

THE SULFUR DYES

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I. INTRODUCTION

Members of the class of tinctorial materials known as the sulfur dyes are numerous and have been widely used for many years, yet, since their compositions and structures remain unknown, no precise definition of the generic term is possible. In a general way the sulfur dyes may be said to be a group of organic compounds which are prepared by heating various nitrogenous organic starting materials with sulfur, sodium sulfide, sodium polysulfide, or other sulfurating agents. The products of such processes are mixtures of sulfur-containing compounds of high molecular weight and low solubility. Pure compounds susceptible of specific characterization have not yet been separated from these mixtures.

Most important of the properties common to the individual members of the class is their ability to serve as vat dyes for cotton. They may be applied to the fiber from baths containing sodium sulfide or hydrosulfite and produce quite fast shades of yellow, brown, blue, violet, and black.

The meager information concerning the structure of the sulfur dyes indicates that the sulfur is present in thiazine rings, thiazole rings, mercaptan groups, and polysulfide linkages. The sulfur dyes may be related to the thiazole dyes (such as the primulines) and the thionine dyes (such as methylene blue or the thioindigos), since it is possible that they are formed by the further sulfuration of compounds containing the ring systems characteristic of these dyes.

It is the purpose of the present review to collect and present as much pertinent information as possible concerning the sulfur dyes. Indicating as it does the paucity of precise chemical information relative to these compounds, this survey establishes clearly the need for further fundamental research in this field of dye chemistry.

II. A BRIEF RÉSUMÉ OF THE HISTORY OF SULFUR DYES

So far as is known, the first of the sulfur dyes was prepared in the year 1861 when Troost, by reducing a crude mixture of 1,5- and 1,8-dinitronaphthalenes

with sodium polysulfide and other reducing agents, obtained substances which in general contained sulfur and which gave reddish, violet, and blue shades on textile fibers (78). Since these substances had little success as dyes, the sulfur dye industry is more properly dated from 1873, when Croissant and Bretonnière observed that the product obtained by melting organic substances with either alkali sulfides or sulfur and sodium hydroxide dyed cotton fibers directly very fast shades which varied with the conditions of the fusion from grayish brown to black. These dyes, which were known as Cachou de Laval (39), were prepared in the main from material resulting from the vital processes of animals and plants and from certain industrial wastes. Among the starting materials employed may be listed humus, moss, blood, horn, animal excrements, sawdust, gums, tanning materials, and carbohydrates, including sugars, starches, paper, and other forms of cellulose. Two different procedures were employed by these workers: By the first of them the starting material was warmed with an aqueous solution of sodium polysulfide, and dyes yielding lilac and gray shades on cotton were obtained. The reaction involved seemed to be one of addition, since no hydrogen sulfide was evolved during the preparation. By the second process the starting material was heated with sodium polysulfides at 100–300°C. for some hours, during which treatment a considerable quantity of hydrogen sulfide was evolved. This latter process was the more important of the two, for by it the first single dye of any importance, Cachou de Laval Brown, was prepared. It was observed that the higher the temperatures employed in this process, the deeper the shade of the dye obtained. Research on the nature of these dyes was undertaken by Witt (84), but his findings are controversial.

Twenty years passed without further developments of any importance in the field, until in 1893 Vidal discovered that by heating benzene and naphthalene derivatives with sulfur alone, or with sulfur and alkalis, there were produced dyes which not only dyed unmordanted cotton directly, but also withstood decomposition on the fiber (7). This discovery was the turning point in the history of sulfur dye chemistry, for it opened up new and unlimited possibilities and instigated great activity in the field.

Shortly after taking his first patent on a sulfur color, Vidal developed a process for the preparation of the fast black dye known as Vidal Black, which does not render a pure tone on the fiber and which does require fixing, but which has been extremely valuable (8). Following this discovery it was found that the acyl derivatives of nitramines and diamines would yield sulfur colors of yellow and brownish yellow hues which were medium fast (9). The examination of a wide variety of organic compounds as starting materials for sulfur dyes proceeded forthwith.

In 1897 Kalischer advanced the industry considerably by the discovery of Immedial Black, a direct dye of great fastness and beauty, which he obtained by heating hydroxydinitrodiphenylamine with sulfur and sodium sulfide (10). The value of this find lay not alone in the inherent virtue of this one dye, but in the fact that through it a whole series of valuable direct black dyes was made possible. It was also during this year that sulfur monochloride (S_2Cl_2) was used for the first time as a sulfurating agent for organic molecules in the preparation of sulfur

dyes (11). As a result of its use a whole series of black dyes was produced from aminophenol, its homologs, and its derivatives. The next year introduced the thiosulfates of the alkali metals as thionating agents in a patent taken by the Clayton Company for the preparation of a black dye from nitrosophenol (12).

With the exception of a few sulfur dyes which yielded yellowish shades, those obtained prior to 1900 were all very dark in color. Thus it was that the discovery in that year of Immedial Pure Blue (13), which gave very fast, bright, methylene blue shades on cotton, marked another high point in the history of these compounds. Its preparation by heating for a number of hours at 110–115°C. a mixture of sulfur, sodium sulfide, and a base made by the reduction of phenol and dialkyl-*p*-phenylenediamine suggested further investigations which soon produced a number of similar compounds.

The period from 1900 to 1902, inclusive, saw the greatest activity in sulfur dye chemistry that has yet occurred. A host of organic compounds were examined as possible starting materials for the preparation of such dyes, and many new dyes of various colors, natures, and conditions of preparation were made as a direct result of these investigations. Reference to the dye patents shows that the processes of commercial value developed during this period far exceed in number those of any other period of equal length (43). From January 1, 1900 to July 1, 1902, there appeared an average of two patents per week. For the most part these were filed by the large manufacturing concerns (44) and may be divided into two groups: those involving the preparation of only a single new product, and those patenting a wide variety of similar starting materials whose future use might possibly be of value (57).

As yet it has not been possible to prepare bright red sulfur dyes, but varying shades of violet, purple, and maroon have been obtained by the thionation of certain of the red dyestuffs such as the azines, safranines, rosindulines, and certain of the red azo dyes, sometimes in the presence of copper or copper salts (14). Some of the simpler diphenylamine derivatives also yield reddish dyes (79). The first of these reddish dyes was patented by Cassella and Company on very nearly the same day that Immedial Pure Blue was patented (15). Through the years there has been no marked progress in the preparation of better red sulfur colors. Schwalbe succeeded in preparing some brighter shades up to a yellowish red, and in some measure increased the fastness of these colors (74); but as a whole they are less fast than the browns and blacks obtained from the same series of starting materials.

A greenish sulfur dye was prepared in 1896 by the polysulfide fusion of *p*-nitro- or *p*-amino-phenol, or their ethers, in the presence of copper sulfate (16), but a true green was not obtained until 1901 when the sodium sulfonate of the indophenol from *p*-aminodimethylaniline and phenol was fused with sodium polysulfide in the presence of copper sulfate (17). By a similar treatment of diamines a number of green dyes have since been prepared; many of these have better properties than their prototype.

From Vidal's discovery of his previously mentioned Thiocatechin¹ until 1902,

¹ Thiocatechin is the name that Vidal gave to the dyes which he prepared by heating acetylated aromatic diamines and other acetylated aromatic compounds with sulfur alone.

some advances were made in the realm of the yellow, orange, and lighter brown shades (18), but they were few in number. In the latter year, however, it was found that dyes of these shades could be made by the thionation with sulfur alone of toluylene-2,4-diamines or of their acyl and other derivatives (19). These dyes, which are soluble in aqueous solutions of sodium sulfide, resemble the thiazole coloring matters in that they are formed from aromatic compounds containing methyl groups and other non-aromatic substituents. Indeed, the side chains are the most important features of the starting materials, for it has been shown that not only the shade, but also the color, of the resulting dye is dependent upon them (75).

One of the most important advances in the sulfur color industry came in 1908 with the discovery of Hydron Blue and its homologs. Because these dyes may be applied as vat dyes, because they give a fine deep blue tone to cotton, and because they are extremely fast to light, scouring, and bleaching agents they are of especial commercial value and are strong rivals of indigo. These Hydron blues are prepared by the polysulfide fusion of indophenols from carbazole, either with or without the presence of copper salts (20). It is worthy of note that in these processes carbazole finds its first important application in the synthetic dye industry (76).

New sulfur colors are prepared from time to time, but since 1908 there has been a gradual decline in the activity within the field. In 1930 Palmer and Lloyd (69) announced the preparation of a new series of sulfur dyes. They stated that almost any volatile organic compound will yield a reproducible sulfur color when its vapor is passed into molten sulfur maintained at 380°C., but it seems doubtful that all of the products so obtained are sulfur dyes in the accepted sense of that term. These colors were applied in a sodium sulfide bath. Haynn (50) has reported the preparation of a new series of Immedial leuco dyes.

As cheap cotton colors of considerable merit many of these sulfur dyes are in great demand and are manufactured in large quantities by several companies, but they are still prepared by pragmatically determined variations of the original empirical methods. The manufacturers, of course, maintain some research work in the field, but this concerns itself largely with the development of occasional new dyes, the standardization of tinctorial properties, the development of greater fastness in their products, the attainment of greater economy of preparation, and other points similar in nature.

III. TYPES OF ORGANIC COMPOUNDS WHICH YIELD SULFUR DYES

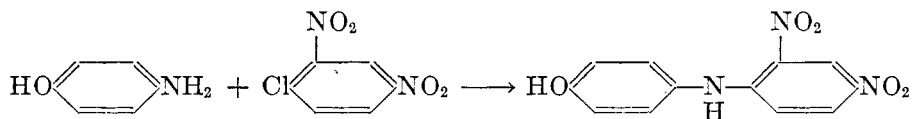
Organic substances exclusively serve as starting materials for the preparation of the sulfur dyes. With the exception of the Cachou de Laval dyes, prepared from a wide variety of plant and animal material, and of those reported by Palmer and Lloyd as prepared from aliphatic substances, the dyes of this class are derived largely from aromatic compounds of the benzene and naphthalene series. Aside from certain mixtures, and from dyes of other classes employed in a few instances, these single aromatic starting materials may be grouped, according to the mother substances of which they are derivatives, into five main

classes: (a) benzene, (b) naphthalene, (c) diphenylamine-nitrated derivatives, (d) diphenylamine-indophenols and indamines, and (e) azine (58).

The benzene derivatives used are substitution products wherein from one to the entire six of the hydrogens have been replaced by groups which are, for the most part, small. These substituent groups are in a majority of cases NH_2 , NO_2 , NO , OH , and the smaller alkyl groups, and any combination of these groups. The carboxyl and sulfonic acid groups are also among the common substituents. A number of dyes are prepared from ureas and thioureas which contain as substituents the benzene ring or substituted benzene rings.

The number of patents (43) involving naphthalene derivatives not contained in indo bodies, although moderately large, is not quite so large as the number requiring the use of benzene derivatives. Of those employed the majority are compounds which contain the substituents listed in the preceding paragraph. It must be noted, however, that sulfonic acids of naphthalene are much more prominent than are those of benzene. A number of naphthalene condensation products also find rather wide application as starting materials. While compounds having double nuclei are being discussed, it should also be pointed out that various derivatives of diphenylmethane give rise to a few important dyes of the family. Carbazole and anthracene are polynuclear compounds whose derivatives are also employed. The former is the parent substance of the Hydron dyes, while the latter, as its nitrated, halogenated, and alkylated derivatives, supplies the starting material for various dyes which yield black and reddish shades on the fiber (21).

By far the most important of the parent substances whose derivatives serve as starting materials for the preparation of the sulfur colors is diphenylamine. As has already been pointed out, its derivatives are most conveniently divided into two groups: one containing those of the hydroxydinitrodiphenylamine type; the other containing those of the leuco-quinone-imide type. The nitro derivatives of diphenylamine result from the condensation of halonitrobenzene or halonitronaphthalene compounds, or their sulfonic acids, with aromatic amino compounds. Upon reduction of the nitro group of these condensation products they change into colorless, easily oxidized diphenylamine derivatives. The condensation of the halomononitro compounds proceeds readily if a small quantity of iodine or cupric iodide be added to the reaction mixture (22); if, however, the halonitro compound is to react readily without outside help the halogen atom must have considerable mobility, which is the case if it is present with at least two nitro groups, or with a nitro group and a sulfonic acid group (6). This is especially true if the two necessary groups are in positions which are ortho and para to the halogen atom. The condensation takes place according to the following scheme:



The products of such condensations are easily obtained in crystalline form.

Other halogenated nitro compounds also form condensation products in a very similar fashion. The dihalonitro compounds are used to a moderate extent, and those which have the halogen atoms replaced with hydroxyl, mercapto, and thiocyanate groups are also used occasionally. The sulfonic acids of halonitrobenzenes with aminophenols and similar compounds also yield condensation products of value in the fabrication of sulfur dyes. On reduction these latter condensation products usually yield sundry aminohydroxysulfinic acids.

The indophenol and indamine derivatives of diphenylamine of the type of the leuco-quinone-imide dyestuffs are very important in the commercial preparation of sulfur dyes, and are obtained from the oxidation of aromatic amines together with phenols or still other amines. That the para positions of both of the uniting rings bear either hydroxyl or amino groups is a condition of the reaction. These indo compounds are usually obtained in crystalline form and are unstable in the presence of a variety of reagents which decompose them into quinone and *p*-diamines. The indophenols frequently undergo further condensation to form phenol ethers. Indophenols which serve for the preparation of green and blue dyes can be formed by the oxidation of naphthalene derivatives with aminophenols (23). Tri- and tetra-phenyl-di- or tri-amine derivatives will also condense with nitrophenol to yield indophenols. The mono- and di-imides of quinone yield indophenols from which a number of good blue sulfur dyes are prepared.

Certain indophenols when treated with neutral sulfites are converted to their water-insoluble sulfonic acid derivatives (24). If these same indophenols be treated with a bisulfite, instead of a sulfite, isomeric water-soluble sulfonic acid derivatives are generated (25). The thiosulfonic acid derivatives can also be prepared, and they find considerable use in industry. Compounds of this variety that are used by the Clayton Company are the di- and tetra-thiosulfonic acids obtained by the oxidation in the presence of sodium thiosulfate of para-substituted benzene derivatives and the subsequent conversion of the oxidation products into indo bodies. The most easily isolated di- and tetra-thiosulfonic acids are those of *p*-phenylenediamine. On account of their solubility and their extreme susceptibility to oxidation, the thiosulfonic acids of *p*-aminophenol, hydroquinone, and other similar substances which contain hydroxyl groups cannot be isolated, and therefore can only be assumed to be analogous to those of *p*-phenylenediamine. The only condition which these starting thiosulfonic acid bodies must fulfill is that upon oxidation they be converted into substances having quinoid linkages. Certain blue dyes of the Badische Anilin und Soda Fabrik are prepared from the indophenols obtained from the quinonethiosulfonic acids.

The azine class of organic starting materials for the sulfur dyes is relatively small and includes three types of derivatives: (a) thiazine, (b) phenazine, and (c) naphthazine. The phenazine division includes the safranines and safraninones, while the members of the naphthazine division are all rosinduline derivatives.

Besides these five general classes of organic starting materials there are also

various and sundry mixtures, as well as a number of single substances, which yield sulfur colors; these, however, are relatively few and of such widely differing natures that it is almost impossible to classify them. The majority of the mixtures are composed of two or more members of the foregoing groups. A few dyes of other classes—azo, etc.—upon sulfuration yield sulfur colors, as do the naphthazarin derivatives and certain condensation products of unknown constitution.

Palmer and Lloyd (69) report that practically any organic compound which can be vaporized will yield sulfur dyes when the vapors are passed into molten sulfur at 380°C. As starting materials they have used a wide variety of aliphatic and aromatic hydrocarbons and their derivatives, but it hardly seems likely that many of the products obtained are sulfur dyes as that term is usually construed.

From this discussion it is immediately obvious that the number and variety of compounds which yield sulfur dyes are very large.

IV. METHODS FOR PRODUCING SULFUR DYES

The methods of sulfurating organic compounds to produce sulfur dyes are few in number and present very few technical difficulties. A survey of the patent literature (43) reveals that a number of sulfurating media are employed; the most common of these is alkaline polysulfide, while pure pulverized sulfur is a none too close second. Fusion in either an open or a closed pot and refluxing with a solvent are the commonest procedures described.

As was previously stated, alkaline polysulfide fusion was the process employed by Croissant and Bretonnière in the production of their Cachou de Laval. This method, with variations of course, has continued to be the most widely used procedure for preparing the sulfur colors. The term "polysulfide" naturally covers a wide range of possible compositions, the use of any particular one of which is dependent upon the compound to be sulfurated and the result desired. This latter matter is more properly the concern of the next section of this paper, where it will be discussed. The usual method of preparing the polysulfide is to melt together sodium sulfide and flowers of sulfur, though sodium hydroxide and flowers of sulfur may be used. The following table (59) gives the proportions of the constituents corresponding to various polysulfide formulas:

Na_2S_2	= 240 parts of Na_2S + 32 parts of sulfur
Na_2S_3	= 240 parts of Na_2S + 64 parts of sulfur
Na_2S_4	= 240 parts of Na_2S + 96 parts of sulfur
Na_2S_5	= 240 parts of Na_2S + 128 parts of sulfur
Na_2S_6	= 240 parts of Na_2S + 160 parts of sulfur

It is said, however, that alkaline sulfides which possess more sulfur than is permitted by the formula Na_2S_4 contain the excess as a mechanical mixture (52). Be that as it may, however, the most stable and the most frequently used in the preparation of these dyes is the tetrasulfide.

Sulfuration by this method may be effected either by introducing the organic material into the molten polysulfide or by adding it to the proper quantities of sulfur and sodium sulfide, after which the fusion is begun. Experience has shown

that better results are obtained by employing the sulfurating medium in excess of the theory. The sulfuration may proceed in an open pot and is completed when the mass has become dry; it may proceed in a closed pot under pressure with, or without, the presence of solvents such as water, alcohol, or glycerol; or it may proceed by long refluxing either with or without the addition of a solvent, as determined by the nature of the organic starting material. If the reaction has taken place in a closed vessel, or if solvents have been used, the product is recovered either by precipitation or by evaporation of the excess liquid present.

A reflux procedure was used for the first time in 1899 by the Aktiengesellschaft für Anilinfabrikation Berlin to produce a black dye from dinitrophenol (26). Patents which involve the use of indophenols and indamines specify reflux processes almost exclusively. The advantages of this procedure are several: (1) the temperature can be held more nearly constant; (2) finer adjustments of the temperature can be made; (3) the concentration can be more easily and exactly maintained; (4) the resulting product is usually the soluble and easily handled leuco compound; and (5) the possibility of overheating is largely excluded. The complex polyhydroxy, aminohydroxy, polyamino, and azine bodies are usually treated in this fashion too. The chief disadvantage of the method is the great length of time required for the reaction to go to completion at the lower temperatures usually employed. The soluble leuco compounds so prepared are usually precipitated by bubbling air through their aqueous solutions.

The usual temperature for open-kettle polysulfide fusion is about 150–200°C. There are instances, however, in which lower temperatures are employed, as well as a few others in which higher temperatures are specified. The reflux procedures are conducted, of course, at lower temperatures—at about 120°C. for those which use water as a solvent and 80–90°C. for those which use alcohol. When it is desirable to use a reflux procedure, but when a higher temperature is imperative, glycerol, amyl alcohol, β -naphthol, and similar substances are employed as solvents. The use of an autoclave permits intensive sulfuration at relatively low temperatures.

Patents which specify the fusion of organic substances with sulfur alone are not nearly so numerous as those requiring the use of polysulfides. This method came into use in 1893 with the preparation of Vidal's black dye (9). Sulfur can be substituted in most instances for polysulfides, but in some instances such a substitution yields different products. For the most part nitro compounds are not treated in this fashion, since they have a strong tendency to explode upon being heated with sulfur. As in the case of the polysulfides open-pot, pressure, and reflux procedures may be used with sulfur. The usual temperature for the open-pot sulfur process is 200–250°C. The patents indicate that in nearly every instance sulfur fusion yields insoluble thio bodies, which can be rendered soluble in water by treatment with molten sodium sulfide or with solutions of sodium sulfide. Palmer, Lloyd, and their coworkers report that the passage of organic vapors into molten sulfur at 240–260°C. yields resinous sulfur dyes which are soluble in sodium sulfide solution, but that identical vapors passed into molten

sulfur at 260–300°C. yield sulfur compounds which are not dyes and which are soluble in neither sodium sulfide nor carbon disulfide (70). By sulfur fusion a number of blue and black dyes are prepared from various amines, diamines, and phenols (27); the method finds its greatest use, however, in the fabrication of the yellow and brown dyes of the thiazole type (28). These latter are prepared, for the most part, in the presence of benzidine, whose participation in the reaction affects the color of the product considerably.

Sulfur monochloride is the third most common sulfurating agent, but even so, the patents citing its use are few. It is either refluxed with the organic material or is merely heated with it, usually in a closed vessel. The common temperature range for processes involving its use is 140–170°C., although the extreme limits are 80–200°C. The higher temperatures insure the reduction of the chloride to a complex mixture of sulfites, polysulfides, and thiosulfates which is apparently the real sulfurating agent. Treatment of the organic starting materials with sulfur monochloride generally yields either insoluble thio bodies, which are rendered soluble by treatment with sodium sulfide or sodium hydroxide, or sulfurated intermediate products which on fusion with sodium sulfide yield the dyes. A solvent may be used, but it must be inactive to both the organic material and the chloride. Carbon tetrachloride is most often used for the purpose, since it fulfills both requirements. The first patent involving the use of the monochloride as a sulfurating agent for the preparation of sulfur dyes was that issued to Cassella in 1897 for the fabrication of a black dye from *p*-aminophenol (29). With the exception of a few violet and reddish colors, all of those made in this manner are black or blue.

There are five other sulfurating agents which find a slight application in the production of the sulfur dyes. Of these five the thiosulfates of the alkali metals should be mentioned first. Upon being heated they decompose in a number of different ways, depending upon the temperature and other conditions, each of which yields one or more sulfurating media. The alkali metal salts of thio-carbonic and orthothiocarbonic acids, made by heating alcoholic carbon disulfide with sodium sulfide and sodium disulfide (Na_2S_2), respectively, are used in a few instances (30). A mixture of sulfur and fuming sulfuric acid which contains some sulfur sesquioxide (S_2O_3) will yield with certain organic compounds dyes which contain sulfur, but which because of their properties do not seem to be true sulfur dyes (31).

In some processes sodium sulfide alone is used to furnish the necessary sulfur. This compound may serve merely as a reducing agent as it does with 1,8- or 1,5-dinitronaphthalene (32), or it may cause dye formation by simultaneously serving as a reducing agent and as a sulfurating agent, as it does with the naphthalenesulfonic acids. The methods of applying sodium sulfide alone are, in general, identical with those for the application of the polysulfides.

A few black and blue dyes are prepared by passing hydrogen sulfide into solutions of the respective organic starting materials contained in a reflux apparatus. Modifications of the process require that an oxidizing agent be present and that the solution be acidic.

V. RESULTS OF VARIATIONS IN METHODS

Observations have been sufficiently extensive to lead to the generalization that in a majority of instances an increase in the temperature at which the sulfuration process takes place does not change the color of the resulting dye, but does deepen the shade of that color. Within limits the alteration of the shade will depend upon the extent of the temperature increase, and is generally regarded as being due to more intensive sulfuration at the advanced temperature (66, 72). A very few easily sulfurated starting materials yield dyes which show no change of shade as more heat is applied.

More intensive sulfuration than is usually to be obtained by an increase of temperature alone frequently produces increasingly deeper colors which may ultimately become black. This change is believed to be due to the formation of a greater number of sulfur-bearing ring structures in the fundamental structural units. Such extensive sulfuration is obtained by increasing the time of heating, by using increased pressures, by employing high-speed stirring, by using greater relative quantities of sulfur or the higher polysulfides, and by employing higher boiling liquids in reflux processes. These various methods may be applied singly or, as is often the case, combinations of them may be used. The choice of one or more of them is often determined by the nature of the starting material and by the result desired. When polysulfides are used as the sulfurating medium, the extent of the sulfuration depends upon the composition of the one chosen, provided all other factors remain constant. For example, *m*-dinitrotoluene yields with a polysulfide of the composition Na_2S_2 - Na_2S_3 a water-soluble red-brown dye, while with $\text{Na}_2\text{S}_4 + \text{S}$ it yields an insoluble deep brown dye (1). Again, starting materials which are easily and more or less completely sulfurated by low polysulfides show little response to treatment with the higher members of the family.

Some organic starting materials yield different dyes with different types of sulfurating agents, while others show no differences. Because of the wide variety of behavior exhibited it is virtually impossible to frame a general statement which will cover all cases. Even among the compounds which show variations when treated with different agents, there seems to be no constant relationship between the properties of the dyes produced and the thionating agents employed. A number of organic substances which are sensitive to alkalis are sulfurated by sulfur melts. A number of other dyes which may be prepared by the use either of sulfur or of polysulfides seem to be identical, save that those prepared from the former are insoluble in water while those from the latter are water-soluble. Sulfur monochloride and trithiocarbonic acid yield dyes which generally are different from those prepared by the action of polysulfides upon identical starting materials.

The foregoing is practically all that can be said in a general way of the changes wrought in the sulfur dyes by variation of the method of thionation; however, it will be well to mention at this juncture several non-sulfurous substances which the patents show are used frequently in the preparation of these dyes and which may influence the color they impart to the fiber. If alcohol be employed as a

solvent in processes which take place at normal pressure, it seems to have no effect upon the product; however, when it is used under pressure, ethylation of the organic material present may occasionally result. The use of benzidine in sulfur fusions has already been referred to. Powdered copper metal and copper salts are frequently added to the dye melts. This treatment usually turns greenish shades to black, reddish ones to brown or violet, and yellowish ones to dull red, but there are recorded instances of its modifying the constitution of certain dyes without affecting the colors which they impart to the fiber (77). Fierz-David and his coworkers have established that the copper atom becomes an integral part of the dye molecule in the case of Pyrogen Green (SCI);² presumably this is true of other dyes fabricated in the presence of copper or copper salts, since the copper can be removed only after disintegration of the molecule has taken place (55). The salts of zinc, iron, chromium, and manganese are used similarly in a few processes, and a patent assigned to the General Aniline Works states that compounds of molybdenum, tungsten, vanadium, uranium, and antimony when added to the polysulfide melt of compounds of the type of 2-methyl-3-amino-7-hydroxy-5-ethylphenazine yield dyes of great color intensity (80).

Because of the present-day production of starting materials of a much more uniform quality and the availability of improved machinery and instruments for large-scale manufacturing, the sulfur dyes produced now are of a much more uniform shade than were those of the past. Careful adherence to empirical procedures based upon practical experience is also a factor in the preparation of more uniform products.

VI. GENERAL PROPERTIES OF THE SULFUR DYES

Although the numerous sulfur dyes are prepared from a great many different organic substances by sundry variations of a few general methods of sulfuration, their properties are very similar, varying in degree rather than in kind.

In general these dyestuffs are dark amorphous powders, many of which possess an almost metallic glint. Most of them are insoluble in water and in ether, acetone, the alcohols, aliphatic and aromatic hydrocarbons, dilute mineral acids, concentrated hydrochloric and acetic acids, and the mono- and poly-haloalkanes. Many of these dyes, however, are soluble in concentrated sulfuric acid, aqueous sodium sulfide, aqueous caustics, hot pyridine, and hot aniline (53). Examination of solutions of certain of the dyes with the ultramicroscope has shown them to be colloidal in nature, and x-ray diffraction photographs of a number of the dyes have been of the type characteristic of non-crystalline substances (41, 54). In the patents the chief properties listed are the colors the dyes exhibit in various solvents, but this is of small value since two or more dyes frequently produce similar colors. Occasionally the characteristic colors imparted to solutions in concentrated sulfuric acid are useful in demonstrating the existence of two differ-

² The letters appearing in parentheses after the trade names of dyes indicate their manufacture: e.g., (SCI) and (SCI in B) refer to the Society of Chemical Industry in Basle, (IG) refers to the German dye trust, and (C) refers to Cassella and Company in Frankfurt a.M.

ent dyes prepared from the same organic compound. The high-boiling organic compounds in which many of them are soluble rarely serve as media for the separation of mixture components. In alcohol those dyes which have been precipitated with acid are invariably insoluble, although the sodium salts of the same dyes are occasionally slightly soluble in it. In the latter case there is some question as to the identity of the soluble material, the suggestion having been made that it may be the sodium salt of an intermediate product (60). In pyridine there seems to be a reaction between the dye molecule and the solvent, and in boiling nitrobenzene the dye molecules undergo decomposition (41).

The insolubility of the dyes in water is, in a measure, dependent upon their method of preparation. All methods which do not employ alkalis or alkali salts produce dyes which are immediately insoluble. Those which result from dry fusion with alkaline substances or from refluxing with alkaline substances, such as alkali mercaptans, are immediately soluble, and the others can be rendered water-soluble by evaporation with alkaline solutions, or even by shaking with solutions of sodium sulfide or sodium hydroxide. These solutions are apparently colloidal, and the dye may be reprecipitated by neutralization with acid save in two recorded instances, or by bubbling air through the solution for a number of hours. The two dyes (33) which are not reprecipitated by acids are shown to possess unchanged amino groups and hence to be not entirely sulfurated. It should be noted that these two dyes which are soluble in dilute mineral acid also serve to dye wool as well as cotton. The materials which remain after treatments calculated to purify the dyes are much less soluble than the untreated dyes. This is presumed to be due to changes in constitution brought about by the treatment. Fierz-David suggests that in certain instances the treatment may possibly have the secondary effect of removing peptizing substances (41). The alkaline earth and heavy metal salts of the dyes are insoluble.

Rarely can a sulfur dye be purified sufficiently for much to be determined concerning its physical constants. Furthermore, the majority of the dyes undergo decomposition below their melting points. Even after preliminary washing to remove excess alkali salts, and further extraction with carbon disulfide to remove excess mechanically held sulfur, there still remains some unreacted sulfur. Frequently there are also present a number of high-molecular-weight compounds of different compositions.

Because of the difficulty of obtaining the dyes in a high state of purity, little can be said of their chemical properties save in a general way. Upon reduction with an aqueous solution of sodium hydrosulfite and sodium hydroxide the majority of the dyes yield soluble leuco compounds of a pale straw color. These, too, may be generally precipitated with dilute mineral acid, but the precipitates are even more quickly reoxidized than is the material held in solution. The sulfur dyes are preëminently dyes for cotton and as such are often applied as vat dyes from their leuco solutions, with the color being developed on the fiber either by air oxidation or by treatment with some one of the well-known oxidizing

agents. The other common method of application is to the unmordanted fiber from the colloidal solution of the dye in sodium sulfide.

The properties of many of the dyes are not altered even by reduction with zinc dust and acid, which causes the evolution of hydrogen sulfide (34). Grape sugar with strong sodium hydroxide solution and certain other strong reducing agents act upon nitrogen-bearing dyes to bring about the evolution of ammonia and a condensation which effects a complete change of properties (61). Reduction with stannous chloride and strong acid of dyes prepared from diphenylamine derivatives brings about the evolution as hydrogen sulfide of a portion of the sulfur contained, with accompanying degradation of the dyestuff (54).

The leuco form of the dyes is readily oxidized, and the dyes themselves undergo oxidation when heated alone or with various strong oxidizing agents. Sodium peroxide fusion converts the sulfur to sodium sulfate, and hot concentrated sulfuric and nitric acid each forms some sulfates also. Upon treatment with the last-named agent, dyes prepared from diphenylamine derivatives yield also a product which has a strong odor of nitrobenzene (53).

So far as is known, only one of the dyes has ever yielded a crystalline bisulfite complex upon treatment with sodium bisulfite. This single success was achieved by Gnehm and his coworkers with Immedial Reinblau (47). By sulfite or bisulfite treatment other dyes are usually converted to water-soluble sulfonic, sulfinic, or thiosulfonic acid derivatives (35).

The majority of reagents either do not attack the dyes at all or else decompose them completely.

One of the most serious disadvantages of the sulfur colors is the extreme sensitivity of a majority of them to chlorine—a sensitivity which is retained after their deposition on the fiber.

It is reported that alkyl substitution of either the dyes or their leuco bases, either on or off the fiber (36), occurs readily provided only that the compound to be alkylated is of a mercaptan nature (37).

Other reported properties are of insufficient generality to warrant mention here.

VII. CONSTITUTION OF THE SULFUR DYES

The discovery of the sulfur dyes, besides instigating much commercial research on intermediates and methods of preparation, also inspired a considerable amount of purely scientific research which had for its aim the determination of their chemical nature and constitution. Work of this kind was begun shortly after the discovery of Croissant and Bretonnière was made public. Given added impetus by Vidal's discoveries and studies on the constitution of his black dye, it was continued by sundry investigators in various laboratories in England and on the Continent until about 1910, when it practically stopped, slowed by the burden of its own discouraging results. During the first half of the last decade there was again a flurry of interest in the constitution of these dyes, but at present activity in the field has again almost reached the vanishing point.

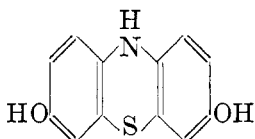
Because of their insolubility, the variability of their composition, and the difficulty encountered in purifying them, their unresponsiveness to any save the most drastic treatments, and the complexity of their structures, the sulfur colors have withstood the majority of attempts to fathom the mystery of their constitutions. As a result of the work that has been done, a number of well-founded theories have been proposed, but the exact constitution of no single dye is authoritatively known. For a time it was thought that the constitution of one dye, Immedial Pure Blue (13), had been established, but there is reason to believe that the proposed structure is that of a fragment rather than of the dye molecule as a whole (41). A study of the assembled data shows that the general nature of the dyestuffs is fairly well agreed upon; the blacks, blues, and some of the greens and Bordeaux-reds are generally held to be thiazine derivatives, while the majority of the yellows and browns are apparently thiazole derivatives. Thianthrene, acrithiole, piazthiole, and other fundamental ring structures have been proposed for various individual dyes, but subsequent investigations do not indicate that such structures are common among the sulfur colors. Investigations into the manner in which sulfur contained in side chains is held have also been interesting.

The sensitivity of the sulfur dyes to heat, the fact that they cannot be obtained in a crystalline form, and their tendency to form colloidal solutions have made molecular-weight determinations impossible, thus blocking the establishment of molecular formulas and largely limiting the work of investigators to the proposal of structural units of the large molecules. All indications are that their molecular weights are large.

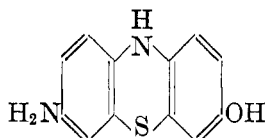
A. Sulfur in the fundamental ring structures

That many of the black, blue, and green sulfur dyes contain the thiazine ring system as the fundamental building unit of their molecules has been established by the collection of a plethora of data. The preparation of sulfur dyes from methylene blue, whose thiazine nature was known, and from certain thiosulfonic acids of benzene derivatives gave an early indication of the thiazine nature of these dyes. Furthermore, certain indophenols and indamines which are starting materials for the sulfur dyes will yield, upon being converted into thiosulfonic acids and treated with dichromate, black and blue dyes which can be distinguished from the sulfur dyes only by a study of their characteristics of fastness (48). These dyes are shown to be derivatives of thiodiphenylamine. Bernthsen (3) has further substantiated this view by the preparation of sulfur dyes from methylene violet and from the product obtained by treating the mercaptan of the condensation product of dihalohydroquinone and dimethyl-*p*-phenylene-diaminethiosulfonic acid. This seems to prove beyond a doubt the thiazine natures of these several dyes, for the stability of the thiazine ring in polysulfide melts follows from the formation of similar sulfur dyes by the treatment of methylene violet with sulfur, trithiocarbonic acid, sulfur monochloride, etc.(62).

Vidal's earlier researches also point to the existence of thiazine rings in the sulfur blues and blacks (81). He found that heating ammonia, sulfur, and quinone together produced leucothionol,

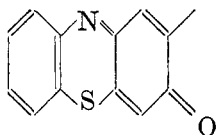


which is also produced along with a black dye when sulfur and *p*-aminophenol are heated together, and again when molecular portions of *p*-aminophenol, quinol, and sulfur are heated together. He also found that by heating together quinol, *p*-phenylenediamine, and sulfur he first obtained leucothionoline,



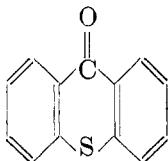
and subsequently, upon further heating of the mixture with sulfur, a black dye. His work, while lacking much in completely elucidating the structure of the dyes which he studied, does offer further evidence for the thiazine nature of such dyes. The Clayton and dinitrophenol blacks (*cf.* Immedial Black) are distinguished from Vidal Black by a considerable difference in properties, but they too have been shown to have the thiazine ring as their fundamental structure (63).

In their investigation of blue, green, and Bordeaux-red sulfur dyes prepared by refluxing some of the simpler derivatives of diphenylamine with polysulfides in an aqueous medium, Jones and Reid (54) found evidence which indicated that the thiazine ring was the fundamental unit of structure in each case. The two Bordeaux-red dyes prepared from *p*-hydroxydiphenylamine and *p*-methyl-*p'*-hydroxydiphenylamine were shown to be very similar in properties to Bernthsen's (4) oxothiodiphenylimide, which is also of a reddish color, and whose formula has been established as



Still more recent work performed by Fierz-David and his coworkers (2, 41, 42, 55) on a variety of blue, green, and black sulfur dyes indicates that here again the thiazine ring is the fundamental structure. The work of these investigators upon Pyrogen Indigo (SCI in B), Hydron Blue (IG), and certain of the other blue dyes is reported as confirmed by Hatirō Hiyama (49).

The formation of thiopyrone rings



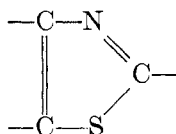
is generally believed to occur in the formation of a few sulfur dyes, notably those prepared from fluorescein by Wichelhaus, Vieweg, and others (38), though

incontrovertible proof remains to be established. There is also a very good likelihood that the dyes prepared from diphenylamine disulfide contain the thianthrene ring, but such dyes are in the minority.

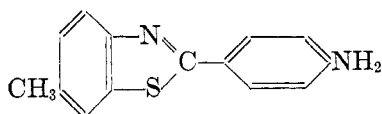
At various times in the past piazthiole, hypothetical acrithiole, and oxazine structures have been proposed as possible components of sulfur dyes, but to date both investigational data and theoretical considerations give no support to the idea.

Thus far the preponderance of evidence indicates that the thiazine ring is the fundamental ring system of black, blue, green, and Bordeaux-red sulfur dyes—especially when derivatives of diphenylamine have been the starting material.

The yellow and brown sulfur dyes, produced largely from toluylene-2,4-diamine, tolidine, and similar compounds containing carbon in the side chain, have been found to resemble dehydrothiotoluidine and primuline in that they contain the thiazole group,

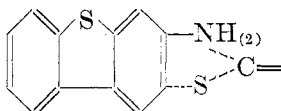


which has been shown to be the fundamental structure of these dyes, although the complete unit structures have been worked out only in a few cases. The initial investigation of dehydrothiotoluidine was begun by Jacobsen (51) and continued by him and others until the constitution of this substance was finally established by Pfitzinger and Gatterman (71) as being that of *p*-aminobenzenyl-aminothiocresol:



In the yellow and brown sulfur dyes the sulfur of the thiazole ring is introduced by the direct interaction of sulfur and the organic starting material. As a result of this treatment there is obtained a colored, insoluble mass which can be rendered soluble by treatment with a hot, concentrated, aqueous solution of sodium sulfide. This treatment introduces mercaptan-groups into the molecule, making it that of a true sulfur dye. The work of Fierz-David and his coworkers (41, 42) also supports the thiazole nature of certain of the yellow, orange, and brown dyes.

It is assumed, though there is no conclusive proof, that the yellow and brown dyes prepared in the presence of benzidine may contain the dibenzothiophene ring system,



either alone or in union with the thiazole ring as indicated.

The proposal of Ris that in certain instances a hypothetical ring isomeric with thiazole, which structure he called acrithiole, might be present has never received any support; on the contrary, in fact, it was largely discredited by the work of Biedermann (5).

At the present time the thiazole nature of the majority of such dyes seems well established.

B. Sulfur in the side chains

Thus far in this discussion of constitution mention has been made only of the sulfur contained in the fundamental ring structures. Sulfur so held is perhaps in the most fundamental union, but usually it represents only a small portion of the total sulfur content of the dye. Dyes prepared both commercially and in the laboratory have been shown to contain both mechanically held sulfur and sulfur-bearing impurities, but even when these have been removed by extraction with dilute acid and base, ether, alcohol, carbon disulfide, etc. (41, 54), the sulfur content of many dye molecules remains relatively high (frequently 30-35 per cent). In the different sulfur colors varying numbers of sulfur-containing side chains are known to be present; although few constitutions are definitely known, of the existence of such side chains there can be no doubt. The work of many investigators substantiates their existence.

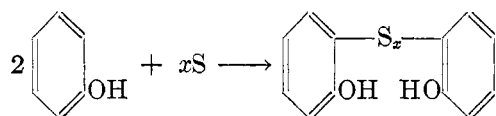
A majority of the sulfur-bearing side chains introduced into the dye molecule by polysulfide fusion are held to be the sodium salts of mercaptan groups, $ZSNa$, which are responsible for the solubility of most dyes prepared by this method. The insoluble, fast, oxidized form of the dye which appears on the dyed fiber is held by this school to be the disulfide, $Z-S-S-Z$ (45). It is further maintained that the mercaptan and disulfide groups, aside from influencing the solubility of the dye, have nothing to do with their ability to dye unmordanted cotton fiber. It was the view of Vidal that the solubility of these dyes was due largely to their phenolic natures (82). The fact that the dyes can be alkylated to form thioethers is irrefutable proof of their mercaptan nature (64). Furthermore, it is well known that even after the dyes have been set to the fiber they may still be alkylated. This would indicate either that if they exist on the fiber as disulfides they still contain unchanged mercaptan groups, or that the mercaptans which were oxidized to disulfides may be reformed by the alkylating agents and then alkylated to produce the color changes usually noted during the process. This latter possibility seems the more likely.

The mercaptan groups, though exerting a great influence on the solubility of the dyes, seem to exert none on their origin and fundamental structure, for frequently by the introduction of a mercaptan group, or of several such groups, into dyestuffs of other classes there will result sulfur dyes which will still retain the tinctorial properties of the class of which they were originally members.

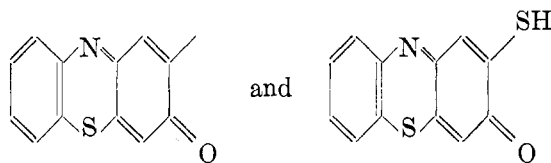
The position of the mercaptan groups in the dye is of considerable importance. A single sulfhydryl group generally enters the position ortho to an amino or hydroxyl group (i.e., to an auxochrome group) of the mother substance (46). The ease with which halogen substituents may be replaced by mercaptan groups

has been of great value in making these determinations of position. The position of mercaptan groups in dyes prepared from halogen-containing indophenols can be established thus with great certainty, for by polysulfide fusion as many sulfhydryl groups as there are halogen groups can be introduced into the indophenol, its leuco base, or its corresponding dinitrodiphenylamine derivative. It must be pointed out, however, that ordinary fusion apparently does not eliminate halogens in the phenylated side chains of an indo body (65).

Not all of the properties of the sulfur colors are explained by the foregoing proved structures. For instance, the production of dyes of several different shades from the same mother substance by variation of the conditions of sulfuration cannot be explained on the basis of a common structure, and variation of the number of mercaptan groups upon a common fundamental ring system has been shown to have no effect upon the color. Such considerations led Möhlaus to propose polysulfide chains rather than the mono- or di-sulfide linkages. He and Seyde (68) began their work on the sulfuration of phenol, a reaction which they represented thus:



From the reaction product they were able to isolate the disulfide, which was poorer in sulfur than the rest of the product from which it was removed. They concluded from their work that the connecting sulfur chain can be as long as eight atoms (67). The work of Jones and Reid further substantiates the existence of polysulfide chains in the dyestuffs of a thiazine nature (54). These investigators were able to show that the compounds



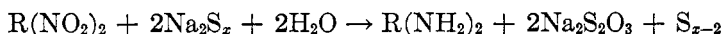
do not yield hydrogen sulfide when treated with stannous chloride and strong acid, but that the sulfur dyes of a thiazine nature do lose as hydrogen sulfide all of their sulfur atoms in excess of those in the thiazine structure and those which are attached directly to the ring. The existence of polysulfide chains seems highly likely from a theoretical consideration, for without them a number of characteristic properties are explained only with difficulty. The existence of such polysulfide bridges helps to explain the existence of the ultra-large molecules, or colloidal aggregates, which are known to exist.

Möhlaus assumes also that in the thiazole, thiazine, and azine structures there may be polysulfides where it is usually the custom to write only a single sulfur atom. The strongest support for this idea is offered by his work of increasing the sulfur chain of Immedial Black to produce a dye of the same color but of different properties. The work of Schultz and Beyschlag (73) substantiates the

polysulfide theory of Möhlaus, and it is their conclusion that the sulfuration of organic substances for the production of sulfur dyes leads to no definite products.

No mention is made here of Erdmann's (40) thiozonide theory, because so little importance attaches to it at the present time.

Further light has been thrown upon the mechanism of the sulfuration process from the standpoint of the sulfur compounds involved, by the work of Khmel'nitzkaya and Verkhovskaya (56), who report that in the formation of the black dye from sodium dinitrophenolate and sodium pentasulfide (Na_2S_5) in water, sulfuration and reduction proceed simultaneously. They represent the reduction thus:

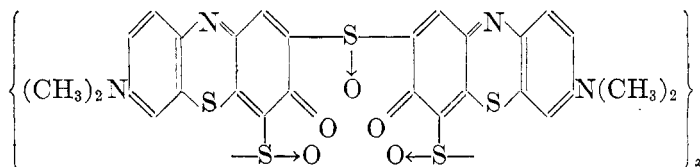


and state that the sulfur set free is in an active form which sulfurizes the amine to produce the dye. Such a mechanism is proposed for the dyes prepared from polysulfides and the various types of organic amines as well as for the Immedial indone dyes. The work of Richard Herz has also been of importance in throwing light upon the possible reactions involved in sulfuration (83).

C. Proposed constitutions of the units making up sulfur dye molecules

The fact that the majority of sulfur dyes cannot be obtained in crystalline form and that in most cases they form colloidal solutions has not only made studies upon constitution difficult, but has also prevented investigators from doing more than proposing the formulas of the units of which the macromolecules are composed. Despite the quantity and excellence of the work upon which these proposals are based, their correctness may still be questioned because of the treatments required to purify the dyes and to convert them into derivatives. Among the most recent suggestions are those of Fierz-David and his coworkers (41) and of Jones and Reid (54).

For the units of which the Immedial Pure Blue (C) molecule is composed, Keller (55) and Fierz-David propose the formula

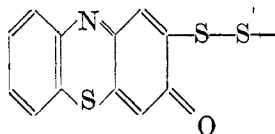


For the other blue, green, and black dyes which they investigated the Fierz-David workers propose similar unit formulas in which two substituted thiazine ring systems are bound together by an SO bridge, save in the case of Pyrogen Green (SCI in B). In this latter case both SO and disulfide links were proposed. This group of workers used both commercially prepared dyes and dyes made by the method of Herz (83) from the same intermediates used for their commercial counterparts. The pairs of dyes made from the same intermediates were not identical in properties nor did they have identical sulfur and oxygen contents.

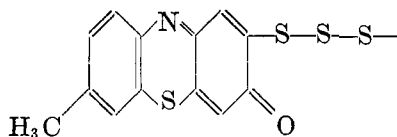
In the case of each dye for which a formula was proposed, the number of thiazine rings in the fundamental structural unit was determined by the titanous chloride titration method of Knecht and Hibbert, but for this titration the dyes had to be rendered soluble by sulfonation. This chemical treatment and the recorded results of the titrations themselves (save in the case of Pyrogen indigo) leave room for question. The presence of the thiazine structure in each case was confirmed, however, by spectroscopic investigation, and the treatment of the leuco compound of Pyrogen indigo with chloroacetic acid produced a derivative which apparently confirmed the existence of two thiazine rings per unit for that dye. The presence in the dyes of groups (presumably disulfides) which upon reduction yield mercaptans is adequately demonstrated.

Continued strong sulfuration of a Bordeaux-red dye prepared by Fierz-David and Zürcher (41) from *p*-anisidine yields a product which becomes darker and darker and finally black, and whose methoxyl content becomes at the same time progressively smaller. It is the assumption of these investigators that further thionation is able to take place at a free para position, or at an occupied para position after elimination of the substituent already there, with the formation of a larger number of thiazine groups, or of other sulfur-bearing groups such as the thioxonium ring. Such drastic treatment apparently introduces also some sulfonic acid groups which, coupled with the mixtures which naturally result from such treatment, make these sulfur blacks of high sulfur content very difficult to purify and to work with in general.

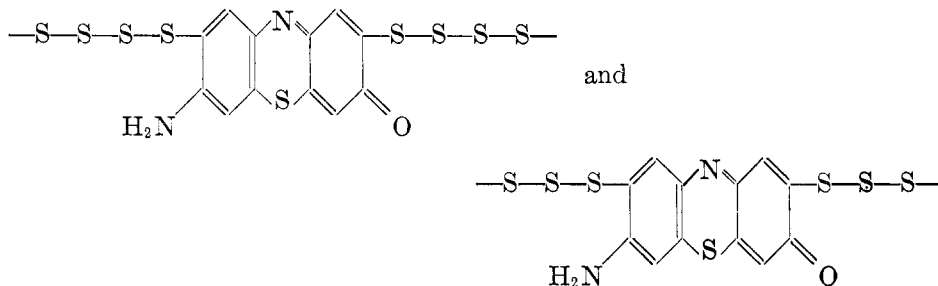
The work of Jones and Reid (54) also indicates the presence of the thiazine ring structure in the blue, green, and Bordeaux-red dyes which they investigated. While not conclusive, their work also indicates the presence of polysulfide side chains of the variety proposed by Möhlaus. There is little evidence of the number of oxygens found by Fierz-David and his coworkers. These investigators, who prepared all of their dyes by treatment of diphenylamine derivatives with aqueous sodium polysulfide, suggest units linked by polysulfide chains as composing the macromolecules. Some of the suggested units are: for the dye from *p*-hydroxydiphenylamine



for the dye from *p*-methyl-*p'*-hydroxydiphenylamine



and for the two green dyes prepared from *p*-amino-*p'*-hydroxydiphenylamine



VIII. CONCLUSION

From the foregoing discussion it is apparent that the sulfuration of organic compounds to produce sulfur dyes proceeds by a few well-defined processes which involve the use of only a limited number of sulfurating agents and which may be so controlled as to produce compounds of given tinctorial properties. Since the first investigation of structure undertaken by Vidal in 1893, many investigators have sought to determine the constitution of a variety of these dyes. As a result of this work the general nature of the dyes is known, but because of the general insolubility of the dyes and their resistance to all save the most drastic treatment, little is known with certitude of the constitutions of the individual dyes. Constitutions of the units of which the macromolecules of a number of the individual dyes are composed have been suggested by several investigators, but though these rest upon good evidence, even they are open to some question.

The researches of the past have been valuable and they have in many instances been ingenious, but perhaps their chief value has been to point the way to further investigations in a field where much remains to be learned and where laborers have been all too few. Investigations conducted with the aid of the new tools of modern physics might succeed in bringing order to the knowledge of this division of tinctorial chemistry.

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- (11) D.R.P. 103,646 (1897).
- (12) D.R.P. 106,030 (1898).
- (13) D.R.P. 134,947 (1900).

³ German patent.

- (14) D.R.P. 152,373 (1903); 161,462 (1903); 177,709 (1905); 181,125 (1905).
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