The Influence of Position Isomerism (Structural Differences) in Azo Dyes Upon Their Fastness to Light and Washing

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CONTENTS

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MARION E. GRIFFITH AND WALLACE R. BRODE[1]

INTRODUCTION

There has been an increasing demand by the consumer for fabrics which will give better service. One of the most important factors to be considered in the selection of any dyed fabric is the fastness of the dyestuffs which have been used to produce the desired color. If the maximum amount of service is to be obtained, the color must be reasonably fast to at least two conditions of use—namely, washing and exposure to light. It is generally understood that the amount of fading depends largely on the type of dyestuff which has been used.
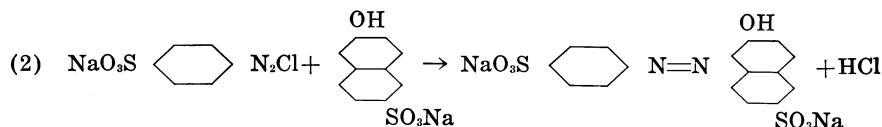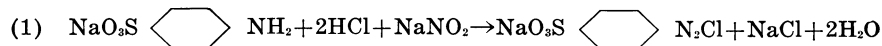
Although many studies have been made of the effects of light and washing upon the fastness properties of dyed fabrics, comparatively little has been done in an effort to determine the extent to which the constitution of the dyestuff affects its fastness properties. The presence of certain groups in the dye molecule has been shown by Watson (11, 12), John (5), and Gebhard (4) to influence the fastness of dyestuffs. Robinson (9) has reported a study of Benzopurpurine 4B and its meta isomer. Jusa and Brewer (6) studied the effect of the mercapto and methyl mercapto groups on the color of mono substituted β naphthol dyes.

The object of the present study was to determine the influence of the position of the sulfonic acid group in a series of isomeric monoazo dyestuffs on the properties of the dyestuffs. Aniline and the ortho-, meta-, and para-sulfonated anilines were coupled to a series of naphthol sulfonic acids. The series of dyes was chosen so as to include a number of commercially important intermediates. This was done in the hope that the information obtained might prove of value in choosing intermediates from which a better type of dyestuff could be obtained. The properties studied included the visible absorption spectra, exhaustive properties, and the amount and kind of fading produced by light exposure and washing tests.

EXPERIMENTAL

PREPARATION OF DYESTUFFS

The dyestuffs were prepared by the usual method of diazotization and coupling (2), the amine being converted into the corresponding diazonium compound and this diazonium compound being allowed to react with the selected naphthol sulfonic acid. An example of the reactions involved is given below:

(1) NaO_3S ⬡ $NH_2 + 2HCl + NaNO_2 \rightarrow NaO_3S$ ⬡ $N_2Cl + NaCl + 2H_2O$

(2) NaO_3S ⬡ $N_2Cl +$ ⬡(OH)(SO₃Na) $\rightarrow NaO_3S$ ⬡ $N=N$ ⬡(OH)(SO₃Na) $+ HCl$

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The amount of time required for diazotization and coupling varies to some extent with the character of the amine used. The preparation of the dyestuffs involved the following steps: precipitation by the addition of sodium chloride, filtering, redissolving in water, salting out, filtering, drying, and grinding.

ANALYSIS OF DYESTUFFS

Due to the very large number of synthetic dyestuffs, with their differences in structure and composition, no one method of analysis is applicable to all dyes. The method of analysis used depends upon the presence in the dyestuff of certain groups which give definite qualitative and quantitative reactions. If the composition of the dyestuff is known and if no other dyestuff is present, titration with titanous chloride will give the exact amount of dyestuff present. This method (7), which depends upon the strong reducing action of the titanous chloride, is especially useful for the analysis of azo dyes. The reduction of the azo group is quantitative and takes place according to the following reaction:

$$R'\text{---}N\text{==}N\text{---}R'' + 4HCl + 4TiCl_3 \rightarrow R'NH_2 + R''NH_2 + 4TiCl_4$$
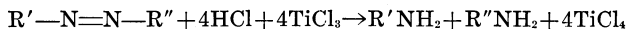
The titanous chloride solution was standardized against a standard sample of Metanil Yellow (meta-sulfonic-benzene-azo-diphenylamine). The Metanil Yellow was prepared and standardized at the Bureau of Standards by Wallace R. Brode.

For analysis a 0.20 gram sample of dyestuff was dissolved in 50 cubic centimeters of distilled water in a 250 cubic centimeter CO_2 flask. To this solution 50 cubic centimeters of a 20% solution of sodium citrate were added and the whole boiled for 3 minutes in an atmosphere of CO_2. The boiling solution was titrated to a colorless endpoint, and about 3 cubic centimeters of titanous chloride were added in excess. Ten cubic centimeters of concentrated HCl were added and the flask and its contents were cooled to 30° C. For the back titration ferric alum was used, 5 cubic centimeters of a 10% solution of ammonium thiocyanate being used as an indicator. All titrations were made in triplicate. From the value of the titanous chloride in terms of the Metanil Yellow, the purity of the dyes, based upon the amount of reducible azo group present, was calculated.

THE APPLICATION OF THE DYESTUFFS

Fabric samples of white wool cashmere weighing 3.25 grams were used. Before dyeing, the wool was scoured by boiling for 15 minutes in an 80 volume bath of 0.5% neutral soap solution and was then thoroughly rinsed. A glycerine-water dyebath was used in dyeing, and in each case dyeings were made in duplicate, according to the following procedure (1):

The wool was wet out hot and entered in a 50 times bath (at 49° C.) containing 1 per cent of dye, 20 per cent of Glauber's salt, and 5 per cent of acetic acid (28%). The temperature was raised to boiling in 15 minutes and boiling continued for 45 minutes.

One per cent of concentrated H_2SO_4 was then added and the boiling continued for 30 minutes. The wool was rinsed, extracted, dried, and ironed with a medium hot iron.

The amounts of dyes and chemicals used are expressed as percentages of the weight of the wool.

TABLE 1.—Properties of the Dyestuffs

No.	Dye formula	Abbreviation	Pct. nitrogen		Relative solubility in water at 20° C.	Color of dye
			Theoretical	Analysis		
1	⬡—N=N—⬡OH	A-a	....	....	Insoluble	Red brown
2	SO₃Na, ⬡—N=N—⬡OH	O-a	8.00	5.02	Slightly soluble	Yellow orange
3	NaO₃S⬡—N=N—⬡OH	M-a	8.00	6.70	Soluble	Dark blue red
4	NaO₃S⬡—N=N—⬡OH	P-a	8.00	5.60	Slightly soluble	Dark blue red
5	⬡—N=N—⬡OH (NaO₃S)	A-a3	8.00	7.22	Very slightly soluble	Orange
6	SO₃Na ⬡—N=N—⬡OH (NaO₃S)	O-a3	6.19	3.96	Slightly soluble	Dark red
7	NaO₃S⬡—N=N—⬡OH (NaO₃S)	M-a3	6.19	3.38	Soluble	Dark orange red
8	NaO₃S⬡—N=N—⬡OH (NaO₃S)	P-a3	6.19	3.87	Soluble	Dark blue red
9	⬡—N=N—⬡OH (NaO₃S)	A-a4	8.00	6.34	Slightly soluble	Red
10	SO₃Na ⬡—N=N—⬡OH (NaO₃S)	O-a4	6.19	5.81	Slightly soluble	Dark red
11	NaO₃S ⬡—N=N—⬡OH (NaO₃S)	M-a4	6.19	4.82	Slightly soluble	Bright red
12	NaO₃S⬡—N=N—⬡OH (NaO₃S)	P-a4	6.19	3.85	Soluble	Red
13	⬡—N=N—⬡OH (SO₃Na)	A-a5	8.00	4.25	Very slightly soluble	Orange
14	SO₃Na ⬡—N=N—⬡OH (SO₃Na)	O-a5	6.19	5.10	Slightly soluble	Very dark brown
15	NaO₃S ⬡—N=N—⬡OH (SO₃Na)	M-a5	6.19	4.58	Soluble	Red

TABLE 1.—Properties of the Dyestuffs—Continued

No.	Dye formula	Abbreviation	Pct. nitrogen		Relative solubility in water at 20° C.	Color of dye
			Theoretical	Analysis		
16	NaO₃S— —N=N— OH / SO₃Na	P-α5	6.19	3.90	Soluble	Red
17	—N=N— OH	A-β	11.25	....	Insoluble	Red orange
18	SO₃Na —N=N— OH	O-β	8.00	3.92	Very slightly soluble	Yellow orange
19	NaO₃S —N=N— OH	M-β	8.00	7.04	Soluble	Orange
20	NaO₃S— —N=N— OH	P-β	8.00	6.77	Soluble	Yellow orange
21	—N=N— OH / SO₃Na	A-β6	6.19	5.02	Soluble	Red orange
22	SO₃Na —N=N— OH / SO₃Na	O-β6	6.19	5.76	Soluble	Bright red
23	NaO₃S —N=N— OH / SO₃Na	M-β6	6.19	4.41	Soluble	Orange
24	NaO₃S— —N=N— OH / SO₃Na	P-β6	6.19	4.11	Soluble	Red
25	—N=N— OH / NaO₃S	A-β7	8.00	6.64	Very slightly soluble	Orange
26	SO₃Na —N=N— OH / NaO₃S	O-β7	6.19	6.12	Soluble	Dark red
27	NaO₃S —N=N— OH / NaO₃S	M-β7	6.19	4.59	Soluble	Orange
28	NaO₃S— —N=N— OH / NaO₃S	P-β7	6.19	3.79	Soluble	Dark orange red
29	—N=N— OH SO₃Na / NaO₃S—	A-α3:8	6.19	3.60	Very slightly soluble	Red

TABLE 1.—Properties of the Dyestuffs—Concluded

No.	Dye formula	Abbreviation	Pct. nitrogen Theoretical	Pct. nitrogen Analysis	Relative solubility in water at 20° C.	Color of dye
30	SO₃Na / OH / SO₃Na —N=N— NaO₃S	O–α3:8	5.39	2.97	Soluble	Red
31	NaO₃S / OH / SO₃Na —N=N— NaO₃S	M–α3:8	5.39	3.68	Soluble	Very dark violet red
32	NaO₃S / OH / SO₃Na —N=N— NaO₃S	P–α3:8	5.39	5.21	Soluble	Dark blue red
33	OH / SO₃Na —N=N— SO₃Na	A–β3:6	6.19	4.95	Soluble	Orange
34	SO₃Na / OH / SO₃Na —N=N— SO₃Na	O–β3:6	5.39	2.48	Soluble	Dark orange red
35	NaO₃S / OH / SO₃Na —N=N— SO₃Na	M–β3:6	5.39	3.75	Slightly soluble	Dark blue red
36	NaO₃S / OH / SO₃Na —N=N— SO₃Na	P–β3:6	5.39	4.42	Slightly soluble	Dark red
37	OH —N=N— NaO₃S / SO₃Na	A–β3:8	6.19	5.57	Soluble	Red orange
38	SO₃Na / OH —N=N— NaO₃S / SO₃Na	O–β6:8	5.39	4.60	Soluble	Yellow orange
39	NaO₃S / OH —N=N— NaO₃S / SO₃Na	M–β6:8	5.39	2.34	Soluble	Orange
40	NaO₃S / OH —N=N— NaO₃S / SO₃Na	P–β6:8	5.39	....	....	....

LAUNDER-OMETER WASHING TESTS

The washing test was made in a Launder-ometer at 49° C., using 100 cubic centimeters of a 0.5% neutral soap solution, as recommended by the American Association of Textile Chemists and Colorists (1). The machine was allowed to run 30 minutes, after which the samples were rinsed several times in warm water. They were then rinsed in cold water, squeezed, and dried in a current of air at room temperature before a fan. Duplicate samples, each measuring 2½ by 3 inches, were placed in each jar.

EXPOSURE TO LIGHT

Two methods are usually used for testing light fastness. The first is exposure to direct sunlight, and the second, exposure to an artificial light. The carbon arc has been found to be the most satisfactory source of artificial light. The Fade-ometer is an instrument using the carbon arc. Since it affords the much more convenient and rapid method of producing fading and is particularly useful for testing in the fall and winter, it was used in the study reported here. The Fade-ometer has a different spectrum from the sun, but its fading action is similar. Robertson (8) made a comparative study of the fading produced by the Fade-ometer (Type LV) and by the sunlight at Columbus, Ohio, and found that there was only a slight difference in the fading produced by the two methods.

Tests of from 40 to 50 Fade-ometer hours are usually adequate to determine whether or not a color will fade (1). Since very little fading (in some cases none) visible to the eye was produced by 40 hours and later 80 hours, the samples in the study reported here were exposed for 120 hours. The average temperature was 120° F. and the average relative humidity, 30 per cent, as recorded by a hygrothermograph.

COLOR ANALYSIS

There are two general broad types of color (2)—one due to interference and the other due to absorption. The latter type includes the color which is involved in the work reported here and is caused by the selective absorption of electro-magnetic waves in the visible spectrum. If white light is passed through a solution which absorbs all light except yellow, the solution will appear yellow. Generally speaking, color is caused by the absorption of a second or complementary substance; for example, if the color absorbed was blue, the color seen is orange.

The most satisfactory method of analyzing visible color is by means of a spectrophotometer. This instrument measures the amount of light reflected from or transmitted by the colored sample at any wave length throughout the spectrum. Spectrophotometric analysis provides a convenient and rapid method for the analysis of dyestuffs and of dyed fabrics. The light absorbed by a dyed sample is proportional to the logarithm of the concentration of the dyestuff taken up by the fabric (10). To obtain numerical expressions for the loss of color due to washing, it is necessary only to express the change in terms of the percentage difference in reflectance at any one wave length. Light fading which involves both a loss in brightness and a change in hue may also be expressed numerically.
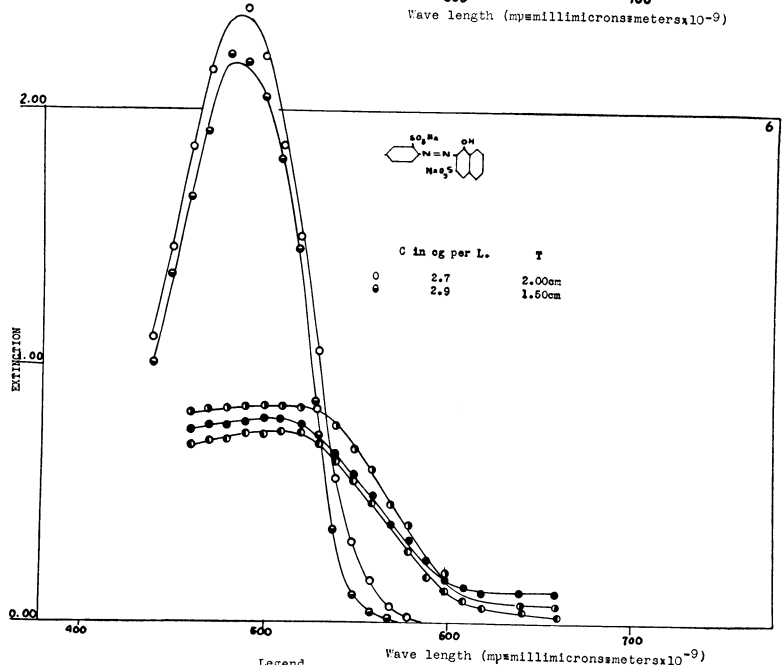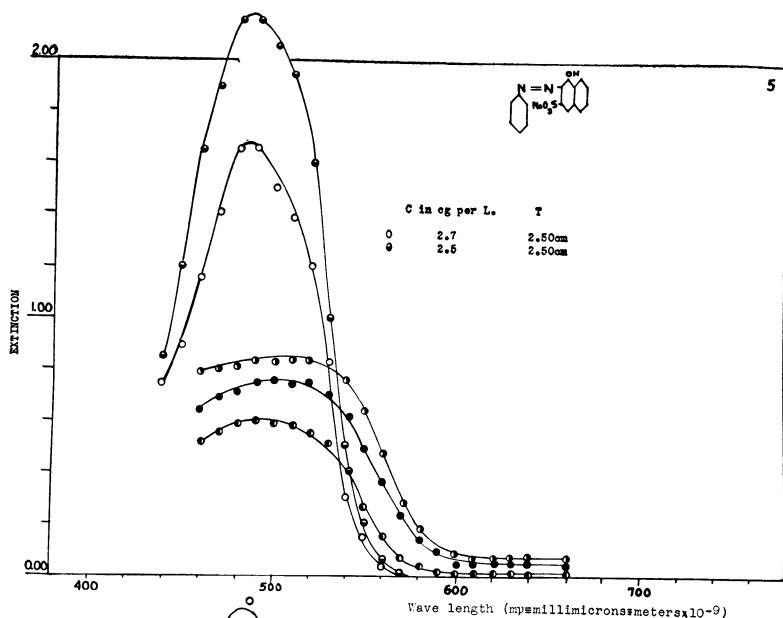
EXHAUSTIVE PROPERTIES

There is no general rule concerning the exhaustive properties of dyestuffs. There are, however, several theories which may explain in part the process of dyeing; if we assume, as has Freundlich (3), that the first stage in every dyeing process is adsorption, then the factors which influence adsorption will have some influence on the degree to which the dye is adsorbed by the fiber. Four of these factors which affect adsorption are: (a) the area of the surface exposed, (b) solution pressure, (c) temperature, and (d) concentration. However, with the same conditions of temperature, pressure, and concentration the degree of adsorption will vary with the nature of the adsorbent and adsorbed substance or in the dyeing process with the nature of the dyestuff and the fabric being dyed.

Solutions of the dyestuffs used in dyeing the fabrics were analyzed for exhaustive properties with a spectrophotometer. The dye solutions were prepared for analysis in the same manner as that used for the dyebath, the same amount of sodium sulfate, acetic acid, sulfuric acid, and dyestuff being added. The exhausted solutions were made up to the original volume and portions taken for analysis. From the curves obtained the difference at the maximum absorption band was obtained, and, from this, the degree of exhaustion of the dyebath was determined. The duplicate exhausted solutions varied in degree of exhaustion by less than one per cent in all cases. The degree of exhaustion varied with the different dyestuffs from 5 to 30 per cent. Observations were made only in the visible portion of the spectrum.

The reflection of light from the dyed samples was measured with the spectrophotometer, using a reflection sphere. Duplicate readings for the original dyed samples, the washed samples, and the samples exposed to light in the Fade-ometer were taken. Corrections were made for the reflection of a piece of the same washed fabric before dyeing. The amount of fading was determined from the relative drop of the extinction coefficient at the maximum of the absorption band. The darkening was determined from the relative increase in extinction of the flat portion of the absorption curve (usually between 610-630 mμ). This value was corrected for pure dye absorption by subtraction of the extinction value observed in the unfaded fabric, which, in turn, had been corrected for loss in fading.

DISCUSSION OF RESULTS

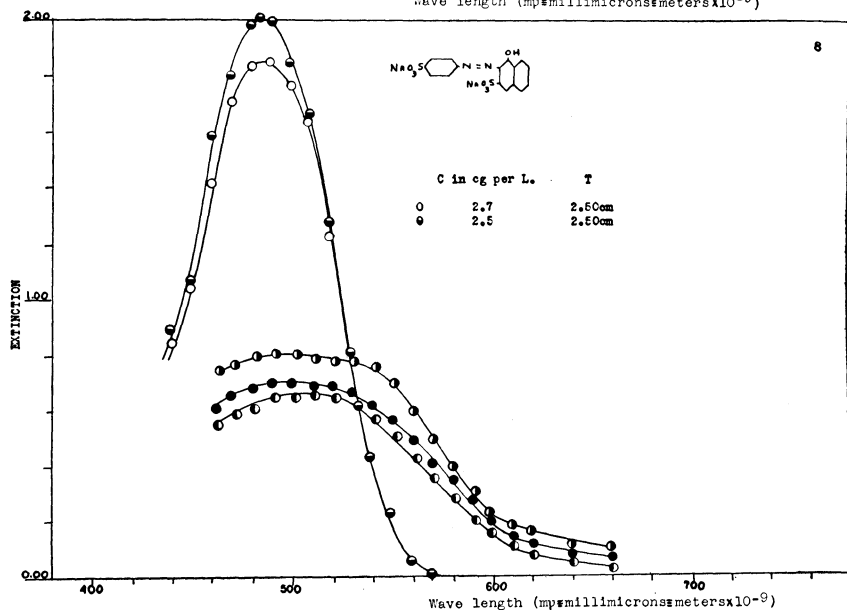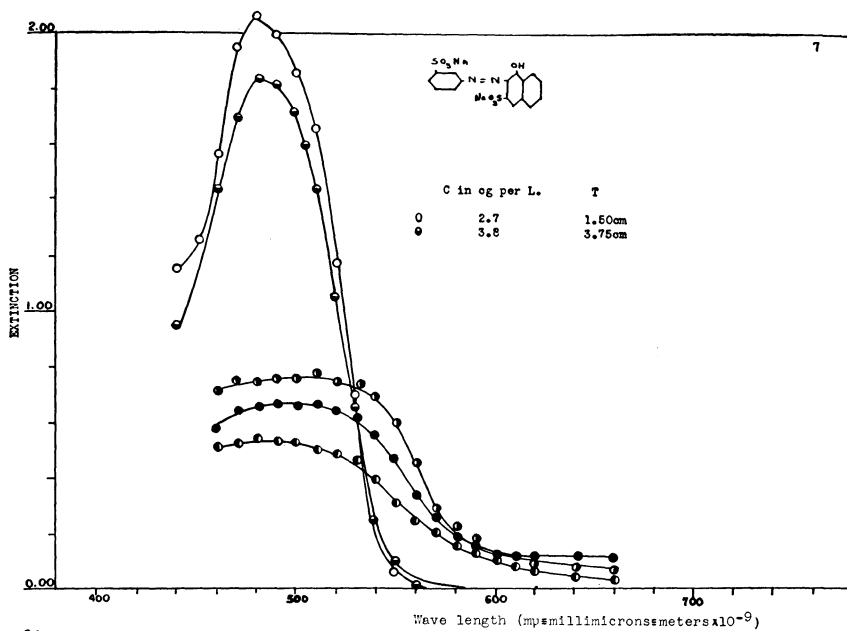### RELATION BETWEEN THE ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF THE DYESTUFFS

The position of the absorption band is an indication of the hue and intensity of the dyestuffs. The position of the sulfonic acid group in the diazotized nucleus appears to have only a slight effect on the position of the absorption band (Column IV, Table 2). With the ortho- and meta-sulfonated compounds the band falls between 470 and 500 mμ. There is a slight shift toward the red with the unsulfonated aniline. When the sulfonic acid group occupies the para position, there is a decided shift of the band towards the red, as well as an increase in the intensity.

Fig. 1

Fig. 2

Legend
O - Original dye solution diluted 1-10
◑ - Exhausted dye solution
◓ - Original dyed fabric
● - Dyed fabric after 120 hours exposure to Fade-ometer light
◐ - Dyed fabric after washing

Fig. 3

Fig. 4

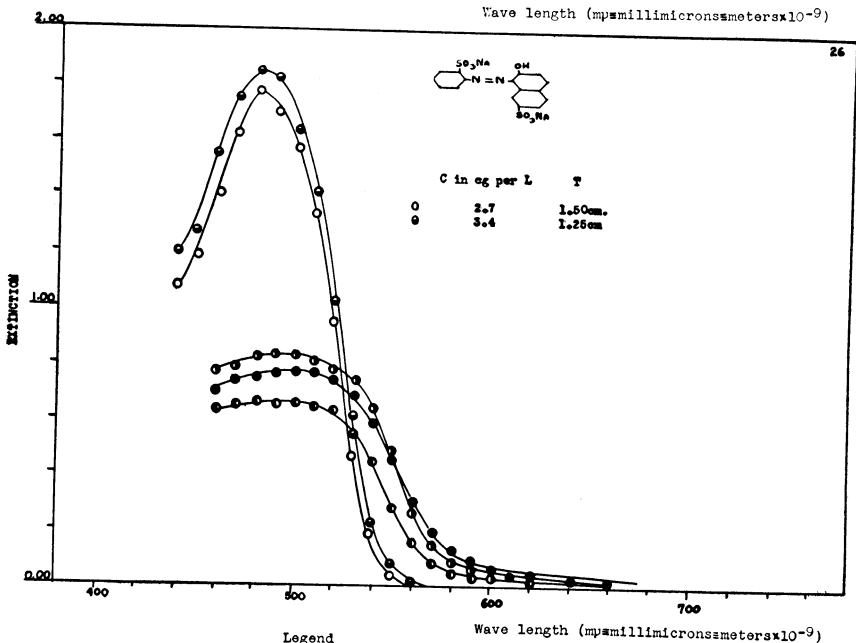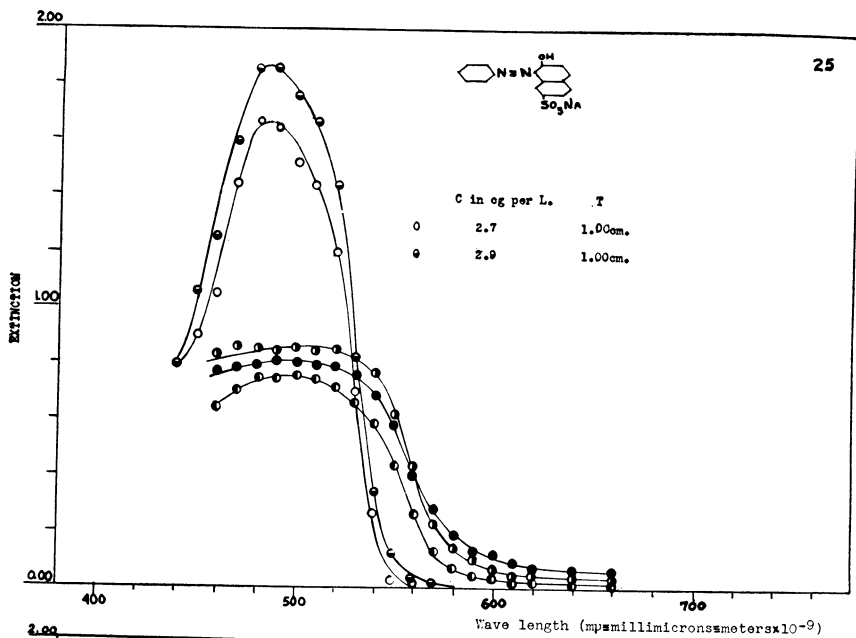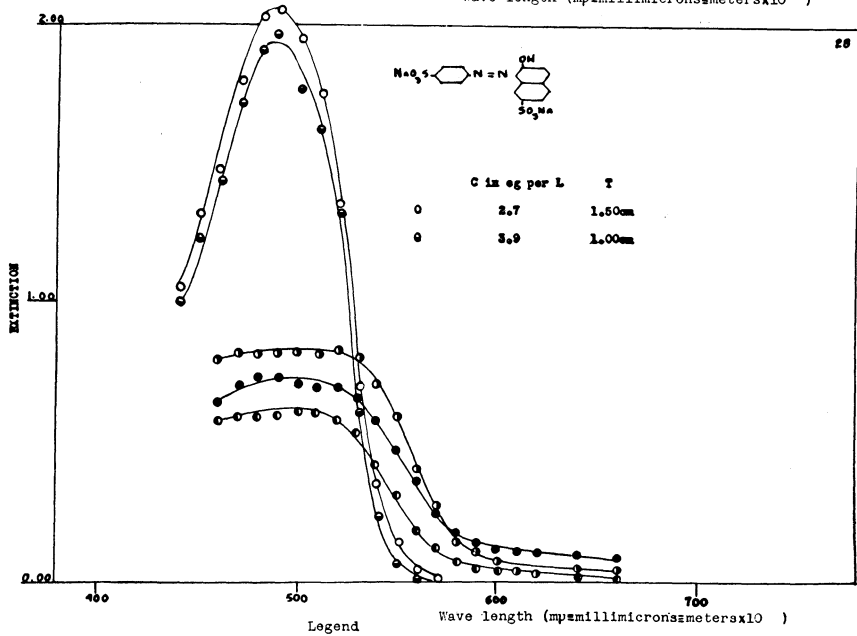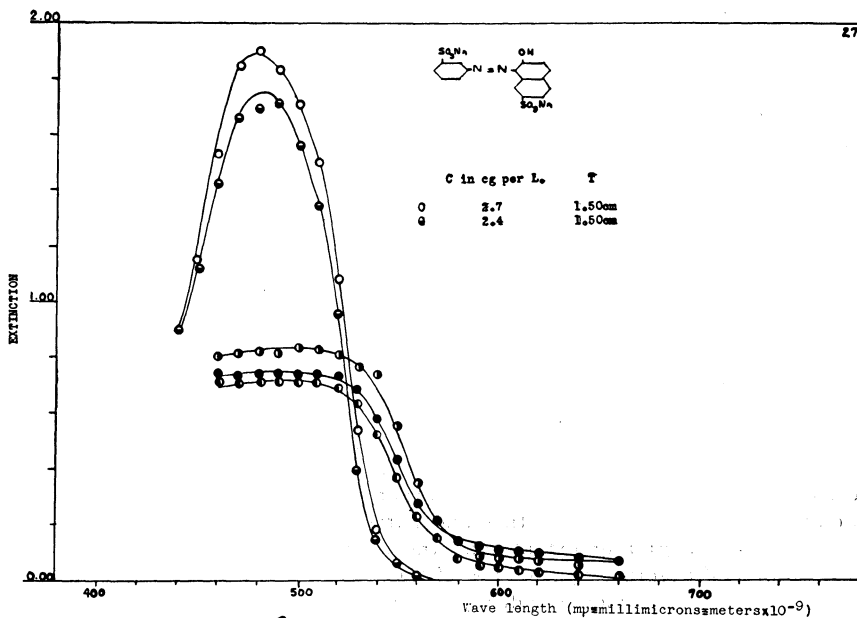Legend

O - Original dye solution diluted 1-10
◑ - Exhausted dye solution
◐ - Original dyed fabric
● - Dyed fabric after 120 hours exposure to Fade-ometer light
◉ - Dyed fabric after washing

In comparing the effect of substitutions in the second component (the naphthol ring) with the position of the absorption band, the greatest transmission in the yellow is found in the α naphthol dyes. The addition of a sulfonic acid group in the *three* position shifts the band towards the red. A still further shift occurs when the substitution is in the *four* position, while the greatest absorption of blue is found when the *five* position is occupied.

The β naphthol dyes have a greater absorption of blue than the α naphthol dyes. Beta naphthol-6-sulfonic acid dyes have a band which is shifted still more toward the red; whereas those in which the *seven* position is occupied have the greatest absorption in the blue.

Very little difference is shown by the disulfonic acid dyes, although the β naphthol-6, 8-disulfonic acid dyes show more absorption of blue than the other disulfonic acid dyes which were studied.

RELATION BETWEEN CONSTITUTION AND FIBER ABSORPTION OF DYESTUFF

The presence of a sulfonic acid group in the diazotized nucleus has a decided influence upon the percentage absorption of the dyestuff by the fiber (Column V, Table 2). The ortho- and para-sulfanilic acid dyes are absorbed by the fiber to a greater extent than the meta-sulfanilic acid dyes. The per cent of dyestuff absorbed by the dyes of the four classes is shown in the following tabulation (the numerals indicate the number of dyes which fall in the various percentage groups):

	Aniline	Ortho-sulfanilic acid	Meta-sulfanilic acid	Para-sulfanilic acid
70– 85 per cent................	6	0	2	0
85– 90 per cent................	1	6	2	4
90– 95 per cent................	1	2	6	4
95–100 per cent................	0	2	0	1

The following tabular form shows the absorption of dyestuffs as affected by substitutions in the naphthol nucleus:

	70–85 per cent	86–90 per cent	91–95 per cent	96–100 per cent
α naphthol dyes.....................	6	10	2	1
β naphthol dyes.....................	4	10	4	....

Substitutions in the naphthol ring appear to have little effect upon the exhaustive properties of the dyestuffs.

RELATION BETWEEN THE CONSTITUTION OF THE DYESTUFF AND THE FASTNESS TO WASHING OF THE DYED FABRIC

The presence of a sulfonic acid group in the diazotized nucleus of these dyes greatly increases their fastness to washing although the position of the sulfonic acid group has little or no effect on the fastness (Column VI, Table 2). Those in the meta and para position are only slightly greater in color fastness than those of the ortho position.

TABLE 2.—Washing Fastness Properties

No.	Dye	Absorption spectra of dye solutions		Per cent of dye absorbed by fabric =Ex	Per cent of dye retained by fabric after washing=w	*W=100-w/Ex
		E=log. lo/l for 2.7 cg. per L. C:T=1 cm.	x=position of band in mμ			
2	O-α...........	2.14	472	89.4	78.6	12.2
3	M-α	2.28	470	82.0	73.4	10.5
4	P-α...........	2.40	471	85.0	67.5	21.0
5	A-α3	1.67	485	74.0	52.1	29.5
6	O-α3...........	1.12	480	88.9	69.5	21.8
7	M-α3	1.73	480	86.0	57.5	33.0
8	P-α3...........	0.81	490	90.0	73.5	18.2
9	A-α4	1.34	495	81.7	55.2	32.2
10	O-α4...........	1.33	490	87.5	73.0	16.6
11	M-α4	1.12	488	90.0	78.0	13.2
12	P-α4...........	1.48	495	85.1	63.8	16.7
13	A-α5	0.91	505	70.5	42.9	30.4
14	O-α5...........	1.01	500	89.9	89.5	10.4
15	M-α5	0.93	495	87.0	76.5	12.0
16	P-α5...........	1.34	500	90.0	69.0	33.2
18	O-β	1.59	480	89.1	74.0	17.0
19	M-β	1.50	480	90.2	88.0	2.5
20	P-β	2.05	480	91.0	75.5	16.7
21	A-β6	1.86	485	80.9	63.5	21.5
22	O-β6..........	1.11	480	89.7	73.5	18.8
23	M-β6	1.17	481	90.1	73.0	19.5
24	P-β6..........	1.46	480	87.0	70.0	19.6
25	A-β7	1.67	484	89.0	80.5	9.5
26	O-β7..........	1.19	480	87.5	68.5	21.7
27	M-β7	1.26	481	90.5	66.1	27.0
28	P-β7..........	1.36	489	85.6	63.9	20.6
29	A-α3:8.........	1.14	492	89.7	79.0	12.0
30	O-α3:8.........	0.96	484	96.4	76.5	20.7
31	M-α3:8.........	1.05	494	90.7	73.8	18.8
32	P-α3:8.........	0.50	498	91.2	75.2	17.6
33	A-β3:6.........	1.29	492	80.5	62.7	21.0
34	O-β3:6.........	0.80	492	96.0	84.6	11.0
35	M-β3:6	1.00	490	91.0	79.0	13.0
36	P-β3:6.........	1.15	495	95.2	82.5	13.4
37	A-β6:8.........	1.23	495	78.9	59.0	25.0
38	O-β6:8.........	0.81	480	89.4	64.3	28.2
39	M-β6:8.........	1.85	485	84.1	68.9	18.2

*W=Per cent loss of dye due to washing, based upon 100 per cent dye on fabric.

Substitutions in the naphthol nucleus do not greatly affect the fastness of the dyes. The greatest fastness is found with β naphthol-6-sulfonic, α naphthol-3,8-disulfonic, and β naphthol-3,6-disulfonic acids. Slightly less fast to washing are the α naphthol-4-sulfonic, β naphthol-7-sulfonic acid, α naphthol, and β naphthol dyes. Alpha naphthol-3-sulfonic acid, α naphthol-5-sulfonic acid, and β naphthol-6,8-disulfonic acid dyes are the least fast to washing.

RELATION BETWEEN DYE CONSTITUTION AND FASTNESS TO LIGHT

Two types of light fading were observed—the loss in intensity of the color and the change in hue. The loss in intensity is expressed as fading (F) (Column IV, Table 3); whereas the change in hue is called darkening (D) (Column VII, Table 3). The combined effects of these two factors indicate the total effect of exposure to light (L) (Column VIII, Table 3).

Ortho-sulfanilic acid dyes are decidedly better than those of the other three series insofar as light fastness is concerned. The para-sulfanilic acid dyes are less fast, and the meta-sulfanilic acid dyes show the greatest fading. The β naphthol dyes fade less than the α naphthol dyes. This relation holds with both the monosulfonic and disulfonic acid substituted dyestuffs.

TABLE 3.—Light Fastness Properties

No.	Dye	f	F=100-f/Ex	δ	d	D=d/Ex	L=D×F	W×L	Color of dyed fabric	Color of light faded sample
2	O-α	66.5	25.5	5	6.25	7.45	189.0	2306	Red orange	Brownish orange—high degree of fading
3	M-α	55.5	32.0	7	9.38	11.40	365.0	3830	Orange	Brownish orange—high degree of fading
4	P-α	75.0	12.5	0	1.00	1.17	14.7	298	Orange	Brownish orange—considerably faded
5	A-α 3	66.0	10.8	0	2.55	3.45	37.2	1110	Orange	Loss of yellow—greyed
6	O-α 3	83.5	6.0	3	6.40	7.22	43.2	940	Red orange	Brownish orange—no great color change
7	M-α 3	75.0	12.7	2	4.90	5.70	72.5	2400	Orange	Brownish orange—high degree of fading
8	P-α 3	78.0	13.0	0	6.60	7.32	95.4	1765	Orange red	Brownish orange—high degree of fading
9	A-α 4	73.2	10.5	0	1.00	1.14	10.9	351	Red orange	Light orange brown—high degree of fading
10	O-α 4	79.2	9.4	6	7.09	8.10	75.3	1260	Red orange	Slightly greyed—loss of yellow
11	M-α 4	83.5	7.2	3	6.14	6.82	49.0	642	Red orange	Slightly greyed—loss of yellow
12	P-α 4	78.0	9.6	4	2.50	2.92	28.0	523	Red orange	Greyed red orange
13	A-α 5	58.0	17.8	6	7.46	9.40	168.0	5130	Orange red	Loss of yellow—high degree of fading
14	O-α 5	80.5	10.5	8	9.40	7.55	100.2	1042	Orange red	Loss of yellow—greyed, high degree of fading
15	M-α 5	76.5	12.0	6	6.50	7.47	89.5	1072	Orange red	Loss of yellow—greyed, high degree of fading
16	P-α 5	88.0	2.2	5	4.35	4.83	10.6	353	Red	Very little change—very slightly lighter in value
18	O-β	83.5	6.4	3	2.90	3.24	23.8	405	Yellow orange	Very little change from original
19	M-β	81.5	9.6	7	6.30	6.97	67.0	168	Yellow orange	Slightly greyed—no great change
20	P-β	85.5	6.0	1	1.55	1.72	10.5	176	Orange	Very slight loss in intensity
21	A-β 6	73.0	9.5	3	2.52	3.07	29.2	627	Yellow	Slightly greyed
22	O-β 6	81.0	9.7	2	2.93	3.26	31.6	596	Orange yellow	Slightly greyed
23	M-β 6	77.0	14.0	2	3.60	3.97	55.5	1062	Orange yellow	Greyed yellow orange
24	P-β6	81.5	6.2	4	5.00	5.77	35.8	702	Yellow orange	Very little change from original
25	A-β 7	83.5	6.2	5	5.00	5.62	34.8	330	Orange	Very slightly greyed
26	O-β 7	81.0	7.2	3	3.11	3.55	25.6	544	Orange yellow	Very slightly greyed
27	M-β 7	81.0	0.5	3	2.15	2.37	1.18	32	Orange yellow	Slightly greyed
28	P-β 7	75.0	13.3	6	7.35	8.59	116.4	239	Yellow orange	Brownish orange—considerable fading

TABLE 3.—Light Fastness Properties—Continued

No.	Dye	f	F=100-f/Ex	δ	d	D=d/Ex	L=D×F	W×L	Color of dyed fabric	Color of light faded sample
29	A-α 3:8	81.0	9.7	4	5.20	5.80	56.2	663	Orange	Loss of yellow—high degree of fading
30	O-α 3:8......	88.5	8.2	5	5.75	5.97	49.0	1015	Orange	Brownish orange—considerable fading
31	M-α 3:8	78.0	13.6	5	5.35	5.90	84.0	1580	Orange	Loss of yellow—high degree of fading
32	P-α 3:8......	80.0	11.3	5	5.10	5.60	61.4	1082	Red orange	Loss of yellow—high degree of fading
33	A-β 3:6	72.5	9.5	9	9.70	8.30	78.8	1592	Orange	Loss of yellow—high degree of fading
34	O-β 3:6......	87.0	8.5	5	4.75	5.00	42.5	468	Orange	Brownish orange—slightly faded
35	M-β 3:6......	82.0	10.0	5	6.04	6.60	66.0	858	Orange	Brownish orange—considerable fading
36	P-β 3:6......	86.0	9.7	6	5.85	6.15	59.6	794	Orange	Loss of yellow—high degree of fading
37	A-β 6:8	76.0	3.8	4	2.13	2.70	10.2	259	Yellow	Very little change from original
38	O-β 6:8......	83.0	6.2	4	3.90	4.36	27.0	750	Yellow	Very little change
39	M-β 6:8	76.0	9.6	6	6.32	7.50	72.1	1320	Yellow	Greyed—considerable fading

f=per cent of dye remaining on fabric (on basis of original solution strength) after light exposure.
F=per cent of fading or loss of dye on fabric after fading on basis of amount of dye on fabric.
δ=observed darkening.

d=darkening expressed in extinction corrected by loss of absorption due to fading of dye or $d = \dfrac{\delta}{Ex} f$.

D=darkening on basis of 100 per cent dye on fabric.
L=light factor or an arbitrary indication of stability of dye to light.
W×L=utility factor.

The degree of darkening seems to be influenced very little by the presence or position of the sulfonic acid group in the benzene nucleus, although there is slightly less darkening in the case of ortho- and para-sulfanilic acid dyes.

The combined effect of fading and darkening (L), which gives the total effect of light on these dyes, again indicates that the ortho-sulfanilic acid dyes are superior to those made from aniline and para- and meta-sulfanilic acids. The meta substitution has decidedly the greatest influence on the degree of fading by light. The aniline dyes are a little more fast to light than the para-sulfanilic acid dyes. With the exception of β naphthol-3,6-disulfonic acid and α naphthol-4-sulfonic acid, the β naphthol dyes are more fast than the α naphthol dyes.

CONSTITUTION AND THE COMBINED EFFECT OF LIGHT AND WASHING

A true index of the fastness of a dyestuff should be arrived at by a comparison of the combined effects of light and washing on the dyestuff, which is reported here as the utility factor (Column IX, Table 3).

As shown by the utility factor, the ortho-sulfanilic acid dyes have the greatest fastness, with para-sulfanilic acid coming second. Meta-sulfanilic acid is only slightly better than aniline.

The effect of substitutions in the naphthol nucleus may be best shown by the following arrangement which shows the relative fastness of the dyes; the dyes are arranged in order from those which show the greatest fastness to those which show the least:

1. β naphthol-7-sulfonic acid
2. β naphthol
3. β naphthol-6-sulfonic acid
4. β naphthol-3, 6-disulfonic acid
5. α naphthol-4-sulfonic acid
6. α naphthol-3, 8-disulfonic acid
7. β naphthol-6, 8-disulfonic acid
8. α naphthol
9. α naphthol-3-sulfonic acid
10. α naphthol-5-sulfonic acid

With the exception of α naphthol-4-sulfonic acid and β naphthol-6,8-disulfonic acid, the β naphthol dyes are superior. The presence of two sulfonic acid groups in the naphthol nucleus does not seem to decrease the fastness of the dyestuff.

SUMMARY

Thirty-seven monoazo isomeric dyestuffs were prepared, and the change in properties of these dyestuffs produced by a shift in the position of the hydroxyl and sulfonic acid groups was studied. Conclusions have been drawn concerning the effect of these changes in position on the color, visible absorption spectra, and exhaustive properties of the dyestuffs and on their fastness to light and washing when applied to wool fabric.

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