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STUDY OF TOLUENE SULFUR DYE

BY

F. A. HODGES

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PART ONE

A Brief History of the Development
of the Dye Industry

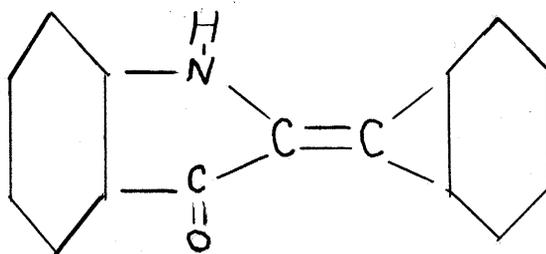
The use of substances as dye materials began thousands of years ago. We have accounts of Ancients who used dyeing materials for developing colors pleasing to the eye almost as early as the art of leaving written records itself. The point to note in this long period of time in the use of dyeing material is the fact that it was always obtained until recent years from natural sources. Chemists interested in the formation of substances learned very little about the structure of dye stuffs until recent years—a fact that must be known before the systematic development of specific new dyes by synthesis can proceed very far.

The substances from which natural dyes are obtained do not furnish very many different shades of colors. We have the true colors but there are not enough to give many varieties of shades and tints. Therefore to have a wide variety of coloring matter much of it must be made synthetically.

The first coloring matter¹ which was made by chemical reaction was prepared by Perkin, an English chemist, who obtained the dye mauve from coal tar, a residue obtained from the distillation of coal.

1. Richardson, L. B., General Chemistry, pp. 778-783.

In the process of dye-making the derivatives of the aromatic compounds are called the intermediates. This process consists in the introduction into the molecule of certain replacing radicals, particularly the amino (NH_2) and the hydroxyl (OH) groups. From these intermediates are built, by various processes, complicated molecular structures which make up the dye itself. The formula of indigo blue,¹ by comparison with some others is not particularly complicated in its molecular structure. It has the following structure:



Considering this structure as a simple dye it is not strange that chemists should know little about their chemical structure and their development by synthesis until a very recent date.

When compounds are colored-substances² they usually contain in their molecules certain definite atomic arrangements or groups known as chromophore groups. This group causes the compound to contain a color although it may not necessarily be a dye.

1. Richardson, L. B., General Chemistry, PP. 778-783.
 2. Ibid.

¹
Dyeing consists in imparting colors to substances of various kinds, usually textile fibers, in such manner that it is not readily removed by those influences to which it is subjected. The term tinting carries the same meaning as dyeing, but this term is applied to light shading.

²
 The mechanical theory of dyeing advanced by Hellat and D Alpligny in 1870 was that particles of coloring matter are embedded in the minute pores of the fiber substance. The chemical theory ³ of Macquer and Bergman is that wool and silk fibres are composed of amino-acids in the fibers and thus have basic and acidic chemical properties. When the dye material comes in contact with these substances under proper conditions a definite color is produced. From a consideration of dye materials ⁴ it seems that a single explanation fails to explain the production of color.

From the view of modern chemistry dyes are ⁵ classified as, (1) mordant dyes, (2) acid dyes, (3) acid-mordant dyes, (4) direct dyes, (5) basic dyes, (6) sulphide dyes, (7) vat dyes, (8) ingrain dyes.

1. Thorpe, E., Dictionary of Applied Chemistry, Vol. VI, P. 574.

2. Ibid.

3. J. Soc. Dyers and Colourists, (1889) II Knecht and Appleyard.

4. Ibid.

5. Thorpe, E., Dictionary of Applied Chemistry, Vol. VI p.574

Until the discovery of congo red there were three dye stuffs only which were capable of dyeing cotton directly from their aqueous solution. These dyes were Turmeric safflower and annato. Now there are a large number of synthetic substantive dyes by means of which any desired shade may be obtained. Vat dyes and sulphide dyes are most important for this purpose. Turmeric is the only important natural dye for cotton. These direct dyes are azo-dyes and contain the chromophore group - N = N. Since the sulphide dyes are the branch of dyes in which we are most interested, we shall consider them alone in detail.

1

In 1861 Troost reduced a crude mixture of 1:5 and 1:8-dinitro-naphthalene with sodium sulphide and other reducing agents and obtained colored products. Croissant and Bretonnaire ² 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 sulphides and polysulphides.

3

Vidal in 1873, found that certain aromatic nitrogen compounds yielded dyes when heated with alkali polysulphides. This discovery directed other investigators into this field of producing sulphur dyes

1. J. (1861) 958; cf Fr. Pat. 244855.
 2. Eng. Pat. (1873) 1489.
 3. Vidal, H. R., D. R. P. 84632 (1873); St Dennis and Vidal, D. R. P. 85330.

from pure coal tar derivatives. These dyes have proved to be very valuable. A few examples of these are Immedial black, from nitro derivatives of hydroxy-diphenyl-amine, and Immedial pure blue and its homologues from dialkyl-p-amino-p-hydroxy-diphenyl amines. Many yellow, orange, and brown sulphur dyes were obtained by heating tolyulene 2:4 diamine and its acyl derivatives from sulphur alone.

Sulphur dyes have yielded practically all colors except bright reds. The production of fast blacks, blues, greens, browns, and yellows are of the greatest importance. Reddish dyes have been obtained by thionating certain red dye stuffs, such as the azines, rosindulines, and saffranines. In some cases copper salts were used as catalysts. ¹ The brown, blue and black sulphur dyes produce colors which are least affected by light. Hence the greatest development of the sulphur dye industry has been in the manufacture of dyes producing these colors.

It appears that sulphur dyes have always been produced by heating or fusing various organic substances with sulphur, alkali sulphides, or polysulphides, using catalysts and varying the temperature. The practical temperature for the preparation of these dyes range from

1. D. R. P. 126175; 152373; 1614621; 177091; 181125.

below 100° C. to approximately 300° C., the majority of these reactions taking place below 200° C. A few sulphur dyes have been prepared above this temperature. The simplest pure substance used in the preparation of sulphur dyes appear, in the aromatic series, to be orthocresol,¹ salicylic acid,² nitro phenol, toluidines, and amino phenols; in products of animal and vegetable origin substances of the type of glucose; in waste products of manufacture, sawdust, cellulose, and similar materials. Sulphur dyes may be prepared from aromatic nitrogen compounds or compounds containing phenolic groups.³ Vidal⁴ succeeded in preparing sulphur dyes from simple pure substances such as p-amino-phenol.⁵ Wyler obtained a sulphur dye from acenaphthene, by heating with sulphur at 250-300°C. Anthracene⁶ when fused with sulphur at 300° yields a vat dye. Retene, when fused with sulphur forms a sulphur dye.⁷ Ellis prepared a sulphur dye from an

1. Bovini, F., Notiz. Chim. Ind. 2 688-90 (1927; D.R.P. 102897 (1895).
2. United States Patent 909154 (Jan. 12, 1909)
3. Rowe, F. M., J. Soc. Dyers and Colourists 33 9 (1917)
4. Vidal, H. R., D. R. P. 84632 (1873); St. Dennis and Vidal, D. R. P. 85330.
5. Wyler, M., United States Patent 1358490 (Nov. 9, 1921).
6. Badische Aniline Soda Fabrik. D. R. P. 186990, (Mar. 23, 1906)
7. Ellis, C., United States Patent 1274351 (July 30, 1918).

oxygenated aromatic hydrocarbon, naphthol, by heating with a solution of sodium sulphide and sulphur.

Binaphthalene dioxide¹ fused with sulphur also forms a sulphur dye. With the exception of these complicated compounds, it appears that at least two groups of atoms must be attached to the benzene ring for sulphur dye formation by all processes used at the present, and that even in the case of cellulose, aromatic substances are formed.

The sulphur dyes come in to the market in the form of powders which are usually insoluble in water, but soluble in a solution of sodium sulphide. The sulphide dyes are commercially known under such names as Sulphurol, thiogene, thional, thionon, thioxine, immedial, kryogan, pyrogen, pyrol, vidal, and auronol dyes.

This group of dye stuffs² is now of great commercial importance in the cotton dyeing because of their relative cheapness and ease of application. Many of them require no treatment after dyeing except exposure to air. The greatest development in these dye stuffs is in the colors brown, blue, and particularly black, which are now manufactured on an enormous scale

1. Farbenind, I. G., A. G. Fr. 653785 (May 1, 1928).
2. Thorpe, E., Dictionary of Applied Chemistry, Vol. II, P. 490.

because of their fastness and ease of application.

The discovery of hydrogen blue¹ and its homologues in 1908 ushered in a new epoch in the history of sulphide dyes because this coloring matter, which is applied as a vat dye, is a serious rival to indigo on account of its fine shades, fastness to light, and to scouring and bleaching agents. It is also deserving of notice because of the fact that the origin of its manufacture is carbazole, $C_6H_5NH \cdot C_6H_4$, a coal tar derivative which has not hitherto been utilizable to any adequate extent in the synthetic color industry.

Vidal black² is produced by heating with alkali polysulfides either p-amino-phenol or substances capable of yielding this compound p-nitro-phenol (100 parts) is slowly added to 400 parts of crystallized sodium sulphide, $(Na_2S \cdot 9 H_2O)$ melted in its water of crystallization, temperature raised to $130^\circ C$. and when reduction is complete 75 parts of sulphur are introduced and the mixture is heated to $150-175^\circ C$. In this reaction H_2S is given off freely.

Sulphide Blues: Pyrogen direct blue³, the first blue sulphide discovered, is prepared from 2:4 dinitro 4' hydroxy-diphenyl-amine (M. P. $187-188^\circ C$) or its

1. C. D. R. pp. 218317; 221215; 222640; and 238857.

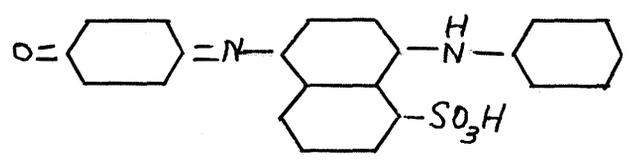
2. Eng. Pats. 23578 (1893); 9943 (1894); D. R. P. PP. 85330; and 90369.

3. Eng. Pat. 5385, (1900); D. R. P. 132424.

Thorpe, E., Dict. of Appd. Chem. Vol. VI p. 498.

products. (M. P. 196-197°C) Ten parts of either of these substances are heated with eighteen parts of anhydrous sodium thiosulphide and sixty parts of alcohol in an iron or enameled autoclave at 135-145°C. The reaction proceeds smoothly in alcoholic solution, coloration begins at 110°C. and after 3-4 hours the pressure reaches 8-10 atmospheres. Cotton is dyed in dark violet blue shades with two percent dye solution and black bluish-violet shades with five percent of the dye.

Sulphide Greens: The 1:8 derivatives¹ of naphthalene are employed in producing sulphide greens. Phenol-a-naphthylamine-8 sulphonic acid and p-amino-phenol yield an indophenol



which gives a green on heating with sodium polysulphide in the presence of copper sulphate. The perimidines produced by condensing 1:8 naphthylenediamine with aldehydes ketones and aliphatic acids² yield indo phenols with p-amino phenols and its chloro derivatives. These indo-phenols when heated for sixty hours in a reflux apparatus with alcoholic sodium polysulphide,

1. A. D. R. P. Anmeldung 20316, (1911).
 2. Annalen (1909); 365, 53; Ber. (1909), 42, 3674.
 Thorpe, E., Dict. of Appd. Chem. Vol. VI, P. 498.

gives rise to very fast dark green coloring matter.

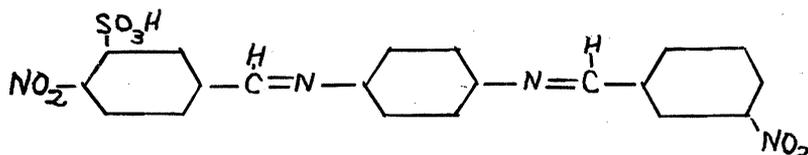
Sulphide Browns: Cachou De Laval¹ is prepared from sawdust and other waste products allied to cellulose by heating these materials with sodium polysulphides at 250-300 °C. A higher temperature produces a darker shade of brown.

Sulphanil Brown:² is produced 2:4 dinitro-4'-amino diphenyl amine, prepared from chloro-2:4-dinitrobenzene and p-phenylene-di-amine, is converted by means of aqueous alkali sulphite at 150 °C. into the sulphonic acid. This compound (40 parts), dissolved in twice its weight of water, is heated at 140-160 ° with sodium sulphide (80 parts) sulphur (30 parts) and water (100 parts) until the mass is dry. The aqueous solution of the dye is violet black changed to brown by caustic alkali.

Pyrogene yellows:³ These coloring matters were the first sulphide yellows discovered and are produced by heating with sodium sulphide and sulphur various condensation products of aromatic p-diamines and amino- and diamino-phenols with formaldehyde, benzaldehyde, the nitrobenzaldehydes and nitro-benzyl chlorides. The compounds with these aldehydes are of the nature of anhydro bases. (Schiff Bases). The following

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1. Richardson and Akroyd; J. Soc. Chem. Ind. (1896), 328.
 2. K. D. R. P. 125584.
 3. D. R. P. 135335; Eng. Pats. 1007, (1900) Fr. Pats. 295.

derivatives which may be regarded as typical of the members of the series give in the polysulphide fusion orange yellow dyes.



Manufacture of Sulphide Dyes.

The apparatus¹ most generally employed in the polysulphide fusion is a cylindrical cast iron jacketed pan about three feet deep by two feet in diameter and having a capacity of about one hundred gallons. The jacket serves for the introduction of super heated steam, a pressure of 4-6 atmospheres sufficing to raise the temperature of the fusion to 125-140°. The pan is fitted with a mechanical stirrer, and its domed lid contains a man hole for introducing the reagents. A thermometer tube dipping into the fusion, an opening leading to the reflux condenser, and an inlet tube for air increased or decreased pressure. The jacket is fitted with a manometer, and if the pan to be used for fusions under pressure it is also fitted with a gauge. This plant serves for a majority of modern sulphide fusions which are carried out at temperatures only slightly above the boiling point of water. In fusions requiring higher temperatures 200-300°C. smaller cast iron pans are employed, heated either by direct fire in

I. Thorpe, E., Dict. of Appd. Chem. Vol. VI, P. 506.

an oil bath, the fittings of the melting pan being similar to those of the jacketed pan. Vaseline or a high boiling point liquid may be employed in the oil bath, which is preferable to heating by direct fires as local overheating is avoided. This mode of heating is employed both in sulphide melts and fusions with sulphur alone in the production of yellow sulphide dyes.

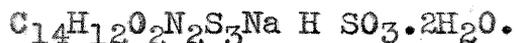
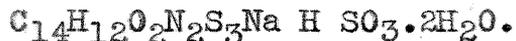
CONSTITUTION OF THE SULPHIDE DYES

The constitution of the sulphide dyes ¹ is not known, but the commercial products are probably mixtures of polymers or homologues and not homologous bodies. These products contain free sulphur varying in amount from one to twelve percent of the dye, and also contain variable amounts of sulphides and polysulphides.

The difficulty in ascertaining the constitution ² of these dyes is due to their non-crystalline form. These dyes tend to form colloidal solutions which render impossible the determination of their molecular weights. Commercial sulphur dyes generally contain colloidal sulphur and thioxone sulphur. Only in the case of the simplest members has it been possible to obtain crystalline derivatives, and through these

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1. Gardner and Hodgson; J. Soc. Chem. Ind. (1910), 672.
 2. Thorpe, E., Dict. of Appd. Chem. Vol. VI, P. 506.

compounds to establish a relationship between the sulphide blues and the blues of the methylene series. Immedial pure blue, referred to above, gives a



Numerous attempts to prepare sulphur dyes from simple organic substances have been made in seeking to determine the structure of the more complicated commercial dyes. Hodgson² has directly sulphurated aniline from 160^o C. to the boiling point of aniline and obtained a small yield of a green complex, insoluble in sodium sulphide solution. He has obtained similar results³ with o-, m-, and p-chloro anilines.

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1. Gnehm and Bots; Jr Pr. Chem. (1904), II. 69, 169.
 2. Hodgson, H. H., J. C. S., 125, 1855, (1924).
 3. Hodgson, H. H., J. Soc. Dyers and Colourists, 42, 82-3, (1926).

PART TWO

Purpose of This Investigation

1

The value of dye stuffs used in the United States per year is enormous. The annual production of dye is 60,000,000 pounds a year. The value of this commodity is \$48,000,000.00. The practical importance of this industry is of even more value when we consider that the entire textile industry with an annual production of \$3,000,000,000.00 worth of textile fibers are largely dependent upon this industry for coloring its materials in an attractive way for the buying public.

Until 1914 the United States bought her dye stuffs from Germany. At this time German Chemists had synthesized 5000 dyes², 900 of these being produced commercially. When the World War began the German markets were excluded from American manufacturers and the United States had to make her own dye materials. This was a great problem for some months for the first American dyes produced were of a very inferior quality. After considerable experiment in research work upon dye synthesis and production the United States were able to cope with the situation. So successful have their efforts been that not only are nearly all the dyes used

1. Richardson, L. B., General Chemistry, PP. 778-783.

2. Ibid.

in this country produced here but a surplus is being made and sold in foreign markets.

These dye products are manufactured in various ways, depending upon the methods and substances required to make each specific dye. Each series of dyes¹ has its advantages and disadvantages as a commercial commodity. Some of these are of great importance in deciding the practical success of an attempt to manufacture them commercially.

The first requirement of a material for dyeing purposes is that its coloring qualities will be fast to all ordinary uses to which textile fabrics are subjected. The next point of importance is that it must be produced at a moderate cost. What might be termed moderate cost depends, of course, upon the price of the particular finished article for which it is used as a dye. Wool and silk materials by having a higher selling price than cotton and rayon, may be dyed profitably with a dye which cost much more per pound than that used in dyeing the cotton fabrics. In other words the price of a dye used in dyeing an article for sale as a commercial commodity bears a ratio to the sale price of the finished article, and

Thorpe, E., Dictionary of Applied Chemistry, Vol. VI.
P. 498.

if the article is to find a ready market this ratio must not exceed a certain percent of the finished article.

As I have mentioned above there are eight divisions of dyes. This division is based upon the methods used in dyeing the fabrics and to the chemical properties possessed by the dyes themselves. We find the sulphide dyes especially important in the cotton textile industry, on account of their fastness, ease of application, and moderate costs. For wool and silk materials the sulphide dyes have not occupied such an important place as dyeing agents because there is a tendency for the compounds forming these substances to be attacked by the dye, or the materials used in the dyeing process.

Another question of vital importance at the present time is the chemical structure of sulphur dyes. Due to the very complex molecular structure of all the sulphide dyes and the various ways the atoms of sulphur combine to form molecular sulphur under varying conditions, chemists have been unable to determine the structures of these dyes. The method by which chemists hope to determine this molecular structure of these compounds is to find some sulphur dyes of very simple molecular structure and study their molecular structure. Then, by synthesis, they hope to build up more complicated

compounds and finally arrive at the structural formulas of the dyes used at the present time.

In the production of this new series (hydrogen containing organic compounds heated in contact with molton sulphur at a temperature of 300-400^oC.) twenty¹ different dyes have been prepared. I have made in this series of experiments a number of tests with toluene and sulphur. My object was to obtain quantitative relations of products formed and materials used. In addition to the dye formed I have tested all by-products obtained, directly or indirectly, to learn whether other products were formed in appreciable quantities during the sulphur-toluene reaction and the resulting dye formation.

The dye produced in this series meets all requirements that a sulphur dye should meet, as I have listed above. This method² was discovered recently by the University of Alabama Chemistry Research Department. The materials used are simple. The molecular structure of toluene is a benzene ring with a methyl group attached. This may be considered as a benzene ring in which a hydrogen atom has been replaced by a methyl group. The sulphur used in the experiments is in the pure state. The dye produced from these two substances must be very simple in structure, though its

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1. Experiments conducted under the direction of the school of Chemistry, Metallurgy & Ceramics, U. of A.
 2. Article to be published by University of Alabama, Chemistry Department.

molecular weight may be large because the compound must be a union of benzene rings with sulphur either attached to a methyl group, benzene ring or possibly both.

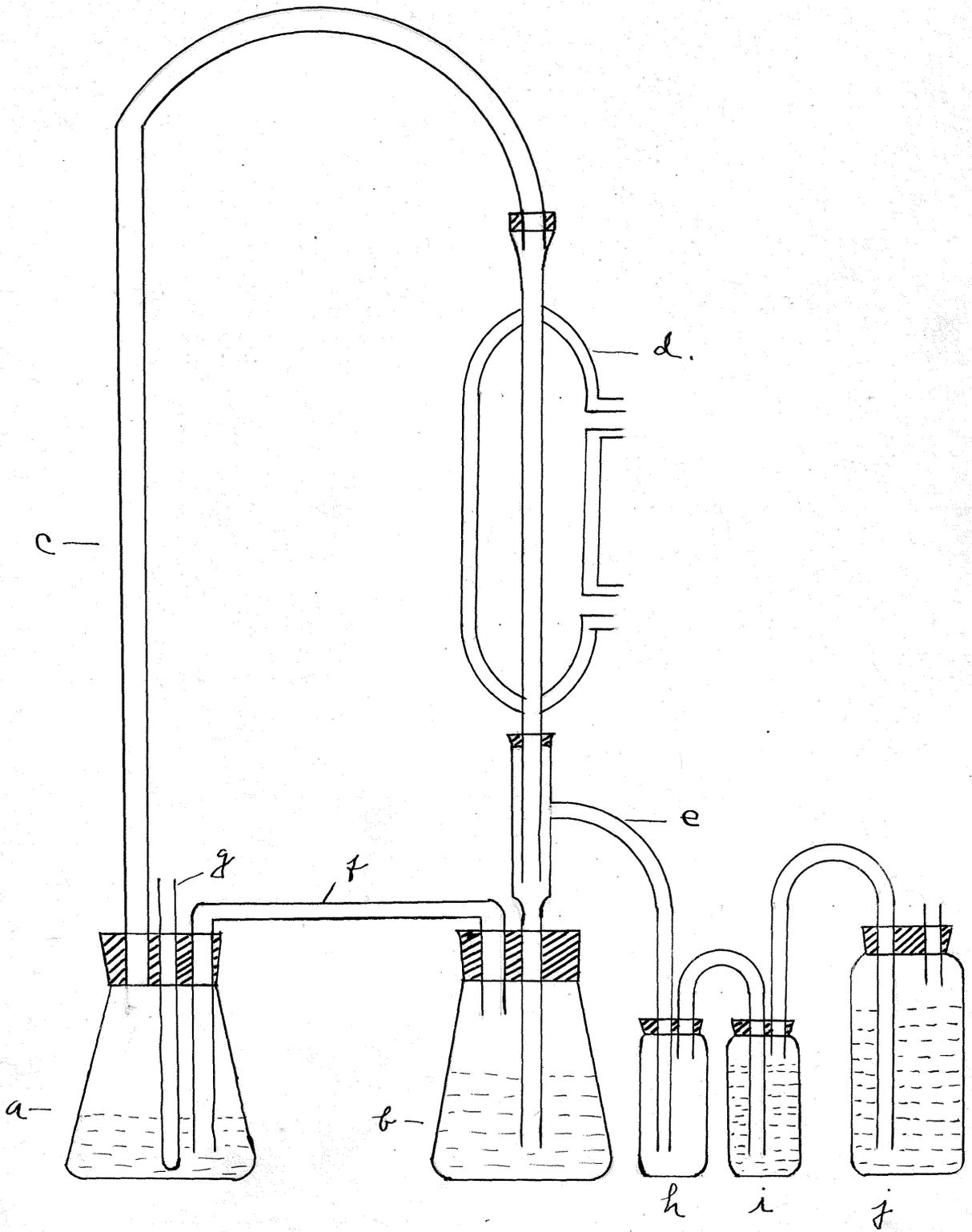
The dyes produced in this series to date give definite colors easily reproduced. This proves that the reaction is definite and reacts invariably in the same way, under the same experimental conditions. The materials are relatively cheap and the yield is large. The manufacturing apparatus need not be very elaborate, and the products can be produced very cheaply.

It would seem that a new series of dyes has been discovered which will have commercial importance and at the same time furnish the materials necessary for the complete determination of the molecular structure of sulphide dyes.

PART THREE

SKETCH AND DESCRIPTION OF APPARATUS

- a. Flask containing sulphur.
- b. Flask containing the toluene.
- c. Air cooled condenser for sulphur-toluene vapors.
- d. Water jacketed condenser.
- e. Tube for conducting gaseous products to lead acetate solution.
- f. Tube for conducting toluene vapors into molten sulphur.
- g. Tube, with lower end sealed, for thermometer.
- h. Water trap.
- i. Bottle containing water.
- j. Bottles containing lead acetate solution.



PART FOUR

Method of Procedure

Two hundred grams of flowers of sulphur are placed in flask (a), and three hundred grams of toluene are placed in flask (b). The apparatus was set up as shown in the diagram and the sulphur was heated to 370-390^o C. and the toluene heated enough to force toluene vapor into the flask containing the sulphur. These experiments were run for varying amounts of time to get data concerning the effect of time on the rate of reaction and differences, if any, in the composition of the products produced during different periods of time. The toluene was kept boiling rapidly enough to keep enough toluene in the flask containing the sulphur to give a small amount condensing in the air condenser and dropping back in to the flask. The toluene vapors are forced through the tube connecting the two flasks and bubbled up through the molten sulphur. The hydrogen sulphide produced by the reaction is sent through the condensers (c) and (d) and forced out through the exit tube (e), water trap (i), pure water bottle (h), and in to the lead acetate solution (j), where it is precipitated as lead sulphide.

At the conclusion of the experiment the apparatus was disconnected and the materials collected.

The lead sulphide was washed, dried, and weighed, and from this the corresponding hydrogen sulphide was calculated. The sulphur dye mixture was ground to a very fine powder and placed on a filter paper in a large funnel and the free sulphur washed out with carbon bisulphide. The remaining dye, practically pure, was then dried and weighed to obtain the amount of pure dye formed by the reaction of sulphur and toluene. The carbon bisulphide used to remove the free sulphur from the dye was carefully distilled to learn if there were any solid or liquid products dissolved in the carbon bisulphide. The toluene remaining after the experiment was also distilled to see if any other materials were dissolved in it which could be produced by the reaction.

The experiments listed above in this work have been performed to obtain data pertaining to products formed and their quantitative relation to the substances reacting to form them. These experiments have been repeated to check all results and thus obtain data which could be relied upon in arriving at these relationships.

PART FIVE

Experimental Work

The experimental data will be found listed below in chronological order. A number of the experiments have not been included because some part of the fragile apparatus broke while the experiment was in operation and no data could be obtained by taking the products at this stage, and consequently these were discarded and new experiments were made. A number of the experiments listed here are incomplete because I could not obtain all the material necessary to make a quantitative report on the materials used and the products produced. This is due to the fact that very little has been done on similar experiments before and I did not have many directions to help me avoid some of my mistakes. Therefore the experiments listed in the beginning are incomplete in regard to data. I have included these experiments, however, for the parts of the results I did obtain can be compared with similar results obtained later.

A number of the tests are complete in all details. From them we can get a very good knowledge of the results we can reasonably expect in experiments involving a comparison of materials used to products produced.

EXPERIMENT ONE

Sulphur (initial)----- 200 grams.
 Toluene (initial)----- 300 " .
 Length of experiment in time----- 7 hrs. 50 min.

Products obtained

Sulphur and dye (mixed)----- 183 grams.
 Lead sulphide----- 31.5 grams.*
 Toluene and dissolved sulphur----- 278.5 grams.
 Weight of dye (purified)----- 22.0 grams.

Sulphur accounted for

Sulphur recovered from dye----- **
 Difference in weight between crude
 and purified dye----- 161 grams.
 Sulphur recovered from toluene----- 0.0 grams.
 Sulphur in lead sulphide----- 4.4 grams.
 Sulphur in tubes----- 5.0 grams.
 Sulphur accounted for----- 166.0 grams.
 Sulphur (PbS plus dye plus by-products) 34 grams.

Toluene accounted for

Amount recovered----- 278.5 grams.
 Toluene (dye and by-products)-----, 21.5 grams.

Remarks: The amount of lead sulphide obtained in this experiment is too small as shown by later tests. The yield of dye is low due to the difficulty encountered in keeping the correct temperature.

EXPERIMENT TWO

Sulphur and toluene used same as in Experiment I.

Length of experiment in time----- 6 1/2 hours.

Products obtained

Sulphur and dye (mixed)----- 151 grams.
 Lead sulphide----- 0.0 grams.
 Toluene and dissolved sulphur----- 225.6 grams.
 Weight of dye (purified)----- 29.5 grams.

Sulphur accounted for

Sulphur recovered from dye----- 121.5 grams.
 Difference in weight between crude
 and purified dye----- 121.5 grams.
 Sulphur recovered from toluene----- 0.0 grams.
 Sulphur in lead sulphide----- 0.0 grams.
 Sulphur in tubes----- 5.0 grams.
 Sulphur accounted for----- 126.5 grams.
 Sulphur (PbS, dye and by-products)---- 73.5 grams.

Toluene accounted for

Amount recovered----- 225.4 grams.
 Toluene (dye and by-products)----- 74.4 grams.

Remarks: Due to an accident I was unable to get weight of the lead sulphide produced.

The amount of sulphur and toluene missing is entirely too much. There must have been a break in the flask through which some of the material escaped and burned in the gas flames.

EXPERIMENT THREE

Materials used same as in experiment one.

Products obtained

Sulphur and dye (mixed)-----	185.6 grams.
Lead Sulphide-----	30.3 grams.
Toluene and dissolved sulphur-----	277.0 grams.
Weight of Dye (purified)-----	23.8 grams.

Sulphur accounted for

Sulphur recovered from dye-----	**
Difference in weight between crude and purified dye-----	161.8 grams.
Sulphur recovered from toluene-----	1.0 grams.
Sulphur in lead sulphide-----	4.2 grams.
Sulphur in tubes-----	3.5 grams.
Sulphur accounted for-----	163.3 grams.
Sulphur (PbS, dye, and by-products)----	33.7 grams.

Toluene accounted for

Amount recovered-----	276 grams.
Toluene (dye and by-products)-----	24.0 grams.

Remarks: From later experiments I find this amount of lead sulphide is too small; this is due to the fact that the solution used at the beginning of the year in a beaker becomes ^{so} dilute that it does not react with all the hydrogen sulphide as it is bubbled into the solution.

EXPERIMENT FOUR

Materials used same as in experiment one.

Length of experiment five hours.

Products obtained

Sulphur and dye (mixed)-----	179.8 grams.
Lead sulphide-----	48.8 grams.
Toluene and dissolved sulphur-----	280.1 grams.
Weight of dye (purified)-----	19.4 grams.

Sulphur accounted for

Sulphur recovered from dye-----	160.4 grams.
Difference in weight between crude and pure dye-----	160.4 grams.
Sulphur recovered from toluene-----	1.8 grams.
Sulphur in tubes-----	3.0 grams.
Sulphur accounted for-----	165.2 grams.
Sulphur in lead sulphide-----	6.7 grams.
Sulphur (dye, PbS and by-products)----	34.8 grams.

Toluene accounted for

Toluene recovered-----	280.1 grams.
Toluene (dye and by-products)-----	19.9 grams.

Remarks: The lead sulphide yield in this experiment is nearer the correct one than the values obtained before. I changed the apparatus for catching the H_2S vapors by sending them through a series of lead acetate solutions contained in bottles.

EXPERIMENT FIVE

Materials used same as in experiment one.

Length of experiment in time----- 8 5/6 hours

Products obtained

Sulphur and dye mixed----- 171.8 grams.
 Lead sulphide----- 80.7 grams.
 Toluene and dissolved sulphur----- 269.5 grams.
 Weight of dye (purified)----- 41.1 grams.

Sulphur accounted for

Sulphur recovered from dye----- 128.5 grams.
 Difference in weight between crude
 and pure dye----- 130.7 grams.
 Sulphur recovered from toluene----- 4.7 grams.
 Sulphur in tubes----- 5.0 grams.
 Sulphur accounted for----- 151.2 grams.
 Sulphur in lead sulphide----- 10.8 grams.
 Sulphur (dye, PbS and by-products)----- 61.8 grams.

Toluene accounted for

Toluene recovered----- 269.5 grams.
 Toluene (dye and by-products)----- 30.5 grams.

Remarks: The amount of lead sulphide is too small in this experiment.

EXPERIMENT SIX

Materials used same as in experiment one.

Length of experiment in time----- 6 hours.

Products obtained

Sulphur and dye mixed-----	189.3 grams.
Lead sulphide-----	99.0 grams.
Toluene and dissolved sulphur-----	279.1 grams.
Weight of dye (purified)-----	34.4 grams.

Sulphur accounted for

Sulphur recovered from dye-----	157.9 grams.
Difference in weight between crude and pure dye-----	159.4 grams.
Sulphur recovered from toluene-----	2.7 grams.
Sulphur in tubes-----	2.0 grams.
Sulphur accounted for-----	162.6 grams.
Sulphur in lead sulphide-----	13.7 grams.

Toluene accounted for

Toluene recovered-----	276.4 grams.
Toluene (dye and by-products)-----	23.6 grams.

Remarks: This is the first experiment that seems to be the one on which most accurate results are obtained. It checks closely with subsequent ones. From these have been tabulated the results given in the table at the end of this part.

EXPERIMENT SEVEN

Materials used same as experiment one.

Length of experiment in time----- 13 hours.

Products obtained

Sulphur and dye (mixed)-----	187.5 grams.
Lead sulphide-----	144.8 grams.
Toluene and dissolved sulphur-----	264.6 grams.
Weight of dye (purified)-----	52.7 grams.

Sulphur accounted for

Sulphur recovered from dye-----	133.3 grams.
Difference in weight between crude and pure dye-----	135.8 grams.
Sulphur recovered from toluene-----	2.0 grams.
Sulphur in tubes-----	3.0 grams.
Sulphur accounted for-----	138.3 grams.
Sulphur in lead sulphide-----	20.0 grams.
Sulphur (PbS, dye and by-products)-----	61.7 grams.

Toluene accounted for

Toluene recovered-----	262.6 grams.
Toluene (dye and by-products)-----	37.4 grams.

Remarks: This experiment was run until the amount of hydrogen sulphide had about ceased. This was carried on as one continuous experiment. Due to the flask breaking after cooling and heating again, it was thought best to make the experiment in this manner.

EXPERIMENT EIGHT

Materials used same as in experiment one.

Length of experiment in time----- 5 hours.

Products obtained

Sulphur and dye (mixed)-----	191.3 grams.
Lead sulphide-----	97.0 grams.
Toluene and dissolved sulphur-----	280.5 grams.
Weight of dye (purified)-----	32.0 grams.

Sulphur accounted for

Sulphur recovered from dye-----	159.8 grams.
Difference in weight between crude and pure dye-----	159.3 grams.
Sulphur recovered from toluene-----	1.4 grams.
Sulphur in tubes-----	2.5 grams.
Sulphur accounted for-----	161.7 grams.
Sulphur in lead sulphide-----	13.4 grams.
Sulphur (dye, PbS and by-products)-----	38.3 grams.

Toluene accounted for

Toluene recovered-----	279.1 grams.
Toluene (dye and by-products)-----	20.9 grams.

EXPERIMENT NINE

Materials same as in experiment one

Length of experiment in time----- 5 hours.

Products obtained

Sulphur and dye (mixed)-----	189.2 grams.
Lead sulphide-----	83.7 grams.
Toluene and dissolved sulphur-----	285.1 grams.
Weight of dye (purified)-----	27.5 grams.

Sulphur accounted for

Sulphur recovered from dye-----	159.8 grams.
Difference in weight between crude and pure dye-----	1617 grams.
Sulphur recovered from toluene-----	37 grams.
Sulphur in tubes-----	3.5 grams.
Sulphur accounted for-----	168.9 grams.
Sulphur (dye, PbS and by-products)-----	31.9 grams.

Toluene accounted for

Toluene recovered-----	281.6 grams.
Toluene (dye and by-products)-----	18.4 grams.

EXPERIMENT TEN

Materials used same as in experiment one.

Length of experiment in time----- 6 hours.

Results obtained

Sulphur and dye (mixed)-----	187.2 grams.
Lead sulphide-----	71.3 grams.
Toluene and dissolved sulphur-----	88.6 grams.
Weight of dye (purified)-----	24.3 grams.

Sulphur accounted for

Sulphur from dye-----	162.9 grams.
Difference in weight between crude and pure dye-----	162.9 grams.
Sulphur recovered from toluene-----	5.0 grams.
Sulphur in tubes-----	5.0 grams.
Sulphur accounted for-----	0172.9 grams.
Sulphur in lead sulphide-----	9.8 grams.
Sulphur (dye, PbS and by-products)-----	27.1 grams.

Toluene accounted for

Toluene recovered-----	283.6 grams.
Toluene (dye and by-products)-----	14.4 grams.

Remarks: In these experiments I have made a distinction between sulphur recovered from dye, and the difference between the crude and purified dye. This is very small. I attribute this difference to the difficulty in weighing the solid sulphur recovered the CS₂ and not to the presence of any other substance in the solution.

TABLE SHOWING QUANTITATIVE RESULTS OF SULPHUR
AND PRODUCTS AND SULPHUR DYE FORMATION

Ex. No.	I.	II.	III.	IV.	V.
Length in Time	5. Hrs.	6. Hrs.	13. Hrs.	5. Hrs.	6. Hrs.
Toluene Reacted in gms.	20.9 Gms.	23.6	37.4	18.4	14.4
Sulphur reacted in gms.	38.3	37.4	61.7	31.9	27.1
Ratio Toluene to Sulphur.	1:1.83	1:1.60	1:1.65	1:1.79	1:1.61
Grams Dye Formed.	32	34.4	52.7	27.5	24.3
Percentage Sulphur* in dye.	63	63.88	64.5	67.53	64.38
Grams Sulphur in dye.	20.2	22.0	34.0	17.56	15.6
Grams Sulphur in H ₂ S.	13.4	13.7	20.0	11.6	9.8
Ratio Sulphur in dye to S. in Toluene	3:2	3:2	3:2	3:2	3:2

* Average of two analyses.

** 3:2 Gm. Atoms.

PART SIX

General Discussion of Results and Observations
From This Series of Experiments

The main point to note in this method of dye production is the temperature required to bring about the reaction. The reason that the reaction of sulphur with hydrogen containing organic compounds was not known until recently when discovered at the University of Alabama is due to the fact that the vapor phase of organic substance and correct temperatures were not used. The writer may be pardoned for stating here that in taking Organic Chemistry at the University of Mississippi in 1923 that special attention was called to the indifference of sulphur toward aromatic hydrocarbons. The reaction does not take place in the case of toluene below 260 degrees and very little reaction is observed below 325^oC. The temperature of maximum reaction as observed from this series of experiments occurs between 370-390^oC. The reaction takes place above 400^oC but seems to be slower.

In the data from the experimental work given above it will be noticed that in a number of experiments there is not sufficient data to calculate the ratio between the amount of sulphur used and the amount of dye produced. This fact may be explained by saying that a number of changes had to be made in the apparatus to meet the needs of the experiment, and through a lack of the correct

results and the inability to arrive at them through the experimental work the first experiments are lacking in the experimental data necessary to determine the amount of sulphur used to the amount of dye produced. With the first experiments the bottles given above in the description were not used but a beaker containing lead acetate solution was tried in place of them. This method was not very satisfactory for two reasons; lead acetate is not very soluble in water at room temperature and after the hydrogen sulphide has bubbled through it for awhile the solution becomes so dilute that it will not react with the hydrogen sulphide, and bubbling the hydrogen sulphide through only one solution is hardly sufficient to catch all this gas, especially if the reaction is proceeding very rapidly. Thus, my results obtained in this way are not very accurate quantitatively because all the sulphide was not caught by the acetate solution. This fault was corrected by replacing the beaker containing the acetate solution with a number of bottles as shown in the diagram.

Another factor of importance to note is the time that elapsed from the time that the toluene vapors were led over into the molton sulphur until hydrogen sulphide was given off as shown in the bottles by the reaction of the sulphide with the acetate solution and the forming of the black lead sulphide precipitate.

From a number of observations from different experiments this time limit ranged between twenty and thirty minutes. At the beginning of the experiment as heat is applied to the flasks air is forced through the solution due, of course, to the fact that the increase of temperature increases the volume of the air. This gas evolution continues for some time but no precipitation is formed due to the absence of hydrogen sulphide. The toluene vapor is not led into the sulphur until molton sulphur has attained a temperature of 375°C . Now from this time to the time hydrogen sulphide reacts with the lead solution is approximately thirty minutes. It seems that the reaction between the sulphur and toluene is prevented by the presence of air. If this were not true it would seem that we should have traces of lead sulphide being deposited immediately after the introduction of the toluene vapor. Of course it is easily possible to get traces of oxidation products with both sulphur and toluene. This could be only a very small amount, however, because of the small amount of oxygen contained in the apparatus at the beginning of the experiment.

I collected some of the gas which had been led through the lead acetate solution, and tests ¹ gave

1. Tests carried out by Mr. Springer under direction of Drs: George D. Palmer and Stewart J. Lloyd.

no indication of unsaturated hydrocarbon being formed in the reaction between the toluene and sulphur.

In the handling of the products from the experiments, it was kept in mind that other products than the dye and hydrogen sulphide might be formed. The dye was purified by washing it thoroughly with carbon bisulphide. In the recovery of the carbon bisulphide I watched for a varying boiling points which would indicate the presence of other compounds with boiling points differing from that of carbon bisulphide. The distillation of carbon bisulphide solution ranged from 46-49°C. With the accuracy of an ordinary thermometer varying by a degree or more, if there are any other compounds in this solvent they are present in very small quantities. The boiling point of carbon bisulphide is 46°C.

In the distillation of the toluene recovered at the end of the experiment the temperature ranged from 109 to 112°C. With the boiling point of toluene being 111°C., there seems to be no other products formed in this case either.

The reaction at 370-390°C proceeds at a constant rate for about five hours. Any more time that the heat is applied at this temperature gives a reaction but it becomes successively slower and slower. I would attribute this slowing up of the reaction to the formation of the dye and this solid tends to prevent

the mixing of the toluene and sulphur.

By the end of the fifth hour the sulphur dye mixture has become a semi-solid at a temperature of 370°C. This allows the bottom of the flask to become heated to a very high temperature and often results in the breaking of the flask. This fact might account for the sulphur variation in two or three of my experiments. A number of times I found the flasks cracked after cooling when I returned to complete the experiment. It is possible that they had cracked before the experiment ended and the sulphur burned in the flames heating the flasks. The leaks, if this were the truth, were so small that I could not detect them.

With the apparatus I was using it is impossible to obtain a very accurate ratio between the amount of toluene used to the amount of dye produced because the toluene is volatile and would also saturate the large corks which I used in the flasks. The quality of these corks varied and some would become more saturated than others.

PART SEVEN

General Conclusions and Summary

The best temperature for the reaction to proceed most rapidly is 370-390°C.

The rate of reaction slows up considerably as it continues. This decrease is quite noticeable by the end of the fifth hour. This would seem to be due to the fact that as the dye is formed by the reaction it interferes with the mixing of the sulphur and toluene vapors. A practical method for overcoming this difficulty would be to have some mechanical device to stir the mixture of dye and sulphur and in this way a larger amount of the surface would be exposed to the toluene vapors and give opportunity for the reaction to proceed at a faster rate.

The toluene vapor needs to pass into the flask containing the sulphur just rapidly enough to condense in the air condenser and fall back into the flask in drops, and not fast enough to have a very large quantity refluxing as this makes it difficult to keep the sulphur at the required temperature.

It is a very good idea to let the hydrogen sulphide pass through a flask containing water before it passes into the acetate solution. By doing this the rate of the reaction can be observed.

The dye formation seems to be one of substitution of the hydrogen in the benzene ring, in the methyl group or both by sulphur as evidenced by the fact that sulphur is found in the analysis¹ of the purified dye and the hydrogen liberated by the reaction is combined² with more sulphur to form hydrogen sulphide. Tests made on some of the gas given off and bubbled through the acetate solution give negative tests for unsaturated hydrocarbons. No evidences are found of any other substances being formed in the reaction by distillation of the liquids remaining or the ones used in purification of the products.

From experiments carried on in this laboratory, the dyes are fast to cotton and rayon. These dyes can be prepared at a moderate cost and therefore offer promise of industrial importance.

Perhaps the most interesting point of study at the present time which these dyes offer is the opportunity of learning, by studying the structure of these simple dyes, the molecular structure of the complicated dyes used at the present time.

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1. Experiment performed by V. D. Padula at this University in analysis of this compound.
 2. Tests of gas made by Mr. Morris Springer at this University.

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