoluble in cold water and alcohol and in acetone. It is slightly soluble in cold alcohol diluted with one-quarter its volume of water, and soluble in the same solvent when hot. It does not melt below  $280^\circ$ . Analysis gave 11.07 and 11.31 per cent sulfur.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rounded grains, in part elongated and rod-like.

*Refractive indices (D)*— $\alpha = 1.583$ ,  $\beta = 1.640$ ,  $\gamma = 1.690$ ,  $\gamma - \alpha = 0.107$ , all  $\pm 0.005$ ; intermediate values are usually shown.

*In parallel polarized light*—Double refraction extremely strong, the colors being second to third order on small grains; extinction inclined, but angle not definitely determinable; elongation variable.

*In convergent polarized light*—Partial interference figure occasionally shown, the sign being apparently negative, and 2 E large.

*Diagnostic features*—The most characteristic feature of this substance is the value of the highest refractive index,  $\gamma$ . On immersion in a mixture of 3 parts  $\alpha$ -monobromonaphthalene with 2 parts of methylene iodide ( $n_D = 1.689$ ), grains so situated as to exhibit index  $\gamma$  will disappear in one direction or the other. Index  $\alpha$  is also fairly distinctive, when taken in connection with the crystal habit; for the other member of this series with the same value of  $\alpha$ , the  $\alpha$ -1,6-compound, is markedly rod-like in habit. Aniline ( $n_D = 1.585$ ) is an immersion liquid coming near to the value of  $\alpha$  in refractive index, and disappearance will occur in this liquid in the case of grains lying in the proper direction.

$\beta$ -NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE,  
 $(C_{10}H_7NH_2)_2 \cdot C_{10}H_6(SO_3H)_2$

This salt forms a dense precipitate of microscopic plates (sometimes needle-like) which are only slightly soluble in hot solvents, and practically insoluble in the cold. It does not melt when heated to  $280^\circ$ . The per cents of sulfur found were 11.02 and 11.02.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, with a more or less rhombic outline.

*Refractive indices (D)*— $\alpha = 1.610$ ,  $\beta = 1.634$ ,  $\gamma = 1.830$ ,  $\gamma - \alpha = 0.220$ , all  $\pm 0.005$ ; indices  $\alpha$  and  $\beta$  are usually shown,  $\gamma$  appearing only on uptilted plates.

*In parallel polarized light*—Double refraction extreme, the colors being first to second order on very thin plates; extinction inclined at large angles, up to  $40^\circ$ , with respect to crystal edges often present, but parallel to the edges of uptilted plates; elongation variable on the usual plates, — on the uptilted ones.

*In convergent polarized light*—An interference figure frequently shown, the sign being +, and 2 E =  $70^\circ \pm 5^\circ$  (2 E calculated from  $n_s = 76^\circ 26'$ ).

**Diagnostic features**—The habit of this substance is characteristic, and, when taken in connection with the indices as listed, renders the identification of the substance an easy matter. The lowest refractive index,  $\alpha$ , is approximately matched by a mixture of equal parts of monobromobenzene and  $\alpha$ -monochloronaphthalene ( $n_D = 1.600$ ), and the intermediate one,  $\beta$ , by  $\alpha$ -monochloronaphthalene ( $n_D = 1.640$ ).

**$\alpha$ -NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE,**  
( $C_{10}H_7NH_2$ )<sub>2</sub>. $C_{10}H_6(SO_3H)_2$

This salt separates very slowly in the form of groups of long needles, when the hot solution is cooled. It is soluble in hot water, in hot and cold 95 per cent alcohol, and in cold alcohol diluted with one-quarter of its volume of water, but practically insoluble in cold water and in acetone. It decomposes gradually without melting when heated above  $220^\circ$ . It gave on analysis 11.01 and 11.24 per cent sulfur (theory 11.16).

**CRYSTALLOGRAPHIC-OPTICAL PROPERTIES.** *Crystal habit*—Rods, the more slender ones slightly curved.

**Refractive indices (D)**— $\alpha = 1.560$ ,  $\beta = 1.650$ ,  $\gamma = 1.675$ ,  $\gamma - \alpha = 0.115$ , all  $\pm 0.005$ ; index  $\alpha$  usually shown lengthwise, and means of the others crosswise.

**In parallel polarized light**—Double refraction extreme, the colors being third order on even slender rods; extinction parallel; elongation —.

**In convergent polarized light**—Partial biaxial figure rarely shown, the sign being +.

**Diagnostic features**—The features most useful in identifying this substance are the value of the lowest refractive index,  $\alpha$ , and the parallel extinction. Monochlorobenzene ( $n_D = 1.561$ ) matches the index in question, and the rods disappear when their long direction lies parallel with the plane of vibration of the polarizer. Between crossed nicols the extinction is parallel, a property which distinguishes this compound sharply from the one likely to be confused with it, the 1,6-disulfonate.

**$\beta$ -NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE,**  
( $C_{10}H_7NH_2$ )<sub>2</sub>. $C_{10}H_6(SO_3H)_2$

This salt forms a mass of long, slender needles on cooling a hot solution. It is soluble in hot water and 95 per cent alcohol, practically insoluble in cold water and alcohol and in acetone, and appreciably soluble in a cold mixture of 4 volumes of alcohol and 1 of water. It does not melt when heated to  $280^\circ$ . Analysis gave 11.07 and 11.16 per cent sulfur.

**CRYSTALLOGRAPHIC-OPTICAL PROPERTIES.** *Crystal habit*—Rods, in part plate-like; sometimes showing a  $130^\circ$  termination; often twinned, that is, grown together in groups of two in definite crystallographic relationship.

**Refractive indices (D)**— $\alpha = 1.530$ ,  $\beta = 1.700$ ,  $\gamma = 1.740$ ,  $\gamma - \alpha = 0.210$ , all  $\pm 0.005$ ; index  $\alpha$  is often shown lengthwise on the twins, but crosswise on rods with parallel extinction;  $\beta$  is shown lengthwise on the latter.

**In parallel polarized light**—Double refraction extreme, colors being second or third order even on thin plates, down to first on parallel-extinguishing rods; extinction inclined, on twins making an angle of  $8^\circ \pm 1^\circ$  with the twinning plane, often parallel on untwinned rods; elongation variable, but usually + on untwinned rods.

**In convergent polarized light**—A biaxial interference figure often shown, the obtuse bisectrix being perpendicular to the plates; 2 E is evidently large and sign —.

**Diagnostic features**—The features most useful for identifying this substance are the habit, especially the frequent twinning;

the unusually low value of the lowest refractive index,  $\alpha$ , and the extinction relations. The lowest index is matched by methyl salicylate ( $n = 1.530$  to  $1.535$ ); and crystals immersed in this liquid disappear in one direction or another with reference to the plane of the polarizer.

SUMMARY

The  $\alpha$ - and  $\beta$ -naphthylamine salts of the naphthalene- $\alpha$ -,  $\beta$ -, 1,5-, 1,6-, 2,6- and 2,7-sulfonic acids and the ferrous salt of naphthalene- $\beta$ -sulfonic acid are described. Their characteristic relative solubilities are shown in Table I and their optical properties in Table II.

TABLE I—RELATIVE SOLUBILITIES OF SUBSTANCES DESCRIBED  
(Except the ferrous salt of the  $\beta$ -acid)

NOTE: d. = difficultly soluble; v. d. = very difficultly soluble; sol. = soluble; s. sol. = slightly soluble; mod. = moderately soluble; insol. = insoluble; v. s. = very slightly soluble.

$\alpha$ -NAPHTHYLAMINE SERIES						
SULFONATE	$\alpha$	$\beta$	1,5	1,6	2,6	2,7
Cold water	d.	d.	v. d.	d.	d.	d.
Hot water	sol.	s. sol.	d.	sol.	mod.	sol.
Cold 95 per cent alcohol	d.	d.	d.	s. sol.	d.	sol.
Hot 95 per cent alcohol	sol.	s. sol.	s. sol.	sol.	s. sol.	sol.
Cold 75 per cent alcohol	sol.	s. sol.	d.	sol.	s. sol.	sol.
Hot 75 per cent alcohol	sol.	s. sol.	d.	sol.	s. sol.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	insol.	insol.	insol.	insol.	insol.	insol.
$\beta$ -NAPHTHYLAMINE SERIES						
Cold water	d.	v. d.	v. d.	d.	v. d.	d.
Hot water	sol.	mod.	s. sol.	sol.	s. sol.	sol.
Cold 95 per cent alcohol	d.	s. sol.	v. d.	s. sol.	v. d.	d.
Hot 95 per cent alcohol	sol.	mod.	s. sol.	sol.	v. s.	sol.
Cold 75 per cent alcohol	sol.	mod.	d.	sol.	d.	s. sol.
Hot 75 per cent alcohol	sol.	sol.	s. sol.	sol.	v. s.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	sol.	insol.	insol.	insol.	insol.	insol.

1 Four volumes of 95 per cent alcohol : 1 volume of water.

TABLE II—OPTICAL PROPERTIES OF SUBSTANCES DESCRIBED

$\alpha$ -NAPHTHYLAMINE SERIES							FERROUS $\beta$
SULFONATE	$\alpha$	$\beta$	1,5	1,6	2,6	2,7	$\beta$
Habit	plates	needles	plates	rods	grains	rods	plates
Indices:							
$\alpha$	1.552	1.600	1.600	1.583	1.583	1.560	1.500
$\beta$	?	1.650	?	1.730	1.640	1.650	?
$\gamma$	1.799	1.725	1.795	1.770	1.690	1.675	1.660
$\gamma - \alpha$	0.243	0.125	0.195	0.187	0.107	0.115	0.160
Usual	$\alpha$ & $\gamma$	$\gamma$	$\alpha$ & $\gamma$	$\alpha$ & $\gamma$	means	$\alpha$ & $\gamma$	
Colors	1-2	1-2	2-3	2-3	3	3	2
Extinction	par.	par.	incl.	17°	incl.	par.	par.
Elongation	indet.	+	indet.	—	indet.	—	indet.
Figure	0	0	rare	occas.	occas.	rare	occas.
2 E	indet.	indet.	indet.	large	large	indet.	large
Sign	indet.	+	indet.	—	—	+	+
$\beta$ -NAPHTHYLAMINE SERIES							$\beta$ -Acid Salt 1,5
SULFONATE	$\alpha$	$\beta$	1,5	1,6	2,6	2,7	1,5
Habit	plates	plates	plates	needles	plates	rods	plates
Indices:							
$\alpha$	1.620	1.640	1.631	1.550	1.610	1.530	1.550
$\beta$	1.670	?	1.647	1.700	1.634	1.700	1.700
$\gamma$	1.850	1.730	1.755	1.755	1.830	1.740	1.850
$\gamma - \alpha$	0.230	0.090	0.124	0.205	0.220	0.210	0.300
Usual	$\alpha$ & $\beta$	$\alpha$	$\alpha$ & $\beta$	$\alpha$	$\alpha$ & $\beta$	$\alpha$ & $\beta$	$\alpha$ & $\beta$
Colors	1-2	1-2	1	3-4	1-2	2-3	3-4
Extinction	par.	indet.	indet.	par.	40°	8°	indet.
Elongation	+	indet.	indet.	—	±	±	indet.
Figure	usual	rare	usual	occas.	usual	usual	occas.
2 E	85°	indet.	75°	large	70°	large	large
Sign	+	indet.	+	—	+	—	+

NAPHTHALENE SULFONIC ACIDS. II—A METHOD FOR THE QUALITATIVE DETECTION OF SOME OF THE NAPHTHALENE SULFONIC ACIDS<sup>1</sup>

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During the course of experiments on the sulfonation of naphthalene it became desirable to have a fairly rapid and convenient way of detecting the presence of the various sulfonic acids formed when naphthalene is subjected to the action of sulfuric acid under varying conditions. No readily applicable method is to be

<sup>1</sup> Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.