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Lead chromate : the relation of the hydrogen ion concentration, dispersion and chemical constitution to the color of lead chromate pigments.

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UNIVERSITY OF LOUISVILLE

LEAD CHROMATE

THE RELATION OF THE HYDROGEN ION
CONCENTRATION, DISPERSION AND CHEMICAL
CONSTITUTION TO THE COLOR OF LEAD
CHROMATE PIGMENTS

A DISSERTATION
SUBMITTED TO THE FACULTY
OF THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE
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MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

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By
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1932

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The
Author Wishes
To Acknowledge His
Appreciation
For All the Kind and Valuable Aid
Given by Dr. R. C. Ernst,
Who Directed This Research.

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INTRODUCTION

Lead chromates are used extensively for pigments. Their color is of great importance, and much attention has been given by investigators and manufacturers to processes and condition of preparation which control the clarity and uniformity of color.

Lead chromate pigments are prepared by the addition of sodium or potassium chromate or dichromate to a solution of a soluble salt of lead, usually lead acetate or nitrate. The color of the pigment obtained by this method of precipitation varies from a medium yellow to a deep orange depending upon conditions of concentration, temperature, acidity and basicity both before and after precipitation.

This investigation was carried out to determine whether the color of the lead chromates resulting from precipitation under varying hydrogen ion concentration was caused by a difference in

particle size, chemical composition, or a combined effect of both.

A study of lead chromate from lead acetate was made by K. Jablonsynski (1) who found that freshly precipitated lead chromate gradually became orange in color. If precipitated from a normal lead acetate solution the lead chromate did not change color while in contact with the mother liquor even on boiling, but changed quickly upon filtering. When basic lead acetate was used the color changed from a golden yellow to a bright red. Jablonsynski attributed this to a loss of water by the basic lead chromate, $Pb_3(OH)_2CrO_4$, to form $PbCrO_4 \cdot PbO$. He concluded that normal lead chromate was slightly soluble, yielding Pb^{++} and CrO_4^{--} ions, the Pb^{++} ions combining with the OH^- ions of the water to form $PbOH^+$ ions, which in turn united with the CrO_4^{--} ions giving $Pb_3(OH)_2CrO_4$, the parent substance of 'chrome red'.

G. Zerr and R. Rubencamp (2) in their

study of lead chromates found that the color varied, depending upon: (a) the concentration of the reacting substances; (b) the temperature of the solutions; (c) the method of reaction -- whether the lead solution was struck into the dichromate solution or vice versa; (d) the rate of mixing the two solutions and; (e) the manner of washing the precipitate.

The effect of the concentration, temperature, basicity, and particle size on the color of lead chromates was investigated by E. E. Free (3). He found that: (a) the particle size varied with the temperature and concentration of the lead nitrate and potassium chromate solutions; (b) an increase in basicity deepened the color and displaced the maximum spectral intensity towards the red; (c) the larger the particles the deeper the color; (d) an increase in temperature varied the color from a very decided yellow to a deep red.

The reaction between lead sulphate and potassium chromate was studied by Milbauer and Kohn⁹ (4). They found that various shades of lead chromate were produced depending upon the concentration and the temperature and time of the reaction.

The color change which lead chromates undergo in the process of drying was investigated by L. Boek³ (5). He attributed this variation in color to a change in physical structure from an amorphous to a crystalline state, and not to a change in chemical composition.

Max Groger (6) studied the reaction between lead acetate and potassium chromate from a standpoint of chemical composition. His results show that the precipitation of normal lead acetate solutions with an equivalent amount of potassium chromate yields an amorphous substance of the composition $\text{CrO}_3 \cdot 0.992\text{PbO} \cdot 0.102\text{K}_2\text{O}$. When precipitated with an excess of potassium chromate a crystalline

precipitate results of the composition $\text{CrO}_3 \cdot 0.953\text{PbO} \cdot 0.049\text{K}_2\text{O}$. Repeated evaporation of an excess of potassium acetate solution with powdered lead chromate gave, after washing with water, a residue approximating the formula $2\text{PbCrO}_4 \cdot \text{K}_2\text{CrO}_4 \cdot \text{H}_2\text{O}$.

J. W. Bain's (7) study of lead chromate pigments led to the conclusions that: (a) the chemical composition of lead chromate was constant although the particle size varied; (b) an increase in particle size resulted in a corresponding darkening of color up to a definite maximum attained at 2.3μ ; (c) an excess of potassium dichromate favored the formation of the orange-yellow pigment while an excess of lead acetate inhibited it; (d) the use of the theoretical amounts of the reacting substances gave the orange-yellow precipitate; and (e) the subsequent filtration and washing of the pale yellow precipitate resulted in the formation of the orange-yellow variety.

According to J. S. Remington (8), when lead chromate is precipitated in an excess of lead

acetate the yellow color does not change if left in contact with the mother liquor or even when boiled, but if decanted and washed with water or acetic acid it acquires an orange tint. In the presence of an excess of basic lead acetate the color changes gradually over to red due to the reaction,

$$\text{Pb}_2(\text{OH})_2\text{CrO}_4 = \text{PbCrO}_4 \cdot \text{PbO} + \text{H}_2\text{O}.$$

R. C. Ernst, E. Pragoff, and E. E.

Litkenhous (9) investigated the effect of the hydrogen ion concentration on the color of lead chromates prepared from lead acetate and potassium dichromate. Their results that the color of the lead chromate varied from yellow at a pH of 3.5 and up to a pH of 9.0, where a sharp change to orange occurred. Above a pH of 9.0 off shades resulted.

This investigation was further extended by R. C. Ernst and A. J. Snyder (10) to chromates prepared from lead nitrates and acetates with sodium and potassium dichromates. The hydrogen

ion concentration was regulated with nitric and acetic acids, and sodium and potassium hydroxides. Their results showed that the acetate series gave lighter shades than the corresponding nitrate series, and that the potassium dichromate gave darker tints than the sodium dichromate. In all cases they obtained yellow pigments below a pH of 9.0 and orange pigments at and above a pH of 9.0.

This investigation is for the purpose of determining the relation between the color, particle size, and chemical constitution of lead chromate pigments when precipitated from solutions of varying hydrogen ion concentrations.

THEORETICAL

Lead chromate pigments precipitated from lead acetate and nitrate with potassium and sodium dichromates vary in color from yellowyellows to distinct oranges. This variation in color has been found to depend upon: (a) concentration of reacting solutions; (b) temperature of reactions; (c) time of reaction; (d) acidity or basicity of solutions; and (e) particle size.

The concentration of the reacting solutions was studied by E. E. Free (3) who found that concentrated solutions gave yellow precipitates while dilute solutions gave orange colored precipitates. His conclusions are open to the objection that in dilute solutions the lead salt is hydrolyzed, thus changing the hydrogen ion concentration which in turn varies the color of the precipitates. Experiments carried on in this laboratory show that lead chromates prepared from varying concentrations of lead acetate and potassium dichromate, the hydrogen ion concentration being held constant, did not change in color, but were yellow below a pH of 9.0 and orange

above a pH of 9.0.

Further experiments show that the time of striking the pigment, when the hydrogen ion concentration is kept constant, does not alter the color of the resulting chromate. But if the precipitated pigment is allowed to stand in contact with water after decantation and washing, or if the acidity or basicity of the struck pigment is changed, a corresponding change in color is noted. This is due to a change in the hydrogen ion concentration of the solution.

The temperature of reaction of the solution is again a case of hydrolysis reactions. If the hydrogen ion concentration of the solution is kept constant no change in color is noted up to temperatures of 85°C. However, it was found that yellow chromates prepared at a definite pH turned orange when boiled, but upon cooling changed back to yellow.

Previous experimental work (9), (10)

has shown that the hydrogen ion concentration, or the acidity and basicity of the solution, controls the color of the precipitated pigment, yellows being produced below a pH of 9.0 and oranges above a pH of 9.0.

Is this change in color due to a change in particle size or chemical composition of the precipitated lead chromate?

It is generally believed that the neutral chromate, PbCrO_4 , is formed by the reaction of any soluble, neutral lead salt with an acid or neutral solution of any chromate or bichromate. Weak solutions of alkalis or carbonates change it wholly or partially into one of the basic orange or red salts. the exact formula for basic lead chromate has never been agreed upon although the most generally accepted is $\text{PbCrO}_4 \cdot \text{PbO}$, a dark red crystalline powder. Lighter shades have been attributed to the addition of water (11), and Wagner (12) has suggested the formula $\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$ for the hydrated compound.

The orange colored lead chromates are probably mixtures of PbCrO_4 and $\text{PbCrO}_4 \cdot \text{PbO}$.

Basic lead chromate occurs native as melanochoite to which Dana (13) assigns the formula $2\text{PbCrO}_4 \cdot \text{PbO}$ or $3\text{PbO} \cdot 2\text{CrO}_3$. Gmelin-Kraut (14) and Moissan (15) favor the formula $\text{PbCrO}_4 \cdot 2\text{PbO}$ or $3\text{PbO} \cdot \text{CrO}_4$.

D. Stromholm (16) added the calculated amount of tenth normal potassium dichromate to lead hydroxide, and as soon as equilibrium was established, there remained an ochre-yellow mass of small needles of the monohydrate of lead trioxychromate, its formula being $\text{Pb}_2\text{CrO}_7 \cdot \text{H}_2\text{O}$.

Lead oxychromate, $2\text{PbO} \cdot \text{CrO}_3$; $\text{PbO} \cdot \text{PbCrO}_4$; or Pb_2CrO_5 was prepared by R. L. Dulong (17) by boiling lead oxide with an aqueous solution of potassium chromate. Lead oxychromate is also a product of the hydrolysis of the normal chromate with water.

If, then, different compounds are formed when the chromate is precipitated in an acid or an alkaline solution, the color will depend upon the nature of the individual compound formed.

The relation between the particle size and the color of lead chromate pigments has been investigated by various experimentors. E. E. Free (3) found that the particle size of the orange variety of lead chromate was much larger than that of the yellow variety. J. W. Bain (7) claimed that the particle size alone caused a change in the color. He found that an increase particle size resulted in a corresponding darkening of color up to a definite maximum where the size of the particle became constant,

The color difference between crystallized lead chromate and the precipitated pigment is very marked. The artificial crystals are a deep orange color, but when finely powdered turn to a yellow,

analogous to that of the precipitated compound. When chrome red is ground it takes on a decided yellow tinge (7).

This behavior of pigments on grinding is explained as the effect of the light reflected from the external surfaces of the crystals. According to Nichols and Snow (18) the reflection spectrum of pigments comes from two distinct sources: (a) light reflected from the surface of the substance; (b) light reflected from the interior faces of the crystals. Quoting them, 'The light reflected from the surface is nearly white - - - It is to the light internally reflected that the pigment owes its color'. The colored light reflected from a crystal is that part of the incident light which has been reflected from the interior faces of the crystal.

In a finely powdered pigment there will be more surface area per unit of mass; the first

of the interior faces will be nearer the external surface so that the layer of material through which the internally reflected ray must pass will be less than in a coarser pigment. Therefore, the selective absorption which takes place in the ray will be relatively weaker so that the effect of pulverisation of the pigment is to weaken the color or dilute it with white light. Thus the finer a substance is divided the more nearly white it will become.

If this is also true in the case of precipitated pigments, then a yellow lead chromate will consist of finer particles than an orange one.

EXPERIMENTAL

A. MATERIALS

Lead nitrate of a C.P. grade was repeatedly crystallized from concentrated C.P. nitric acid. It was then washed thoroughly with alcohol and ether and dried at 80°C.

Sodium dichromate of a high quality was repeatedly recrystallized from a saturated solution and dried at 110°C.

Both the sodium hydroxide and nitric acid were of C.P. grade and were made up to ap-
five normal solutions for use.

Boiled, raw linseed oil was used for rubbing up the colors.

B. PREPARATION OF SAMPLES

Five samples were prepared for examination ranging from a pH of 6.0 through a pH of 10.0. The hydrogen ion concentration of the solutions was determined by the potentiometric method of Ernst, Pragoff, and Litkenhous (9) using quinhydrone (19) as the indicator electrode, and a saturated calomel electrode as the standard half cell. Figure I shows a sketch of the wiring diagram.

The hydrogen ion concentration of the lead nitrate solution was varied by the addition of five normal nitric acid and sodium hydroxide solutions. The nitrate solution was made up so that when the desired pH was attained the solution occupied a volume of three hundred c.c. and was 0.5 normal. Three hundred c.c. of 0.5 normal sodium dichromate solution were then struck into the nitrate solution in thirty seconds with constant

FIGURE I

WIRING DIAGRAM

S.P. is a Student Potentiometer (range 0 to 1.6 volts).

Battery is a dry cell battery of 1.5 volts.

P is a protective resistance of 10,000 ohms.

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

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

G is a D'Arsonal Galvanometer (0.5 microamperes per mm. sensitivity, three seconds, critical dampening resistance 2400 ohms.)

W is a Western Cadmium Standard Cell (U.S. Bureau of Standard calibration 1.01878 International Volts at 22°C.

K,K are Tap Keys.

stirring. The solution was stirred vigorously for fifteen minutes, allowed to settle and decanted. One hundred c.c. of distilled water were added, stirred again, and a sample taken in a ground glass stoppered bottle for microscopic examination. The remaining pigment was filtered on a buchner funnel and washed five times with fifty c.c. portions of cold distilled water. The chromate was then washed well with alcohol and ether, dried for twelve hours at 85°C, ground in a mortar and pestle and analyzed for lead and chromium content. The pH of the samples along with the corresponding E.m.f. are shown in Table I.

The dried pigments were rubbed up in linseed oil to compare their mass tone and strength, and are shown in Table II. They are yellow below a pH of 9.0 and orange above a pH of 9.0.

TABLE I

HYDROGEN ION CONCENTRATION OF SAMPLES

Sample number	pH of $\text{Pb}(\text{NO}_3)_2$	E.m.f. millivolts
6	6	- 98
7	7	- 40
8	8	+ 20
9	9	+ 80
10	10	+140

Sodium dichromate, pH 2.5 (E.m.f., -305 millivolts),
not varied.

TABLE II

RUBBED UP SAMPLES

$\text{pH} = 6.0$ $\text{pH} = 7.0$ $\text{pH} = 8.0$ $\text{pH} = 9.0$ $\text{pH} = 10.0$

C. CHEMICAL CONSTITUTION

The samples were analyzed for lead and chromium content to determine the composition of the pigments when precipitated from solutions of varying hydrogen ion concentrations.

The lead content of the samples was determined gravimetrically by weighing as lead sulphate while the chromium was determined volumetrically by the iodimetric method of titrating the iodine liberated by the chromium against standard sodium thiosulphate, using starch as an indicator.

From 0.2 to 0.3 grams of chromate were boiled in two hundred c.c. of concentrated nitric acid until dissolved. One hundred c.c. of distilled water were carefully added, the solution was warmed, and ten c.c. of four molar sulphuric acid added. The solution was then boiled down to white fumes of sulphur trioxide in order to remove all traces

of nitric acid. It was then diluted to one hundred c.c. and a few c.c. of ethyl alcohol were added to convert any remaining chromate over to the chromic state. The lead sulphate was then filtered cold on a weighed gooch crucible, and washed with cold water containing a little acetic acid. It was dried by heating to a dull red heat, and then weighed.

The filtrate, containing the chromium, was boiled down to about one hundred c.c., cooled, and neutralized with ten per cent sodium hydroxide solution. Three grams of sodium peroxide were then added, and the solution was boiled fifteen minutes to expel all of the hydrogen peroxide. After cooling, it was neutralized with four molar sulphuric acid and ten c.c. added in excess, diluted to one hundred c.c. and ten c.c. of ten per cent potassium iodide were added. The solution was allowed to stand for two minutes and then it was titrated against standard 0.1 normal sodium thiosulphate,

using starch solution as an indicator.

This method gave good checks for the lead determination, but gave inconsistent and low results for the chromium content. It is referred to hereafter as method no.1.

The method used by G. Sirois (20) for the determination of chromium in paint pigments was tried and gave more consistent and higher results. His method is as follows :

'Boil 0.2 - 0.5 grams of pigment with twenty c.c. of concentrated hydrochloric acid, dilute to sixty c.c. with hot water, boil five minutes, and filter off any insoluble residue. Make barely alkaline with ammonium hydroxide and add hydrochloric acid until all of the lead hydroxide is dissolved. Dilute to three hundred c.c. and add three grams of sodium peroxide. Boil twenty minutes to convert all chromium to chromate and destroy any excess of hydrogen peroxide. Make acid with hydrochloric acid, adding five c.c. excess. Cool

quickly to 85°C, add ten c.c. of twenty per cent potassium iodide solution, and titrate immediately with standard tenth normal sodium thiosulphate solution. At this temperature there should be no precipitation of lead iodide, but the titration must proceed rapidly or there will be a loss of iodine.'

This is referred to hereafter as method no. 2. It gave a sharp end point, the blue coloration disappearing by the addition of one drop of sodium thiosulphate solution. A faint trace of iodine vapors was noticed escaping from the hot solution during the titration.

A sample of pure potassium dichromate was carried through both procedures as a check on the accuracy of the methods. From method no. 1 the chromium analysis showed the sample to contain 91.8 per cent potassium dichromate. Method no. 2 gave 95.5 per cent potassium dichromate.

In the calculation of the percentage composition of the lead chromates, the chromium content was based upon the results obtained by method no. 2, taking into account the fact that this method gave but 95.5 per cent of the total chromium present. In the orange colored samples, the lead remaining after the calculation of PbCrO_4 content from the chromium analysis was calculated as Pb(OH)_2 .

The composition of the samples is shown in Table III along with a comparison of the methods of analysis for the chromium content.

The examination of the chemical composition indicates the formation of normal lead chromates, PbCrO_4 , in solutions whose hydrogen ion concentration is kept below a pH of 9.0. These pigments are all yellow in color and have constant chemical composition.

At a pH of 9.0 and above a mixture of lead chromate and lead hydroxide is obtained, with a possibility of the formation of a double salt corresponding to the formula, $\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$. There is no reason to believe that $\text{PbCrO}_4 \cdot \text{PbO}$ is obtained, for in the preparation of the samples a heavy precipitate of lead hydroxide was obtained in bringing the hydrogen ion concentration of the lead nitrate solution up to a pH of 9.0.

The fact that sample no. 10 contained a larger per cent of lead hydroxide than sample no. 9 indicates that the precipitate is a mixture of lead chromate and lead hydroxide, and the more basic the solution the greater the percentage of lead hydroxide. Also, the fact that neither of the orange samples gave the theoretical per cent of PbCrO_4 and $\text{Pb}(\text{OH})_2$ in the double salt $\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$ indicates that a mixture is obtained above a pH of 9.0.

TABLE III

CONSTITUTION OF SAMPLES

	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10
Per cent PbCrO_4 from PbSO_4	99.8	99.7	99.1	-----	-----
Per cent PbCrO_4 from Method No. 1	84.4	82.1	87.2	43.6	38.2
Per cent PbCrO_4 from Method No. 2	100.5	96.5	100.3	54.0	49.5
Per cent Pb(OH)_2 by Pb left from PbCrO_4 calculation	-----	-----	-----	43.0	51.4
$\text{Pb(OH)}_2 + \text{PbCrO}_4$	99.8	99.7	99.1	97.0	99.9
Composition	PbCrO_4	PbCrO_4	PbCrO_4	PbCrO_4 and Pb(OH)_2	PbCrO_4 and Pb(OH)_2

D. PARTICLE SIZE

In the determination of the particle size of pigments three procedures may be followed: (a) screen analyses, (b) sedimentation methods, and (c) microscopic methods.

Screen analyses give but rough approximations of the particle size. It is doubtful whether the actual crystal itself is measured by this method, the most probable result being the measurement of large agglomerates rather than the crystal itself.

Sedimentation methods involve the calculation of the particle size on the assumption that the particle is either a perfect cube or sphere. This assumption is seldom true and here again the measuring of agglomerates instead of individual crystals may result.

Microscopic methods are by far more accurate than either of the above methods. Also, by the use of high magnifications, the possibility of measuring agglomerates instead of individual crystals is avoided.

In this investigation a Bausch and Lomb metallographic microscope was used. The samples were examined by transmitted light, a two hundred watt, concentrated filament bulb being used as the source. A 'Bulls Eye' condenser was used to bring the light to a focus on the concave mirror of the microscope. An eyepiece containing a graduated scale was used to measure the size of the particles.

In taking photographs of the particles a Leitz micro camera attachment for 9 x 12 cm. plates was used. An inspection tube with a prism transmitting about 75 per cent of the admitted light is fitted at the side of the camera, Figure II. With the aid of this inspection tube the image may be

FIGURE II. LEITZ CAMERA

watched during the actual exposure. A wire release is attached to the prism so that the image may be put out of action for any length of time while the exposure is being made. This wire release is fitted with a small screw, by means of which the prism may be locked out of action. The magnification of the camera attachment is 1X so that it reproduces the image in the same size in which it is seen by visual observation.

Photographs at four magnifications, 150, 350, 750, and 1400 diameters were taken of each sample. Table IV shows the plate number, pH, magnification, objective, ocular, tube length, and time of exposure for each plate. The plates were special make, Wratten and Wainwright 'M', and are particularly adapted to microscopic work.

The photographs are shown according to their magnification so that the particle size of the five samples may be compared at each magnification.

TABLE IV

PHOTOGRAPHIC DATA

Plate no	Sample pH no.	Approx. Mag.	Objective mm.	Ocular	Tube Length mm	Time sec Exposure
1	6	150	16	15X	160	5
2	6	350	4	8X	165	12
3	6	750	1.9	8X	160	26
4	6	1400	1.9	15X	160	48
5	7	150	16	15X	160	5
6	7	350	4	8X	165	12
7	7	750	1.9	8X	160	26
8	7	1400	1.9	15X	160	48
9	8	150	16	15X	160	5
10	8	350	4	8X	165	8
11	8	750	1.9	8X	160	15
12	8	1400	1.9	15X	160	30
13	9	150	16	15X	160	5
14	9	350	4	8X	165	8
15	9	750	1.9	8X	160	15
16	9	1400	1.9	15X	160	35
17	10	150	16	15X	160	5
18	10	350	4	8X	165	8
19	10	750	1.9	8X	160	15
20	10	1400	1.9	15X	160	20

Plate No. 1

Plate No. 5

Plate No. 9

Plate No. 13

Plate No. 17

Magnification = 150

At a magnification of 150 diameters, agglomerates of the pigments are visible. Plates nos. 1, 5, and 9 (pH of 6, 7, and 8 respectively) show larger agglomerates than plates 13 and 17 (pH of 9 and 10). These photographs show that the particle size of the yellow lead chromates is larger than that of the orange pigments. The agglomerates formed at a pH of 7, plate no. 5, are somewhat smaller than those formed at a pH of 6 and 8, plates 1 and 9. They are, however, larger than the particles obtained at a pH of 9 and 10, plates 13 and 17.

At a magnification of 350 diameters, agglomerates are still prevalent. Here again the pigments struck at a pH of 6, 7, and 8 show larger agglomerates than those struck at a pH of 9 and 10. In plate no. 10 the individual crystals may be faintly distinguished. From the scale shown at this magnification and approximate estimation of the particle size was made. Two and one half scale divisions are equal to 0.01 mm. The agglomerates

Plate No. 2

Plate No. 6

Plate No. 10

Plate No. 14

Plate No. 18

Magnification = 350

Plate No. 3

Plate No. 7

Plate No. 11

Plate No. 15

Plate No. 19

Magnification = 750

in plate no. 2 are approximately 0.005 mm. in diameter. Plate no. 6 shows longer agglomerates whose approximate width and length are 0.002 mm. and 0.11 mm. respectively. From plate no. 10 the approximate width and length of the individual crystals was estimated as being 0.0002 mm. and 0.0005 mm. The agglomerates in plates 14 and 18 are approximately 0.001 mm. in diameter.

At a magnification of 750 diameters the individual crystals of the yellow pigments are visible. They are approximately 0.0001 mm. wide and 0.0004 mm. long, as shown in plate nos. 3, 7, and 11. The oranges are still seen as agglomerates, although small particles which seem to be clusters of two or three crystals are discernable, (plate nos. 15 and 19).

At a magnification of 1400 diameters, the individual needle-like crystals in the agglomerates of the yellow precipitates are readily discernable,

Plate No. 4

Plate No. 8

Plate No. 12

Plate No. 16

Plate No. 20

Magnification = 1400

as can be seen from plate nos. 4, 8, and 12. The agglomerates of the orange pigments do not resolve into individual crystals at this magnification --- plate nos. 16 and 20. The few individual particles which may be picked out however, do not appear to be long needle-like crystals as in the case of the yellow precipitates. Instead, they appear to be very small cubical bodies. This conclusion is open to the objection that the crystal is viewed from the end and not from the side.

The photographs as a whole show that lead chromates precipitated at varying hydrogen ion concentrations up to a pH of 9 form large, loose agglomerates of long needle-like crystals. Above a pH of 9 smaller and more compact agglomerates are formed. Since the orange colored chromates were composed of smaller agglomerates and crystals than the yellow variety, it is evident that the particle size does not cause the variation in color of lead chromates when they are precipitated from solutions of varying hydrogen ion concentrations.

E. OPTICAL PROPERTIES

Most solids are crystalline and show constant properties in parallel directions because there is a similar arrangement of particles. Crystals are classified according to definite axes drawn within the crystal so that its surfaces are symmetrically arranged about them. Crystals whose physical properties are the same in all directions are termed 'isotropic', while those in which the values are dependant upon the direction in which the measurements are made are termed 'anisotropic'.

Crystals may be classified into six systems:

- (1) The Regular System --- three axes of equal length, intersecting each other at right angles.
- (2) The Tetragonal System --- two axes of equal length and the third axis either longer or shorter, all three intersecting at right angles.

- (3) The Hexagonal System --- three axes of equal length, all in the same plane and intersecting at angles of 60° , and a fourth axis, either longer or shorter and perpendicular to the plane of the other three.
- (4) The Rhombic System --- three axes of unequal length, all intersecting each other at right angles.
- (5) The Monoclinic System --- three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not the other.
- (6) The Triclinic System --- three axes of unequal length no two of which intersect at right angles.

The class to which a crystal belongs may be determined by its optical behavior towards

polarized light. For this purpose, a Spencer polarizing microscope was used. The main features of a polarizing microscope over an ordinary microscope for laboratory use are the polarizer, analyzer, rotating stage, and condenser, Figure III.

Polarizer. For illuminating the specimen with polarized light a nicol prism is mounted in the substage. The polarizer mounting should permit it to be readily removed when polarized light is not required, or when some other illumination is to be used. It is essential that the nicol prism be replaceable in a fixed position, so that the plane of vibration of the polarized light will be definitely oriented with respect to the microscope. This is accomplished by means of a notch and stud in the mountings.

Analyzer. A specimen illuminated by polarized light appears much the same as if unpolarized light were used. By placing a second

FIGURE III. POLARIZING MICROSCOPE

polarizing prism above it, however, any effect which the material may have upon the original plane of vibration of the light will be rendered evident. A Glan-Thompson prism is usually employed for this purpose. It is mounted so that it may be conveniently set 'crossed' with respect to the polarizer, so that their planes of vibration are perpendicular to each other. Under these conditions the analyzer stops all the light that the polarizer transmits.

Rotating Stage. By means of the circular stage which rotates on an axis coincident with the center of the field, specimens may be orientated in different directions with reference to the planes of vibration of the nicols. The stage is provided with graduations and a pointer for angular measurements.

Condenser. A condenser mounted above the polarizer is necessary in order to obtain convergent light for the study of interference figures. It

should have a numerical aperture of at least 1.0, and as long a focal length as possible. On account of its necessarily small field, accurate centration of the condenser is important.

The samples were examined liquids of various refractive indices, for it is desirable to have an appreciable difference between the refractive index of the immersion liquid and the substance under examination. The following liquids were tried : Acetone $n = 1.358$, Ethylene glycol $n = 1.41$, Xylene $n = 1.494$, and Quinoline $n = 1.62$.

The particles examined were very small and no sharp extinction of the crystals could be obtained upon rotating the stage. There seemed to be some definite crystalline form in that they all had the same shape, but instead of becoming extinct upon rotation of the field, they merely seemed to blur and go out of focus. They were so small that sharp distinction was impossible. They were ex-

examinated by transmitted parallel and convergent light and by dark field illumination with no results.

The individual particles or crystals are too small to be studied with the view of crystal classification.

CONCLUSIONS

When lead chromates are precipitated from lead nitrate solutions of varying hydrogen ion concentrations by means of sodium dichromate, normal/lead chromate, PbCrO_4 , results below a pH of 9.0. At a pH of 9.0 and above, a mixture of lead chromate and lead hydroxide is obtained, with the possibility of the formation of a double salt corresponding to the formula, $\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$.

Larger particles and agglomerates are obtained below a pH of 9.0 than above a pH of 9.0 when lead chromates are precipitated from lead nitrate solutions of varying hydrogen ion concentration by means of sodium dichromate. This indicates that the particle size does not cause the variation in color of lead chromates when precipitated from solutions of varying hydrogen ion concentrations.

No results were obtained as to the crystal classification of precipitated lead chromates.

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