

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, WEST VIRGINIA UNIVERSITY]

LIESEGANG RINGS. II. RHYTHMIC BANDS OF DYES ON FILTER PAPER AND CLOTH BY EVAPORATION. THE REFRACTIVITY, SURFACE TENSION, CONDUCTIVITY, VISCOSITY, AND BROWNIAN MOVEMENT OF DYE SOLUTIONS

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Introduction

The attention of the author was drawn to this phenomenon by lecture experiments performed in a course on colloids. It is a well-known fact that filter paper immersed in water acquires a negative charge if its dielectric constant is lower than that of the water. Hence when a strip of filter paper is put in a dye solution (almost all dyes are negative), the water is drawn up by the capillarity, followed by the colored solute. With a positive colloid there is a precipitation a short distance above the solution surface. After making a series of these demonstrations the beakers with solutions and papers were allowed to stand. On "cleaning up" after the lapse of about 2 weeks it was noticed that the dye had given the filter paper a banded appearance. It was also at that time observed that the white porous clay cup which had been used in a demonstration of electro-endosmosis had also a banded appearance due to evaporation of the dye.

Experimental

These accidental results seemed to show the possibility of developing rhythmic bands by evaporation. The first experiments were carried out at room temperatures which varied greatly. The results were some irregular bands. It was then decided to use constant temperature and slow evaporation. The air oven was regulated to about 37°. This not only gave constant rate of evaporation but insured the absence of light.¹

Preliminary experiments with 7 different makes of filter paper and varying concentrations of dyes resulted in the choice of 0.04% and 0.005% solutions and the use of 3 different makes of filter paper. Paper designated B was ordinary analytical 12.5cm. paper bought from Welch Chem. Co. of Chicago. Paper D was an English make put up by J. Green, grade 588 J. G. Folded, size 18.5 cm. Paper H was "ashless," C. Schleicher and Schull, no. 589, 15 cm.

The next point to be decided was how the evaporation should be carried out. The experiments were finally performed as follows; 150 cc. of the dye solution was put in a 250cc. Pyrex beaker. Strips of filter paper were cut about 2.5 cm. wide and as long as possible. Two strips across the sheet were not completely severed and were folded so as to form one strip of

¹ For influence of light on some rhythmic bands see Davies, *THIS JOURNAL*, **44**, 2698 (1922).

double length. It was found that this fold did not greatly disturb the formation of bands. The paper was then creased over the edge of the beaker so that one end touched the bottom of the inside while the other hung over the outside. A sample of each of the 3 different makes of filter paper was put in each beaker. This was done for 62 dyes with both concentrated (0.04%) and dilute (0.005%) solutions. Ordinary distilled water was used.²

The measurements on refraction of light recorded in Table I were made at 25° with a Zeiss total immersion refractometer. It was found necessary to use the auxiliary prism because of the depth of some of the colors. The instrument was checked each day with the distilled water used in the solutions. Surface tension was measured by the method of DuNouy³ at 22°. Conductivity ($1/\omega$) was determined with a Wheatstone bridge. Values are accurate to about 2%. Viscosity (η) experiments were carried out at 25° with an Ostwald viscosity tube.

Brownian movement (B. M.) was observed with a microscope fitted with Abbe condenser and opaque disc. A projection lantern was used for light. In the column under B. M., 1 means "slight," 2 is "fair," 3 is "good," 4 is "very good." The last 3 columns show positive (+) or negative (-) re-

² Since this paper was written, Mr. C. D. L. Ropp, working with the author, after experimentation with various methods, has prepared some remarkable bands on filter paper and on cotton cloth. It was found that some cotton cloths will give fairly good bands when treated exactly as were the filter papers. However, the bands were on the whole a disappointment. Some of the cloths acted as siphons giving drops from the outer ends.

Pads of filter paper were put under the beakers to catch the drops and some interesting rhythmic bands were thus accidentally obtained. An attempt to substitute dropping funnels for the "wicks" proved unsatisfactory. Hence it was decided to use the "wicks" and let the drops fall on filter papers and on cotton cloth. With this arrangement a number of beautiful sets of bands were obtained (Fig. 1).

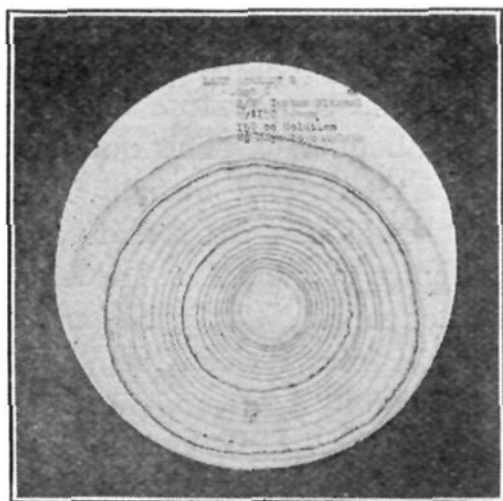


Fig. 1.

in the rate of flow as evaporation progresses and this is automatically secured with the wick.

It has been found that when the experiment is carried on until a good series of bands is obtained and then the temperature is lowered, the bands are wiped out. Hence uniform temperature is one of the essential factors.

³ DuNouy, *J. Gen. Physiol.*, 1, 521 (1919).

sults with band formation. B is "Welch," D is "J. Green" and H is "S and S. ashless" filter paper; c means concentrated (0.04%) and d is dilute (0.005%). All dyes showed good Tyndall cones.

TABLE I

Name	η_D	γ	$1/\omega$ $\times 10^4$	η	B.M.	B		D		H	
						c	d	c	d	c	d
Erie Red 4 B	1.33259	70.6	2.69	1.0090	4	-	-	-	-	-	-
Brilliant Scarlet 3 R	63	70.6	2.84	1.0048	3	-	+	-	+	-	+
Duroil Black B	61	70.0	3.55	1.0024	3	-	-	+	-	-	-
Erie Pink 2 B	69	71.2	4.02	1.0068	3	+	+	-	-	-	+
Alizarol Black 3 G	66	75.4	4.67	1.0000	4	+	+	+	+	-	+
Erie Black N R Extra	59	74.6	4.10	1.0048	3	+	-	+	+	+	+
Methylene Blue BB	68	74.5	3.58	1.0042	3	-	-	-	+	-	-
Fast Wool Blue B	70	73.7	3.55	1.0090	4	+	+	+	+	+	-
Erie Orange 2 R	72	74.4	2.92	1.0024	3	-	-	-	-	-	-
Fast Crimson 6 B	63	74.6	4.74	1.0023	3	+	+	+	+	+	+
Fast Red S Conc.	63	75.1	1.29	1.0045	3	+	-	+	-	-	-
Buffalo Chrome Black 2 BN	63	72.2	5.2	1.0202	3	-	-	-	-	-	-
Sulfur Brown CG	63	74.8	3.87	1.0024	3	-	-	-	-	-	-
Lake Scarlet R	67	74.5	3.14	1.0068	3	+	+	-	+	+	+
Sulfur Black F paste	66	75.0	1.59	1.0071	3	+	-	-	-	-	-
Fast Crimson R	57	76.6	5.96	1.0024	3	+	-	+	-	-	+
Erie Fast Red FD	66	74.5	3.51	1.0048	3	-	-	-	-	-	-
Buffalo Black NBR	70	72.6	3.80	1.0048	3	-	-	-	-	-	-
Erie Black GXOO	74	73.8	7.10	1.0090	4	+	+	+	+	-	-
Niagara Blue 2 B	59	75.5	7.78	1.0045	3	-	-	-	-	-	-
Diazine Black H Extra	70	74.4	5.55	1.0024	3	-	-	-	-	-	-
Cloth Red B	63	68.2	2.21	1.0048	3	-	+	-	-	-	+
Erie Brown C	55	68.5	3.81	1.0071	3	-	-	-	-	-	-
Erie Brown 3 RB	55	74.5	4.30	1.0071	3	-	-	-	-	-	-
Alizarol Yellow 3 G	59	74.4	4.11	0.9976	3	+	+	-	+	+	-
Azo Yellow A 5 W	53	74.4	2.99	1.0000	4	+	-	-	-	-	-
Alizarine Sapphire	66	75.0	3.92	1.0112	2	+	+	+	+	-	-
Wool Orange 2 G Cryst.	59	76.2	1.95	1.0090	3	+	+	+	+	-	+
Croceine Scarlet MOO	55	74.4	2.42	1.0045	4	+	+	+	+	-	-
Wool Yellow Extra Conc.	70	75.2	3.97	1.0000	3	+	+	+	+	-	-
Super Chrome Black 6 BP	63	70.4	3.89	1.0112	4	-	-	-	-	-	-
Azo Rubine Extra	63	75.1	4.95	1.0095	4	+	+	+	+	-	-
Wool Orange A Conc.	78	75.0	1.05	1.0000	3	+	+	+	+	-	+
Erie Yellow F	55	74.3	3.64	1.0095	3	-	-	-	-	-	-
Erie Brown GB	59	69.2	4.02	1.0090	3	-	-	+	-	-	-
Erie Green MT	59	71.3	4.58		3	+	-	-	-	-	-
Niagara Blue G Conc.	55	71.5	3.30	1.0090	2	-	-	+	-	-	-
Alphazurine B	25	73.0	4.87	1.0000	4	+	-	+	+	+	-
Erie Fast Yellow WB	63	75.2	0.495	1.0068	3	+	+	+	+	+	-
Fast Wool Cyanone R	59	63.8	3.28	0.9976	3	+	-	-	-	-	-
Wool Violet 4 BN	66	65.5	2.18	1.0068	3	+	+	+	+	-	-
Chrome Blue GN Conc.	55	75.4	1.95	1.0000	4	-	-	-	-	-	-
Fast Acid Green S	51	61.7	1.68	1.0045	3	+	+	+	+	+	-
Alizarol Orange R	43	74.5	4.58	1.0090	4	-	-	-	-	-	-
Buffalo Black 10 B	57	74.2	2.30	1.0023	2	+	-	+	+	+	+

TABLE I (Continued)

Name	η_D	γ	$1/\omega$ $\times 10^4$	η	B.M.	B		D		H	
						c	d	c	d	c	d
Alizarol Brown 2 R	43	76.3	2.10	1.0135	4	-	-	+	+	-	+
Erie Violet 3 R	36	75.2	4.27	1.0021	3	+	-	-	-	-	-
Primuline NAC	51	74.0	2.54	1.0119	3	+	-	+	-	+	-
Alizarine NAC 20% paste	43	75.1	0.483	1.0048	4	-	-	-	-	-	-
Niagrazine 128 B	57	74.9	0.726	0.9955	3	-	+	+	+	+	+
Safranine A	57	74.7	4.95	0.9977	3	+	-	-	-	-	-
Chrome Green CB	62	74.7	2.15	1.0112	1	-	-	-	-	-	-
Alizarol Brown RB	61	76.0	4.16	1.0083	3	+	-	+	-	-	-
Victoria Green WB Cryst.	43	72.8	4.29	1.0180	3	-	-	-	-	-	-
Niagara Sky Blue	59	75.6	6.82	1.0250	3	-	-	-	-	-	-
Methyl Violet 2 B Conc.	55	65.7	2.85	1.0119	3	-	+	-	-	-	-
Super Chrome Blue Extra	59	71.5	2.76	1.0000	3	+	+	+	+	-	-
Erie Orange Y	59	61.2	4.17	1.0238	3	-	-	-	-	-	-
Chrysoidine Y Extra	63	70.2	3.31	1.0071	4	+	+	+	+	-	-
Bismark Brown 53	36	73.8	5.08	1.0157	1	-	-	-	-	-	-
Acid Green L Extra	51	64.0	6.91	1.0048	3	+	+	+	+	-	-
Azo Wool Violet 4 B	66	71.4	4.88	1.0135	3	+	+	-	+	-	-

Discussion

It is obvious that when the bands begin to form we have considerable dye at the band. In nearly all cases the dye was almost entirely removed from the beaker at the end of the evaporation. Thus the dye contained in the 150 cc. of solution is at the end mostly collected in the bands. At the time of band formation we have, therefore, much greater viscosity than in the original solution. We have in fact what appears to be a film of oriented molecules. The phenomenon is thus very similar to the rhythmic crystallization⁴ observed by E. Küster when trisodium orthophosphate, cupric sulfate, ferrous sulfate, potassium ferrocyanide and ammonium sulfate separated from gelatin solutions by drying at room temperature. It is also similar to rhythmic agate-like structures observed by A. v. Fischer⁵ when very thin layers of molten sulfur solidify. Fischer explained the formation of the ridges of sulfur as follows: the sulfur on solidifying contracts and then draws up the liquid sulfur about it by capillarity, thus forming a ridge of sulfur deeper than the average depth while adjacent to the ridge is a depression where solidification has overtaken the sulfur before that lost to the ridge can be gained from the surrounding belt.

This is another case of Liesegang bands which differs enough from the usual type to further emphasize the folly of attempting to cover all cases of formation of rhythmic bands by any one general theory. Each type needs a different explanation. In this as well as in the cases discussed in the first paper of the series we may have films of oriented molecules⁶

⁴ Küster, *Kolloid-Z.*, **14**, 307-19 (1914).

⁵ Fischer, *ibid.*, **16**, 109 (1915).

⁶ Harkins, Davies and Clark, *THIS JOURNAL*, **39**, 541 (1917).

playing an important role. There are no striking relations between the formation of bands and the physical properties of the dye solutions (Table I). It is probable that by using different papers from ours and different concentrations it would be possible to form bands in still other cases than those indicated.

Summary

Rhythmic bands of dyes have been made on filter paper, cotton cloth, and unglazed porcelain by regulated evaporation. Several varieties of filter paper were used with both 0.04% and 0.005% solutions of each of 62 dyes. A table gives measurements of the following physical properties of the 0.04% solutions: refractive index for light, surface tension, conductivity, viscosity, Brownian movement, Tyndall cone, and band formation. Uniform temperature and a gradual decrease in the rate of flow are the important factors in the formation of bands. It is probable that just before the band forms we have a film of oriented molecules.

In conclusion I wish to thank the National Aniline and Chemical Company of New York for samples of the dyes used in these experiments.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

THE USE OF MALIC, MALEIC AND FUMARIC ACIDS IN VOLUMETRIC ANALYSIS

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Malic, maleic and fumaric acids¹ are now available in large quantities and at comparatively low prices, and an investigation was, therefore, made to determine whether they might replace the more costly succinic acid² for standardizing basic solutions. A. Astruc³ has shown that when phenolphthalein is used as the indicator many of the dicarboxylic acids, including the acids mentioned above, behave as though they have 2 replaceable hydrogen atoms, whereas with methyl orange the end-point is uncertain. No methods of purification nor data of titrations were given for these acids.

In the experiments below, the sodium hydroxide solutions free from carbon dioxide were prepared in the usual manner by the addition of barium chloride and then standardized against hydrochloric acid, the normality of which was determined by precipitation of silver chloride; the normality of the sodium hydroxide was also determined by titration with pure succinic acid.

¹ U. S. pat. 1,318,631-2, -3.

² Phelps and Weed, *Am. J. Sci.*, **26**, 138 (1908); *Z. anorg. Chem.*, **59**, 114 (1908).

³ Astruc, *Z. anal. Chem.*, **40**, 418 (1901); *Compt. rend.*, **130**, 253 (1900).