Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. III. Spectrophotometric Specifications of Colors of Cobalt Soaps

By Hirotaro KAMBE

(Received February 28, 1961)

Cobalt soaps of higher saturated fatty acids have been described generally as pink crystals. Recently Herron and Pink[1] described rose-pink cobalt laurate dihydrate and purple anhydrate, which was obtained by the dehydration of pink soap in boiling organic solvents.

In a previous paper of this series[2], three species of cobalt soap of different colors were obtained by metathesis in aqueous ethanol under some conditions. From results of analyses, it was ascertained that blue soap is anhydrate, red soap is dihydrate, and pink soap has a degree of hydration near to that of dihydrate[3].

In the present paper, the colors of these soaps will be specified by spectrophotometry. Reflection spectra and a chromaticity diagram of these colors will be shown. Relations of these colors with each other will also be discussed.

Experimental

Materials.—The same samples of cobalt stearates were used as for the previous papers[2,3].

Reflection Spectra.—Reflection spectra of soaps were measured with a Shimadzu QR-50 quartz spectrophotometer, to which an integrating sphere was attached. Reflection coefficients expressed in percentages were plotted against wavelengths between 350 and 700 mμ to get reflection curves.

Graphical Representation of Chromaticity.—Reflection curves were analyzed by a method proposed by the International Commission on Illumination (I. C. I.)[4]. Tristimulus values, X, Y and Z, were determined from reflection curves by graphical integrations with the thirty-selected-ordinate method[4].

$$X=0.03268\sum R_x(\lambda_n) \qquad Y=0.03333\sum R_y(\lambda_n)$$

$$Z=0.03938\sum R_z(\lambda_n) \tag{1}$$

where $R(\lambda_n)$'s are reflection coefficients of the sample at selected wavelengths (Table I).

Trichromatic coefficients, x, y and z were calculated by the formulas

$$x=\frac{X}{X+Y+Z} \qquad y=\frac{Y}{X+Y+Z}$$

TABLE I. THIRTY SELECTED ORDINATES FOR ILLUMINANT C

Ordinate number	(X) Wavelength mμ	(Y) Wavelength mμ	(Z) Wavelength mμ
1	424.4	465.9	414.1
2	435.5	489.4	422.2
3	443.9	500.4	426.3
4	452.1	508.7	429.4
5	461.2	515.1	432.0
6	474.0	520.6	434.3
7	531.0	525.4	436.5
8	544.3	529.8	438.6
9	552.4	533.9	440.6
10	558.7	537.7	442.5
11	564.1	541.4	444.4
12	568.9	544.9	446.3
13	573.2	548.4	448.2
14	577.3	551.8	450.1
15	581.3	555.1	452.1
16	585.0	558.5	454.0
17	588.7	561.9	455.9
18	592.4	565.3	457.9
19	596.0	568.9	459.9
20	599.6	572.5	462.0
21	603.3	576.4	464.1
22	607.0	580.5	466.3
23	610.9	584.8	468.7
24	615.0	589.6	471.4
25	619.4	594.8	474.3
26	624.2	600.8	477.7
27	629.8	607.7	481.8
28	636.6	616.1	487.2
29	645.9	627.3	495.2
30	663.0	647.4	511.2

$$z=\frac{Z}{X+Y+Z} \tag{2}$$

They were plotted on an I. C. I. chromaticity diagram. Dominant wavelength λ_d, purity p_c, and brightness Y were determined for each sample.

Results and Discussion

The reflection spectra of several samples of each typical color are shown in Figs. 1—3. Their tristimulus values and trichromatic coefficients have been calculated in Table II and plotted on an I. C. I. chromaticity diagram in Fig. 4. Their dominant wavelengths, purities,

---

* Present address. Aeronautical Research Institute, The University of Tokyo, Meguro-ku, Tokyo.

1) R. C. Herron and R. C. Pink, *J. Chem. Soc.*, **1956**, 3948.

2) H. Kambe, This Bulletin, **34**, 1786 (1961).

3) H. Kambe, ibid., **34**, 1790 (1961).

4) A. C. Hardy, "Handbook of Colorimetry", Cambridge, Mass. (1936).

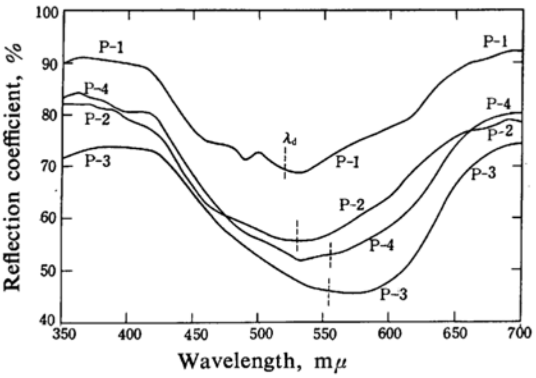

Fig. 1. Reflection curves of pink cobalt stearates.

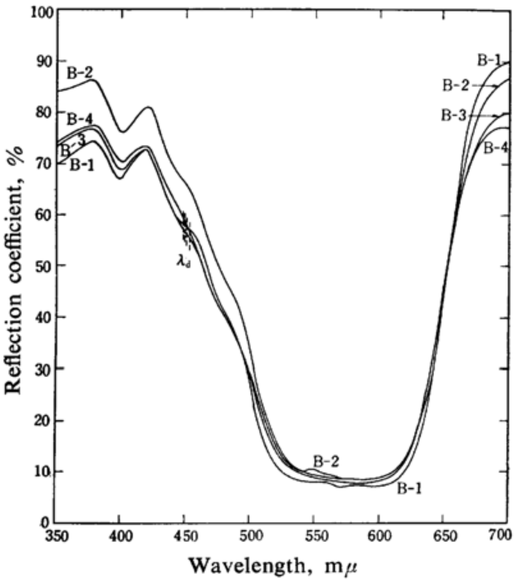

Fig. 2. Reflection curves of blue anhydrous cobalt stearates.

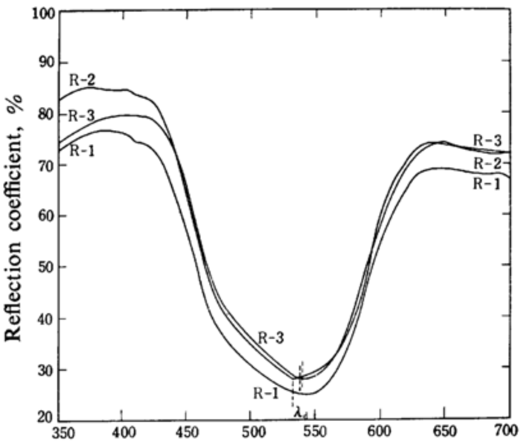

Fig. 3. Reflection curves of red cobalt stearate dihydrates.

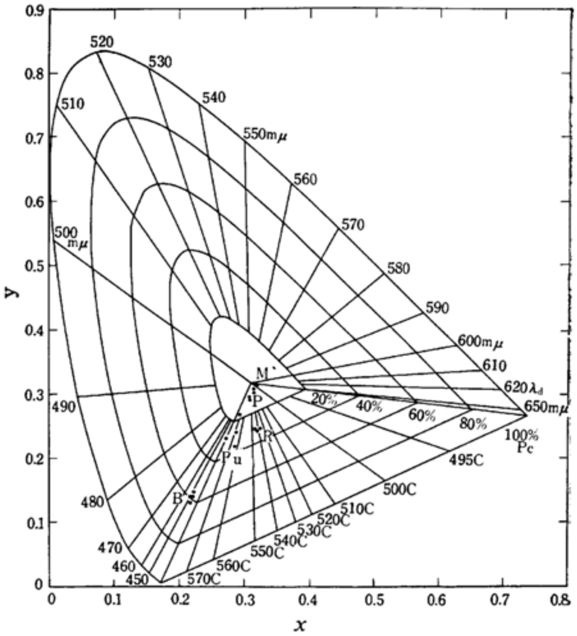

Fig. 4. I. C. I. chromaticity diagram.

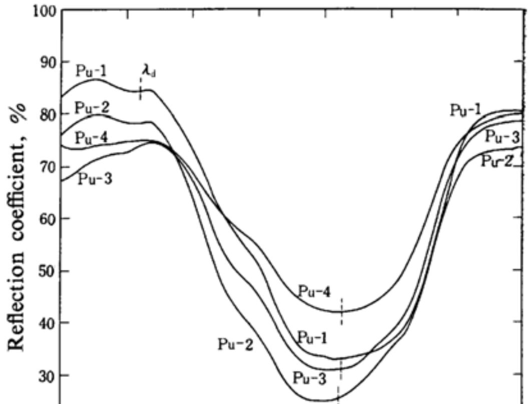

Fig. 5. Reflection curve of purple cobalt stearates.

and brightnesses are also tabulated in Table II.

The dominant wavelengths λ_d of each spectrum are shown with dotted lines. In color language, blue and red soaps must be called violet and magenta respectively.

Pink soaps (Fig. 1) show a broad absorption band with a maximum at 530~540 mμ. The dominant wavelength of pink soaps varies within a wide range, from pure pink at 520c mμ to bluish pink at 565c mμ, but it does not essentially differ from that of red soaps. Pink soaps have smaller purities and larger brightnesses than red soaps.

TABLE II. CHROMATICITY COEFFICIENTS OF COLORS OF SEVERAL TYPICAL COBALT STEARATES

System	Tristimulus values			Trichromatic coefficients			Dominant wave-length	Purity	Bright-ness
	X	Y	Z	x	y	z	λ_d, mμ	p_c, %	Y, %
(Pink soaps)									
P-1	76.24	73.81	91.78	0.315	0.305	0.380	520c*	5.5	73.81
P-2	63.38	59.74	77.52	0.316	0.298	0.386	530c	8.5	59.74
P-3	67.13	63.79	86.23	0.309	0.294	0.397	554c	9.0	63.79
P-4	59.65	55.86	77.89	0.308	0.289	0.403	555c	10.5	55.86
(Blue soaps)									
B-1	21.26	12.67	64.43	0.216	0.129	0.655	448	62.5	12.67
B-2	24.45	15.45	73.07	0.216	0.137	0.647	452	60.5	15.45
B-3	21.76	13.74	63.20	0.220	0.139	0.641	449	57.0	13.74
B-4	22.63	14.78	64.49	0.222	0.145	0.633	450	56.5	14.78
(Red soaps)									
R-1	48.84	36.22	62.96	0.330	0.245	0.425	533c	32.5	36.22
R-2	53.78	40.25	71.30	0.325	0.243	0.431	538c	32.5	40.25
R-3	53.34	40.25	71.21	0.324	0.244	0.432	540c	31.5	40.25

* 520c mμ means complementary to color of 520 mμ.

TABLE III. CHROMATICITY COEFFICIENTS OF SOME PURPLE COBALT STEARATES AND PINK COBALT STEARATES OBTAINED IN AQUEOUS METHANOL

System	Tristimulus values			Trichromatic coefficients			Dominant wave-length	Purity	Bright-ness
	X	Y	Z	x	y	z	λ_d, mμ	p_c, %	Y, %
(Purple soaps obtained from blue soaps)									
Pu-1	46.22	39.17	84.23	0.272	0.231	0.497	410	27.5	39.17
Pu-2	39.06	29.53	67.90	0.286	0.216	0.497	561c	36.0	29.53
(Purple soaps obtained from red and pink soaps)									
Pu-3	45.26	37.66	74.94	0.287	0.239	0.475	562c	27.0	37.66
Pu-4	52.34	47.41	78.73	0.293	0.266	0.441	564c	17.0	47.41
(Pink soaps obtained in aqueous methanol)									
M-1	83.21	81.61	95.46	0.320	0.314	0.367	493c	3.0	81.61
M-2	85.91	84.42	98.34	0.320	0.314	0.366	493c	3.0	84.42

Blue anhydrates (Fig. 2) show a large absorption band with a broad maximum at 580~590 mμ, and a shallow but sharp absorption band at 400 mμ. The blue color of this species originates from a large reflection at shorter wavelengths.

Red dihydrates (Fig. 3) show a deep but relatively sharp absorption band at 540~550 mμ. Sometimes the spectra of blue soaps have a small shoulder at a corresponding position, arising from the red soap also present.

When blue soap was taken out of the solution at a half-turned-red state, purple soap was obtained. Pink and red soaps also became purple when they were immersed in pure ethanol for a long time. These samples are shown in Figs. 4 and 5, and their trichromatic coefficients are tabulated in Table III.

Purple soaps have dominant wavelengths between those of pink and blue soaps. Purple soaps obtained from blue soap have relatively larger purities. In these samples the dominant wavelength seems to change abruptly from 564c mμ to 410 mμ, but it is clear from the chromaticity diagram (Fig. 4) that these dominant wavelengths are continuous. The main origin of purple color changes in this range, however, from an absorption band at 560 mμ to a reflection band at 400 mμ.

In this way, it is established that among cobalt soaps of different colors, red and pink soaps are the same in nature, although their colors differ in purity and brightness, and that blue soap continues to pink or red soap through purple soaps.

Cobalt stearate may be formed by metathesis in aqueous methanol instead of ethanol[2)], but the color of the soaps thus formed is pale pink. Their reflection curves are very flat, with a maximum at about 500 mμ, as shown in Fig. 6 and in Table III. It is characteristic for them that their purities are small and

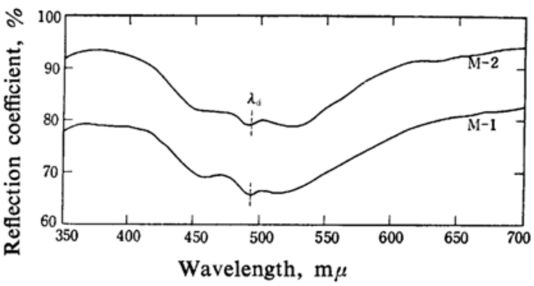

Fig. 6. Reflection curves of cobalt stearates obtained in aqueous methanol.

their brightnesses are large, and their maximum absorption occurs at a shorter wavelength.

Summary

The colors of three species of cobalt stearates were specified by I. C. I. chromaticity coefficients. Reflection spectra have been compared with each other, and it has been found that these colors are continuous in nature.

Pink soaps have dominant wavelengths in a wide range from 520c～555c mμ and show small purities and large brightnesses. Red soaps have essentially the same dominant wavelengths as that of pink soaps at 530c～540c mμ, but they show comparatively large purities and small brightnesses, because they are darker than pink soaps. They must be called magenta in color language.

Blue soaps must be called violet rigorously, for they show dominant wavelengths at about 450 mμ. They have larger purities and smaller brightnesses. Between blue and pink, many tones of color from violet to purple exist continuously. It is certain that these colors are related to each other.

The pale pink cobalt stearates obtained in aqueous methanol were specified in the same way.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi, for his advice throughout this work. He is also indebted to Messrs. Hiroshi Kayano and Teijiro Mizuno for their assistance in spectrophotometry.

Institute for Science and Technology
The University of Tokyo
Meguro-ku, Tokyo