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The effect of hydrogen ion concentration on the color of metallic chromates.

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UNIVERSITY OF LOUISVILLE

**THE EFFECT OF HYDROGEN ION CONCENTRATION
ON THE COLOR OF METALLIC CHROMATES.**

A Dissertation

Submitted to the Faculty

Of the Graduate School

**In Partial Fulfillment of the
Requirements for the Degree of
Master of Science**

Department of Chemistry

By

John E. Morris

1938

16 June 33 M.P.S.

Table of Contents.

| | |
|---------------------------|------------|
| Introduction | 1 |
| Experimental | 4 |
| Apparatus | 9 |
| Materials | 12 |
| Metallic Chromates | 15 |
| Copper Chromate | 18 |
| Silver Chromate | 33 |
| Magnesium Chromate | 45 |
| Calcium Chromate | 48 |
| Strontium Chromate | 51 |
| Barium Chromate | 54 |
| Zinc Chromate | 69 |
| Cadmium Chromate | 84 |
| Mercuric Chromate | 94 |
| Aluminum Chromate | 104 |
| Titanium Chromate | 107 |
| Stannous Chromate | 109 |
| Arsenic Chromate | 112 |
| Antimony Chromate | 116 |
| Bismuth Chromate | 118 |

| | |
|------------------------|------------|
| Iron Chromate | 124 |
| Cobalt Chromate | 127 |
| Nickel Chromate | 134 |
| Summary | 139 |
| Bibliography | 142 |

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INTRODUCTION

Introduction.

Several of the insoluble metallic chromates are used extensively as colored pigments in the paint industry. The most important of these is lead although others, as cadmium and barium, form insoluble or slightly soluble chromates which are also suitable for use as pigments.

The lead salts have been investigated by various experimenters who have studied the relation of the color of these chromates to such factors as hydrogen ion concentration, dispersion, particle size, chemical constitution, etc.

The insoluble chromates are precipitated from a dilute solution of the metallic salt either with sodium or potassium chromates or dichromates. Ernst (1) and others found that the variation of the hydrogen ion concentration of the solutions does effect the resulting color of lead chromate pigments but the acid or base used to affect this change of pH does not change the color. Neither does the use of the different alkali chromates of sodium or potassium nor the dichromates of these metals have any marked effect on the color. The time of striking

and the temperature of the solutions had no effect. Therefore it is believed the hydrogen ion concentration of the solutions is a determining factor in controlling the color of the chromate pigment.

It is the purpose of this investigation to prepare other metallic chromates and study the effect the hydrogen ion concentration of the solutions has on the resulting color.

EXPERIMENTAL

Experimental.

The purpose of this investigation was the preparation of different metallic chromates by precipitation from solutions having different hydrogen ion concentrations and the study of the color of the resulting chromates.

The hydrogen ion concentration of the solution was determined by the potentiometric method of Ernst, Pragoff, and Litkenhaus, (1). In this method the electromotive force of a cell consisting of the solution with the saturated calomel electrode as a half-cell and the quinhydrone electrode of Bülmann (34) as the indicator electrode, is measured. The relation between the measured electromotive force and the pH (according to Sørensen) (35) is

$$E = 0.4526 - 0.0591 \log \text{pH at } 25^{\circ} \text{ C.}$$

The electromotive force was determined by the use of the potentiometer using the circuit shown in Figure 1. The quinhydrone electrode used dipped directly into the solution during the titration. The calomel electrode was connected to the solution by means of the salt bridge (potassium chloride and agar-agar).

The hydrogen ion concentration was varied by the acid having the common ion of the metallic salt, that is all solutions made from the metallic chloride were varied with hydrochloric acid and those from metallic nitrates were varied with nitric acid. Since only sodium dichromate was used in this investigation sodium hydroxide was the only base used. The acids and base used were approximately 5 normal.

The pH of the solutions were varied from 1 to 11. All pH above 9 are doubtful (37). The pH of the dichromate solutions corresponding to the observed values of the E. M. F. are probably not the true pH values.

It was attempted to prepare the colors under three different conditions in order to see if the method of precipitating had any marked effect on the resulting color.

1. The dichromate solution was run into the metallic ion solution, the hydrogen ion concentration of the metallic ion solution varied, while that of the dichromate solution was held constant.

2. The dichromate solution was run into the metallic ion solution, the hydrogen ion concentration of the dichromate solution varied, while that of the metallic ion was held constant.

3. The metallic ion solution was run into the dichromate solution, the hydrogen ion concentration of the metallic ion solution was varied while that of the dichromate was held constant.

All solutions used were .5 normal when struck. The solutions were made up so that after the addition of the acid or base the volume could be made up so the concentration of the desired ion would be .5 normal. A quantity of metallic ion solution was taken that would give approximately 15 grams of dried pigment, and was precipitated with a volume of dichromate solution that would give a slight excess of the chromate ion. This insured a more complete precipitation of the metallic chromate.

The solution was agitated during and approximately ten minutes after the mixing. After this period of agitation the final pH of the solution was recorded and a sample of the pulp color was removed and placed in a stoppered test tube, the remainder of the color was washed five times by decantation, with approximately a liter of water each washing. The color was then filtered and placed in an oven, at a temperature of 75 - 80 degrees Centegrade for 24 hours, or until dry.

The pulp colors, after having been placed in stoppered test tubes were compared with the color plates in Maertz and Paul Dictionary of Color (37). All refernces to this dictionary are given in the form PS -10L, which means that the color is on color plate number 8 and in the area corresponding to 10L on the chart.

The mass tones were rubbed in bleached linseed oil to a paste, and then placed on glass slides and compared with the Dictionary of Color. The colors shown herein were prepared the same way and placed on cardboard.

The pH values for the solutions when struck corresponded to the following E.M.F. listed in volts.

| | | | |
|---|--------|----|--------|
| 1 | -.3943 | 7 | -.0396 |
| 2 | -.3352 | 8 | +.0196 |
| 3 | -.2726 | 9 | +.0787 |
| 4 | -.2169 | 10 | +.1400 |
| 5 | -.1578 | 11 | +.2000 |
| 6 | -.0967 | | |

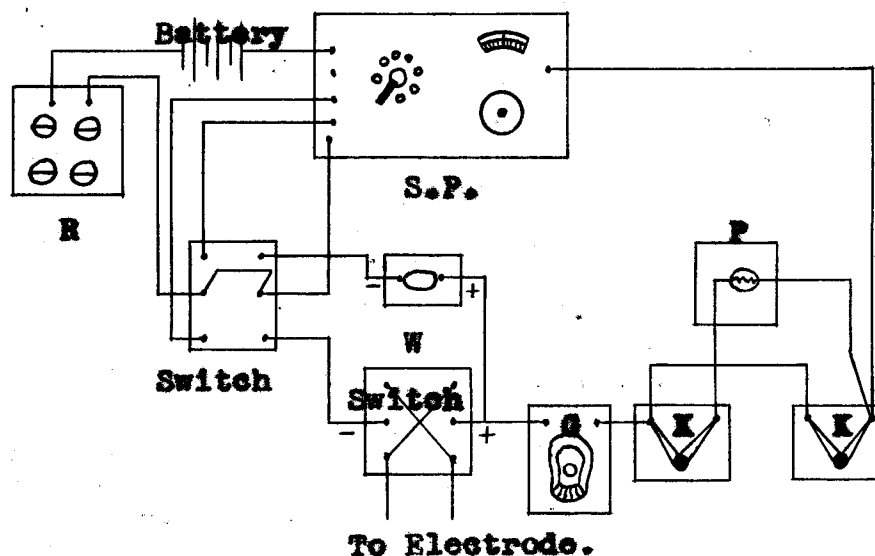
All values were taken from a Leeds-Northrup Conversion Table.

APPARATUS

Apparatus.

The apparatus used in this investigation for measuring the hydrogen ion concentration consisted of a Leeds and Northrup Student Potentiometer circuit.

Figure I.



S.P. is a student potentiometer (range 0 to 1.6 volts, 200 division scales, 0.5 millivolt accuracy).

Battery is a dry cell battery of 1.5 volts.

R. is a resistance box (1 to 1000 ohms).

Switches are D.P.D.T. switches.

P. is a protective resistance of 10,000 ohms

G. Is a D'Arsenal Galvanometer (0.5 microamperes per mm. sensitivity, three seconds, critical damping resistance 2400 ohms.

W. is a Weston Cadmium Standard cell (U.S. Bureau of Standard calibration 1.01868 International Volts at 22° Centigrade.

K, K are tap Keys.

MATERIALS

Materials.

The materials used in this investigation were either C.P. salts or were recrystallized. The sodium dichromate was recrystallized from a distilled water solution having a boiling point 120 - 125 degrees Centegrade. It was found that below 120 degrees no crystals would form and above 125 degrees the solution would solidify. Small crystals were obtained by rapid cooling and constant stirring the solution.

The following metallic salts were used in the preparation of the chromates.

1. Copper nitrate
2. Silver nitrate
3. Magnesium nitrate
4. Calcium nitrate
5. Strontium chloride
6. Barium chloride
7. Zinc nitrate
8. Cadmium nitrate
9. Mercuric nitrate
10. Aluminum nitrate
11. Titanium trichloride
12. Stannous chloride

13. Arsenic oxide
14. Antimony trichloride
15. Bismuth nitrate
16. Manganese chloride
17. Ferrous chloride
18. Ferric chloride
19. Cobaltous chloride
20. Nickelous nitrate.

The acids and base used were of the highest
purity.

METALLIC CHROMATES

Metallic Chromates.

The metallic chromates are salts of chromic acid, and are analogous to sulphates in many respects, especially solubility. Thus, the alkali chromates and those of magnesium and calcium are soluble while lead and barium are practically insoluble. The metallic dichromates are salts of dichromic acid. In a solution of an alkali dichromate both the chromate and the dichromate ion are present. Therefore when a metallic salt is added to a dichromate solution the chromate or dichromate may precipitate, depending on which is the least soluble. This accounts for the fact that lead chromate, and other metallic chromates, are precipitated from dichromate solutions.

Most insoluble metallic chromates are of some shade of yellow. (). The lead and barium probably being the most common, are both yellow the barium chromate being a lighter shade. Metallic dichromates are usually a reddish color, silver, being a good example is a reddish brown.

Metallic chromates do not form acid salts as do the sulphates but they do form basic salts.

H.T.S. Britton (2) found that by titrating metallic salts with potassium chromate a basic salt would form at the same pH as the hydroxide of the metal. He investigated several metallic salts (Ni, Co, Al, Zn, Th, and other rare elements) and found this to be a general fact.

COPPER CHROMATE

Copper Chromate.

The normal copper chromate was prepared by J. Schulze (8) by heating copper hydroxide and potassium dichromate in a sealed tube at 220 degrees. He described the product as being iron-black or reddish brown with the appearance of hematite. The normal salt was insoluble in water, but hydrolyzed in hot water to a basic salt. Under ordinary conditions Schulze and others found a basic salt was formed from a boiling solution of copper hydroxide and a dichromate.

L. N. Vauquelin (9) found that a chestnut brown precipitate formed when a neutral salt of copper was treated with potassium chromate. This salt upon analysis consisted of $K_2O \cdot 3CrO_3 \cdot 2H_2O$. M. Greger (33) obtained a greenish-yellow precipitate from copper chloride and sodium chromate, which changed to a rusty brown when left in contact with the mother liquor. The composition of the greenish-yellow was $2Cu(OH)_2 \cdot CuCrO_4$. The rusty-brown precipitate reverted to the greenish-yellow upon washing.

Table I.

**Effect of Variation of Hydrogen Ion Concentration of
Copper Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Sodium dichromate* added to copper nitrate.)

| Sample | pH $\text{Cu}(\text{NO}_3)_2$ | Final E.M.F. (volts) | Final pH | Remarks. |
|--------|----------------------------------|----------------------------|-------------|-------------|
| 1 | 1 | -.3706 | 1.4 | Soluble |
| 2 | 2 | -.3056 | 2.5 | " |
| 3 | 3 | -.2820 | 2.9 | " |
| 4 | 4 | -.2583 | 3.3 | Slight ppt. |
| 5 | 5 | -.2051 | 4.2 | Medium ppt. |
| 6 | 6 | -.1992 | 4.3 | Heavy ppt. |
| 7 | 7 | -.1785 | 4.6 | " |
| 8 | 8 | -.1975 | 4.3 | " |
| 9 | 9 | -.1750 | 4.7 | " |
| 10 | 10 | -.1685 | 4.9 | " |
| 11 | 11 | -.1210 | 5.6 | " |

* The pH of the sodium dichromate 2.5.

Time of striking was 21 seconds.

On washing the precipitate the resulting solutions were colored due to the slight solubility of the pigment or to hydrolysis.

Table II.

Comparison of Pulp Colors prepared from Copper Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|------------------------|
| 4 | P14-12F | Gold Brown |
| 5 | P14- 9K | Bunny |
| 6 | P14-12C | Tortoise |
| 7 | P14-10J | |
| 8 | P14-10K | Tiffin |
| 9 | P14-11K | Cigarette, Antique Br. |
| 10 | P14- 9K | Bunny |
| 11 | P14- 9L | Sudan Br. |

* Pulp colors as precipitated under conditions
of Table I.

Numbers 1,2,3 were almost completely soluble so were not considered in the color chart. Number 5 was an offshade, no apparent reason. There was a slight break at pH of 10 (No. 10) from a red-brown to a green-brown. Number 5, 8, 10, 11 showed a slight change in color where the pigment was in contact with the supernatant liquid, which contained chromate and quinhydrone. The others showed little or no change.

All the changes were to a darker brown. The series except for offshades varied from a red-brown to a green-brown.

Table III.

Comparison of Mass Tene of Colors Prepared from Copper Nitrate and Sodium Dichromate*.

| Sample | Index | Name of Color. |
|--------|---------|---------------------------------|
| 4 | P8 -12L | Mandalay, Frair ⁺ |
| 5 | P15- 9L | |
| 6 | P8 -12H | Cattail, Cafe Noir ⁺ |
| 7 | P8 -12A | Autumn |
| 8 | P8 -12A | Autumn |
| 9 | P16-12C | |
| 10 | P8 -12A | Autumn |
| 11 | P13- 1L | |

* Color prepared under conditions of Table I.

The series varies from a brown (No. 4) through a greenish brown (Nos. 5 - 10) then to a light green-yellow (No. 11). Numbers 5 and 9 are offshades being more green than brown. All the colors are brighter than the duplicate in color chart. All the green-browns are a dirty color.

Color Chart 1.

| Sample | pH | Name of Color. |
|--------|----|----------------------|
| 4 | 4 | Mandelay Friar |
| 5 | 5 | ----- |
| 6 | 6 | Cattail Cafe Noir |
| 7 | 7 | Autumn |
| 8 | 8 | Autumn |
| 9 | 9 | ----- |
| 10 | 10 | Autumn |
| 11 | 11 | ----- |

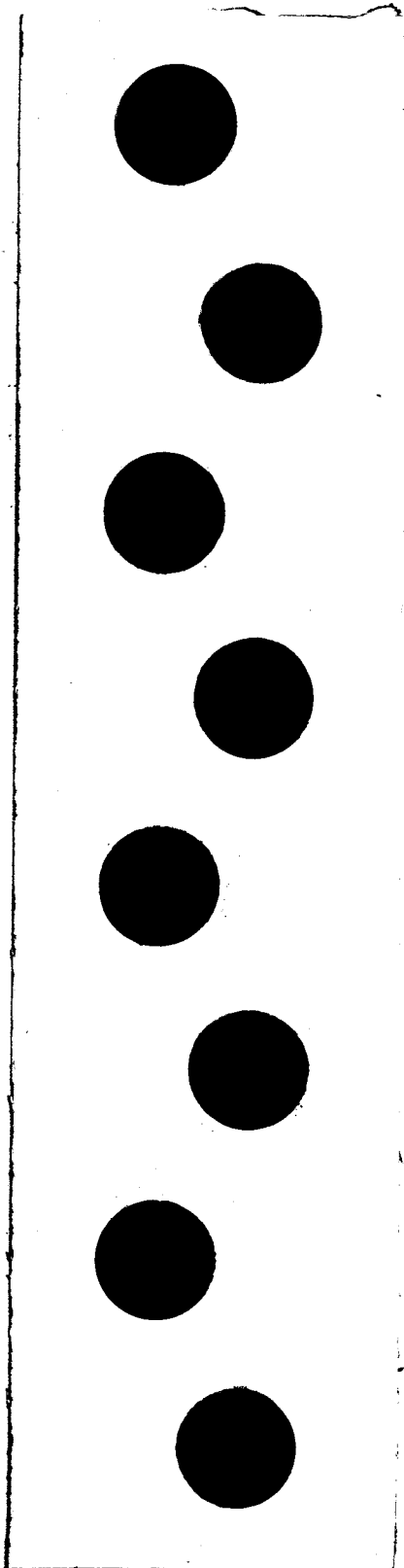


Table IV.

Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate added to copper nitrate^{*}.)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks. |
|--------|--|-------------------|-------------|-------------|
| 12 | 1 | -.4255 | .5 | Slight ppt. |
| 13 | 2 | -.4350 | .3 | " |
| 14 | 3 | -.4520 | .1 | " |
| 15 | 4 | -.4690 | | Medium ppt. |
| 16 | 5 | -.4830 | | Large ppt. |
| 17 | 6 | -.4490 | .1 | " |
| 18 | 7 | -.4215 | .6 | " |
| 19 | 8 | -.4195 | .7 | " |
| 20 | 9 | -.4120 | .7 | " |
| 21 | 10 | -.4085 | .8 | " |
| 22 | 11 | -.4325 | .3 | " |

* The pH of the copper nitrate 1.8

The time of striking was 21 seconds. The
final E.M.F. of these precipitates is indoubtedly
not true pH values.

Table V.

**Comparison of Pulp Colors prepared from Copper Nitrate
and Sodium Dichromate.***

| Sample | Index | Name of Color. |
|--------|---------|-----------------------------|
| 15 | P14-10D | Mustard Br ⁺ |
| 16 | P14-12A | Alamo ⁺ |
| 17 | P15-12A | Burnt Umber ^P |
| 18 | P14-12H | Bombay |
| 19 | P15-12A | Burnt Umber ^P |
| 20 | P14-10E | Seminole |
| 21 | P14-11E | |
| 22 | P14-12B | Arab-Rugby tan ⁺ |

* Pulp colors as precipitated under conditions of Table IV.

Samples Numbers 12, 13, 14 were almost completely soluble so were not considered in the color chart. Numbers 18 and 20 were offshades. All the colors except Number 20 showed a change of color where in contact with the supernatant liquor containing chromate and quinquhydrone. The series varies from a tan to a red-brown, all colors being a shade or two darker than those listed in the chart. There was no definite break in color at any point except offshades.

Table VI.

Comparison of Mass Tone of Colors Prepared from Copper
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|---------------------------------------|
| 15 | PS -12C | Bracken |
| 16 | PS -12H | Cattail, Cafe Noir ⁻ |
| 17 | PS -11H | Conga ⁺ |
| 18 | PS -12E | Bronche, Old English Br. ⁺ |
| 19 | PS -12H | Cattail, Cafe Noir ⁻ |
| 20 | PS -12A | Autumn |
| 21 | PS -12E | Bronche, Old English Br. ⁺ |
| 22 | PS -12H | Conga ⁺ |

* Colors prepared under conditions of
Table IV.

This series was very constant with no definite break at any point. All colors were a dirty green-brown, with no particular offshades except Number 20 was a little darker and Number 22 was a little lighter than others. Number 15 was a more distinct green than any other. The colors were all different but not so distinctly different as those in the preceding group (Table III).

Color Chart 2.









| Sample | pH | | Name of Color. |
|--------|----|---|----------------------------|
| 15 | 4 |  | Bracken |
| 16 | 5 |  | Cattail Cafe Noir |
| 17 | 6 |  | Conga |
| 18 | 7 |  | Broncho Old English Br |
| 19 | 8 |  | Cattail Cafe Noir |
| 20 | 9 |  | Autumn |
| 21 | 10 |  | Broncho Old English Br. |
| 22 | 11 |  | Conga |

Table VII.

**Effect of Variation of Hydrogen Ion Concentration of
Copper Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Copper nitrate added to sodium dichromate^{*})

| Sample | pH Cu(NO ₃) ₂ | E.M.F. (volts) | Final pH | Remarks. |
|--------|---|-------------------|-------------|-------------|
| 23 | 1 | -.4240 | .5 | Soluble |
| 24 | 2 | -.3975 | 1.0 | Slight ppt. |
| 25 | 3 | -.3710 | 1.4 | " |
| 26 | 4 | -.3540 | 1.7 | Medium ppt. |
| 27 | 5 | -.3290 | 2.1 | Large ppt. |
| 28 | 6 | -.3000 | 2.6 | " |
| 29 | 7 | -.2845 | 2.9 | " |
| 30 | 8 | -.2467 | 3.5 | " |
| 31 | 9 | -.2197 | 4.0 | " |
| 32 | 10 | -.1675 | 4.8 | " |
| 33 | 11 | -.1195 | 5.7 | " |

* The pH of the sodium dichromate 2.5

This series is very comparable to the series produced in Table I, in quantity of precipitate and the pH of the solution containing the precipitated color.

Table VIII.

Comparison of Pulp Colors Prepared from Copper Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|------------------------|
| 26 | P14-12D | Hippane |
| 27 | P14-12H | Bombay |
| 28 | P14-11D | |
| 29 | P14-11H | |
| 30 | P14-11K | Cigarette, Antique Br. |
| 31 | P14-10L | Antique Bronze |
| 32 | P15- 8H | Rubber |
| 33 | P15-10L | Whippet. |

* Pulp colors prepared under conditions of
Table VII.

Numbers 23, 24, 25 were almost completely soluble so were not considered in the color chart. The series runs from a reddish brown (No. 26) to a tan (No. 31) and then to a dark greenish brown (Nos. 32 - 33). Some colors were a shade or two darker than the corresponding color in the chart. There is a definite break in the series at the pH of 9 (No. 31), with no particular offshades. The colors showed the characteristic color change where in contact with the supernatant liquid.

Table IX.

**Comparison of Mass Tone of Colors Prepared from Copper
Nitrate and Sodium Dichromate.***

| Sample | Index | Name of Color. |
|--------|---------|---------------------------------|
| 25 | P16- 8H | |
| 26 | P15- 9H | |
| 27 | P15- 9H | |
| 28 | P 8-12H | Cattail, Cafe Noir ^m |
| 29 | P 8-12A | Autumn |
| 30 | P15- 8L | |
| 31 | P15- 8L | |
| 32 | P15- 8L | |
| 33 | P15- 8L | |

* Colors prepared under conditions of
Table VII.

The series of colors varies slightly from a green-brown (No. 25) to a light brown (Nos. 26-27) then to a dark brown (Nos. 28 - 29) and the last colors are a light greenish brown (Nos. 30 - 33). All the changes were distinct and very pronounced. This series of colors are very comparable to those discussed under Table III. The changes were at approximately the same pH but the colors at any particular pH did not match.

Color Chart 3

Sample pH Name of Color.

25 3 -----

26 4 -----

27 5 -----

28 6 Cattail
Cafe Noir

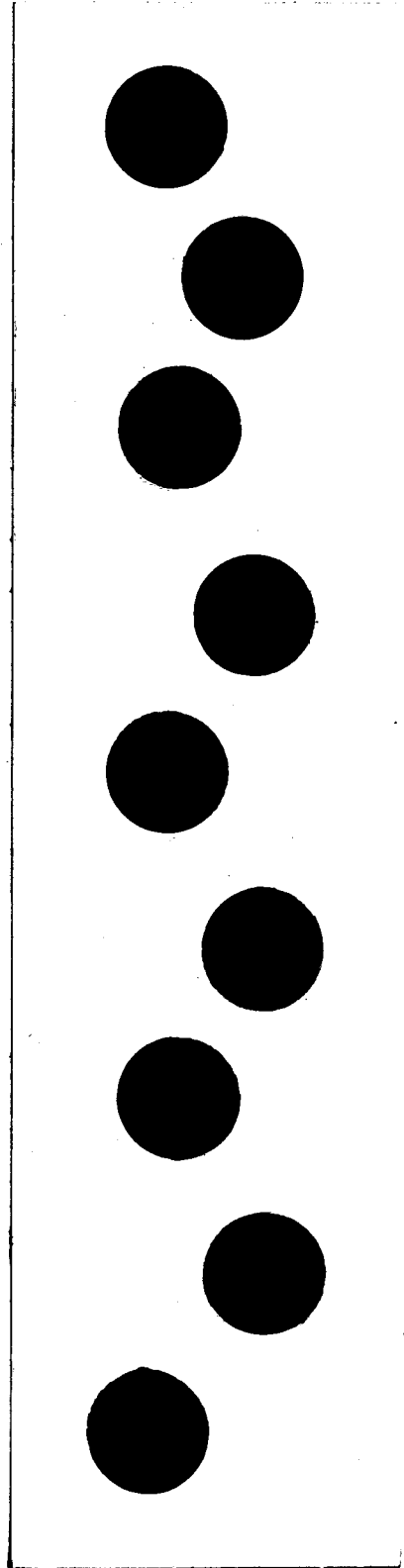
29 7 Autumn

30 8 -----

31 9 -----

32 10 -----

33 11 -----



**General Comparison of Colors Produced
from Copper Nitrate.**

The pulp colors of these precipitates are all browns or green-browns. The method of striking seemingly had little effect on the color since the two series of colors produced by reverse methods of striking (Tables II and VIII) are very similar. The colors compared in Tables II and VIII varied approximately the same from brown to a green-brown at the same pH values. The pulp colors in the other series where the pH of the dichromate solution was varied were very different from the other two series. These were mostly reds or red-browns with little change at the various pH values.

The method of striking had little effect on the mass tone of the different precipitates. The mass tones of Tables III and IX (reverse method of striking copper nitrate solutions) were very comparable, although the individual colors at any particular pH were not identical. The series as a whole varied from a brown to a green-brown, being nearly similar at pH of 9 and 10. The other series of colors (Table VI) was very constant with no definite breaks at any point, nor any offshades.

SILVER CHROMATE

Silver Chromate.

Silver chromate has been prepared in several ways. L. N. Vauquelin (3) found that the method of striking concentrated solutions formed different colored precipitates. When the chromate solution was dropped into the silver nitrate solution a reddish brown precipitate formed while the reverse method of striking formed an orange red precipitate which was contaminated with the potassium salt. Silver chromate has also been prepared from silver oxide and potassium chromate, silver carbonate and chromic oxide, silver oxide and potassium chromate, silver bromide and chromic acid, and silver dichromate. The normal silver dichromate was prepared by H. Moser (36) from chromic acid and silver nitrate.

Silver chromate varies in color with the way of preparation. R. Hunt believed that dichromate solution exposed to sunlight caused the variation of color. F. Bush (5) found the time of precipitation of the color produced different colors. C. Freese (6) and others found that if the silver salt was in excess when the chromate was produced

from a silver salt and a chromate, the red variety was produced, and the result was not affected by temperature. On the other hand when silver dichromate was decomposed by hot or cold water or when a solution of silver chromate or dichromate was evaporated several observers have found that green crystals were formed. F. Kohler (7) found that the pure silver chromate was greenish-black but the solid took in nitrates of either potassium or ammonium, and in each case the color was red. He therefore attributed the color to impurities in the solid. It is interesting that the specific gravity of the different colored silver chromate varies being 5.536 for the green and 5.523 for the red variety.

Table X.

**Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Nitric**

Acid and Sodium Hydroxide.

(Silver nitrate^{*} added to sodium dichromate.)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | Excess | Remarks |
|--------|--|----------------|-------------|
| 34 | 1 | Chromate | Slight ppt |
| 35 | 2 | " | Medium ppt. |
| 36 | 3 | " | " |
| 37 | 4 | Silver Nitrate | " |
| 38 | 5 | " | Large ppt. |
| 39 | 6 | " | " |
| 40 | 7 | " | " |
| 41 | 8 | " | " |
| 42 | 9 | " | " |
| 43 | 10 | " | " |
| 44 | 11 | " | " |

* It was found impossible to determine the pH of silver nitrate solutions with the quinhydrone electrode, so the pH of the dichromate was varied and the silver nitrate held constant.

The time of striking was 25 seconds.

Table XI.

Comparison of Pulp Colors Prepared from Silver Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|------------------------|
| 34 | P7 - 7L | Maroon |
| 35 | P6 -10L | Cuba , Wallflower. |
| 36 | P6 -11L | Egyptian R., Alcasar |
| 37 | P6 -12L | Indian Red. |
| 38 | P6 -11K | Kobe |
| 39 | P7 -10L | Kettledrum, Mansanita, |
| 40 | P7 - 9L | Kozak, Captie |
| 41 | P8 - 4L | Andona |
| 42 | P7 -11J | Cordova, Castillon |
| 43 | P7 - 9L | Kozak, Captie |
| 44 | P7 - 1L | Malaya. |

* Colors prepared under conditions of

Table X.

The series of colors runs from a reddish-purple at 34 to reds, then to reddish-browns. There is a definite break at pH of 8 (No. 41) from a red to a reddish-brown. The series is variable, having a light peak at pH of 4 (No. 37) and pH 7 (No. 40).

Table XII.

**Comparison of Mass Tone of Colors Prepared from Silver
Nitrate and Sodium Dichromate.***

| Sample | Index | Name of Color. |
|--------|---------|------------------------------|
| 34 | P8 - 6J | Briarwood |
| 35 | P7 - 8L | Massaya |
| 36 | P7 - 7L | Maroon |
| 37 | P7 - 7L | Maroon |
| 38 | P7 - 5L | Algerian Red, Crimson Maple- |
| 39 | P7 -10L | Kettledrum, Manzanita |
| 40 | P7 -10L | Kettledrum, Manzanita |
| 41 | P8 - 5L | Zanzibar |
| 42 | P7 -11L | Coromandel, Tuscany |
| 4 43 | P7 -11L | Coromandel, Tuscany |
| 44 | P7 -10L | Kettledrum, Manzanita |

* Colors prepared under conditions of

Table X.

This series of colors were all reds varying only slightly. Nos. 34 and 41 were offshades while No. 38 was a little lighter than the other reds.

Color Chart 4.



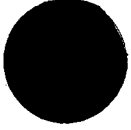

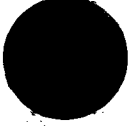






| Sample | pH | | Name of Color. |
|--------|----|---|-------------------------------|
| 34 | 1 |  | Brierwood |
| 35 | 2 |  | Maccara |
| 36 | 3 |  | Mareon |
| 37 | 4 |  | Mareon |
| 38 | 5 |  | Algerian Red Crimson Maple |
| 39 | 6 |  | Kettle drum Mansanita |
| 40 | 7 |  | Kettle drum Mansanita |
| 41 | 8 |  | Zansibar |
| 42 | 9 |  | Coromandel Tuscany |
| 43 | 10 |  | Coromandel Tuscany |
| 44 | 11 |  | Kettle drum Mansanita |

Table XIII.

**Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Sodium Dichromate added to Silver nitrate.*)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | Excess | Remarks. |
|--------|--|----------------|-------------|
| 45 | 1 | Chromate | Slight ppt. |
| 46 | 2 | " | Medium ppt. |
| 47 | 3 | " | " |
| 48 | 4 | Silver Nitrate | " |
| 49 | 5 | " | Large ppt. |
| 50 | 6 | " | " |
| 51 | 7 | " | " |
| 52 | 8 | " | " |
| 53 | 9 | " | " |
| 54 | 10 | " | " |
| 55 | 11 | " | " |

* Since it was found impossible to obtain the pH of silver nitrate solutions with the quinhydrone electrode, the pH of the sodium dichromate was varied, and that of the silver nitrate held constant.

Table XIV.

Comparison of Pulp Colors Prepared from Silver Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|---------------------------------------|
| 45 | P8 - 6A | |
| 46 | P8 - 6E | Rose Ebony |
| 47 | P8 - 6J | Garnet , Spanish Wine. |
| 48 | P6 -11L | Egyptian R., Alcazar. |
| 49 | P7 - 9L | Kazak, Coptic |
| 50 | P7 -10L | Kettledrum, Manzanita. |
| 51 | P6 -11L | Egyptian R., Alcazar. |
| 52 | P7 - 1L | Malaga |
| 53 | P7 -12J | Chutney |
| 54 | P8 - 9L | Maracaibo, Domingo Brown ⁻ |
| 55 | P7 - 4L | Akbor ⁻ |

* Pulp colors prepared under conditions of
Table XIII.

This series of colors runs from a dark purple (No. 45) to a red (No. 51) then to a red brown. There is a definite break at pH of 8 (No. 52) to a red brown. The series is variable having a light peak at pH of 4 (No. 48) and pH of 7 (No. 51).

Table XV.

**Comparison of Mass Tone of Colors Prepared from Silver
Nitrate and Sodium Dichromate.***

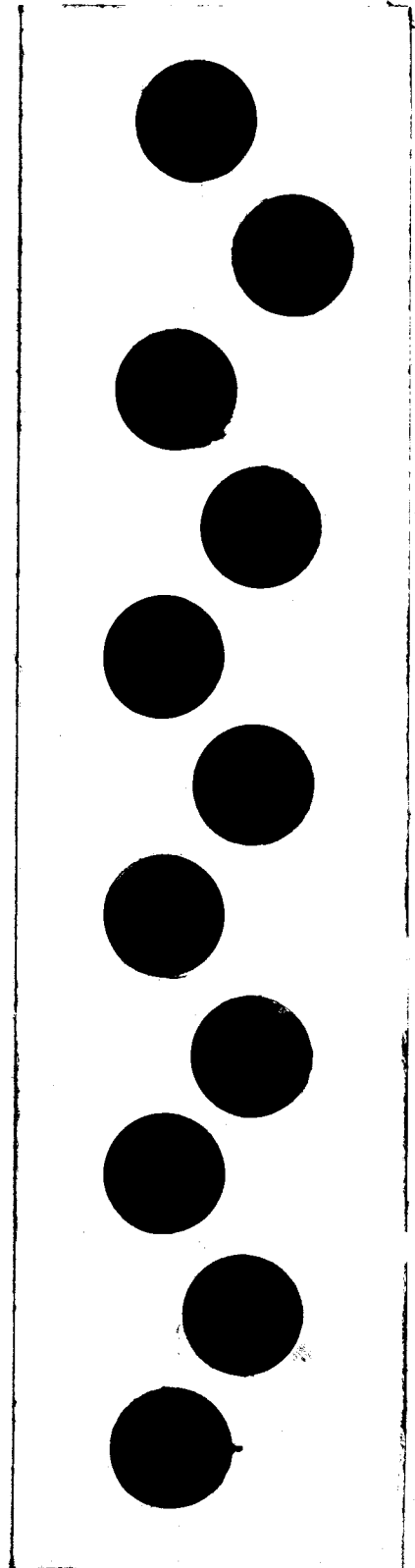
| Sample | Index | Name of Color |
|--------|---------|---------------------------|
| 45 | P8 - 6J | Briarwood - |
| 46 | P7 - 7L | Maroon |
| 47 | P7 -11L | Coromandel, Tuscany |
| 48 | P7 - 9L | Kozak, Captic |
| 49 | P7 - 7L | Maroon |
| 50 | P8 - 9L | Maracaibo, Domingo Brown- |
| 51 | P8 - 7L | Carbuncle |
| 52 | P8 - 7L | Carbuncle |
| 53 | P7 -11L | Coromandel, Tuscany |
| 54 | P8 - 7L | Carbuncle |
| 55 | P8 - 6L | Mirador, Art Brown |

* Colors prepared under conditions of
Table XIII.

This series of colors were all reds. Nos. 45 and 46 were a little darker than others, while Nos. 51 and 52 had a slight brown tint. There were no definite breaks or offshades.

Color Chart 5.

| Sample | pH | Name of Color. |
|--------|----|---|
| 45 | 1 | Briarwood ^m |
| 46 | 2 | Maroon |
| 47 | 3 | Coromandel Tuscany |
| 48 | 4 | Kozak Captie |
| 49 | 5 | Maroon |
| 50 | 6 | Maracaibo Domingo Brown ^m |
| 51 | 7 | Carbuncle |
| 52 | 8 | Carbuncle |
| 53 | 9 | Coromandel Tuscany |
| 54 | 10 | Carbuncle |
| 55 | 11 | Mirador Art Brown |



**General Comparison of Colors Produced
from Silver Nitrate.**

The two series produced pulp colors very comparable to each other. At pH of 6 (Nos. 39 and 50) the colors produced were exactly the same. The series as a whole break at the same pH value of 8, with corresponding light peaks at pH of 4 and 7. The first color in each series are the only ones showing a distinct color difference.

The mass tones were also very comparable. The method of striking had little or no effect on the color produced. At pH of 1 the colors were exactly the same and at other pH values the variation was slight. No 41 was the only color that was distinctly different from the corresponding color in the other series.

MAGNESIUM CHROMATE

Magnesium Chromate.

Magnesium chromate is completely soluble in water, (60 grams per 100 cc.). The crystals are orange-yellow six sided. Magnesium chromate is prepared, under a canadian patent (10), by treating a magnesium salt with an alkali chromate, the alkali metal and the acid radical of the magnesium salt forming a more difficultly soluble salt than the chromate. Many double salts of magnesium and chromium have been prepared.

Table XVI.

**Effect of Variation of Hydrogen Ion Concentration of
Magnesium Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Sodium dichromate^{*} added to magnesium nitrate)

| Sample | pH Mg(NO ₃) ₂ | E.M.F. (volts) | Final pH | Remarks. |
|--------|---|-------------------|-------------|------------|
| 56 | 1 | -.7525 | | Soluble |
| 57 | 2 | -.5100 | | " |
| 58 | 3 | -.3565 | 1.7 | " |
| 59 | 4 | -.3200 | 2.3 | " |
| 60 | 5 | -.3200 | 2.3 | " |
| 61 | 6 | -.3150 | 2.4 | " |
| 62 | 7 | -.3200 | 2.3 | " |
| 63 | 8 | -.3150 | 2.4 | " |
| 64 | 9 | -.3250 | 2.2 | " |
| 65 | 10 | -.1200 | 5.6 | large ppt. |
| 66 | 11 | -.1335 | 5.4 | " |

* The pH of the sodium dichromate 2.5.

Upon setting for 12 hours Nos. 58 - 64
formed a dark solution from which was filtered a
small amount of color.

The time of striking was 25 seconds.

CALCIUM CHROMATE

Calcium Chromate.

Calcium chromate is completely soluble in water (22.2 grams per 100 cc.). T. Thomson (11) and H. Moser (36) found that a solution of calcium chloride and potassium dichromate slowly formed a precipitate which when analyzed by J. P. Bahr (12) was found to vary from CaCrO_4 to $5\text{CaCrO}_4 \cdot \text{K}_2\text{CrO}_4$. When free acetic acid was present H. Kammerer (13) and F. T. Frerichs (14) observed no precipitate. Calcium chromate is prepared under a Canadian patent (15) by roasting an intimate mixture of finely ground ferrochrome, lime and alkali metal carbonate. The compound is easily converted into other chromates and chromic acid. The basic salt has also been prepared which yielded lemon-yellow monoclinic prisms. Many double salts of calcium and chromium have been prepared.

Table XVII.

Effect of Variation of Hydrogen Ion Concentration of
Calcium Nitrate Solutions with Nitric

Acid and Sodium Hydroxide.

(Sodium dichromate added to calcium nitrate.)

| Sample | pH $\text{Ca}(\text{NO}_3)_2$ | Final E.M.F. (volts) | pH | Remarks. |
|--------|----------------------------------|----------------------------|-----|----------|
| 67 | 1 | -.7200 | | Soluble |
| 68 | 2 | -.5325 | | " |
| 69 | 3 | -.4200 | 0.6 | " |
| 70 | 4 | -.3550 | 1.7 | " |
| 71 | 5 | -.3775 | 1.3 | " |
| 72 | 6 | -.3005 | 2.5 | " |
| 73 | 7 | -.3015 | 2.6 | " |
| 74 | 8 | -.2950 | 2.7 | " |
| 75 | 9 | -.2950 | 2.7 | " |
| 76 | 10 | -.2850 | 2.8 | " |
| 77 | 11 | -.2650 | 3.2 | " |

* The pH of the sodium dichromate 2.5.

The time of striking was 30 seconds.

No further investigation was made of this group since all proved to be soluble.

STRONTIUM CHROMATE

Strontium Chromate.

Strontium chromate is precipitated from concentrated solutions of strontium chloride and a chromate, but J. D. Smith (16) observed that no precipitate formed in dilute solutions. Strontium chromate is not precipitated from strontium hydroxide, neither will it precipitate from an acetic acid solution. L. Bourgeois (17) obtained the crystalline salt by fusing strontium chloride with sodium and potassium chromates. Strontium chromate has been used as a pigment, and is commonly known as lemon-yellow, and strontium yellow.

Table XVIII.

**Effect of Variation of Hydrogen Ion Concentration of
Strontium Chloride Solutions with Sodium
Hydroxide and Hydrochloric Acid.**

(Sodium Dichromate* added to strontium chloride)

| Sample | pH SrCl ₂ | E.M.F. (volts) | Final pH | Remarks. |
|--------|-------------------------|-------------------|-------------|----------|
| 78 | 1 | -.5545 | | Soluble |
| 79 | 2 | -.3375 | 2.0 | " |
| 80 | 3 | -.2515 | 3.4 | " |
| 81 | 4 | -.2515 | 3.4 | " |
| 82 | 5 | -.2370 | 3.7 | " |
| 83 | 6 | -.2310 | 3.8 | " |
| 84 | 7 | -.2310 | 3.8 | " |
| 85 | 8 | -.2195 | 4.0 | " |
| 86 | 9 | -.2110 | 4.1 | " |
| 87 | 10 | -.2005 | 4.3 | " |
| 88 | 11 | -.1870 | 4.5 | " |

* The pH of the sodium dichromate 2.5.

The time of striking was 20 seconds.

No further investigation was made of this group since all proved to be soluble.

BARIUM CHROMATE

Barium Chromate.

Barium chromate has been prepared by many experimenters in many different processes. When an aqueous solution of a barium salt is treated with an alkali chromate or dichromate, a pale yellow precipitate of barium chromate is formed. Barium dichromate can be prepared either from barium chloride or barium chromate and concentrated chromic acid. The dichromate decomposes to the monochromate in cold water. Barium chromate and barium sulphate are about equally soluble, both being more insoluble than the carbonate. H. Moser (36) found the pale yellow barium chromate changed to a dark yellow upon heating. Barium chromate has been used as a pigment being commonly known as ultramarine yellow, lemon yellow, and permanent yellow. Several double salts of barium and chromium have been formed.

Table XIX.

**Effect of Variation of Hydrogen Ion Concentration of
Barium Chloride Solutions with Sodium
Hydroxide and Hydrochloric Acid.
(Sodium dichromate* added to barium chloride)**

| Sample | pH BaCl ₂ | Final E.M.F. (volts) | Final pH | Remarks. |
|--------|-------------------------|----------------------------|-------------|---------------|
| 89 | 1 | -.6425 | | Granular ppt. |
| 90 | 2 | -.6150 | | " |
| 91 | 3 | -.6100 | | " |
| 92 | 4 | -.5990 | | " |
| 93 | 5 | -.5935 | | " |
| 94 | 6 | -.5840 | | " |
| 95 | 7 | -.6225 | | " |
| 96 | 8 | -.6350 | | " |
| 97 | 9 | -.6400 | | " |
| 98 | 10 | -.6375 | | " |
| 99 | 11 | -.6380 | | " |

* The pH of the sodium dichromate 2.5.

The time of striking was 25 seconds.

The final E.M.F. was not a true pH value.

Table XX.

Comparison of Pulp Colors Prepared from Barium Chloride
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|----------------|
| 89 | P10- 1K | |
| 90 | P10- 1K | |
| 91 | P10- 1K | |
| 92 | P10- 1K | |
| 93 | P10- 1K | |
| 94 | P9 - 1L | |
| 95 | P9 - 1L | |
| 96 | P10- 1L | |
| 97 | P9 - 1J | |
| 98 | P9 - 1L | |
| 99 | P9 - 1J | |

* Pulp Colors prepared under the conditions
of Table XIX.

The series of colors varied slightly from
a light yellow to a darker yellow at pH of 8 (No. 95)
then to a lighter yellow. The only break in the
group was at the pH of 8.

Table XXI.

Comparison of Mass Tens of Colors Prepared from Barium
Chloride and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|-----------------------------|
| 89 | P10- 1K | Aureolin ^P |
| 90 | P10- 1L | |
| 91 | P10- 1L | |
| 92 | P10- 1L | |
| 93 | P10- 1L | |
| 94 | P10- 2L | |
| 95 | P10- 2L | |
| 96 | P10- 4L | Light Chrome Y ^P |
| 97 | P10- 1K | Aureolin ^P |
| 98 | P10- 2L | |
| 99 | P10- 1J | |

* Colors produced under conditions of
Table XIX.

All colors were either a yellow or a cream.
Nos. 96 and 98 were yellows, Nos. 97 and 99 were a
cream, while Nos. 89 - 95 varied from a cream to a
medium yellow.

Color Chart 6.


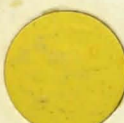




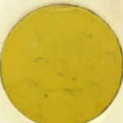




| Sample | pH | | Name of Color. |
|--------|----|---|-----------------------------|
| 89 | 1 |  | Aureolin ^P |
| 90 | 2 |  | ----- |
| 91 | 3 |  | ----- |
| 92 | 4 |  | ----- |
| 93 | 5 |  | ----- |
| 94 | 6 |  | ----- |
| 95 | 7 |  | ----- |
| 96 | 8 |  | Light Chrome Y ^P |
| 97 | 9 |  | Aureolin ^P |
| 98 | 10 |  | ----- |
| 99 | 11 |  | ----- |

Table XXII.

Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Sodium
Hydroxide and Hydrochloric Acid.

(Sodium dichromate added to barium chloride.*)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks. |
|--------|--|-------------------|-------------|-----------------|
| 100 | 1 | -.6090 | | Granular ppt. |
| 101 | 2 | -.6245 | | " |
| 102 | 3 | -.6245 | | " |
| 103 | 4 | -.6150 | | " |
| 104 | 5 | -.6005 | | " |
| 105 | 6 | -.2330 | 3.7 | Flocculent ppt. |
| 106 | 7 | -.1390 | 5.3 | " |
| 107 | 8 | -.1055 | 5.9 | " |
| 108 | 9 | -.0950 | 6.0 | " |
| 109 | 10 | -.0915 | 6.1 | " |
| 110 | 11 | -.0450 | 8.4 | " |

* The pH of the barium chloride 2.4

Time of striking 25 seconds.

It will be noticed that when the E.M.F.
became equivalent to a pH value the character of
the precipitate changed.

Table XXIII.

Comparison of Pulp Colors Prepared from Barium Chloride
 and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|----------------|
| 100 | P9 - 1L | |
| 101 | P10- 1L | |
| 102 | P10- 1L | |
| 103 | P10- 1E | |
| 104 | P10- 1E | |
| 105 | P10- 1F | |
| 106 | P10- 1D | |
| 107 | P10- 1F | |
| 108 | P10- 1F | |
| 109 | P10- 1D | |
| 110 | P10- 1D | |

* Pulp Colors prepared under conditions of
 Table XXII.

None of the above colors were named in the
 Dictionary of Color. The series of colors runs
 slightly to a darker yellow (Nos. 100 - 104), but
 with the change in the character of the precipitate
 there is a corresponding change in the color, to

a light cream gradually becoming whiter, with the rise in pH.

Table XXIV.

Comparison of Mass Tons of Colors Prepared from Barium Chloride and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|----------|-----------------------|
| 100 | P10- 1K | |
| 101 | P10- 2L | Aureolin ^D |
| 102 | P10- 2L | Aureolin ^D |
| 103 | P10- 1H | |
| 104 | P10- 1H | |
| 105 | P10- 1G | |
| 106 | P10- 1G | |
| 107 | P10- 1G | |
| 108 | P10- 1G | |
| 109 | P10- 1G | |
| 110 | P10- 1G. | |

* Colors prepared under conditions of

Table XXII.

This series of colors were all yellows or creams. Nos. 100 - 102 were yellows with 100 a little lighter shade, while Nos. 103 - 110 were all creams, varying only slightly.

Color Chart 7

| Sample | pH | Name of Color |
|--------|----|-----------------------|
| 100 | 1 | ----- |
| 101 | 2 | Aureolin ^P |
| 102 | 3 | Aureolin ^P |
| 103 | 4 | ----- |
| 104 | 5 | ----- |
| 105 | 6 | ----- |
| 106 | 7 | ----- |
| 107 | 8 | ----- |
| 108 | 9 | ----- |
| 109 | 10 | ----- |
| 110 | 11 | ----- |



Table XXV.

Effect of Variation of Hydrogen Ion Concentration of
Barium Chloride Solutions with Sodium
Hydroxide and Hydrochloric Acid.
(Barium chloride added to sodium dichromate.)*

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | Final E.M.F. (volts) | Final pH | Remarks |
|--------|--|----------------------------|-------------|---------------|
| 111 | 1 | -.5900 | | Granular ppt. |
| 112 | 2 | -.5875 | | " |
| 113 | 3 | -.5650 | | " |
| 114 | 4 | -.5490 | | " |
| 115 | 5 | -.5430 | | " |
| 116 | 6 | -.6400 | | " |
| 117 | 7 | -.6340 | | " |
| 118 | 8 | -.6400 | | " |
| 119 | 9 | -.6395 | | " |
| 120 | 10 | -.6340 | | " |
| 121 | 11 | -.6325 | | " |

* The pH of the sodium dichromate 2.5.

The time of striking was 25 seconds.

The results are very comparable to the results in Table XIX, in the kind, quantity and color of precipitates produced.

Table XXVI.

Comparison of Pulp Colors prepared from Barium Chloride
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|----------------|
| 111 | P10- 1K | |
| 112 | P10- 1K | |
| 113 | P10- 1L | |
| 114 | P10- 1L | |
| 115 | P10- 1L | |
| 116 | P9 - 2L | |
| 117 | P9 - 3L | |
| 118 | P9 - 3L | |
| 119 | P9 - 1K | |
| 120 | P9 - 2L | |
| 121 | P9 - 1K | |

* Pulp colors prepared under conditions of
Table XXV.

None of the above colors were named in the
Dictionary of Color. There was very little change in
the series, Nos. 111 - 116 being practically the
same. Nos. 117 and 118 changed slightly to a darker
yellow while Nos. 119 - 121 gradually changed to a

cream. Number 120 (pH 10) was an offshade. The break in the series was at 118 (pH 8). Numbers 116 and 117 showed a change in color where in contact with the supernatant liquid.

Table XXVII.

Comparison of Mass Tone of Colors Prepared from Barium Chloride and Sodium Dichromate.*

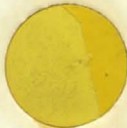
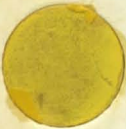

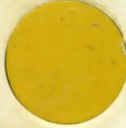
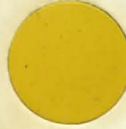





| Sample | Index | Name of Color |
|--------|---------|-----------------------------|
| 111 | P10- 1K | |
| 112 | P10- 1L | |
| 113 | P10- 1L | |
| 114 | P10- 1L | |
| 115 | P10- 1L | |
| 116 | P9 - 2L | |
| 117 | P9 - 2L | |
| 118 | P10- 4L | Light Chrome Y ^P |
| 119 | P10- 1K | |
| 120 | P10- 2L | |
| 121 | P10- 1J | Sulphur Y, Citrus. |

* Colors prepared under conditions of

Table XXV.

All colors are yellows or creams. Nos. 118 and 120 were a deeper yellow than others while Nos. 119 and 121 were creams. Nos. 111 - 117 varied gradually from a cream to a light yellow.

Color Chart 8.

| Sample | pH | | Name of Color. |
|--------|----|---|-----------------------------|
| 111 | 1 |  | |
| 112 | 2 |  | |
| 113 | 3 |  | |
| 114 | 4 |  | |
| 115 | 5 |  | |
| 116 | 6 |  | |
| 117 | 7 |  | |
| 118 | 8 |  | Light Chrome Y ^P |
| 119 | 9 |  | |
| 120 | 10 |  | |
| 121 | 11 |  | Sulphur Y Citrus |

**general Comparison of Colors Prepared
from Barium Chloride.**

The pulp colors of the precipitates from barium chloride were very similar, especially those prepared from solutions of the barium salt having varying hydrogen ion concentrations. The character of the precipitate in each is also similar. The series in each case broke at the same pH value, although the variation was slight. The series as a whole varied little from each other, showing the method of striking had little effect on the resulting color. The other series of colors, except for the flocculent precipitate, produced colors almost the same as the two other series. The flocculent precipitates were much lighter yellows and at the higher pH values was almost a white.

The reverse method of striking the colors had no effect on the mass tones since the colors at different pH values were almost identical (Tables XXI and XXVII). All the colors were either yellows or creams. The other series, prepared by varying the pH of the sodium dichromate, produced mostly creams. The first three colors in that series were yellows while the others were some shade of cream.

ZINC CHROMATE

Zinc Chromate.

Normal zinc chromate is not easily prepared since in concentrated solutions at high temperatures oxygen is given off and in more dilute solutions the basic salt is formed. (38) Several experimenters have however obtained the normal salt. J. Schulze (8) described it as being a lemon-yellow microscopic crystals, which are insoluble in water. The basic zinc chromates that form are of indefinite composition and have been used as pigments in paints. They are commonly called zinc yellow, zinc chrome, or yellow ultramarine. Four basic salts of definite composition have been prepared by different experimenters. They are zinc trioxychromate, $(4ZnO \cdot CrO_3 \cdot 3H_2O)$, zinc dioxychromate $(3ZnO \cdot CrO_3 \cdot 2H_2O)$, zinc oxychromate $(2ZnO \cdot CrO_3 \cdot 1\frac{1}{2}H_2O)$, and zinc oxybischromate $(3ZnO \cdot 2CrO_3 \cdot H_2O)$. Zinc chloride in an aqueous solution of N. or 3N. potassium dichromate formed a yellow granular precipitate $(4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O)$ which when washed with hot water several times was converted into a dark yellow precipitate $(ZnCrO_4 \cdot 3Zn(OH)_2)$. A darker precipitate is formed when an excess of potassium dichromate is used than when an excess of the zinc salt.

Table XXVIII.

Effect of Variation of Hydrogen Ion Concentration of
Zinc Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate* added to zinc nitrate)

| Sample | pH Zn(NO ₃) ₂ | E.M.F. (volts) | Final pH | Remarks |
|--------|---|-------------------|-------------|------------|
| 122 | 1 | -.6465 | | Soluble |
| 123 | 2 | -.3550 | 1.7 | " |
| 124 | 3 | -.3000 | 2.6 | " |
| 125 | 4 | -.2500 | 3.4 | " |
| 126 | 5 | -.2350 | 3.7 | " |
| 127 | 6 | -.2000 | 4.3 | " |
| 128 | 7 | -.1525 | 5.1 | Heavy ppt. |
| 129 | 8 | -.1160 | 5.7 | " |
| 130 | 9 | -.0945 | 6.1 | " |
| 131 | 10 | -.0945 | 6.1 | " |
| 132 | 11 | -.0950 | 6.1 | " |

* The pH of the sodium dichromate 2.5

All precipitates were formed from solutions
in which a large amount of basic salt was precipitated,
before the addition of the sodium dichromate.

Table XXIX.

Comparison of Pulp Colors Prepared from Zinc Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 128 | P14-12L | Sudan Br |
| 129 | P13- 9L | Chipsunk |
| 130 | P14-11L | Oak, Briar |
| 131 | P14-10K | Tiffin |
| 132 | P14-12L | Sudan Br |

* Colors prepared under conditions of
Table XXVIII.

This series of colors were all browns. Samples Nos. 129 - 130 showed a light yellow precipitate which was heterogeneously mixed in with the dark brown precipitate. All the precipitates were very flocculent and about the same shade of brown. No precipitate formed from solutions that were not basic enough to precipitate the hydroxide, before adding the chromate.

Table XXI.

Comparison of Mass Tone of Colors Prepared from Zinc
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|---------------------------------|
| 127 | P8 -10J | Java , Nomad Brown ^m |
| 128 | P13-11L | Buffalo |
| 129 | P13- 9L | |
| 130 | P13-11L | Buffalo |
| 131 | P13- 9L | |
| 132 | P13-10L | Whippet |

* Colors prepared under conditions of
Table XXVIII.

This group of colors were all some shade
of brown, varying slightly from a green-brown to
a medium brown.

Color Chart 9.

| Sample | pH | Name of Color |
|--------|----|---------------------|
| 127 | 6 | Java Honed Brown |
| 128 | 7 | Buffalo |
| 129 | 8 | ----- |
| 130 | 9 | Buffalo |
| 131 | 10 | ----- |
| 132 | 11 | Whippet |

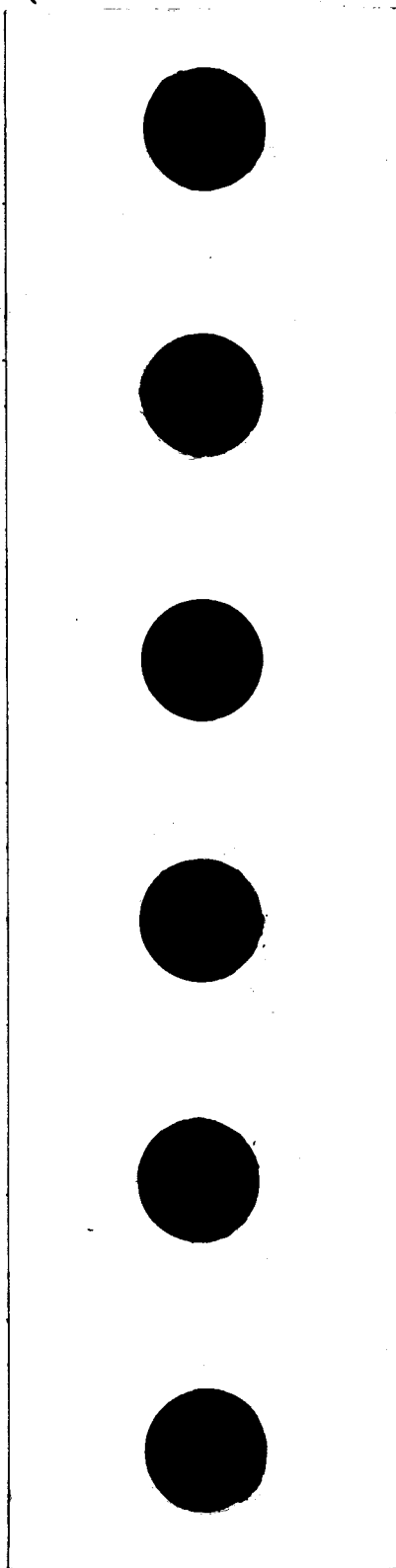


Table XXXI.

Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate added to zinc nitrate.)*

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks |
|--------|--|-------------------|-------------|------------|
| 133 | 1 | -.3550 | 1.7 | Soluble |
| 134 | 2 | -.3250 | 2.2 | " |
| 135 | 3 | -.3025 | 1.5 | " |
| 136 | 4 | -.3150 | 2.4 | " |
| 137 | 5 | -.1880 | 4.5 | Heavy ppt. |
| 138 | 6 | -.1884 | 4.5 | " |
| 139 | 7 | -.1790 | 4.6 | " |
| 140 | 8 | -.1660 | 4.9 | " |
| 141 | 9 | -.1520 | 5.1 | " |
| 142 | 10 | -.1435 | 5.2 | " |
| 143 | 11 | -.1370 | 5.4 | " |

* The pH of the zinc nitrate 1.6.

The precipitates in this series are very similar to those in the preceding series.

Table XXXII

Comparison of Pulp Colors Prepared from Zinc Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|-------------------------|
| 137 | P13- 8L | Buckthorn Br, Sumac |
| 138 | P13- 8L | Buckthorn Br, Sumac |
| 139 | P13-11L | Peruvian Br |
| 140 | P13-11L | Peruvian Br |
| 141 | P13-10L | Raw Sienna ^P |
| 142 | P13-10L | Raw Sienna ^P |
| 143 | P13-10L | Raw Sienna ^P |

* Pulp colors prepared under conditions of Table XXXI.

This series of colors was very constant, all being browns, with Nos. 137 - 138 nearly a tan, and Nos. 139 - 140 dark browns while Nos. 141 - 143 were medium browns. All the precipitates were flocculent similar to those in Table XXIX.

Table XXXIII.

Comparison of Mass Tone of Colors Prepared from Zinc
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|--------------------------|
| 137 | P8 - 8J | Java Brown |
| 138 | P8 - 8J | Java Brown |
| 139 | P8 - 8J | Java Brown |
| 140 | P8 -12E | Broncho, Old English Br |
| 141 | P8 -11H | Congo |
| 142 | P8 -12E | Broncho, Old English Br. |
| 143 | P8 -10J | Falcon, Muskrat |

* Colors prepared under conditions of
Table XXI.

This group of colors varied only slightly,
all colors being a medium brown.

Color Chart 10.








| Sample | pH | | Name of Color |
|--------|----|---|----------------------------|
| 137 | 5 |  | Java Brown |
| 138 | 6 |  | Java Brown |
| 139 | 7 |  | Java Brown |
| 140 | 8 |  | Broncho Old English Br. |
| 141 | 9 |  | Congo |
| 142 | 10 |  | Broncho Old English Br |
| 143 | 11 |  | Falcon Muskret |

Table XXXIV.

**Effect of Variation of Hydrogen Ion Concentration of
Zinc Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Zinc nitrate added to sodium dichromate.)*

| Sample | pH Zn(NO ₃) ₂ | E.M.F. (volts) | Final pH | Remarks. |
|--------|---|-------------------|-------------|-------------|
| 144 | 1 | -.6280 | | Soluble |
| 145 | 2 | -.5000 | 2.6 | " |
| 146 | 3 | -.3115 | 2.6 | " |
| 147 | 4 | -.2855 | 2.9 | " |
| 148 | 5 | -.2500 | 3.4 | " |
| 149 | 6 | -.2300 | 3.8 | Slight ppt. |
| 150 | 7 | -.1675 | 4.9 | Heavy ppt. |
| 151 | 8 | -.1215 | 5.6 | " |
| 152 | 9 | -.0950 | 6.1 | " |
| 153 | 10 | -.0100 | 7.5 | " |
| 154 | 11 | -.0950 | 6.1 | " |

* The pH of the sodium dichromate 2.5.

This series is very comparable to the series produced in Table XXVIII, which is the reverse method of striking.

Table XXIV

Comparison of Pulp Colors Prepared from Zinc Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------------|
| 149 | P13- 8L | Buckthorn Br, Sumac |
| 150 | P13- 9L | Chipmunk |
| 151 | P13- 8L | Buckthorn Br, Sumac |
| 152 | P13- 9L | Chipmunk |
| 153 | P13- 6L | |
| 154 | P13- 9L | Chipmunk |

* Pulp colors prepared under conditions of Table XXIV.

All the precipitates, except No. 150, had a light yellow color heterogeneously mixed in with the brown precipitate, which made up the bulk of the color. The series of colors, except for the yellow precipitate, was constant with no definite break in color and no particular offshades.

Table XXXVI.

Comparison of Mass Tones of Colors Prepared from Zinc Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color |
|---------------|--------------|----------------------|
| 150 | P15-10H | |
| 151 | P15- 8L | |
| 152 | P15- 9L | |
| 153 | P14- 7L | Old Bronze |
| 154 | P15- 9L | |

* Colors prepared under conditions of Table XXXIV.

This group varied only slightly, all colors were a medium brown or a green brown.

Color Chart 11.

| Sample | pH | Name of Color |
|--------|----|---------------|
|--------|----|---------------|

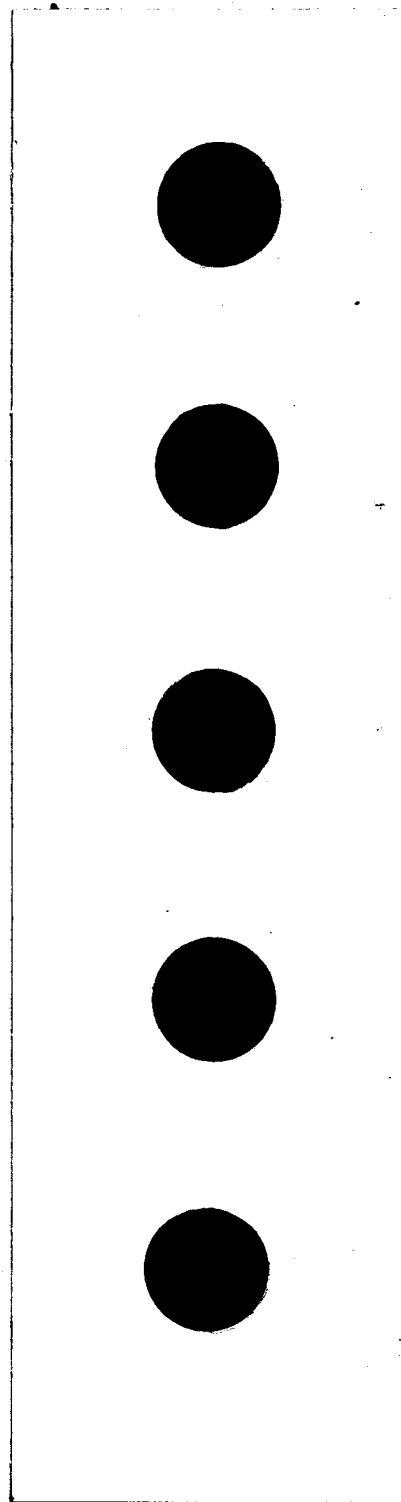
| | | |
|-----|---|-------|
| 150 | 7 | ----- |
|-----|---|-------|

| | | |
|-----|---|-------|
| 151 | 8 | ----- |
|-----|---|-------|

| | | |
|-----|---|-------|
| 152 | 9 | ----- |
|-----|---|-------|

| | | |
|-----|----|------------|
| 153 | 10 | Old Bronze |
|-----|----|------------|

| | | |
|-----|----|-------|
| 154 | 11 | ----- |
|-----|----|-------|



**General Comparison of Colors Prepared
from Zinc Nitrate.**

The precipitates from zinc nitrate and sodium dichromate were formed only when the basic salt of zinc hydroxide was present before striking. All the colors were brown except where the precipitate was intermingled with a light yellow color. The method of striking had little effect on the variation of the pulp color, since the two series of colors prepared by reverse methods of striking (Tables XXVIII and XXXIV) were practically the same. The other series of colors (Table XXXI) was more constant and the colors a more distinct brown than the other colors produced from zinc nitrate.

The mass tones were all browns or green-browns. The method of striking had little effect on the mass tones, as it had on the pulp colors. Most of the colors were a dirty color and not a good color as those produced from other metals.

CADMIUM CHROMATE

Cadmium Chromate.

Normal cadmium chromate has been prepared by S. H. C. Briggs (18) by heating a mixture of cadmium oxide and chromium trioxide in a sealed tube for three hours at 200 degrees Centegrade. It was also prepared by J. Schulze (8) from cadmium dichromate and cadmium hydroxide under practically the same conditions. The normal salt is a yellow crystalline powder. Basic salts have been formed that have a orange-yellow color varying slightly with different compositions. The basic chromate, according to F. Rose (19), has been used as a yellow pigment but its cost limits it to fine art work.

Table XXXVII.

Effect of Variation of Hydrogen Ion Concentration of
 Cadmium Nitrate Solutions with Nitric
 Acid and Sodium Hydroxide.
 (Sodium dichromate* added to cadmium nitrate)

| Sample | pH Cd(NO ₃) ₂ | Final E.M.F. (volts) | Final pH | Remarks |
|--------|---|----------------------------|-------------|---------------|
| 155 | 1 | -.5000 | | Soluble |
| 156 | 2 | -.2750 | 3.0 | " |
| 157 | 3 | -.2650 | 3.2 | " |
| 158 | 4 | -.2650 | 3.2 | " |
| 159 | 5 | -.2750 | 3.0 | " |
| 160 | 6 | -.2700 | 3.1 | " |
| 161 | 7 | -.2700 | 3.1 | " |
| 162 | 8 | -.1350 | 5.4 | Granular ppt. |
| 163 | 9 | -.0650 | 6.6 | " |
| 164 | 10 | -.0310 | 7.2 | " |
| 165 | 11 | -.0100 | 8.0 | " |

* The pH of the sodium dichromate 2.5.

The time of striking was 18 seconds.

It is interesting to note that no precipitate formed at a pH value below 3.1 for the mother liquor.

Table XXXVIII.

Comparison of Pulp Colors Prepared from Cadmium Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 162 | P9 - 1J | |
| 163 | P9 - 1K | |
| 164 | P9 - 1K | |
| 165 | P9 - 1L | |

* Colors prepared under conditions of

Table XXXVII.

This series of colors varied little, all were yellows characteristic of insoluble cadmium chromate. No break or offshades were noticed.

Table XXXIX.

Comparison of Mass Tone of Colors Prepared from Cadmium
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|----------------|
| 162 | P12- 4L | Sulphine Y |
| 163 | P10- 2L | |
| 164 | P12- 3K | Cloudy Amber |
| 165 | P12- 3L | Pyrite Y |

* Colors prepared in Table XXXVII.

All the colors were yellows with slight variations from a cream to a medium yellow.

Color Chart 12.





| Sample | pH | | Name of Color |
|--------|----|---|---------------|
| 162 | 8 |  | Sulphine Y |
| 163 | 9 |  | ----- |
| 164 | 10 |  | Cloudy Amber |
| 165 | 11 |  | Pyrite Y |

Table XL.

Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate added to cadmium nitrate.)*

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks |
|--------|--|-------------------|-------------|-------------|
| 166 | 1 | -.3350 | 2.0 | Soluble |
| 167 | 2 | -.2880 | 2.8 | " |
| 168 | 3 | -.2825 | 2.9 | " |
| 169 | 4 | -.2353 | 3.7 | Slight ppt. |
| 170 | 5 | -.2280 | 3.8 | " |
| 171 | 6 | -.2000 | 4.3 | " |
| 172 | 7 | -.2000 | 4.3 | " |
| 173 | 8 | -.1900 | 4.5 | " |
| 174 | 9 | -.1750 | 4.7 | " |
| 175 | 10 | -.1520 | 5.1 | " |
| 176 | 11 | -.1245 | 5.6 | " |

* The pH of the cadmium nitrate 4.0.

The precipitates from this series either dissolved or were of such small quantity that no further work could be done on them.

Table XLI.

Effect of Variation of Hydrogen Ion Concentration of
Cadmium Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.

(Cadmium nitrate added to the sodium dichromate.)*

| Sample | pH Cd(NO ₃) ₂ | E.M.F. (volts) | Final pH | Remarks |
|--------|---|-------------------|-------------|---------------|
| 177 | 1 | -.5000 | | Soluble |
| 178 | 2 | -.3160 | 2.3 | " |
| 179 | 3 | -.2900 | 2.8 | " |
| 180 | 4 | -.3000 | 2.6 | " |
| 181 | 5 | -.2860 | 2.8 | " |
| 182 | 6 | -.2835 | 2.9 | " |
| 183 | 7 | -.2625 | 3.2 | " |
| 184 | 8 | -.1595 | 5.3 | Granular ppt. |
| 185 | 9 | -.0875 | 6.2 | " |
| 186 | 10 | -.0680 | 6.5 | " |
| 187 | 11 | -.0450 | 6.9 | " |

* The pH of the sodium dichromate 2.5.

This series of colors is very comparable to
Table XXXVII, in the quantity of precipitate, the pH
at which precipitates formed and the color.

Table XLII.

Comparison of Pulp Colors Prepared from Cadmium Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 184 | P9 - 1L | |
| 185 | P9 - 1K | |
| 186 | P9 - 1K | |
| 187 | P9 - 1K | |

* Pulp colors prepared under conditions of

Table XLI.

All the colors were the characteristic
yellow of cadmium chromate, with No. 184 slightly
darker than others.

Table XLIII.

Comparison of Mass Tone of Colors Prepared from Cadmium
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 184 | P9 - 1L | |
| 185 | P9 - 1K | |
| 186 | P9 - 1K | |
| 187 | P9 - 1K | |

* Colors prepared from Table XLI.

All the colors were yellows.

Color Chart 13.

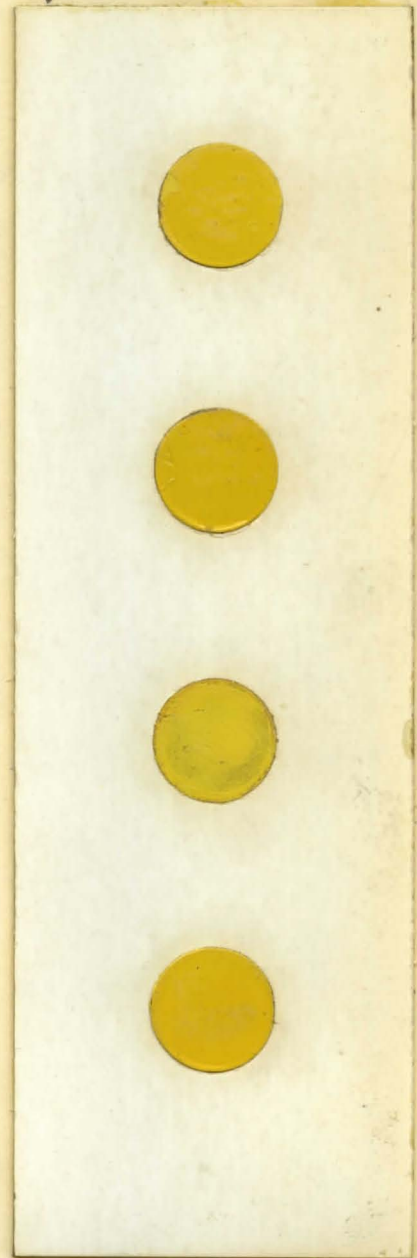
| Sample | pH | Name of Color |
|--------|----|---------------|
|--------|----|---------------|

| | | |
|-----|---|-------|
| 184 | 8 | ----- |
|-----|---|-------|

| | | |
|-----|---|-------|
| 185 | 9 | ----- |
|-----|---|-------|

| | | |
|-----|----|-------|
| 186 | 10 | ----- |
|-----|----|-------|

| | | |
|-----|----|-------|
| 187 | 11 | ----- |
|-----|----|-------|



**General Comparison of Colors Prepared
from Cadmium Nitrate.**

It will be noticed that only four colors in each group were compared, and that each color was formed from a solution with a final pH greater than 5.0. In Table XL the slight precipitate was not the color of cadmium chromate until the final pH of the solution was greater than 5.0. The precipitates that formed in solutions of lower final pH values dissolved when washed, and a very small quantity of precipitate formed in the solutions of pH value of 5.0 or greater. The quantity of precipitate in this group did not warrant further consideration.

The pulp colors and the mass tones were almost identical in each case. They were all yellows varying only slightly either to a cream or a medium yellow.

MERCURIC CHROMATE

Mercuric Chromate.

Normal mercuric chromate was prepared by A. Geuther (20) and A. J. Cox (21) by boiling equimolar parts of chromic oxide and yellow mercuric oxide with water. The normal salt hydrolyzes in cold water and $7\text{HgO} \cdot 2\text{CrO}_3$ is formed. Mercuric dioxochromate has been prepared by several experimenters, in as many processes. Its formula is $2\text{HgO} \cdot \text{HgCrO}_4$ or $3\text{HgO} \cdot \text{CrO}_3$. Many other basic salts have been prepared, and many complex salts form with mercury and chromium. The basic salts have been, according to F. Rose (19), used as pigments, under the common names of purple red or chrome red. F. Fichter (22) and G. Oesterheld (22) claim the color of the precipitate depends upon the temperature, a yellow or golden brown precipitate results from a cold solution with an excess of chromate, while a darker precipitate results from a hot solution. Basic mercuric chromate ($\text{Hg}_3\text{Cr}_3\text{O}_{15}$) results from hydrolysis of mercuric chromate in cold solutions. A brick red mercuric chromate ($\text{Hg}_6\text{Cr}_2\text{O}_9$) formed slowly in cold but rapidly in hot solutions when an excess of mercuric nitrate was present.

Table XLIV.

Effect of Variation of Hydrogen Ion Concentration of Sodium Dichromate Solutions with Nitric Acid and Sodium Hydroxide.

(Sodium dichromate added to Mercuric nitrate.)*

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | Excess | Remarks |
|--------|--|------------|-------------|
| 188 | 1 | Dichromate | Slight ppt. |
| 189 | 2 | " | Heavy ppt. |
| 190 | 3 | " | " |
| 191 | 4 | " | " |
| 192 | 5 | " | " |
| 193 | 6 | " | " |
| 194 | 7 | " | " |
| 195 | 8 | " | " |
| 196 | 9 | " | " |
| 197 | 10 | " | " |
| 198 | 11 | " | " |

* It was found impossible to obtain the pH of mercuric nitrate solutions with the quinhydrone electrode, so the pH of the sodium dichromate was varied and added to the mercuric nitrate solution, which was as near neutral as could be obtained without hydrolysis.

Table XLV.

Comparison of Pulp Colors Prepared from Mercuric Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|--------------------|
| 189 | P4 -11L | Redfeather, Buddha |
| 190 | P4 -12K | Brazil R |
| 191 | P3 -12I | Tomato R, Khiva |
| 192 | P4 -12K | Brazil R |
| 193 | P4 -12K | Brazil R |
| 194 | P3 -12H | |
| 195 | P3 -12J | Bitter Sweet |
| 196 | P3 -12J | Bitter Sweet |
| 197 | P3 -12J | Bitter Sweet |
| 198 | P3 -12K | |

* Pulp colors prepared under conditions of

Table XLIV.

The colors of this series varied from a deep red to a deep reddish orange, with no offshades. No. 191 (pH 4) was slightly lighter showing a reddish orange comparable to Nos. 195 - 198 (pH 8 - 11). There was the yellowish brown precipitate on top or the settled color similar to that already mentioned.

Table XLVI.

Comparison of Mass Tone of Colors Prepared from Mercuric Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|-------------------------|
| 188 | P6 -12F | |
| 189 | P4 -12I | Nasturtium |
| 190 | P6 -12K | Kobe |
| 191 | P4 -12I | Nasturtium |
| 192 | P6 -12L | Indian Red ^P |
| 193 | P4 -12J | Totem |
| 194 | P3 -12E | Burnt Orange |
| 195 | P3 -12E | Burnt Orange |
| 196 | P5 -12J | Monterey |
| 197 | P4 -12L | Buccaneer |
| 198 | P4 -12L | Buccaneer |

* Colors prepared under conditions of

Table XLIV.

The series of colors varied from a brown to a red orange. No. 188 was brown, Nos. 189 - 191 were a medium orange, Nos. 192 - 193 were red browns, Nos. 194 - 195 were a good orange, and Nos. 196 - 198 were a red brown.

Color Chart 14.












| Sample | pH | | Name of Color |
|--------|----|---|-------------------------|
| 188 | 1 |  | ----- |
| 189 | 2 |  | Nasturtium |
| 190 | 3 |  | Kobe |
| 191 | 4 |  | Nasturtium |
| 192 | 5 |  | Indian Red ^P |
| 193 | 6 |  | Toten |
| 194 | 7 |  | Burnt Orange |
| 195 | 8 |  | Burnt Orange |
| 196 | 9 |  | Monterey |
| 197 | 10 |  | Buccaneer |
| 198 | 11 |  | Buccaneer |

Table XLVII.

**Effect of Variation of Hydrogen Ion Concentration of
Mercuric Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Mercuric Nitrate^{*} added to sodium dichromate.)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | Excess | Remarks |
|--------|--|------------|------------|
| 199 | 1 | | Soluble |
| 200 | 2 | | " |
| 201 | 3 | | " |
| 202 | 4 | | " |
| 203 | 5 | Dichromate | Heavy ppt. |
| 204 | 6 | " | " |
| 205 | 7 | " | " |
| 206 | 8 | " | " |
| 207 | 9 | " | " |
| 208 | 10 | " | " |
| 209 | 11 | " | " |

* The pH of the Mercuric nitrate could not be determined with the quinhydrone electrode, so the solution was made as near neutral as could be obtained without hydrolysis.

The final E.M.F. was constant at $-.6490$ millivolts.

Table XLVIII.

Comparison of Pulp Colors Prepared from Mercuric Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|-------------------|
| 203 | P2 -12E | Midnight Sun |
| 204 | P2 -12F | Mandarin R |
| 205 | P2 -12G | Orange Vermillion |
| 206 | P2 -12G | Orange Vermillion |
| 207 | P2 -12G | Orange Vermillion |
| 208 | P2 -12G | Orange Vermillion |
| 209 | P2 -12G | Orange Vermillion |

* Pulp colors prepared under conditions
of Table XLVII.

The series varies little with no offshades.
Nos. 205 - 209 were the same, while the others were
only a slight shade lighter orange. All the colors
were a good orange.

Table XLIX.

Comparison of Mass Tons of Colors Prepared from Mercuric
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|------------------|
| 203 | P3 -12D | Tile R, Cherokee |
| 204 | P3 -12C | |
| 205 | P3 -12I | Tomato R, Khiva |
| 206 | P3 -12H | |
| 207 | P3 -12H | |
| 208 | P3 -12H | |
| 209 | P3 -12H | |

* Colors prepared under conditions of

Table XLVII.

This series varied little all being orange. Nos. 203 - 204 were a light shade of orange, No. 204 a more reddish orange, and the others (Nos. 206 - 209) were typical oranges.

Color Chart 15.

| Sample | pH | Name of Color |
|--------|----|---------------|
|--------|----|---------------|

| | | |
|-----|---|--------------------|
| 203 | 5 | Tile R Cherokee |
|-----|---|--------------------|

| | | |
|-----|---|-------|
| 204 | 6 | ----- |
|-----|---|-------|

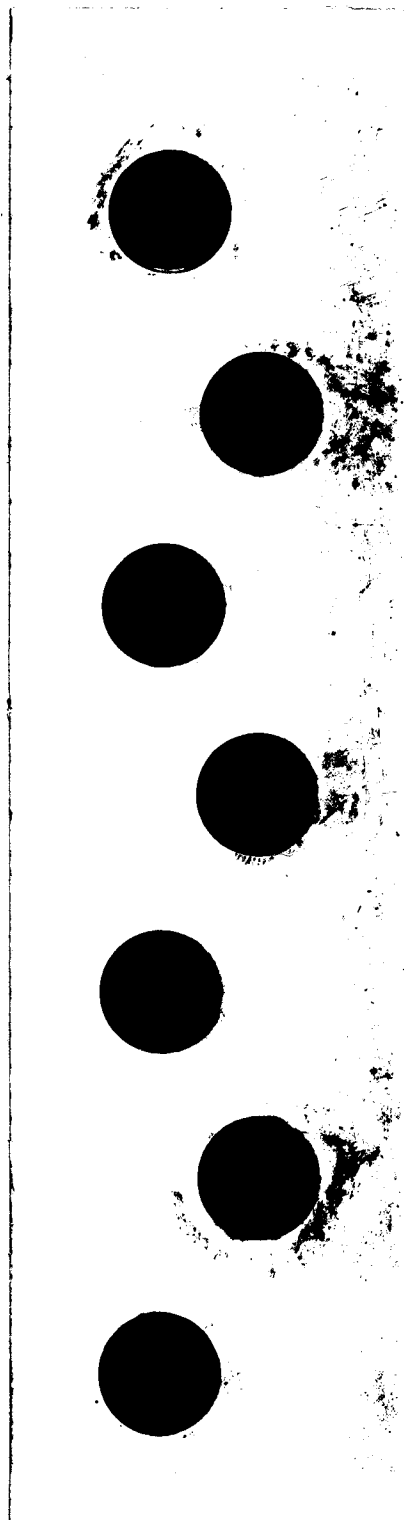
| | | |
|-----|---|-------------------|
| 205 | 7 | Tomato R Khiva |
|-----|---|-------------------|

| | | |
|-----|---|-------|
| 206 | 8 | ----- |
|-----|---|-------|

| | | |
|-----|---|-------|
| 207 | 9 | ----- |
|-----|---|-------|

| | | |
|-----|----|-------|
| 208 | 10 | ----- |
|-----|----|-------|

| | | |
|-----|----|-------|
| 209 | 11 | ----- |
|-----|----|-------|



**General Comparison of Colors Prepared
from Mercuric Nitrate.**

Since it was found to be impossible to obtain the pH of mercury ion solutions with the Quinhydrone electrode, the final E.M.F. of the solutions were undoubtedly not true pH values. The quantity of precipitate in each series was almost the same. The pulp colors of the precipitates from the two groups of colors were very different, having only a slight resemblance in all being some shade of red or orange.

The mass tones of the two series of colors were very different. The first group of colors was very variable (from a brown to a red), while the second group was very constant. No colors were the same in the two series.

ALUMINUM CHROMATE

Aluminum Chromate.

According to Moller (23) no satisfactory evidence has been obtained that aluminum chromate exists as a normal salt, but all evidence proves several basic salts have been identified. Some experimenters claim aluminum dioxychromate, $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, is formed when a solution of potassium alum and potassium chromate were mixed. Others claim it is impossible to obtain such a precipitate from these solutions. M. Gröger (24) obtained a yellow precipitate from aluminum chloride and potassium chromate. When the ratio of aluminum chloride and potassium chromate was one mole to three moles the precipitation was complete. S.H.C. Briggs (25) obtained, by experiments similar to those already discussed, a lemon yellow, insoluble product which corresponded to aluminum oxydichromate, $3\text{Al}_2\text{O}_3 \cdot 2\text{CrO}_3 \cdot 6\text{H}_2\text{O}$.

Table L.

Effect of Variation of Hydrogen Ion Concentration of
Aluminum Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate^{*} added to aluminum nitrate)

| Sample | pH Al(NO ₃) ₃ | E.M.F. (volts) | Final pH | Remarks |
|--------|---|-------------------|-------------|-------------|
| 210 | 1 | | | Soluble |
| 211 | 2 | | | " |
| 212 | 3 | | | " |
| 213 | 4 | -.3485 | 1.8 | Slight ppt. |
| 214 | 5 | -.2550 | 3.4 | Heavy ppt. |
| 215 | 6 | -.1530 | 5.1 | " |
| 216 | 7 | -.1350 | 5.4 | " |
| 217 | 8 | -.1105 | 5.8 | " |
| 218 | 9 | -.0900 | 6.2 | " |
| 219 | 10 | -.0510 | 6.8 | " |
| 220 | 11 | +.0530 | 8.6 | " |

* The pH of the sodium dichromate 2.5

At pH of 4 (No. 213) Al(OH)₃ was precipitated,
and at pH of 11 (No. 220) sodium aluminate was formed.
All the chromate color was washed from the precipitate
leaving only aluminum hydroxide.

TITANIUM CHROMATE

Titanium Chromate.

M. Blondel (26) found that a concentrated aqueous solution of chromic acid dissolved titanous acid in amounts depending on the concentration and temperature of the solution and the previous history of the titanous acid. He obtained several basic salts of titanium chromate from the above solutions. Some of the salts he prepared are listed below. Titanium tetroxychromate ($3\text{TiO}_2 \cdot 2\text{CrO}_3 \cdot \text{H}_2\text{O}$), Titanium trioxychromate ($\text{TiO}_2(\text{TiO})\text{CrO}_4 \cdot 2\text{H}_2\text{O}$), Titanium pentoxychromate ($2\text{TiO}_2(\text{TiO})\text{CrO}_4 \cdot 3\text{H}_2\text{O}$). These compounds have not yet been verified.

In this investigation titanium trichloride and sodium dichromate was used. It was found impossible to obtain the pH of the titanium solutions with the quinhydrone electrode so samples were tried from acid and basic solutions to determine what effect such hydrogen ion concentrations would have on the solutions when mixed.

From the acid solutions no precipitate formed, but from the basic solutions where a heavy precipitate of the basic titanium salt had been formed a greenish gray precipitate formed which when thoroughly washed left only the basic titanium salt.

STANNOUS CHROMATE

Stannous Chromate.

J. J. Berzelius (29) found that when stannous chloride is added to an excess of a solution of potassium chromate, and the liquid agitated, yellow, curdy flocks of stannous chromate are precipitated. He also observed that if to a solution of stannous chloride a dilute solution of potassium chromate is added in small portions at a time, with constant agitation, a greenish precipitate of chromic stannate is formed. If the solution of the tin salt contains free acid, no precipitate is formed and the solution is green.

In this investigation stannous chloride was used. It was found to be impossible to obtain the pH of stannous chloride solutions with the quinhydrone electrode. Samples were tried with an acid solution of stannous chloride which contained no hydrolyzed salt. In each case the solution when dichromate was added formed no precipitate. When more basic solutions were used the basic salt was formed, and a colored precipitate was obtained, which however lost all its color when thoroughly washed, and the white hydrolyzed stannous precipitate remained.

When the sodium dichromate was added to the more acid solutions the solutions turned green, showing the formation of chromium stannate. When the solution contained only a small amount of precipitated stannous salt before striking the green solution formed, but where large amounts of the precipitate was present no green formed. All the solutions showing the green chromium stannate formation were very acid to litmus.

ARSENIC CHROMATE

Arsenic Chromate.

A review of the literature revealed no information on the compounds of arsenic and chromium, either as chromates or chromites.

Table LI.

Effect of Variation of Hydrogen Ion Concentration of Arsenic Oxide Solutions with Hydrochloric Acid and Sodium Hydroxide.

(Sodium dichromate* added to arsenic oxide.)

| Sample | pH As ₂ O ₃ | Final E.M.F. (volts) | pH | Remarks |
|--------|--------------------------------------|----------------------------|-----|---------------|
| 221 | 1 | | | Soluble |
| 222 | 2 | | | " |
| 223 | 3 | | | " |
| 224 | 4 | | | " |
| 225 | 5 | -.0835 | 6.3 | granular ppt. |
| 226 | 6 | -.0560 | 6.7 | " |
| 227 | 7 | -.0400 | 7.0 | " |
| 228 | 8 | -.0200 | 7.3 | " |
| 229 | 10 | -.0000 | 7.6 | " |

* The pH of the sodium dichromate 2.5.

On mixing the solutions no noticeable

reaction took place but upon agitation for approximately two or three minutes a greenish precipitate formed. It required a large amount of sodium hydroxide to obtain the pH values from which the precipitate formed.

Table LII.

Comparison of Pulp Colors Prepared from Arsenic Oxide
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 225 | P21- 7E | |
| 226 | P21- 7E | |
| 227 | P21- 7E | |
| 228 | P21- 7D | |
| 229 | P18- 7C | |

* Pulp colors prepared under conditions of Table LI.

All the colors were practically the same shade of green. No. 225 was more flocculent than the others and had several shades of color heterogeneously mixed in it. The higher the pH the more homogeneous the color.

Table LIII.

Comparison of Mass Tone of Colors Prepared from Arsenic
Oxide and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|----------------|
| 225 | P31-10H | Marine Green - |
| 226 | P31-11E | |
| 227 | P31-12E | |
| 228 | P31-11C | |
| 229 | P31-12C | |

* Colors prepared under conditions of
Table LI.

This group of colors were all practically
the same. Nos. 226 - 228 were medium greens while
Nos. 225 and 229 were slightly darker.

Color Chart 16.

Sample pH

Name of Color

225 5

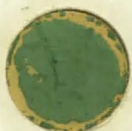


Marine Green

226 6



227 7



228 8



229 10



ANTIMONY CHROMATE

Antimony Chromate.

No evidence has been produced to show that antimony forms a normal chromate. S.H.C. Briggs (25) in experiments similar to those in which he formed many normal chromates produced, by varying the amounts of reactants, two different compounds of definite composition. One was antimony oxychromite ($2Sb_2O_3 \cdot Cr_2O_3$), and the other antimony tetroxybischromate ($3SbO_2 \cdot 2CrO_3$). The former was a brown powder insoluble in alkali-lye, water, acids and aqua regia. The latter was orange-yellow, insoluble in water, and slowly soluble in nitric acid. The reactants used were antimony oxide, chromic oxide, and water. The latter two reactants were varied in the experiments.

In this investigation antimony trichloride solutions were used. Several samples at different pH values were struck with sodium dichromate solution. In each case any precipitate that formed washed completely free of chromate after one or two washings. No further study was made of this group.

BISMUTH CHROMATE

Bismuth Chromate.

Normal bismuth chromate has not yet been prepared but several complex and basic salts have been. Most of these basic and complex salts were prepared from hot concentrated solutions of bismuth nitrate and potassium chromate or dichromate. J. Löwe (30) prepared a substance, probably bismuthyl paradichromate, by pouring a solution of bismuth nitrate, containing as little free nitric acid as possible, into an excess of a solution of potassium chromate. The product was a lemon yellow, micro-crystalline powder, which formed a red basic salt when boiled with soda-lye. M. K. P. Muir (31) obtained bismuthyl chromate $((\text{BiO})_2\text{CrO}_4)_2$, a red powder, from a mixture of solutions of bismuth nitrate and potassium chromate or dichromate and a few drops of nitric acid, when the solutions were boiled for several hours. J. Löwe (30) obtained bismuth hydroxy-chromate from nearly neutral solutions of the nitrate and an excess of potassium dichromate by boiling the solutions for some time.

Table LIV.

**Effect of Variation of Hydrogen Ion Concentration of
Bismuth Trinitrate Solutions with Nitric
Acid and Sodium Hydroxide.**

(Sodium dichromate* added to bismuth trinitrate)

| Sample | pH Bi(NO ₃) ₃ | Final E.M.F. (volts) | Final pH | Remarks |
|--------|---|----------------------------|-------------|-----------------|
| 230 | 1 | | | Soluble |
| 231 | 2 | -.4710 | | Flocculent ppt. |
| 232 | 3 | -.4595 | | " |
| 233 | 4 | -.3900 | 1.1 | " |
| 234 | 5 | -.3550 | 1.7 | Granular ppt. |
| 235 | 6 | -.3400 | 1.9 | " |
| 236 | 7 | -.1000 | 6.0 | " |
| 237 | 8 | -.2400 | 3.6 | " |
| 238 | 9 | -.2000 | 4.2 | " |
| 239 | 10 | -.2150 | 4.0 | " |
| 240 | 11 | -.2020 | 4.2 | " |

* The pH of the sodium dichromate 2.5

At pH of 2 and 3 the color was soluble until nearly all the dichromate solution had been added to the bismuth solution. Below the pH of 5 the solution was free of precipitate of bismuth hydroxide which formed at that pH.

Table LV.

**Comparison of Pulp Colors Prepared from Bismuth Nitrate
and Sodium Dichromate.***

| Sample | Index | Name of Color |
|--------|---------|-----------------------------|
| 231 | P9 - 5L | |
| 232 | P9 - 5L | |
| 233 | P10- 5L | Primerlin Y, Golden Red |
| 234 | P10- 4L | Light Chrome Y ^P |
| 235 | P10- 4L | Light Chrome Y ^P |
| 236 | P13- 7L | Tensel, Deep Stone |
| 237 | P10- 5J | Corn |
| 238 | P10- 5J | Corn |
| 239 | P10- 5J | Corn |
| 240 | P10- 5J | Corn |

* Colors prepared under conditions of

Table LIV.

This group of colors varied from a light orange to a yellow at No. 233, then to a slightly darker yellow at No. 235. Nos. 236 - 240 all had about the same color with a definite metallic luster.

Table LVI.

Comparison of Mass Tone of Colors Prepared from Bismuth Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|-----------------------------------|
| 231 | P14- 9L | |
| 232 | P15-11L | Buffalo |
| 233 | P15-12L | Partridge, Raw Umber ^P |
| 234 | P10- 4J | Primrose Y, Snapdragon |
| 235 | P12- 7L | Burnished Gold |
| 236 | P11- 2J | Pinapple |
| 237 | P11- 5J | Buttercup |
| 238 | P11- 4J | Mustard |
| 239 | P11- 4J | Mustard |
| 240 | P12- 4L | Sulphine Y |

* Colors prepared under conditions of

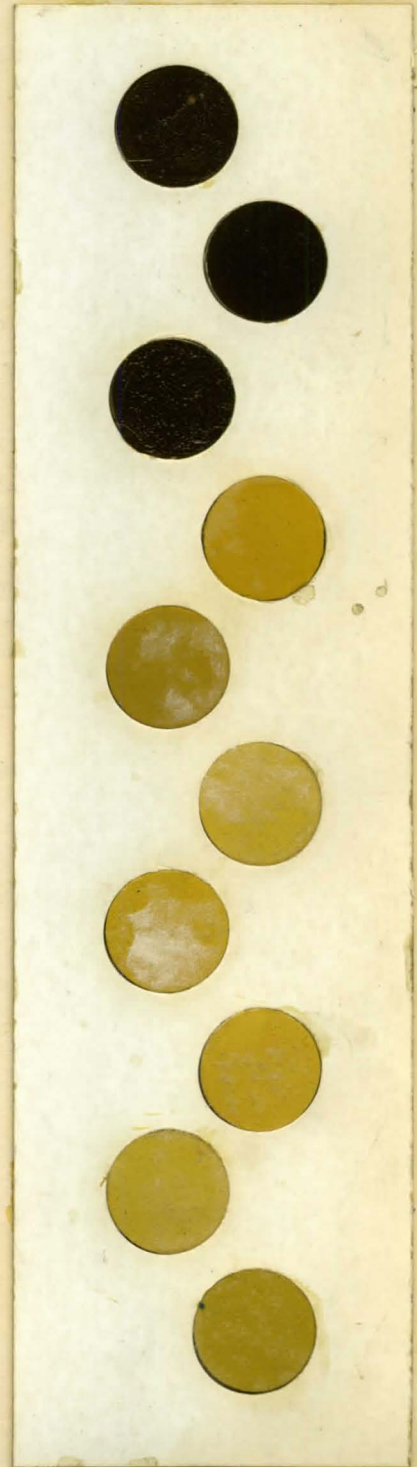
Table LIV.

This group of colors was very variable.

Nos. 231 - 233 were browns, No. 234 was a medium yellow No. 235 a tan, and Nos. 236 - 240 were a light tan or a cream. The break was at PH of 4 (No. 233) from a brown to a yellow.

Color Chart 17.

| Sample | pH | Name of Color. |
|--------|----|-------------------------------------|
| 231 | 2 | ----- |
| 232 | 3 | Buffalo |
| 233 | 4 | Partridge Raw Umber ^P |
| 234 | 5 | Primrose Y Snapdragon |
| 235 | 6 | Burnished Gold |
| 236 | 7 | Pinnacle |
| 237 | 8 | Buttercup |
| 238 | 9 | Mustard |
| 239 | 10 | Mustard |
| 240 | 11 | Sulphine Y |



IRON CHROMATE

Iron Chromate.

It is scarcely to be expected that normal ferrous chromate could be prepared in aqueous solutions because of the oxidizing power of the chromates and chromic acid. L.M. Vauquelin (3) obtained a yellowish-brown precipitate from ferrous sulphate and potassium chromate, which upon analysis was found to be a basic complex ferric salt. Several experimenters failed to obtain the normal ferric chromate. Ferryl chromate ($(\text{FeO})_2\text{CrO}_4$) a brown precipitate is prepared by the action of potassium chromate on a solution of a ferric salt.

In this investigation both the ferrous and the ferric chloride solutions were used. As the sodium hydroxide was added to the ferrous salt, ferrous hydroxide was precipitated which soon changed to the ferric hydroxide. The precipitate that formed, when the solutions of varying hydrogen ion concentrations were struck with the dichromate solution, had the characteristic appearance and color of ferric hydroxide, so were not studied further.

When the pH of the ferric salt was varied and the solution struck with dichromate solution, the

solution changed color, varying as the pH value increased. When the solution was basic enough to precipitate ferric hydroxide before striking, a brown precipitate formed that was a little darker than those previously formed. Each washing removed some of the chromate from the precipitate, until only the ferric hydroxide was left.

COBALT CHROMATE

Cobalt Chromate.

Potassium chromate with solutions of cobalt salts gives reddish-brown precipitates which are probably a basic salt. Briggs (18) obtained the normal cobaltous chromate, greyish-black crystalline substance, by a method similar to those he used for the preparation of other chromates, by heating the carbonate in chromic acid at high temperatures in a sealed tube. C. Freese (6) precipitated the cobaltous oxychromate from boiling solutions of potassium chromate and a cobaltous salt. More complex salts of cobalt and chromium have been prepared than possibly any other element and chromium.

Table LVII.

Effect of Variation of Hydrogen Ion Concentration of
Cobaltous Chloride Solutions with Sodium
Hydroxide and Hydrochloric Acid.
(Sodium Dichromate* added to cobaltous chloride.)

| Sample | pH CoCl ₂ | R.M.F. (volts) | Final pH | Remarks |
|--------|-------------------------|-------------------|-------------|------------|
| 241 | 1 | | | Soluble |
| 242 | 2 | | | " |
| 243 | 3 | | | " |
| 244 | 4 | | | " |
| 245 | 5 | | | " |
| 246 | 6 | | | " |
| 247 | 7 | | | " |
| 248 | 8 | -.0330 | 7.1 | Heavy ppt. |
| 249 | 9 | -.0190 | 7.3 | " |
| 250 | 10 | -.0165 | 7.4 | " |
| 251 | 11 | -.0105 | 7.5 | " |

* the Ph of the sodium dichromate 2.5.

The precipitates were formed from the basic
salt which was either a light blue or almost a purple.

Table LVIII.

Comparison of Pulp Colors Prepared from Cobaltous Chloride
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|--------------------------|
| 248 | PS -10L | Java, Nomad Brown |
| 249 | PS -11L | Leaf Mold, Weathered Oak |
| 250 | PS -12L | Mandalay, Friar |
| 251 | PS -11L | Leaf Mold, Weathered Oak |

* Colors prepared under conditions of

Table LVII.

All the colors were a deep brown, and all practically the same. Nos. 248 - 249 were slightly redder than others.

Table LIX.

Comparison of Mass Tons of Colors Prepared from Cobaltous
Chloride and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|---------------|
| 248 | PS--10H | Chocolate |
| 249 | PS -10H | Chocolate |
| 250 | PS -10H | Chocolate |
| 251 | PS -10H | Chocolate |

* Colors prepared under conditions of

Table LVII.

All the colors were identical, being a chocolate brown.

Table IX.

Effect of Variation of Hydrogen Ion Concentration of
Sodium Dichromate Solutions with Sodium
Hydroxide and Hydrochloric Acid.

(Sodium dichromate added to cobaltous chloride.)*

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks |
|--------|--|-------------------|-------------|------------|
| 252 | 1 | | | Soluble |
| 253 | 2 | | | " |
| 254 | 3 | | | " |
| 255 | 4 | | | " |
| 256 | 5 | | | " |
| 257 | 6 | | | " |
| 258 | 7 | | | " |
| 259 | 8 | -.0700 | 6.5 | Heavy ppt. |
| 260 | 9 | -.0625 | 6.6 | " |
| 261 | 10 | -.0750 | 6.4 | " |
| 262 | 11 | -.0810 | 6.3 | " |

* The pH of the cobaltous chloride 6.5.

This group very similar to those in Table

LVII.

Table LXI.

Comparison of Pulp Colors Prepared from Cobaltous chloride
and Sodium Dichromate.*

| Sample | Index | Name of Color. |
|--------|---------|----------------|
| 259 | P7 -12E | Cocoa, Turtle |
| 260 | P7 -12E | Cocoa, Turtle |
| 261 | P7 -12H | Mohawk, Mecca |
| 262 | P7 -12H | Mohawk, Mecca |

* Colors prepared under conditions of

Table IX.

All colors were a medium brown.

Table LXII.

Comparison of Mass Tone of Colors Prepared from Cobaltous
Chloride and Sodium Dichromate.*

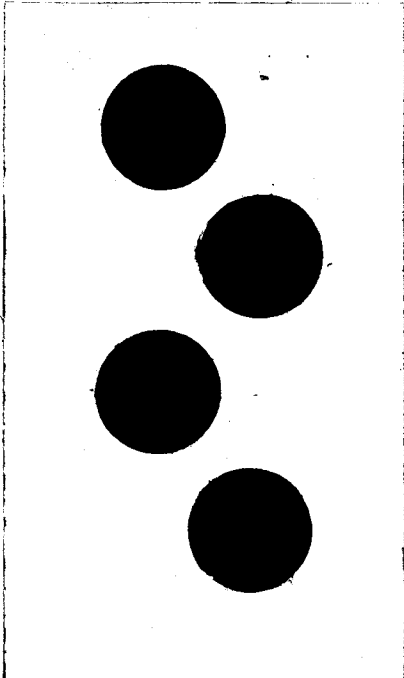
| Sample | Index | Name of Color. |
|--------|---------|-----------------|
| 259 | P8 -12L | Mandalay, Friar |
| 260 | P8 -12L | Mandalay, Friar |
| 261 | P8 -12L | Mandalay, Friar |
| 262 | P8 -12L | Mandalay, Friar |

*Colors prepared under conditions of

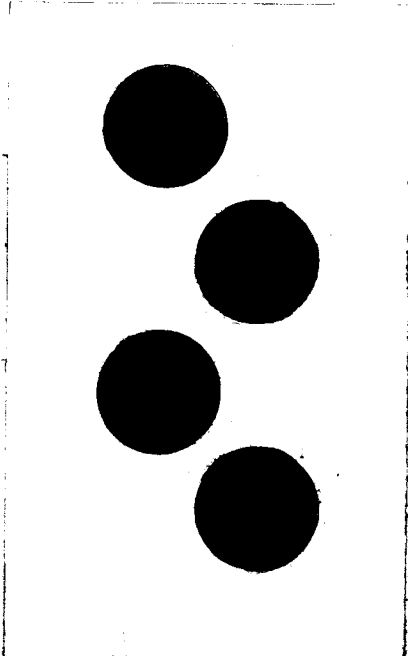
Table IX.

All colors were a medium brown.

Color Chart 18.

| Sample | pH | | Name of Color |
|--------|----|--|---------------|
| 248 | 8 |  | Chocolate |
| 249 | 9 | | Chocolate |
| 250 | 10 | | Chocolate |
| 251 | 11 | | Chocolate |

Color Chart 19.

| | | | |
|-----|----|---|-------------------|
| 259 | 8 |  | Mandaley Friar |
| 260 | 9 | | Mandaley Friar |
| 261 | 10 | | Mandaley Friar |
| 262 | 11 | | Mandaley Friar |

NICKEL CHROMATE

Nickel Chromate.

Briggs (18) obtained the normal chromate by methods similar to those already discussed in the preparation of other chromates. He said that altho nickel chromate is insoluble in water it will not precipitate from nickel salt solutions and it must therefore be polymerized. The normal nickel salt he prepared was a black crystalline substance. When nickel hydroxide was dissolved in chromic acid a yellow solution was formed, which deposited non-deliquescent red crystals. R. Tuppute (32) observed that if the solution was treated with nickel carbonate or an alkali-lye, a reddish-yellow insoluble powder of nickel oxychromate was deposited. M. Greger (33) obtained a brown amorphous precipitate from a mixture of 3 normal sodium chromate and normal nickel chromate, which was probably a basic sodium nickel chromate. He obtained a reddish brown precipitate from similar solutions of potassium chromate and nickel chromate, which became potassium nickel chromate when allowed to stand under its mother liquor.

Table LXIII.

Effect of Variation of Hydrogen Ion Concentration of
Nickel Nitrate Solutions with Nitric
Acid and Sodium Hydroxide.

(Sodium dichromate added to nickel nitrate.)

| Sample | pH $\text{Na}_2\text{Cr}_2\text{O}_7$ | E.M.F. (volts) | Final pH | Remarks |
|--------|--|-------------------|-------------|-------------|
| 263 | 1 | | | Soluble |
| 264 | 2 | | | " |
| 265 | 3 | | | " |
| 266 | 4 | | | " |
| 267 | 5 | | | " |
| 268 | 6 | | | " |
| 269 | 7 | -.1825 | 4.6 | Slight ppt. |
| 270 | 8 | -.0440 | 6.9 | Heavy ppt. |
| 271 | 9 | -.0105 | 7.5 | " |
| 272 | 10 | -.0050 | 7.6 | " |
| 273 | 11 | -.0805 | 9.0 | " |

* The pH of the sodium dichromate 2.5.

No nickel was precipitated at the pH value of 6 before striking, at pH value of 7 a slight precipitate formed, and above a pH of 7 a heavy precipitate of nickel hydroxide was formed.

Table LXIV.

Comparison of Pulp Colors Prepared from Nickel Nitrate
and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|-----------------------|
| 270 | P6 -12E | Copper Br |
| 271 | P6 -12E | Copper Br |
| 272 | P6 -12E | Copper Br |
| 273 | P7 -12E | Cocoa, Turtle, Sahara |

* Pulp colors prepared under conditions of
Table LXIII.

All colors were a brown varying only slightly
to a red brown at No. 273.

Table LXV.

Comparison of Mass Tone of Colors prepared from Nickel
Nitrate and Sodium Dichromate.*

| Sample | Index | Name of Color |
|--------|---------|-----------------|
| 270 | P8 -10J | Falcon, Muskrat |
| 271 | P8 -10J | Falcon, Muskrat |
| 272 | P8 -10J | Falcon, Muskrat |
| 273 | P8 -10J | Falcon, Muskrat |

* Colors prepared under conditions of
Table LXIII.

All colors were identical being a dark
red brown.

Color Chart 20.

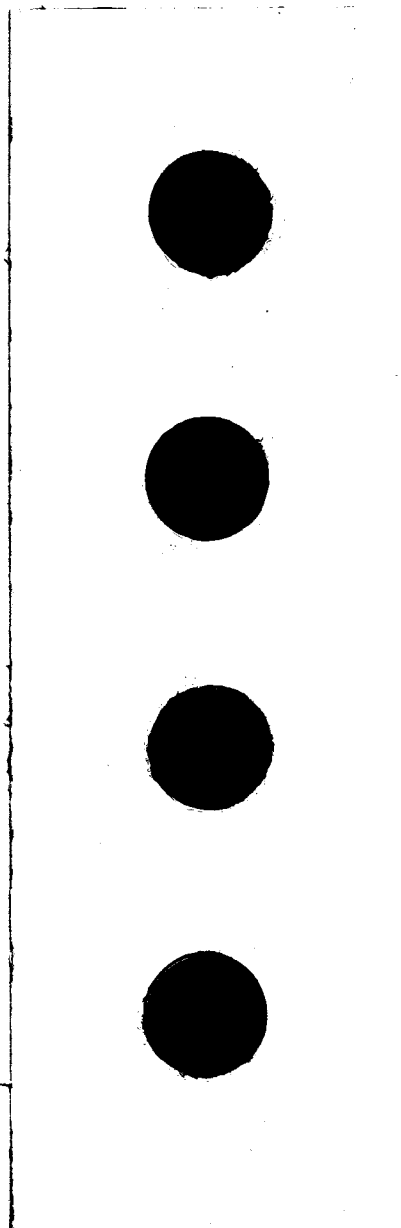
| Sample | pH | Name of Color |
|--------|----|---------------|
|--------|----|---------------|

| | | |
|-----|---|-------------------|
| 270 | 8 | Falcon Muskrat |
|-----|---|-------------------|

| | | |
|-----|---|-------------------|
| 271 | 9 | Falcon Muskrat |
|-----|---|-------------------|

| | | |
|-----|----|-------------------|
| 272 | 10 | Falcon Muskrat |
|-----|----|-------------------|

| | | |
|-----|----|-------------------|
| 273 | 11 | Falcon Muskrat |
|-----|----|-------------------|



SUMMARY

Summary.

The precipitates prepared in this investigation were either yellows, reds or some combination of these except in the case of arsenic, in which case the precipitate was a green. The precipitates in many cases did not form from acid solutions and in cases in which they did form the precipitate was usually very definite in color, and varied only slightly. Precipitates that formed from neutral or basic solutions were variable in color and in some cases were entirely different from that formed in the acid solutions. It is believed that the variable colors are due to variable basic chromates.

The method of striking had little or no effect on the color in most cases, since most of the groups of colors prepared by reverse methods of striking were very comparable, and in some cases were identical.

The effect of the variation of the hydrogen ion concentrations had a marked effect in most cases, and in all cases slightly varying colors were produced. The variation of the hydrogen ion concentration of the metallic salt had a more marked effect on the color

than the variation of the pH of the sodium dichromate. The colors prepared from solutions that had the pH of the sodium dichromate varied were more or less constant in color with the increase in the PH. The precipitates formed from solutions that had the hydrogen ion concentration of the metallic ion solution varied were, in many cases, very different and in some cases even the character of the precipitate changed as the pH value was increased. The change in the color at a particular pH was not as definite as that of lead chromate, investigated by Ernst (1) and others, although many of the groups had a definite change at about the same pH value as that of the lead chromate (pH of 8). This change was usually to a darker color. It was noticed that for a particular metal, except those that formed completely insoluble chromates, the precipitate formed in solutions having a final pH of approximate the same, regardless of the method of striking, or the solution that had the hydrogen ion concentration varied.

No attempt was made to determine the composition of the precipitated colors.

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