part of the picric acid. This was filtered off and the remainder extracted with ether. The hydrochloride of the base was made strongly basic, the free base extracted with ether and subsequently distilled under reduced or atmospheric pressure.

Reduction of Metanicotine.—As a standard run 0.1 mole (23.5 g.) of metanicotine hydrochloride in 150 cc. of 95% ethyl alcohol with 0.2 g. of platinum-oxide platinum black was used. The time required for the reduction to dihydrometanicotine (absorption of 0.1 mole of hydrogen) was thirty minutes, while the reduction to octahydrometanicotine (absorption of 0.4 mole of hydrogen) required three to four hours. The catalyst was removed and the free bases were recovered from the hydrochlorides as in the reduction products of nicotine. The yields are practically quantitative in each case.

The ethylenic linkage in the aliphatic chain in metanicotine is much more easily reduced than the unsaturated bonds in the pyridine nucleus as practically all of the metanicotine is converted into dihydrometanicotine before the reduction of the pyridine ring is started.

Summary

Nicotine hydrochloride has been reduced to a mixture of hexahydronicotine hydrochloride and octahydronicotine hydrochloride with hydrogen using platinum-oxide platinum black as catalyst. Metanicotine hydrochloride has been reduced to both dihydrometanicotine hydrochloride and octahydronicotine hydrochloride, the yields being quantitative.

A method is given for the separation of the reduction products of nicotine involving the solubilities of the hydrochlorides and picrates.

Pure nicotine can be conveniently obtained by crystallization of the hydrochloride from an ether–acetone solution of the commercial 95% nicotine. The hydrochloride recrystallizes from hot absolute ethyl alcohol upon the addition of acetone.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALABAMA]

SULFUR DYES. I. PREPARATION OF A NEW SERIES[1]

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Introduction

In 1861 Troost,[2] by reducing a crude mixture of 1,5- and 1,8-dinitronaphthalenes with sodium sulfide and other reducing agents, obtained colored products. Croissant and Bretonnière[3] obtained a patent in 1873 which included the conversion to dyes of a heterogeneous collection of organic substances (animal and vegetable products, chiefly) when heated with alkali sulfides and polysulfides.

Vidal,[4] in 1893, found that certain aromatic nitrogen compounds yielded

[1] Presented at the Atlanta meeting of the American Chemical Society, April, 1930.

[2] Troost, *Jahresber*, 958 (1861); *cf.* French Patent 244,885.

[3] Croissant and Bretonnière, English Patent 1489 (1873).

[4] H. R. Vidal, German Patent 84,632 (1893); St. Dennis and Vidal, German Patent 85,330, etc.

dyes when heated with alkali polysulfides. This discovery directed other investigators into the field of producing sulfur dyes from pure coal tar derivatives. These dyes have proved very valuable. A few examples are Immedial black, from nitro derivatives of hydroxydiphenylamine, and Immedial pure blue and its homologs, from dialkyl-*p*-amino-*p*-hydroxydiphenylamines. Also, many yellow, orange and brown sulfur dyes were obtained by heating toluylene-2,4-diamine and its acyl derivatives with sulfur alone.

The sulfur dyes have yielded practically all colors except bright reds. Reddish shades have been obtained by thionating certain red dyestuffs, such as the azines, rosindulines and safranines. In some cases copper salts were used as catalysts. The brown, blue and black sulfur dyes produce colors which are least affected by light. Hence, the greatest development of the sulfur dye industry has been in the manufacture of dyes producing these colors.

It appears that sulfur dyes have always been produced by heating or fusing various organic substances with sulfur, alkali sulfides, or mixtures of these. Various modifications of this process have been effected, such as boiling an aqueous solution of the organic substance with alkali sulfides or polysulfides, using catalysts, and varying the temperature.

The practical temperatures for the preparation of sulfur dyes range from below 100° to approximately 300°, the vast majority of reactions taking place below 200°. A few sulfur dyes have been prepared by heating above this temperature.[5]

The simplest pure substances used in the preparation of sulfur dyes appear, in the aromatic series, to be *o*-cresol,[6] salicylic acid,[7] nitrophenols, toluidines and aminophenols; in products of animal and vegetable origin, substances of the type of albumin and glucose; in waste products of manufacture, sawdust, cellulose, etc. According to theory, sulfur dyes may be prepared from aromatic nitrogen compounds, or compounds containing phenolic groups.[8]

Vidal succeeded in preparing sulfur dyes from simple pure substances such as *p*-aminophenol. Wyler[9] obtained a sulfur dye from the aromatic hydrocarbon, acenaphthene, by heating with sulfur at 250–300°. Anthracene,[10] when fused with sulfur at 300°, yields a sulfur vat dye. Retene, when fused with sulfur, forms a sulfur dye. Ellis[11] prepared a sulfur dye

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[5] German Patents 97,285, 118,701, 129,495, 198,049, 161,516; Ö. P. 2336 *Kopp B.*, **7**, 1746 (1874).

[6] F. Bovini, *Notiz. chim. ind.*, **2**, 688–690 (1927); German Patent 102,897 (1895).

[7] U. S. Patent 909,154 (Jan. 12, 1909).

[8] F. M. Rowe, *J. Soc. Dyers Colourists*, **33**, 9 (1917).

[9] M. Wyler, U. S. Patent 1,358,490 (Nov. 9, 1921).

[10] Badische Anilin und Soda Fabrik, German Patent 186,990 (March 23, 1906).

[11] C. Ellis, U. S. Patent 1,274,351 (July 30, 1918).

from an oxygenated aromatic hydrocarbon, naphthol, by heating with a solution of sodium sulfide and sulfur. Binaphthalene dioxide,[12] fused with sulfur, also forms a sulfur dye. With the exception of these few complicated compounds, it appears that at least two groups must be attached to the benzene ring for sulfur dye formation by all processes used at present, and that, even in the case of cellulose, aromatic substances are formed which subsequently react with sulfur.

Numerous attempts to prepare sulfur dyes from simple organic substances have been made in seeking to determine the structure of the more complicated commercial dyes. Hodgson[13] has directly sulfurated aniline from 160° to the boiling point of aniline, and obtained a small yield of a green complex, insoluble in sodium sulfide. He has obtained similar results with *o*-, *m*- and *p*-chloro-anilines.[14]

We have found that practically all organic substances in the vapor phase react with sulfur at higher temperatures to form sulfur dyes.

Apparatus and Procedure

In the preparation of these dyestuffs, we proceeded as follows, referring to Fig. 1.

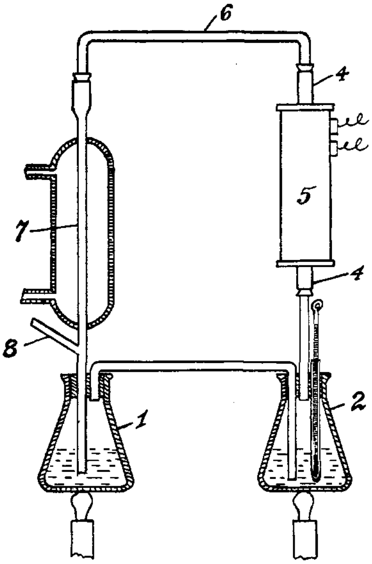

Fig. 1.

The organic material was placed in a vessel, such as flask (1), heated to its boiling point or to a temperature at which the material vaporized, and the vapor passed through the tube as shown, into a vessel (2) containing sulfur heated above its fusing point and above the boiling point of the organic material (preferably to 300° or more.) The bulb of the thermometer was inserted beneath the surface of the sulfur.

The vapors were so introduced as to bubble upward through the molten sulfur, thereby insuring their intimate contact, and hastening the reaction. In the vessel (2) the organic vapor combined with the sulfur to form the dyestuff.

Uncombined vapors of the organic compound and gaseous products of the reaction passed through the tube shown, into the tube (4), which is adapted to be heated, as by an electric furnace (5), and from this were carried by means of the tube (6) into a condenser (7), where that portion of the gases which formed liquids or solids at the temperature of the condenser was returned to the flask (1), while that part which remained gaseous escaped through the opening (8), and was collected as desired.

When the organic material was a gas, as ethylene, or acetylene, the flask (1) was,

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[12] I. G. Farbenind. A.- G., Fr. 653,785 (May 1, 1928).

[13] H. H. Hodgson, *J. Chem. Soc.*, **125**, 1855 (1924).

[14] H. H. Hodgson, *J. Soc. Dyers Colourists*, **42**, 82–83 (1926).

of course, not necessary. In the reaction between the organic material and sulfur a considerable quantity of hydrogen sulfide was produced.

With organic compounds such as benzene, alcohol, ether, etc., having a comparatively low boiling point, the furnace (5) was not necessary. In the case of a solid, such as anthracene, or naphthalene, having a comparatively high boiling point, the furnace prevents the condensation of the solid in the connecting tubes.

On the completion of the reaction, the material in flask (2) was removed and pulverized. This pulverized mass was washed with carbon bisulfide until all free sulfur was dissolved out.

Three hundred grams of organic substance, such as benzene or toluene, was placed in flask (1) and two hundred grams of flowers of sulfur in flask (2). These were heated for several hours. In some cases the operation was continued until hydrogen sulfide ceased to be given off. Our procedure consisted of first heating the sulfur to approximately 380°, then allowing the vapor of the organic substance to bubble slowly through the sulfur. The heat was so regulated that a constant drip of excess organic substance could be observed in the condenser. The hydrogen sulfide was allowed to bubble into an excess of lead acetate solution; the lead sulfide was washed, dried and weighed, and the corresponding amount of hydrogen sulfide calculated. The dye formed and the sulfur and organic substance remaining were weighed. From these weights the ratio of sulfur in hydrogen sulfide to sulfur in the dye, and the amount of organic substance used were determined. The dyes were analyzed for sulfur.

Results

Apparently, all types of organic substances, when vaporized and passed over or through molten sulfur above 300°, formed sulfur dyes in good yields, practically without carbonization. Better yields were obtained at approximately 380°. They are true sulfur dyes in the sense that they dissolve in an aqueous solution of sodium sulfide, and dye cotton, rayon and other vegetable fibers directly. Apparently these dyes are not oxidized in the dyeing process, as the color of the dyed skein is approximately the same as that of the aqueous sodium sulfide solution of the dye. The dye dissolved in aqueous sodium sulfide may be precipitated upon addition of acid, and redissolved in aqueous alkali sulfide solution.

Sulfur dyes of various colors were prepared by passing separately the vapors of pure benzene, toluene, aniline, phenol, benzaldehyde, naphthalene, anthracene, diphenyl, chlorobenzene, dichlorobenzene, diethylaniline, furfural, acetic acid, ethyl alcohol, ether, kerosene and turpentine over, or through, molten sulfur above 300°, preferably between 350 and 400°. Sulfur dyes were also obtained from ethylene, acetylene and by-product gases when these were passed over or through sulfur under the same conditions. The colors of all the dyes are specific and easily reproduced. They are fast to repeated washings with soap and water, and to all organic solvents of which we are aware. In fact, most of the properties are those of sulfur dyes prepared in the usual manner.

Discussion

Through this process we have prepared sulfur dyes which give to vegetable fibers all colors except distinct reds, yellows, blues and blacks.

Undoubtedly many of these colors will later be produced, as many other substances are yet to be tried.

In Table I it appears that the reddish color of these sulfur dyes is connected with the benzene ring. On rayon the benzene sulfur dye gives a red color with very little brown. The replacement of a hydrogen atom of a benzene ring by an amino group makes a great change in color.

TABLE I

SUBSTANCES VAPORIZED THROUGH SULFUR

		Color on cotton and rayon
Benzene	↑	Reddish-brown
Naphthalene		Reddish-brown
Anthracene		Reddish-brown
Dichlorobenzene		Reddish-brown
Monochlorobenzene		Reddish-brown
Furfural		Reddish-brown
Ethylene		Reddish-brown
	Toward Red	
Carbolic acid		Brown
Benzaldehyde		Brown
By-product gas		Brown
Diethyl ether		Grayish-brown
Ethyl alcohol (abs.)		Grayish-brown
Acetylene		Gray
	Toward Green	
Kerosene		Khaki
Turpentine		Khaki
Diethylaniline		Khaki
Acetic acid		Khaki
Diphenyl		Khaki
Toluene	↓	Khaki
Aniline		Green

It is of interest to know that carbon tetrachloride, when passed through sulfur under conditions for dye formation, failed to yield a dye. Dye formation appears to be directly proportional to the amount of hydrogen sulfide evolved. Hence, it would appear that hydrogen-containing organic compounds are necessary to produce sulfur dyes when passed through or over sulfur at 300° or more.

We have always found that a definite relationship exists between the amount of hydrogen sulfide evolved and the amount of dye formed. In Table II, in the case of the benzene sulfur dye, for every one atom of sulfur that went into dye formation, one atom of sulfur was evolved as hydrogen sulfide. In the case of the toluene sulfur dye, Table III, for every three atoms of sulfur that went into dye formation, two atoms of sulfur were evolved as hydrogen sulfide.

It also appears that for every five molecules of benzene that went into dye formation, eight atoms of sulfur reacted. Apparently no appreciable amounts of by-products are formed in the benzene and toluene sulfur dyes. By-products have been obtained in other cases. It is quite likely that the weights of benzene used are too high, owing to loss of benzene by volatilization. Therefore, the benzene–sulfur ratio should not be regarded as significant in this case. In a similar manner, for each molecule of toluene that went into dye formation, five atoms of sulfur reacted. No appreciable amount of toluene was lost by volatilization. The following reaction appears to take place: $[C_6H_5CH_3 + 5S \longrightarrow \text{Dye (3S)} + 2H_2S]_x$. The sulfur in hydrogen sulfide evolved, subtracted from the total sulfur reacted (obtained by weighing all sulfur throughout the reaction) is identical with the sulfur in dye obtained by multiplying the weight of pure dye by percentage sulfur.

TABLE II

BENZENE SULFUR DYE (370–390°)

No.	Time Hours	Min.	Benzene, g.	Sulfur, g.	Benzene to sulfur ratio	Dye formed, g.	Sulfur, in dye, %	g.	Sulfur in H_2S, g.	Ratio of Sulfur in dye to sulfur in H_2S
1	1	32	35.4	23.0	1.54:1	15.5	63.40	9.8	10.3	1:1
2	4	21	38.3	24.9	1.54:1	19.2	65.25	12.5	10.8	1:1
3	4	27	38.2	23.4	1.63:1	17.0	64.40	11.0	10.6	1:1
4	6	34	45.9	29.3	1.56:1	23.0	64.50	14.8	14.9	1:1
5	12	23	41.4	26.5	1.56:1	21.4	66.10	14.0	11.2	1:1
Av.					3:2 g.					1:1 g.
Av.				5 moles:8 g. atoms			64.73			1:1 g. atoms

TABLE III

TOLUENE SULFUR DYE (370–390°)

No.	Time, Hours	Min.	Toluene, g.	Sulfur, g.	Toluene to sulfur ratio	Dye formed, g.	Sulfur in dye, %	g.	Sulfur in H_2S, g.	Ratio of sulfur in dye to sulfur in H_2S
1	4	30	16.4	26.5	1:1.61	24.3	64.38	15.6	9.8	3:2
2	5	0	20.9	38.3	1:1.83	32.0	63.00	20.2	13.4	3:2
3	6	0	23.6	37.4	1:1.60	34.4	63.87	22.0	13.7	3:2
4	13	0	37.4	61.7	1:1.65	52.7	64.50	34.0	20.0	3:2
Av.					1:1.67 g.					3:2 g.
Av.					1 mole:5 g. atoms		63.93			3:2 g. atoms

From Tables II and III it may be noted that the percentage of sulfur in dye remains fairly constant for each dye (benzene and toluene), regardless of the length of the run. The small differences in different runs are undoubtedly due to slight amounts of carbon formed in some runs. Also, the sulfur analysis of the benzene sulfur dye prepared at the boiling point of sulfur (444°) is identical with that of the benzene sulfur dye prepared at 380°. The colors of these dyes on rayon and cotton skeins are constant, regardless of the time and temperature of preparation. The twenty sulfur dyes that we have prepared (Table IV) represent practically all types of organic compounds. From the percentages of sulfur in the dyes prepared from aromatic substances, it appears that each benzene ring is attached to four or five sulfur atoms. This seems to be true in the case of most of the benzene derivatives used.

Table IV

Colors and Sulfur Analyses

Dye	Color of solid dye	Percentage of sulfur Found		Av.
Benzene	Brick red	64.60	64.84	64.72
Naphthalene	Brick red	71.40	71.10	71.25
Anthracene	Blackish-red	72.91	73.13	73.02
p-Dichlorobenzene	Orange	73.96	74.11	74.03
Monochlorobenzene	Reddish-brown	73.52	72.90	73.21
Furfural	Bluish-black	80.20	80.37	80.28
Ethylene	Bluish-black	61.54	61.15	61.34
Carbolic acid	Bluish-black	63.76	64.25	64.00
Benzaldehyde	Bluish-black	63.51	63.46	63.48
Ethyl alcohol (abs.)	Gray	10.13	9.56	9.84
Acetylene	Bluish-black	68.15	67.85	68.00
Kerosene	Bluish-black	61.98	61.78	61.88
Turpentine	Greenish-black	62.64	62.29	62.46
Diethylaniline	Bluish-black	60.30	60.12	60.21
Acetic acid	Bluish-black	49.47	49.61	49.54
Toluene	Greenish-brown	63.58	63.99	63.78
Aniline	Green	58.60	58.00	58.30

We hesitate to attempt to write the structure of these sulfur dyes until we have more data. The high sulfur content appears to show that chains of sulfur atoms must be attached to the benzene, toluene, etc., rings.

Probably a chromophore group, consisting of sulfur atoms in certain formations, exists. The colors of the dyes are apparently modified by various groups which are attached to such a chromophore.

Many hydrocarbons[15] heated with sulfur have yielded various non-dye substances. Ziegler,[16] in 1890, stated that the stability of the benzene ring toward sulfur is remarkable, and that certain basic groups attached to the benzene nucleus are necessary for reactivity with sulfur. Szperl[17] succeeded in reacting sulfur with benzene in a sealed tube. He obtained non-dye substances in which the sulfur was not substituted for hydrogen of the benzene ring. Glass and Reid[18] have shown that sulfur can be introduced

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[15] V. Meyer and Sandmeyer, *Ber.*, **16**, 2176 (1883); E. Baumann und E. Fromm, *ibid.*, **28**, 890–895, 895–907, 907–914 (1895); a review of the literature of the subject, Ludwik Szperl, *Chemik Polski*, **15**, 8–10 (1917).

[16] J. H. Ziegler, *Ber.*, **23**, 2472 (1890).

[17] Ludwik Szperl, *Roczniki Chem.*, **6**, 155 (1926).

[18] H. B. Glass and E. Emmet Reid, This Journal, **51**, 3428 (1929).

directly into aromatic hydrocarbons, such as benzene and ethylbenzene, without catalysts, in a steel bomb at 350°. Thiophenol was produced from benzene and sulfur along with other related sulfur compounds. This work suggests that the brownish-red dye which we have obtained by passing the vapor of benzene over or through molten sulfur at atmospheric pressure is prepared through the mechanism of thiophenol formation.

In the case of aniline and sulfur, we obtained a green dye, soluble in an aqueous solution of sodium sulfide. Hodgson's work[19] indicates, at least in the case of aniline, that our process of using the vapor of the organic substance in contact with sulfur at high temperatures give to the sulfurated substance the property of solubility in an aqueous solution of sodium sulfide.

We have substituted selenium for sulfur in the above process, and have obtained similar reactions.

The production of a sulfur dye in this simple manner from substances such as benzene and ethylene naturally arouses the hope that definite ideas on the structure of sulfur dyes may shortly be obtained. Work directed to this end is now proceeding in the laboratory of the University.

Summary

1. Practically all types of hydrogen-containing organic compounds, such as benzene, toluene, furfural, ethylene, ether, kerosene, etc., when vaporized and passed over or through molten sulfur above 300°, form true sulfur dyes in good yields, practically without carbonization.

2. Twenty dyes, which give to vegetable fibers all colors except distinct reds, yellows, blues and blacks, have been prepared.

3. Sulfur analyses, ratios of sulfur in dyes to sulfur in hydrogen sulfide evolved, and ratios of organic substances to sulfur reacted are given.

4. Some ideas as to the structures of the sulfur dyes prepared from these simple substances are presented.

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[19] H. H. Hodgson, *J. Chem. Soc.*, **125**, 1855 (1924); *J. Soc. Dyers Colourists*, **42**, 82–83 (1926).