

The Influence of Position Isomerism in Azo Dyes Upon Their Fastness to Light and Washing

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INTRODUCTION

The color fastness of dyed fabrics is a problem which has received considerable attention during the past few years with the increasing trend toward consumer education. To be satisfactory, a dye must be fast to both light and washing. Many factors determine the fastness of a dyestuff. It is generally understood that the fiber content of the fabric, the method of application of the dyestuff, the type of dyestuff, and the conditions of wear, use, and care influence fastness properties. The extent to which variations among the dyes in any one particular class or of any one particular type affect these properties has not been widely studied. In any class of dyestuffs there are almost unlimited possibilities of arrangement of elements or groups of elements. These almost unlimited possibilities may account for variations in the fastness properties of different dyes in one class or type. The work described here is part of a general problem dealing with the relationship between the chemical constitution, especially the arrangement of certain groups in the dye molecule, and the properties of the dyestuffs. The properties studied were color, the degree of exhaustion, and the fastness to light and washing.

In a previous publication¹ such a study of a series of sulfonated phenylazo-alpha-and beta-naphthol dyes was reported. The dyes in the series reported here are sulfonated phenylazo-alpha-and beta-naphthylamine dyes (see table 1). In each series of dyes one object was to determine the influence of the position of the sulfonic acid group in both the benzene and the naphthalene nucleus. In addition, it was also possible to study the comparative effects of the presence and the position of the hydroxyl and amino groups in the naphthalene ring.

EXPERIMENTAL

DYES AND PREPARATION

The dyes in this series were prepared by the diazotization of ortho-sulfanilic acid, metanilic acid, or para-sulfanilic acid and coupling to form the monoazo dyes with the available naphthylamines and their monosulfonated derivatives. Thirty-six of these dyes were prepared and used. This series of dyes was prepared, purified, and analyzed by Dr. D. R. Eberhart of the Calco Chemical Company.²

The alpha-naphthylamine series included isomeric sulfonic acids in which the sulfonic acid group occupied the 2, 3, 4, 5, 6, 7, or 8 position. The beta series included the 5, 6, and 7 naphthylaminesulfonic acids and beta-naphthylamine (see table 1). The method of purification was improved through the use of the diphenylguanidine method.³

¹Griffith, M. E. and W. R. Brode. 1936. Ohio Agr. Exp. Sta. Bull. 565.

²Eberhart, D. R. and W. R. Brode. 1936. Doctors' Dissertations 18: 123. The Ohio State University Press.

³Rose, R. E. 1933. Ind. and Eng. Chem. 25: 1028.

The dyes were analyzed by the titanous trichloride method.⁴ The preparation and analysis of these dyes have been described in part in a previous publication.¹

DYEING AND EXHAUSTIVE PROPERTIES

Duplicate samples of scoured white wool cashmere were dyed according to the procedure previously described.¹ The degree of exhaustion of the dye bath was determined by spectrophotometric analysis of the original and exhausted dye solutions.

LIGHT AND WASHING TESTS

The light fastness test was made by exposing duplicate samples for 120 hours to the light of the Fade-Ometer (Type LV). The washing test was made in a Launder-Ometer using a temperature of 49° C. and 100 cubic centimeters of a 0.5 per cent solution of neutral soap. The samples were washed for 30 minutes; rinsed in warm water; squeezed; and dried in a current of air at room temperature, as recommended by the American Association of Textile Chemists and Colorists.⁵

COLOR ANALYSIS

The loss of color due to washing or exposure to light may be expressed numerically in terms of the percentage difference in reflectance of the original and faded fabrics at any wave length. The amount of fading was determined from the relative drop of the extinction coefficient at the maximum of the absorption band. Light fading often involves a change in hue as well as a loss in intensity and produces a darkening of the color. The darkening was determined from the relative increase in extinction of the flat portion of the absorption curve (usually between 610-630 $m\mu$).

DISCUSSION OF RESULTS

The data obtained from this study are indicated in tabular form in tables 1 and 2 and examples are given of individual dyes in figures 2 and 3. In order to permit better observation and comparison, a portion of these data has been arranged in graphic form in figures 4, 5, 6, and 7. The data in the tables were obtained from spectrophotometric observations on the original dye solution, the exhausted dye solution, the dyed fabric, the washed fabric, and the light-faded fabric. These five sets of observations are represented by curves of typical dyes in figures 2 and 3. From a study of these data and an examination of the dyed and treated samples (figure 8) it has been possible to draw certain conclusions.

Absorption spectra.—In the alpha-naphthylamine series the position of the maximum absorption band (figure 1) shifts toward the red as the position of the sulfonic acid groups goes from the 2 to the 8 position. The least absorption of red occurs in the para-substituted dyes. Less absorption of red is evident with the beta-naphthylamine dyes than with those of the alpha-naphthylamine series.

⁴Kolthoff, I. M. and Conmar Robinson. 1926. *Rec. Trav. Chim.* 45: 169; Calcott, W. S. and F. L. English. 1923. *Ind. and Eng. Chem.* 15: 1042.

⁵American Association of Textile Chemists and Colorists. 1933. 1932 Yearbook. Howes Publishing Co., New York, N. Y.

TABLE 1.—Absorption spectra and exhaustive properties of the dye solutions

No.	Dye	E=log I ₀ /I for 2.7 cg. per liter C:T=1 cm.	X=position of band in spectra	Ex=per cent of dye absorb- ed by fabric
1.....	O-a2	1.75	460	89.1
2.....	M-a2	0.92	450	75.0
3.....	P-a2	0.88	500	82.8
4.....	O-a3	1.10	465	90.8
5.....	M-a3	0.70	460	96.1
6.....	P-a3	0.84	480	95.4
7.....	O-a4	0.80	470	81.9
8.....	M-a4	0.80	470	89.3
9.....	P-a4	0.76	480	82.3
10.....	O-a5	1.01	480	79.9
11.....	M-a5	0.66	480	88.2
12.....	P-a5	0.74	490	91.5
13.....	O-a6	1.76	480	82.7
14.....	M-a6	3.68	500	97.8
15.....	P-a6	1.58	500	84.3
16.....	O-a7	1.52	510	78.0
17.....	M-a7	1.80	500	85.6
18.....	P-a7	2.10	500	86.1
19.....	O-a8	1.42	510	83.1
20.....	M-a8	2.00	520	94.1
21.....	P-a8	2.92	520	96.3
22.....	O-β	0.91	480	76.0
23.....	M-β	1.18	460	92.5
24.....	P-β	1.25	470	93.1
25.....	O-β5	0.78	460	94.1
26.....	M-β5	0.70	440	70.8
27.....	P-β5	0.54	460	91.6
28.....	O-β6	0.76	465	91.5
29.....	M-β6	2.80	460	92.6
30.....	P-β6	0.84	460	87.4
31.....	O-β7	0.97	460	95.0
32.....	M-β7	0.66	460	70.0
33.....	P-β7	0.82	460	90.3

O, M, and P indicate ortho-, meta-, and para-sulfanilic acids, respectively. α and β indicate position of NH₂; and 2, 3, 4, etc., indicate position of sulfonic acid group in the naphthalene nucleus.

E=log I₀/I (2.7 cg. per liter; 1-cm. cell).

X=Position of band in spectra.

Ex=per cent of dye absorbed by fabric.

Exhaustive properties.—The lowest degree of exhaustion is shown by the dyes of the ortho-sulfanilic acid series. The ortho-substituted dyes are most consistent, with very little difference in the 1-3, 1-4, 1-5, 1-7, 1-8, 2-6, and 2-7 dyes. The greatest degree of exhaustion is evident in the meta-sulfanilic-1-naphthylamine-7-sulfonic acid; whereas the meta-sulfanilic-2-naphthylamine-5-sulfonic acid and ortho-sulfanilic-beta-naphthylamine are the poorest in exhaustive properties. In the beta-naphthylamine series less difference is shown among the dyes of para-sulfanilic acid than those of ortho- and meta-sulfanilic acid.

Washing fastness properties.—In general the fastness of these three series of dyestuffs to washing (figure 4) increases as the sulfonic acid group moves from the 2 to the 8 position. The para-substituted dyes are the poorest. Those of the alpha-naphthylamine series are better than those of the beta-naphthylamine series.

TABLE 2.—Washing and light fastness properties

	w	W=100-w	f	F=100-f	δ	L= δ +F	U=W+2L
O-a2	20.9	79.1	74.6	25.4	5	30.4	140.4
M-a2	3.3	96.7	90.2	9.8	15	24.8	146.4
P-a2	7.7	92.3	79.5	20.5	14	34.5	171.3
O-a3	35.0	65.0	74.0	26.0	13	39.0	143.0
M-a3	12.5	87.5	49.0	51.0	14	65.0	217.5
P-a3	6.7	93.3	66.7	33.3	12	45.3	183.6
O-a4	4.7	95.3	74.7	25.3	12	37.3	170.0
M-a4	1.9	98.1	63.2	36.8	14	50.8	199.7
P-a4	15.6	84.4	68.2	31.8	12	43.8	172.1
O-a5	20.9	79.1	70.0	30.0	15	45.0	169.1
M-a5	28.8	71.2	58.8	41.2	7	48.2	167.6
P-a5	5.9	94.0	63.7	36.3	12	48.3	190.6
O-a6	37.1	62.9	65.5	34.5	8	42.5	147.9
M-a6	36.1	63.9	78.8	21.2	12	33.2	130.3
P-a6	52.6	47.4	73.8	26.2	13	39.2	123.8
O-a7	29.5	70.5	65.0	35.0	10	45.0	161.0
M-a7	20.6	79.4	90.5	9.5	15	24.5	129.0
P-a7	41.2	58.8	81.2	18.8	20	38.8	136.6
O-a8	39.3	60.7	61.5	38.5	9	47.5	156.0
M-a8	50.0	50.0	70.0	30.0	10	40.0	130.0
P-a8	40.5	59.5	75.5	24.5	4	28.5	117.0
O- β	18.7	81.3	65.5	34.5	10	44.5	170.3
M- β	47.0	53.0	41.0	59.0	10	69.0	191.0
P- β	62.0	38.0	46.2	53.8	11	64.8	164.6
O- β 5	11.0	89.0	82.0	18.0	6	24.0	137.0
M- β 5	10.0	90.0	68.7	31.3	11	42.3	174.6
P- β 5	52.0	48.0	66.2	33.8	8	41.8	131.6
O- β 6	10.2	89.8	78.5	21.5	8	29.5	148.8
M- β 6	7.2	92.8	62.5	37.5	6	43.5	177.7
P- β 6	17.0	83.0	70.0	30.0	12	42.0	167.0
O- β 7	24.0	76.0	82.0	18.0	9	27.0	130.0
M- β 7	23.4	76.6	60.0	40.0	11	51.0	173.6
P- β 7	28.0	72.0	72.0	28.0	12	40.0	112.0

w=per cent of dye retained by fabric after washing.

W=per cent of dye removed from fabric by washing=100-w.

f=per cent of dye retained by fabric after light exposure.

F=per cent of dye removed from fabric after light exposure=100-f.

δ =darkening.

L= δ +F.

U=Utility factor=W+2L.

Darkening.—There is a great similarity in the amount of darkening shown by these dyes. The least darkening occurs in the ortho-sulfanilic acid series.

Light fading.—The effect of light on the intensity of these dyes is least with the alpha-naphthylamine-2-sulfonic acid dyes. In the meta-sulfanilic acid series light fastness increases in the group from alpha-naphthylamine-3-sulfonic acid to alpha-naphthylamine-7-sulfonic acid. With the ortho series the alpha-naphthylamine 6-, 7-, or 8-sulfonic acid dyes are the best. A very high degree of fading is evident in the beta-naphthylamine series; the ortho-substituted dyes are the most fast to light.

When the amount of darkening and of light fading is treated as one factor, a decrease in fastness from the 1-2 to the 1-8 dyes of the ortho series is observed. The para series decreases in fastness to the 1-5 dye, after which there is an increase in fastness. With the exception of metanilic-2-naphthylamine-7-sulfonic acid there is an increase in fastness as the position of the sulfonic acid group moves from the 5 to the 7 position.

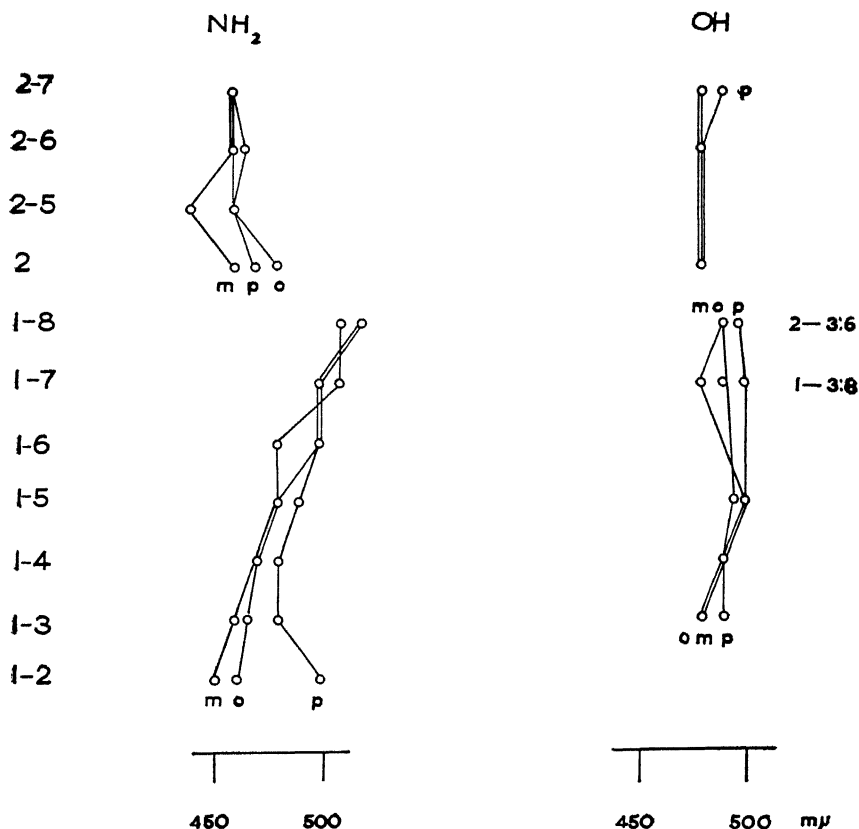


Fig. 1.—Shift of position of principal band (in $m\mu$) with a change in position of substituents of sulfonated phenylazonaphthols and naphthylamines

Utility factor.—The combined effect of washing and light fastness properties has been used as an arbitrary index of the value of the dyestuff when applied to wool fabrics. The fastness of the ortho series decreases as the sulfonic acid group goes from the 2 to the 8 position, with the exception of the dye where the sulfonic acid group occupies the 6 position. This series of dyes is more nearly uniform in fastness properties than those of the meta- and para-sulfanilic acid series. With the beta-naphthylamine dyes of the ortho series the fastness increases as the sulfonic acid group goes from the 5 to the 7 position. In both the meta- and para-substituted sulfanilic acids a shift of the sulfonic acid group increases the fastness properties with the exception of the para-sulfanilic acid 1-naphthylamine-5-sulfonic acid and 2-naphthylamine-6-sulfonic acid dyes. The meta-sulfanilic acid 1-naphthylamine-3-sulfonic acid and the meta-sulfanilic acid coupled to beta-naphthylamine-sulfonic acids are extremely fugitive as measured by the utility factor.

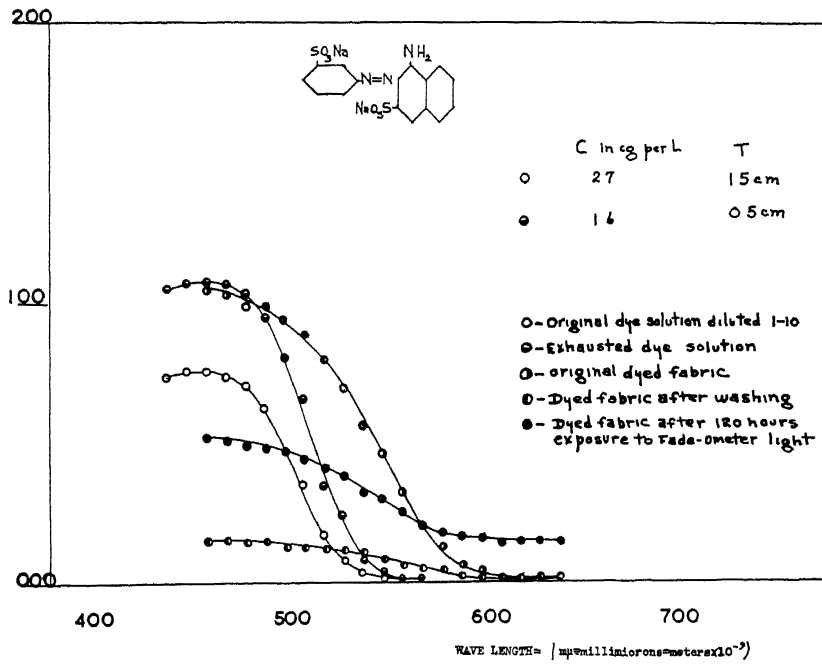


Fig. 2.—Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

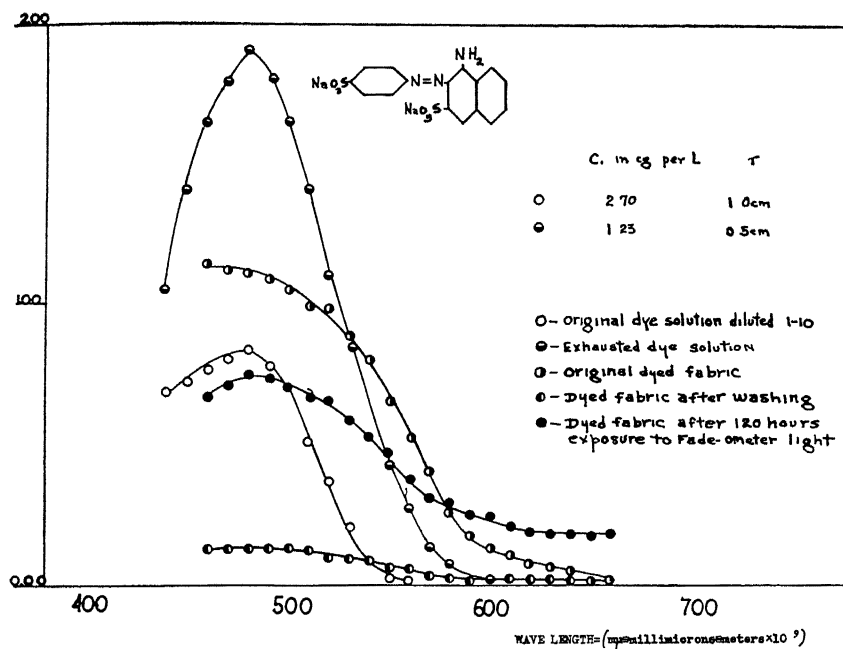


Fig. 2.—(Continued) Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

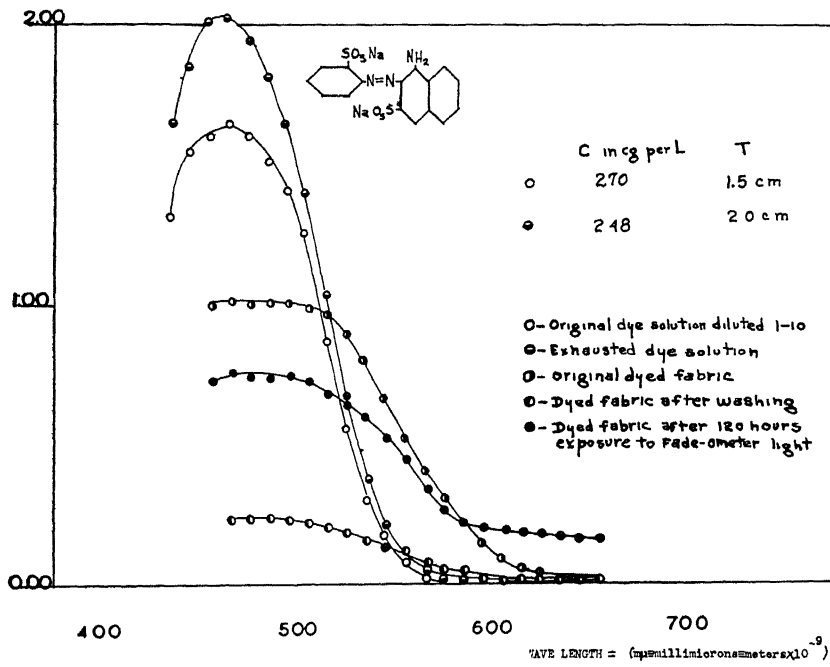


Fig. 2.—(Continued) Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

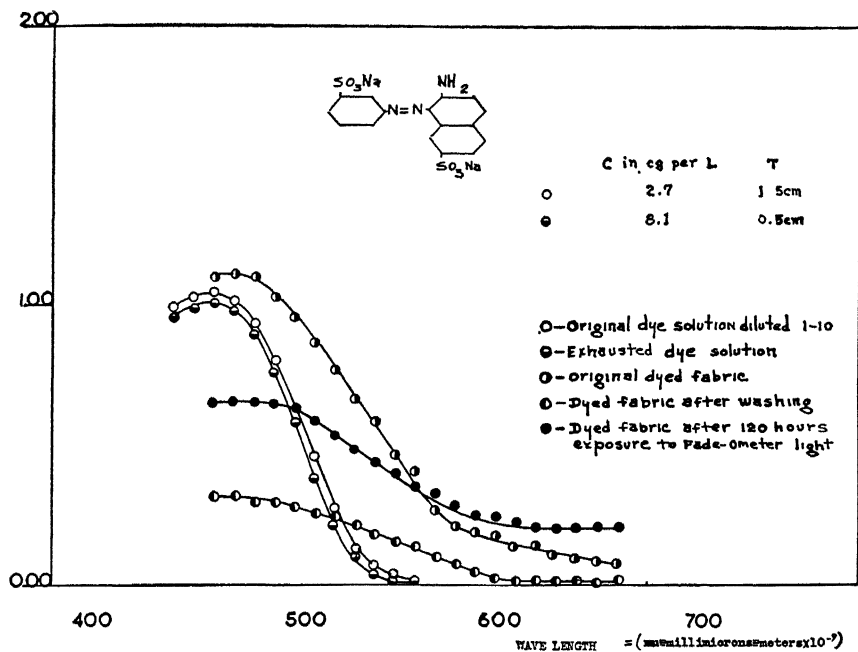


Fig. 3.—Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

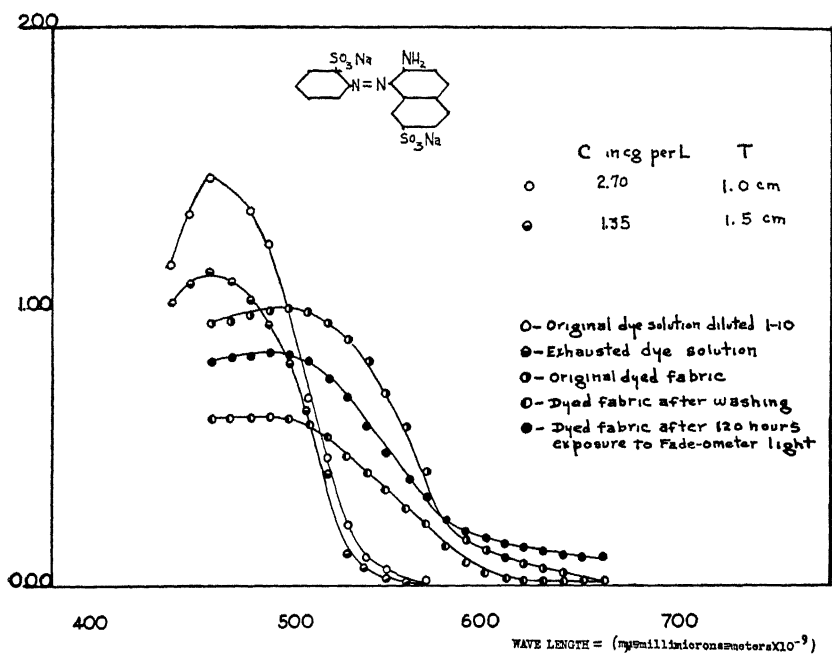


Fig. 3.—(Continued) Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

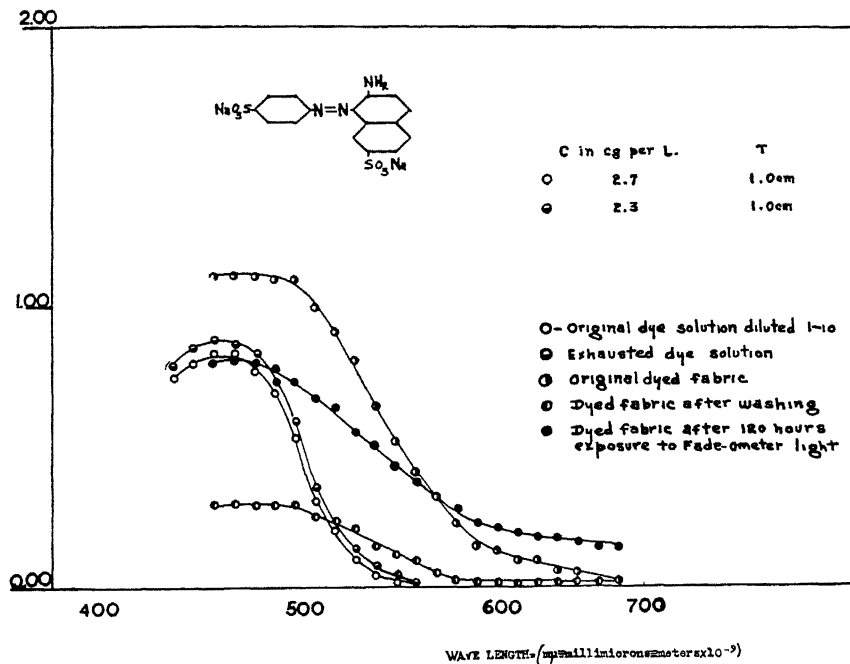


Fig. 3.—(Continued) Spectrophotometric measure of washing and fading properties of the indicated dyestuffs

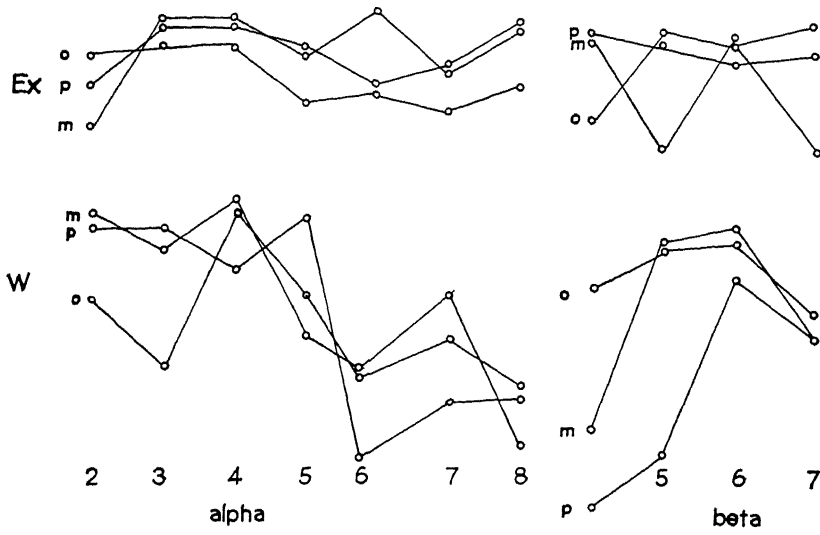


Fig. 4.—Graphical indication of per cent of dye absorbed by fiber (E x) and per cent of dye removed by washing (W)

o, m, and p indicate position of SO_3H group in phenyl rings; α , β , 1, 2, 3, etc., indicate position of NH_2 and SO_3H groups in naphthyl rings.

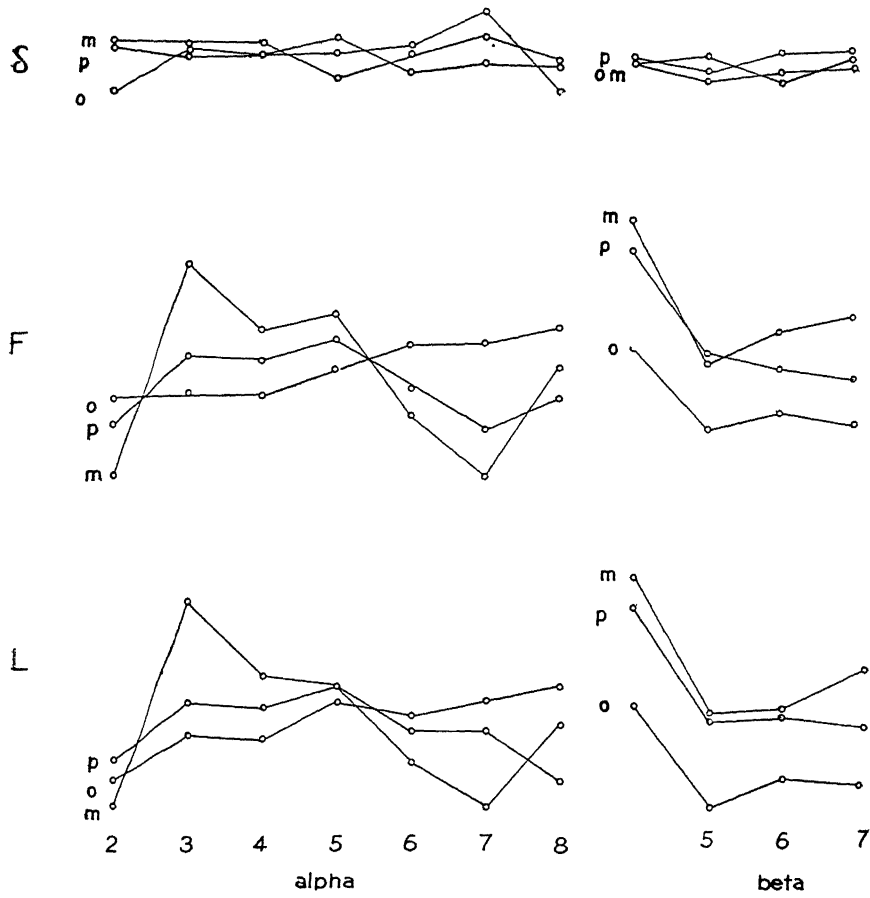


Fig. 5.—Darkening (δ), fading (F), and light fastness factor (L)
 (See figure 4 and table 2 for explanation of ordinates and factors.)

UTILITY FACTOR

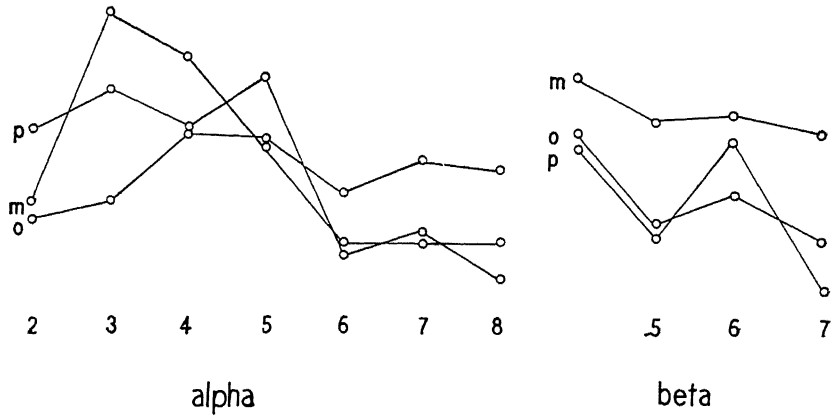


Fig. 6.—Utility factor (U) for the dye series

(See figure 4 and table 2 for explanation of ordinates and factors.)

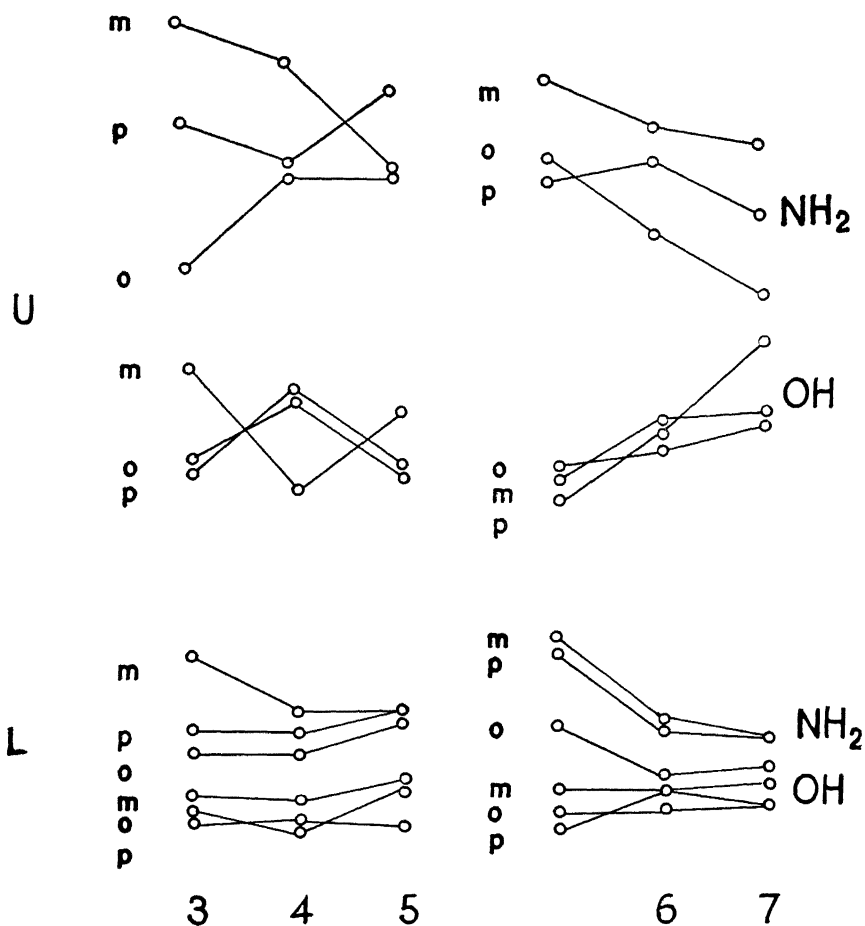


Fig. 7.—Comparison of utility (U) and light (L) factors of similar naphthol and naphthylamine dyes

(See figure 4 and table 2 for explanation of ordinates and factors.)

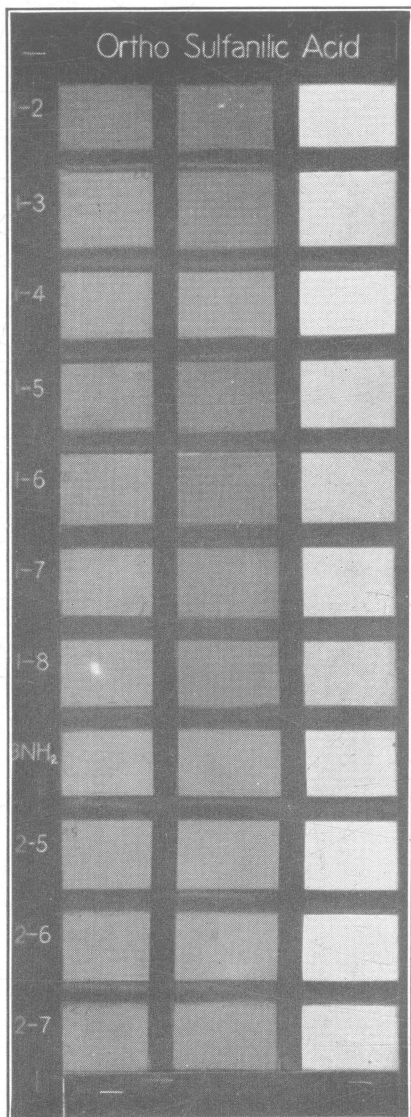


Fig. 8.—Sample card of the ortho (o) sulfonated phenylazonaphthylamines. (The first number indicates the position of NH₂ groups, the second number the position of SO₃H groups.)

The left-hand column represents the faded sample, the center the original dyed fabric, and the right-hand column the washed sample. (See figures 2 and 3 and table 2 for numerical data on these samples.)

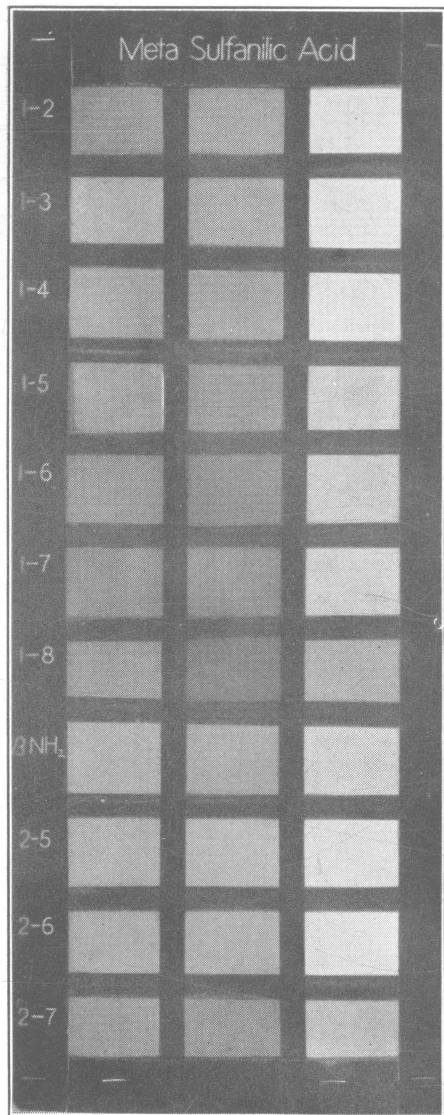


Fig. 8.—(Continued) Sample card of the meta (m) sulfonated phenylazonaphthylamines. (The first number indicates the position of NH₂ groups, the second number the position of SO₃H groups.)

The left-hand column represents the faded sample, the center the original dyed fabric, and the right-hand column the washed sample. (See figures 2 and 3 and table 2 for numerical data on these samples.)

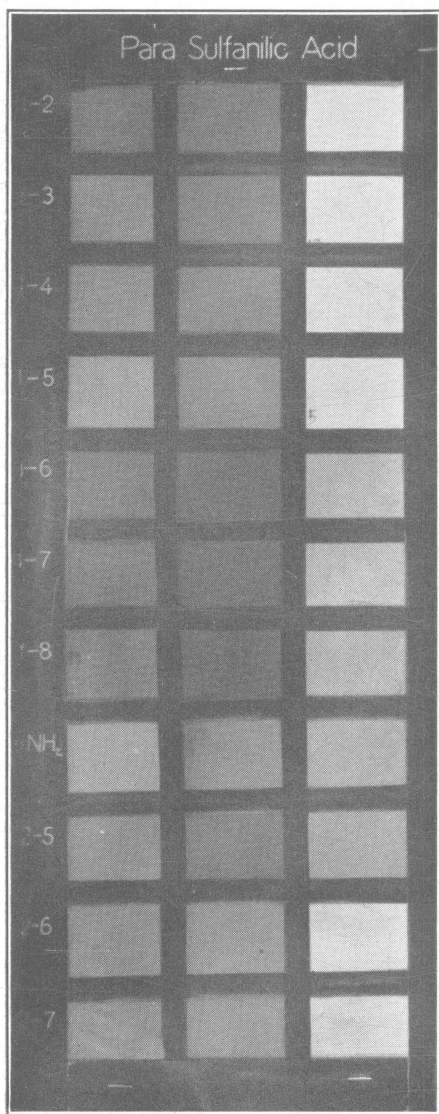


Fig. 8.—(Continued) Sample card of the para (p) sulfonated phenylazonaphthylamines. (The first number indicates the position of NH₂ groups, the second number the position of SO₃H groups.)

The left-hand column represents the faded sample, the center the original dyed fabric, and the right-hand column the washed sample. (See figures 2 and 3 and table 2 for numerical data on these samples.)

SUMMARY

The effect of the position of the sulfonic acid group in the benzene and naphthalene nucleus in a series of 36 monoazo dyes has been studied. Conclusions have been drawn concerning the effect of these changes in position on the color, exhaustion, and washing and light fastness. It has been possible also to show the comparative effect of the presence of the amino and the hydroxyl group in the naphthalene ring upon the properties listed.