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When it is more important that cells have low hysteresis than that their electromotive forces agree with the established value¹⁶ cells can be made more acid and a fine grained mercurous sulfate used.

Summary

1. Weston standard cells made with finely divided mercurous sulfate had electromotive forces 40 to 100 mmv. higher than cells made with coarser mercurous sulfate.

2. Hysteresis varied greatly with the characteristics of the mercurous sulfate, being largest in the case of a coarse, white mercurous sulfate and practically zero in the case of a fine, gray mercurous sulfate. Both smallness of the particles and the presence of finely divided mercury appeared to influence the prevention of hysteresis.

3. The addition of acid to cells lowered the hysteresis considerably.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE, CALCUTTA]

STUDIES IN DYES WITH MULTIPLE CHROMOPHORES

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A careful examination of the literature on dyes shows that the introduction of an additional chromophore into a dye may have one of the following consequences: (1) the color becomes deeper in some cases; (2) it becomes lighter in some; and (3) it remains practically unaltered in others; at any rate the effect is not perceptible to the naked eye.

In the light of the modern researches of Hartley, Baly, Hewitt, Purvis, Watson and their collaborators regarding the absorption spectra of colored substances, the change of color is intimately associated with the shifting of the absorption bands, and the deepening of color is caused by the shifting of the absorption band (or bands) towards the red end of the spectrum. When, however, the shifting takes place to such an extent that the absorption band (or bands) reaches the infra-red region, the color of the compound attributable to that absorption band or to those bands disappears and a second color termed "the color of the second order"¹ may appear due to another absorption band entering into the visible part of the spectrum from the ultra-violet region. This theory of color of the second order offers a plausible explanation of the apparently anomalous phenomenon of the color of a compound sometimes becoming lighter by the multiplication of chromophores.

¹⁶ This is the case with unsaturated cells to be used at room temperature, and with any working standards which can be checked occasionally.

¹ Piccard, Ber., 46, 1843 (1913).

The present investigation was the outcome of attempts to prepare several dyes of mixed type (that is, dyes containing different chromophores), with a view to studying the effect of multiplying the number of chromophores.

Attention was first directed towards the preparation of dyes of the triphenylmethane series containing one or more azo groups in the molecule with a view to studying the effect of the additional chromophore (azo group).

The azo-triphenylmethane dyes studied in the present work may be conveniently classified into three types according to whether they contain one, two or three azo groups in the molecule, respectively.

1. The dyes of the first type containing only one azo group in the molecule, studied before by Green and Sen,² have been prepared by three different methods: (a) by condensing one molecule of an azo aldehyde, such as phenetole-azo-benzaldehyde sulfonic acid, with two molecules of an amino compound, namely, dimethylaniline, in the presence of moderately concentrated hydrochloric acid; (b) by condensing one molecule of tetramethyldiamido-benzohydrol prepared by the oxidation of tetramethyl-diamido-diphenylmethane with one molecule of an azo compound, such as benzene-azo-dimethylaniline, in the presence of strong sulfuric acid; (c) by condensing one molecule of methylene disalicylic acid with one molecule of an azo compound, namely, benzene-azo-salicylic acid, in the presence of strong sulfuric acid and an oxidizing agent such as sodium nitrite.

2. The dye belonging to the second type has been prepared by condensing one molecule of benzaldehyde with two molecules of an azo compound, such as benzene-azo-dimethylaniline.

3. The dye of the third type has been prepared by condensing one molecule o an azo aldehyde, such as phenetole-azo-benzaldehyde sulfonic acid, with two molecules of an azo compound, such as benzene-azo-dimethyl-aniline.

With the introduction of a single azo group in the *para* position to the triphenylmethane carbon atom, the color usually deepens to a marked degree, as previously found by Green and Sen, whereas the color is lightened by the introduction of two azo groups; the addition of a third azo group makes the color lighter still. Thus, with the introduction of one azo group into dyes of the type of the methyl violets, the color becomes deeper; as for example, in Table I, Compound 1 is green and Compound 2 is blue. A similar effect is also produced by the introduction of an azo group into dyes of the chrome violet type; thus, Compound 3 in Table I dyes unmordanted wool a deep red which, on chroming becomes deep black, while unmordanted wool alone is dyed only a pink shade and chrome-mordanted wool a violet by chrome violet. By the addition of two azo chromophore groups to dyes of the malachite green series, however, it is found that the

² Green and Sen, J. Chem. Soc., 101, 1113 (1912).

color becomes lighter, Compound 4 in Table I being violet; and with the introduction of three azo groups the color becomes lighter still; for example, Compound 5 is yellow, while rosaniline is red.

It was next attempted to introduce an azo group as well as an azomethine group into a few dyes and for this purpose, several dyes containing free amino groups, such as (1) chrysoidine, (2) rosaniline, (3) safranine and (4) congo red, were condensed with an azo aldehyde such as phenetoleazo-benzaldehyde sulfonic acid. It has been found that the joint effect of the two additional chromophores, -N=N- and -N=CH- is to lighten the color more or less; moreover, the direct dyeing property of congo red appears to have been destroyed by the joint effect of the two additional chromophores -N=N- and -N=CH-.

The effect of the addition of an azo group to dyes of the indamine series was next studied, and for this purpose nitroso-dimethylaniline hydrochloride was condensed with benzene-azo-dimethylaniline in equimolecular proportions in an alcoholic medium. Here the introduction of an azo group (a chromophore) deepens the color; for example, indamine is *blue* and this compound is *olive-green*.

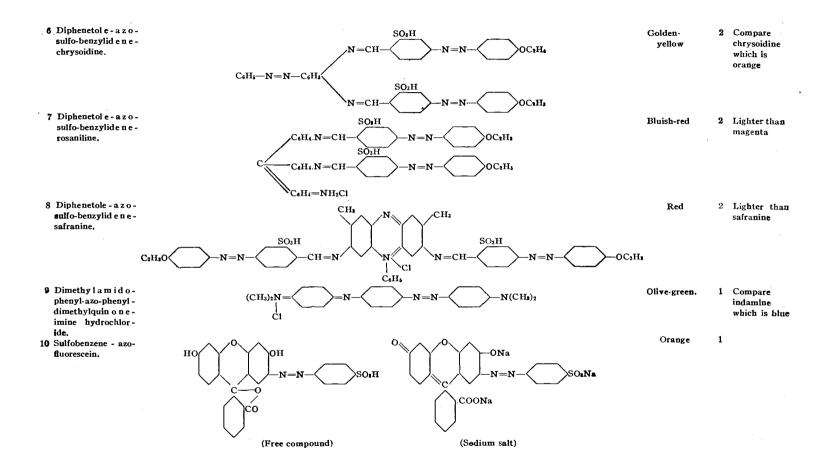
Next, the effect of the addition of azo groups to fluoresceins was studied. For this purpose, sulfanilic acid was diazotized and the diazo compound was coupled with fluorescein in an alkaline medium. By the introduction of the azo group, the color was changed from yellow to orange; moreover, the azo compound shows a red-green fluorescence, whereas fluorescein itself shows yellow-green fluorescence. It may also be remarked here that this substance is not so strongly fluorescent as fluorescein itself. Thus, by the introduction of an azo group, fluorescence is more or less diminished and the shade is deepened to a certain extent.

Experimental Part

1. Phenetole-azo-sulfophenyl-tetramethyl-diamidodiphenyl Carbinol (Condensation product of phenetole-azo-benzaldehyde sulfonic acid and dimethylaniline).—To a solution of 3.5 g. of phenetole-azo-benzaldehyde sulfonic acid in 10 cc. of hot water in a round-bottom flask fitted with a reflux condenser heated by a water-bath, was gradually added 2.5 g. of dimethylaniline dissolved in 2.1 cc. of strong hydrochloric acid. The water in the bath was kept boiling briskly and the heating was continued for 17-18 hours. A green color gradually developed. At this stage, the azo aldehyde was absent from the contents of the flask, as indicated by failure to obtain the orange-colored compound formed between the azo aldehyde and phenylhydrazine acetate. Thus, from the absence of the azo aldehyde, it was presumed that the reaction was complete. The color of the product also indicated that condensation and oxidation had taken place simultaneously.

The heating was then stopped and the flask was taken out of the bath. The hydrochloric acid solution was poured off. The solid that was formed in the flask was dissolved in a very dilute solution of sodium hydroxide, the solution filtered and the coloring matter precipitated by the addition of dil. hydrochloric acid. The precipitate was filtered off and washed. This process of solution and precipitation was repeated thrice. Two g.

	TABLE I			
COMPOUNDS PREPARED AND STUDIED				
No. Name	Molecular formula	Shade of dyeing		
1 Phenetole - azo-sul - fophenyl - tetra -	SO ₂ H	Green	1	Compare
methyl-diamido-				the methyl violets
diphenyl carbinol.				
	$(HO) - C \longrightarrow N(CH_{t})_{t}$			
	N(CH _t)1			
2 Dimethyl-a m i d o -		Blue	1	Compare,
phenyl-azo-phenyl - tetramethyl-diami -				the methyl violets
do-diphenyl carbi-	(HO) - C			violets
nol,				
	N(CH ₄)			
3 Salicylyl-azo- phenyl - disalicylyl	Соон	Red	1	Compare
carbinol.	N=N-OH	Black on chrome		chrome violet
	Соон	Reddish-		
	(HO) - C / OH	brown (on chrom e-		
	Соон	mordanted		
	ОН	wool)		
4 Phenyl - di(dimeth-		Violet	2	Compare
ylamido - p h e n y l- azo-phenyl) carbi-				malachite green
nol.	$(HO) \sim C / N = N - (CH_a)_a$			0
5 Phenetole - azo-sul-		Yellow	2	Compare
foph e n y l - di (d i -	SO ₄ H	renow	4	rosaniline
methylamido-				
phenyl- azo-phenyl) carbinol.	$(HO) - C - N = N - (N(CH_1))$			
	N=N-N(CH _a)t			



of the compound was thus obtained. The compound was purified by crystallization from hot dil. alcohol and then obtained in the form of a microcrystalline powder.

Analysis. Subs., 0.1545: 14.2 cc. of N_2 (30°, 757.3 mm.). Calc. for $C_{22}H_{34}O_5N_4S$: N, 10.03. Found: 9.89.

It is a green powder; it dyes wool directly in a green shade. It is insoluble in cold water and soluble in alcohol. The solution in sulfuric acid is brown.

2. Dimethylamidophenyl-azo-phenyl-tetramethyldiamido-diphenyl Carbinol (Condensation product of benzene-azo-dimethylaniline and tetramethyl-diamidobenzohydrol).—A mixture of 2.5 g. of benzene-azo-dimethylaniline and 3 g. of tetramethyldiamidobenzohydrol (prepared by oxidizing tetramethyl-diamido-diphenylmethane by means of lead peroxide) was introduced into a conical flask containing about 6 cc. of concd. sulfuric acid (d., 1.840). The contents of the flask were then thoroughly mixed and heated under a short air-condenser for four hours in a boiling water-bath. The concd. sulfuric acid solution was treated with ice and ice-cold water, and the cold solution was filtered through a fluted filter paper. The coloring matter was then precipitated from the filtrate by the addition of cold sodium hydroxide solution. The precipitate was washed with water by decantation, filtered off and again washed. The compound was then further purified by solution in chloroform and reprecipitation by addition of the chloroform solution to benzene.

It is a bluish-violet powder that dyes wool and tannin-mordanted cotton in a blue shade. It has not yet been obtained in a sufficiently pure condition for analysis.

3. Salicylyl-azo-phenyl-disalicylyl Carbinol (Condensation product of methylene disalicylic acid and benzene-azo-salicylic acid).—A mixture of 5 g. of dry methylene disalicylic acid (obtained by the condensation of 1 molecular equivalent of formaldehyde with 2 of salicylic acid in the presence of concd. hydrochloric acid and a little alcohol) and 4 g. of dry benzene-azo-salicylic acid was dissolved in 17 cc. of concd. sulfuric acid (d., 1.840) in a conical flask. The flask was then placed in a freezing mixture and 2.5 g. of finely powdered sodium nitrite (dried between folds of blotting paper) was added a little at a time and mixed thoroughly with the contents of the flask. After all the nitrite had been added, the flask was kept at a temperature of $40-50^{\circ}$ for about four hours. The contents of the flask were then transferred into a beaker by means of ice and ice-cold water; the solid portion was filtered off and washed free from sulfuric acid. It was then dissolved in dil. sodium hydroxide, the solution filtered and precipitated by acidification of the filtrate with dil. hydrochloric acid. The precipitate was dissolved in a large volume of boiling water from which the dye was precipitated by the addition of a few drops of strong hydrochloric acid, and subsequent cooling. The precipitate was filtered off, washed and dried in a steam-oven.

It is a red powder, soluble in dil. alcohol and also in hot water giving a red solution. It dyes wool directly in a red shade which turns black on chroming. It dyes chromemordanted wool in a brown shade. This compound slowly decomposes at about 195°.

Analysis. Subs., 0.1455: 7 cc. of N_2 (31°, 753 mm.). Calc. for $C_{28}H_{20}O_{10}N_2$: N, 5.15. Found: 5.12.

4. Phenyl-di(dimethylamidophenyl-azo-phenyl) Carbinol (Condensation product of benzaldehyde and benzene-azo-dimethylaniline).—To a solution of 4 g. of dry benzeneazo-dimethylaniline in 7 to 8 cc. of concd. sulfuric acid (d., 1.840) in a conical flask was added 1.2 g. of benzaldehyde. The mass was thoroughly mixed by means of a glass rod, and the flask fitted with a short air-condenser and heated on a boiling water-bath. After some time, a strong odor of sulfur dioxide developed, the presence of which was proved by reaction with potassium iodide-starch paper. A portion of the contents of the flask was removed at intervals by means of a rod and the color of the aqueous solution examined; it was observed that the color gradually changed from light red through

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reddish-violet to violet. The heating was continued for seven hours until there was no further change in color. Finally, the flask was heated in an oil-bath at about 110° for 15 to 20 minutes, and allowed to cool; the contents were mixed with ice and cold water and the mixture was filtered. The residue on the filter paper was dissolved in dil. hydrochloric acid and the solution filtered. The two filtrates were mixed and the dye was precipitated by the addition of dil. sodium hydroxide solution from which unaltered benzaldehyde was removed by steam distillation. After the solution had cooled, the precipitate was filtered off, washed with cold water and dried. The product was finally purified from hot dil. alcohol and obtained in the form of a microcrystalline powder; m. p., 180–181°.

The compound dissolves in alcohol, giving a violet solution. It dyes wool and tannin-mordanted cotton in violet shades.

Analysis. Subs., 0.0935: 13 cc. of N_2 (30°, 758.3 mm.). Calc. for $C_{35}H_{34}ON_6$: N, 15.16. Found: 14.98.

5. Phenetole-azo-sulfophenyl-di(dimethyl amidophenyl-azo-phenyl) Carbinol (Condensation product of phenetole-azo-benzaldehyde sulfonic acid and benzene-azodimethylaniline).—A mixture of 3.3 g. of phenetole-azo-benzaldehyde sulfonic acid and 4.5 g. of benzene-azo-dimethylaniline dried at 100° was introduced into a conical flask that contained 8 to 9 cc. of concd. sulfuric acid (d., 1.840), mixed thoroughly and the whole heated in a boiling water-bath under an air condenser. A strong odor of sulfur dioxide developed and this substance was tested for as before. The heating was discontinued after about four hours. The contents of the flask, when cold, were mixed with a few bits of ice and stirred. The mixture was filtered and the precipitate was washed free from sulfuric acid by means of ice-cold water.

The precipitate was then dissolved in dil. hydrochloric acid and precipitated by the addition of dil. sodium hydroxide. It was next crystallized from dil. alcohol and recrystallized from the same solvent. This compound dyes wool yellow.

Analysis. Subs., 0.1045: 14.4 cc. of N₂ (35°, 755.3 mm.). Calc. for C₄₃H₄₂O₈N₈S: N, 14.33. Found: 14.4.

6. Diphenetole-azo-sulfo-benzylidene-chrysoidine (Condensation product of chrysoidine hydrochloride and phenetole-azo-benzaldehyde sulfonic acid).-Two g. of chrysoidine hydrochloride and 5.3 g. of phenetole-azo-benzaldehyde sulfonic acid were separately dissolved in 100 cc. and 500 cc. of water, respectively. Both the solutions were heated to about 70° , and the azo aldehyde solution was added to the chrysoidine solution while the mixture was stirred; a red compound was formed; the addition of the azo-aldehyde solution was continued until the mixed solution was found to contain a slight excess of the azo aldehyde (tested with phenylhydrazine acetate solution); 5 to 10 cc. of dil. hydrochloric acid was then added and the solution vigorously shaken for about 5 minutes. After the mixture cooled, the precipitate was filtered off, washed free from hydrochloric acid, again washed with a little cold dil. sodium hydroxide solution and finally with water until the wash water was found to be free from chloride. The product was then dried. It is a red powder; it dyes wool and silk directly in golden-yellow shades; it has no affinity for cotton. It is insoluble in cold water, slightly soluble in hot water as well as in dil. sodium hydroxide solution, and in alcohol, and insoluble in dil. hydrochloric acid. The solution in concd. sulfuric acid is deep red.

Analysis. Subs., 0.1403: 16.8 cc. of N_2 (30°, 755 mm.). Calc. for $C_{42}H_{36}O_8N_8S_2$: N, 13.27. Found: 12.9.

7. Diphenetole-azo-sulfo-benzylidene-rosaniline Hydrochloride (Condensation product of rosaniline and phenetole-azo-benzaldehyde sulfonic acid).—Two g. of rosaniline (base) was dissolved in 60 to 70 cc. of water acidulated with a few drops of hydro-

chloric acid, and 4.6 g. of phenetole-azo-benzaldehyde sulfonic acid was dissolved in about 350 cc. of water. Both the solutions were heated to $50-60^\circ$. The azo aldehyde solution was then added to the rosaniline solution while the mixture was stirred. The precipitated compound was filtered off and washed free from hydrochloric acid, dissolved in alcohol, the hot alcoholic solution filtered and the filtrate poured into water acidulated with a little hydrochloric acid. The dye was precipitated, filtered, washed with water and dried in a steam-oven.

This compound is a deep chocolate color, is insoluble in cold water, slightly soluble in hot water, and more soluble in alcohol. It dyes wool in a bluish-red shade. The solution in coned. sulfuric acid is brownish-red.

Analysis. Subs., 0.0745: 7.2 cc. of N_2 (30°, 750 mm.). Calc. for $C_{49}H_{41}O_8N_7S_2C1$: N, 10.27. Found: 10.20.

8. Diphenetole-azo-sulfo-benzylidene-safranine Hydrochloride (Condensation product of safranine and phenetole-azo-benzaldehyde sulfonic acid.—To 1.5 g. of safranine dissolved in 100 cc. of water heated to $50-60^{\circ}$ was added (while the mixture was stirred) an approximately 1% solution of phenetole-azo-benzaldehyde sulfonic acid, also heated to $50-60^{\circ}$, until the mixed solution contained a slight excess of the azo aldehyde. A precipitate was formed which was filtered off, washed with cold water and purified from dil. alcohol in the same manner as in the case of the compound described above. It is a chocolate-colored powder, insoluble in cold water, slightly soluble in hot water and more soluble in alcohol. It dyes wool in a red shade.

Analysis. Subs., 0.1253: 13.3 cc. of N_2 (31°, 759 mm.). Calc. for $C_{50}H_{43}O_8N_8S_2C1$; N, 11.4. Found: 11.37.

9. Dimethylamido-phenyl-azo-phenyldimethyl-quinone-imine Hydrochloride (Condensation product of nitroso-dimethylaniline hydrochloride and benzene-azo-dimethylaniline).—A mixture of 4 g. of nitroso-dimethylaniline hydrochloride with 5 g. of benzene-azo-dimethylaniline was dissolved in 140 cc. of absolute alcohol in a round-bottomed flask and the solution heated on a water-bath under a reflux condenser for 11 hours. The color gradually changed from yellowish-brown, to a black that in thin layers was greenish. The alcohol was distilled, the product extracted with dil. hydrochloric acid and again precipitated by the addition of dil. sodium hydroxide solution, an excess being avoided. The base thus precipitated was filtered off and washed with water. It was redissolved in dil. hydrochloric acid and reprecipitated by dil. sodium hydroxide solution. The precipitate was again dissolved in dil. hydrochloric acid and again precipitated by dil. ammonia solution. Finally, the base was crystallized from dil. alcohol. It is a greenish-black powder soluble in hot water as well as in alcohol; m. p., 150°. It dyes wool in an olive-green shade.

Analysis. Subs., 0.1210: 20.2 cc. of N₂ (29°, 752.3 mm.). Calc. for $C_{22}H_{25}ON_5$ (free base): N, 18.66. Found: 18.0.

10. Sulfobenzene-azo-fluorescein.—A solution of 2.6 g. of sulfanilic acid in a cold, concentrated solution of sodium hydroxide (containing about 0.6 g.) was further cooled by placing the beaker inside a freezing mixture bath, 1.2 g. of sodium nitrite dissolved in a little water was added and the solution was stirred. When the temperature was near 0°, 5 cc. of concd. hydrochloric acid (d., 1.16) in 20 cc. of ice-cold water was gradually added and the solution in the beaker was mechanically stirred. When the diazotization was complete, that is, when free nitrous acid could be detected in the solution (as indicated by starch-iodide paper), the beaker was removed from the bath and kept cold. A solution of 5 g. of fluorescein in a solution of sodium hydroxide containing about 2 g. was cooled in the freezing mixture bath and a few pieces of ice were added; when the temperature was about 0°, the cold diazo solution was added a little at a time

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and the contents of the beaker were vigorously stirred. The coupling was completed as much as possible before adding a fresh quantity of the diazo solution, the presence of unaltered diazo compound being tested by means of an alkaline solution of β -naphthol. After all the diazo solution had been added, the stirring was continued for about an hour. The beaker was taken out of the cold bath, and the solution acidified with dil. acetic acid when unaltered fluorescein separated as a yellow precipitate. The solution was cooled and then filtered. To a test portion of the filtrate, dil. acetic acid was added drop by drop but no further precipitate was formed. Dil. sulfuric acid was next added to the filtrate and the red precipitate formed was filtered off and washed with cold water, dissolved in a dil. solution of sodium hydroxide, and the dye precipitated by means of dil. sulfuric acid. The precipitate was filtered off, washed and dried. This compound is a red powder soluble in hot water; it dyes wool orange. The alkaline solution shows redgreen fluorescence.

Analysis. Subs., 0.1340: 6.4 cc. of N_2 (29°, 759.6 mm.). Calc. for $C_{26}H_{16}O_8N_2S$: N, 5.43. Found: 5.19.

Summary

1. Three types of azo-triphenylmethane dyes have been studied containing, respectively, one, two and three azo groups in the *para* position to the central carbon atom. It has been found that the introduction of one azo group deepens the color, of two azo groups lightens the color, and of three makes it still lighter.

2. The effect of the multiplication of chromophores has also been studied by introducing simultaneously an azo-methine group and an azo group into chrysoidine, rosaniline, safranine and congo red, and in each case the color becomes lighter. The direct dyeing property of congo red also disappears.

3. The introduction of one azo group has been found to deepen the color in the case of an indamine dye as well as in the case of fluorescein.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CONDENSATION OF CITRAL WITH KETONES AND SYNTHESIS OF SOME NEW IONONES¹

By HAROLD HIBBERT AND LAURA T. CANNON Received June 8, 1923

Theoretical Discussion

In connection with a series of studies on the condensation and polymerization of aldehydes and ketones, it seemed desirable to reinvestigate the behavior of citral towards acetone in the presence of alkaline condensing media. This offered the possibility of obtaining further evidence on

¹ This paper is constructed from a dissertation presented by Laura T. Cannon in June, 1921, to the Faculty of the Graduate School, Yale University, in candidacy for the degree of Doctor of Philosophy. The thesis contains a review of the scientific and patent literature on citral, ionones and related compounds as well as of the work on "the relation between odor and constitution."